Seven-Membered Conjugated Carbo- and Heterocyclic Compounds and Their Homoconjugated Analogs and Metal Complexes. Synthesis, Biosynthesis, Structure, and Reactivity

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Received August 2, 1972 (Revised Manuscript Received January 31, 1973)

Contents

I. Introduction

This review is concerned with seven-membered carbo- and heterocyclic compounds for which fully conjugated 6-π-electron structures can be written. Also included here are those compounds in which the seven-membered ring may be viewed as a homoconjugated system.

The mere possibility of writing a plausible fully conjugated, or homoconjugated, 6-π-electron structure for a certain compound (as distinct from the requirement of experimental evidence for full conjugation, or homoconjugation) is sufficient to include it here. This classification is thus independent of the progress of our knowledge of the properties of these compounds and should therefore be a lasting one.

Insofar as their chemistry is strictly connected to that of the free ligands, metal (either π or chelate) complexes of the compounds having the above specifications are also included here. In any case, both π and chelate complexes are presented here from an organic chemical point of view. As a consequence of this, chelate complexes having mainly inorganic chemical interest receive limited attention here.

Synthesis, physical properties and structure, and reaction modes of all the above compounds are considered. The aim is to give a unified picture for compounds which (according to the author's conviction) are linked together by basically similar chemical behavior and are therefore best treated together.

For natural products biosynthetic studies are also briefly reviewed because of their implications on and similarities with organic chemical behavior, while isolation of new natural products is only sporadically mentioned and biological properties are not considered at all. The present unifying treatment does not suffer at all for the omission of such topics.

Priorities in the discoveries and personal names are omitted so as to aid in the conciseness of exposition and not distract the reader from the chemistry involved. As a consequence of this, often only recent papers are referred to, and no historical material is included. With this proviso, the literature has been covered up to June 1972. References to papers appearing after this date, up to November-December 1972, have been added in the revised version of the manuscript.

Long-established trivial names are usually used here because of the troublesomeness of the IUPAC nomenclature with these compounds. When the latter is used for recent compounds, *Chemical Abstracts* has been followed.

Several general reviews, mainly concerned with cycloheptatrienones, were already available. Three of them[1] are frequently quoted here. No general review has appeared after 1966.

II. Synthesis

This section is divided into four main subsections dealing with "cycloheptatrienones," "other species," "radicals and ion radicals," and "metal complexes." Syntheses of cycloheptatrienones from preformed ones are not included here. To avoid repetitions, these will be presented in section V when dealing with reactivity problems. Such repetitions cannot be avoided to some extent when dealing with the "other species." In some cases, in fact, the best synthetic entries (or even the only ones so far devised) to these compounds are from preformed seven-membered conjugated cyclic compounds. This has the logical consequence that the wider space is given to the synthesis of cycloheptatrienones.

This subdivision is merely based on grouping together what appears to be similar from drawings on paper. For example, among cycloheptatrienones are included dibenzotropones and perhalotropones where much of the typical characteristics of tropones are lost. However, this subdivision has both mnemonic value and, more fundamentally, the advantage that this classification will not demand a change when a deeper understanding of the behavior of these compounds is arrived at.

Synthetic entries to seven-membered conjugated ring compounds from their metal π complexes (obtained from simpler organic compounds) are dealt with only in section II.D which is concerned with such complexes.

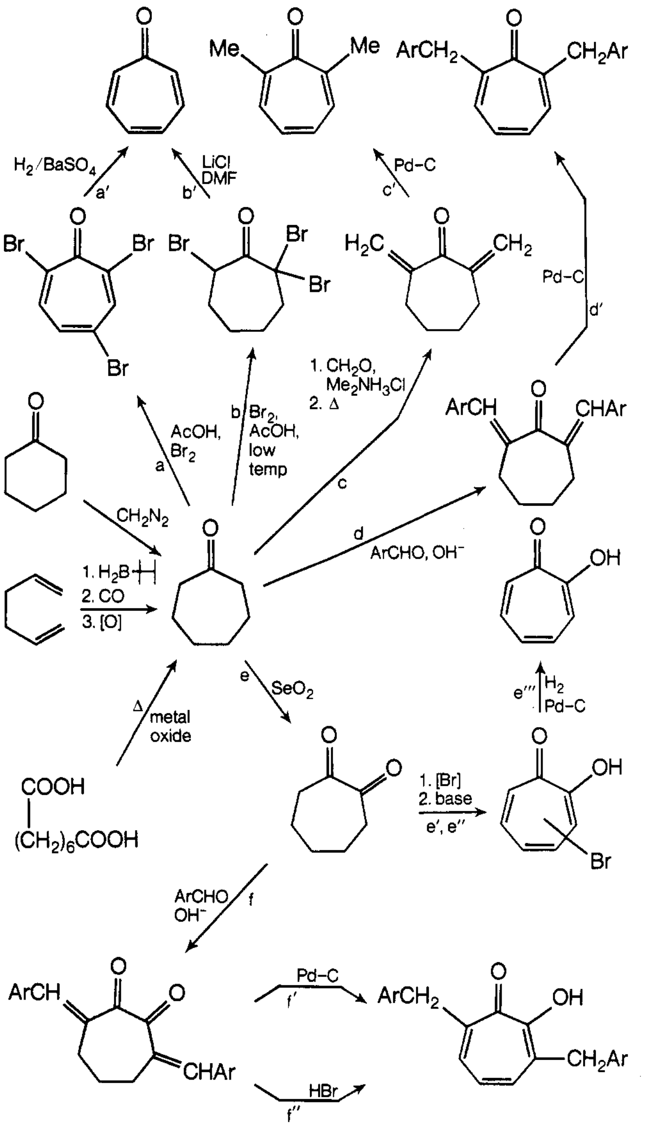
A. Cycloheptatrienones

1. From Cycloheptanone Derivatives

a. From Cycloheptanones

Most useful syntheses of cycloheptatrienones from cycloheptanones (and the most useful synthetic entries to these) are shown in Scheme I for cycloheptanone itself. Cycloheptanones can be obtained by ring enlargement reactions of cyclohexanones or their derivatives,[2] by cyclization of metal salts of 1,7-dicarboxylic acids,[3] and by hydroboration of 1,5-hexadienes with 2,3-dimethyl-2-butylborane followed by carbonylation and oxidation.[4] Reaction of cycloheptanone enamines with reactive alkyl halides is also a useful route to 2-alkylcycloheptanones.[5]

SCHEME I



Bromination-debromination of cycloheptanones leads to bromocycloheptatrienones (Scheme I, route a). This can be followed by catalytic reduction to cycloheptatrienones (Scheme I, route a′). This has been used for tropone itself[6a] and for 2-substituted tropones such as 2-phenyltropone.[6b]

Only carbons in the α position to the carbonyl group are brominated by bromine at low temperature. Successive treatment with lithium chloride or carbonate in DMF

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(1) (a) P. L. Pauson, *Chem. Rev.*, **55,** 9 (1955); (b) T. Nozoe, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience, New York, N. Y., 1959, pp 339-464; (c) D. Lloyd, "Carbocyclic Non-Benzenoid Aromatic Compounds," Elsevier, Amsterdam, 1966.

(2) C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968.

(3) H. Gilman, Ed., "Organic Synthesis," Wiley, New York, N. Y.: Collect. Vol. I, 1941, p 192; Collect. Vol. IV, 1963, p 854.

(4) H. C. Brown and E. Negischi, *J. Amer. Chem. Soc.*, **89,** 5477 (1967).

(5) G. Opitz and H. Mildenberger, *Justus Liebigs Ann. Chem.*, **649,** 47 (1961).

(6) (a) T. Nozoe, Y. Kitahara, T. Ando, and S. Masamune, *Proc. Jap. Acad.*, **27,** 231 (1951); *Chem. Abstr.*, **46,** 7558 (1952); T. Nozoe, Y. Kitahara, T. Ando, S. Masamune, and H. Abe, *Sci. Rep. Tohoku Univ., Ser. 1*, **36,** 166 (1952); *Chem. Abstr.*, **49,** 11615 (1955); (b) T. Nozoe, S. Ito, and K. Sonobe, *Proc. Jap. Acad.*, **29,** 101 (1953); *Chem. Abstr.*, **48,** 10716 (1954); (c) G. Jones, *J. Chem. Soc. C*, 1230 (1970); (d) E. W. Collington and G. Jones, *Chem. Commun.*, 958 (1968); (e) E. W. Collington and G. Jones, *J. Chem. Soc. C*, 2656 (1969).

(Scheme I, route b, b′) affords cycloheptatrienones. This route has been used, other than for tropone itself, for 2- and 4-alkyl-substituted tropones like 2-*n*-propyl- and 4-isopropyltropone (*ca.* 20 and 22% yields, respectively).[6c] It was suggested that in the dehydrobromination step (b′) double bond migration is involved.[6d] Competing bromination to other bromocycloheptanones, which are not dehydrobrominated to tropones, limits the yields obtainable by this method.[6e]

2,7-Dialkyl- and 2,7-dibenzyltropones are also accessible *via* the Mannich reaction (Scheme I, route c)[7] or *via* the dibenzilidene derivative (Scheme I, route d)[8] from cycloheptanones having free 2 and 7 positions, followed by dehydrogenation on palladium/charcoal (steps c′ and d′).

The most general route from cycloheptanones to tropolones involves their oxidation to α-diketones with SeO_2 followed consecutively by bromination with bromine[9] or with *N*-bromosuccinimide,[10] dehydrobromination by heat or alkali, and catalytic reduction. This route (Scheme I, e, e′, e″, e‴) has been used for tropolone itself,[9,10] and for a variety of alkyl- and aryl-substituted tropolones.[11] It is clear that with substituted cycloheptanones a mixture of tropolones will be generated. This is the case, for example, of 4-phenylcycloheptanone, which gives a mixture of 4-phenyl- and 5-phenyltropolone.[12] Generally, the bromination–dehydrobromination stage gives rather poor yields.

Alternatively, dibenzylidene formation from the α-diketone followed by dehydrogenation leads to 3,7-benzyl-disubstituted tropolone[13] (Scheme I, routes e, f, f′ or e, f, f″; the second route gives better yields[13]).

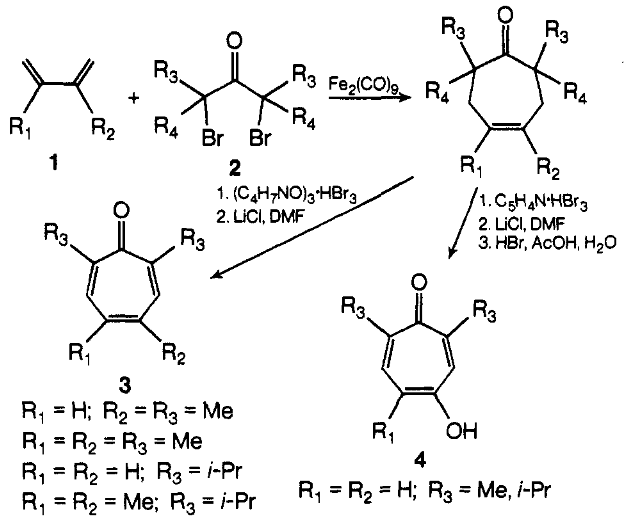
b. From 2-Hydroxycycloheptanones

2-Hydroxycycloheptanones, accessible by acyloin condensation[14] of dialkyl pimelates, give tropolones, free from bromotropolones, on treatment with bromine.[15] This method has been used for tropolone itself[15] and for substituted tropolones.[13b,15]

c. From Cycloheptenones or Arenecycloheptanones

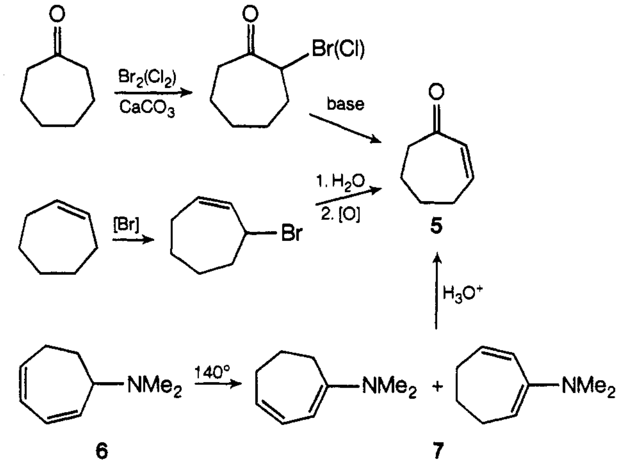
4-Cycloheptenones have been elegantly synthesized (Scheme II) by the cycloaddition of butadiene or 2,3-dialkyl-substituted butadienes (**1**) with secondary α,α'-dibromo ketones (**2**) in the presence of $Fe_2(CO)_9$ (iron pentacarbonyl operates less effectively).[16] Only the cases of the cycloheptenones suitable for further transformation into cycloheptatrienones are illustrated in Scheme II. Thus, bromination of 4-cycloheptenones with pyrrolidone hydrotribromide followed by dehydrobromination with LiCl in DMF leads to tropones **3**.[16] When 4-cycloheptenones with unsubstituted 4 and 5 position were brominated with pyridine hydrotribromide followed by partial debromination (to 4-bromotropones) and the products were subjected to acid hydrolysis, 4-hydroxytropones **4** were obtained.[16] Yields from 4-cycloheptenones range from 46 to 66%. A mechanistic investigation of this cyclization indicates that an oxyallyl-Fe(II) intermediate is involved.[16]

SCHEME II



Less versatile use of 2-cycloheptenones has been made so far. 2-Cycloheptenone itself (**5**) has been brominated in a single step to 2,4,7-tribromotropone, which has then been catalytically reduced to tropone (Scheme I, step a′).[17] 2-Cycloheptenone is available either *via* dehydrohalogenation of 2-chloro- or 2-bromocycloheptanone (which are easily obtained from cycloheptanone),[18] or by allylic bromination of cycloheptene followed by hydrolysis and oxidation[19] (Scheme III).

SCHEME III



A further route to **5** is by thermal rearrangement of α-methyltropidine (**6**) to **7** and acid hydrolysis of the latter.[20]

Finally, a new entry to 2-cycloheptenones (in mixture with 3-cycloheptenones) by ring enlargement of methylene-2-cyclohexenes with cyanogen azide has been re-

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[7] M. Mühlstädt, *Naturwissenschaften*, **45**, 240 (1958).

[8] N. J. Leonard, L. A. Miller, and J. W. Berry, *J. Amer. Chem. Soc.*, **79**, 1482 (1957).

[9] J. W. Cook, A. R. Gibb, R. A. Raphael, and A. R. Somerville, *J. Chem. Soc.*, 503 (1951).

[10] T. Nozoe, S. Seto, Y. Kitahara, M. Kunori, and Y. Nakayama, *Proc. Jap. Acad.*, **26**, 38 (1950); *Chem. Abstr.*, **45**, 7098 (1951).

[11] References 61–71 in ref 1a above.

[12] W. von E. Doering and A. R. Sayigh, *J. Org. Chem.*, **26**, 1365 (1961).

[13] (a) N. J. Leonard and J. W. Berry, *J. Amer. Chem. Soc.*, **75**, 4989 (1953); (b) N. J. Leonard and G. C. Robinson, *ibid.*, **75**, 2143 (1953).

[14] K. T. Finley, *Chem. Rev.*, **64**, 573 (1964).

[15] J. D. Knight and D. J. Cram, *J. Amer. Chem. Soc.*, **73**, 4136 (1951).

[16] (a) R. Noyori, S. Makino, and H. Takaya, *J. Amer. Chem. Soc.*, **93**, 1272 (1971); R. Noyori, Y. Hayakawa, M. Funakura, H. Takaya, S. Murai, R. Kobayashi, and S. Tsutsumi, *ibid.*, **94**, 7202 (1972).

[17] T. Nozoe, T. Mukai, K. Takase, and T. Nagase, *Proc. Jap. Acad.*, **28**, 477 (1952); *Chem. Abstr.*, **48**, 2678 (1954).

[18] E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 607 (1954).

[19] N. Heap and G. H. Whitham, *J. Chem. Soc. B*, 164 (1966).

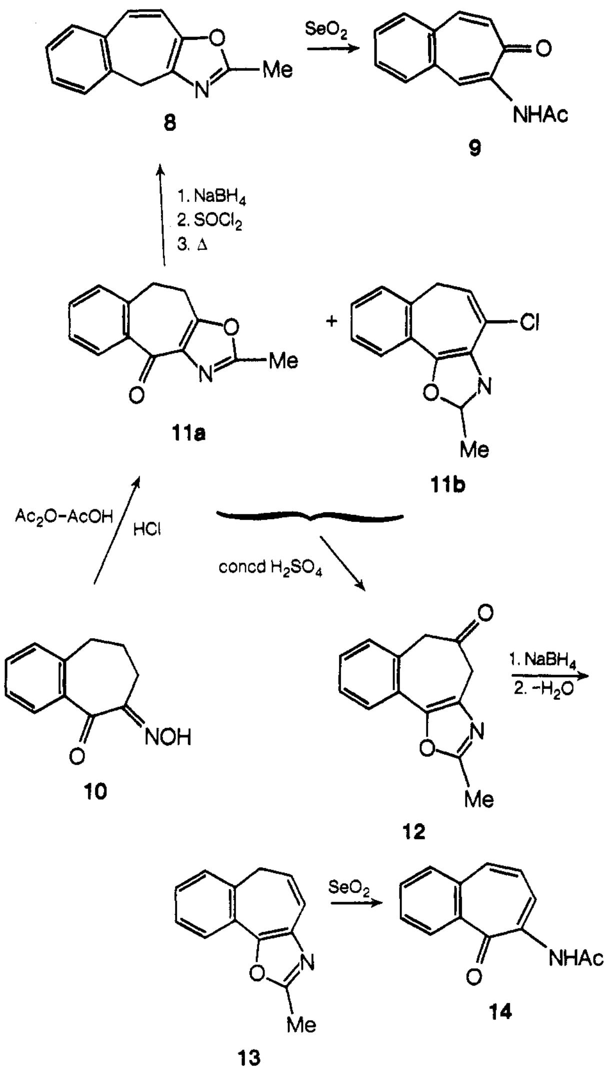
[20] H. J. Dauben and H. J. Ringold, *J. Amer. Chem. Soc.*, **73**, 876 (1951).

ported.[21] So far, however, no adaptation to the synthesis of cycloheptatrienones has been reported.

Fused arenecycloheptanones may be formally considered as a special case of cycloheptenones, and their transformation into cycloheptatrienones is therefore considered here. Bromination with bromine of 2,3-benzocycloheptanones, followed by dehydrobromination with LiCl in DMF, leads to 2,3-benzotropones in 90% yield.[6c] This method is an amelioration of previous ones.[22] Also 1',2'2,3-naphthotropone has been obtained by bromination–dehydrobromination sequences.[23]

Fused arenetropolones have been obtained from arenecycloheptanones also by the other routes shown in Scheme IV.[24] Thus, *α*-oximinobenzosuberone (**10**) reacts with Ac_2O–AcOH–HCl to give a mixture of **11a** and **11b** *via* a "non-Beckmannian" pathway.[24] Treatment of this mixture with concentrated sulfuric acid gives **12** which can be transformed into **13** (65% yield from **10**).[24] Treatment of **13** with SeO_2 in dioxane at reflux gives **14** which undergoes easy acid hydrolysis to give 3,4-benzotropolone.[24] The isomeric 4,5-benzotropolone can be obtained from **11a** *via* **8** and **9** as indicated in Scheme IV.[24]

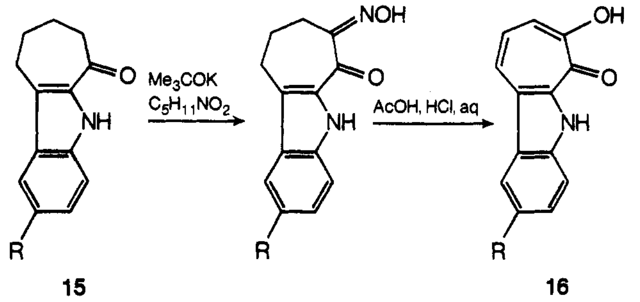
SCHEME IV

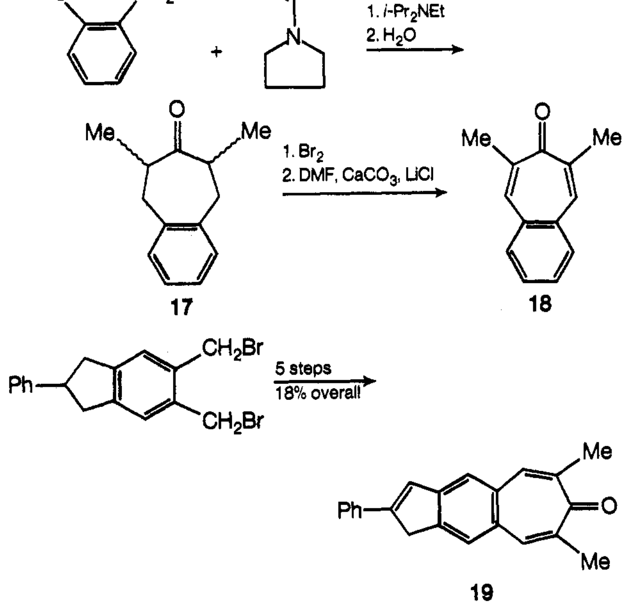


Advantages of the routes shown in Scheme IV are high yields and adaptability to the synthesis of benzotropolones bearing reducible substituents (*e.g.*, nitro groups) on the benzene ring.[24]

Indolocycloheptanones (**15**) may also be formally viewed as cycloheptenones. Recently the smooth transformation of **15** into indolotropolones (**16**) on treatment with amyl nitrite and *t*-BuOK followed by acids has been reported.[25]

A new entry to benzocycloheptanones[26] has been devised on adaptation of a cyclization method for smaller rings. Thus, *α*,*α*'-dibromo-*o*-xylene was condensed with the pyrrolidine enamine of pentan-3-one to give **17**.[26] Bromination–dehydrobromination of **17** gave 2,6-dimethyl-4,5-benzotropone (**18**).[26] The indenotropone **19** was obtained analogously.[26]





d. From Cycloheptadienones

Tropinone (**20**), under carefully controlled conditions for Hofmann degradation, gives 2,6-cyclohexadienone (**21**)[27a] (Scheme V). Under less carefully controlled conditions, a mixture of 2,4- (**22**) and 3,5-cyclohexadienone (**25**) was obtained.[27b]

The same mixture of cyclohexadienones was also obtained by bromination of the tropane derivative **23** followed by alkali treatment,[28a] whereas the solvolytic ring

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(21) J. E. McMurray, *J. Amer. Chem. Soc.*, **91**, 3675 (1969).

(22) G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, 3586 (1959).

(23) D. Elad and D. Ginsburg, *J. Chem. Soc.*, 1286 (1957).

(24) E. Galantay and W. R. J. Simpson, *Chem. Commun.*, 754 (1970).

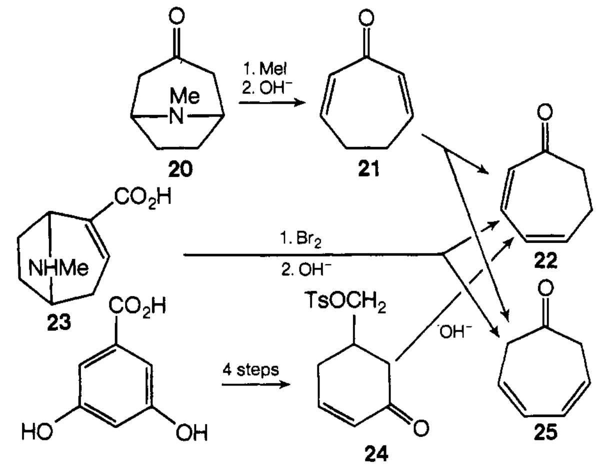
(25) M. Mühlstädt and H. Lichtman, *J. Prakt. Chem.*, **312**, 466 (1970).

(26) F. G. Bordwell and M. Winn, *J. Org. Chem.*, **32**, 42 (1967).

(27) (a) E. E. van Tamelen, J. McNary, and F. A. Lornitzo, *J. Amer. Chem. Soc.*, **79**, 1231 (1957); (b) J. Meinwald, S. L. Emerman, N. C. Yang, and G. Buchi, *ibid.*, **77**, 4401 (1955).

(28) (a) A. Eichengrun and A. Einhorn, *Ber.*, **23**, 2870 (1890); (b) E. E. van Tamelen and G. T. Hildahl, *J. Amer. Chem. Soc.*, **75**, 5451 (1953); (c) E. E. van Tamelen and G. T. Hildahl, *ibid.*, **78**, 4405 (1956).

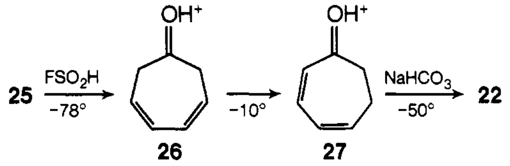
SCHEME V



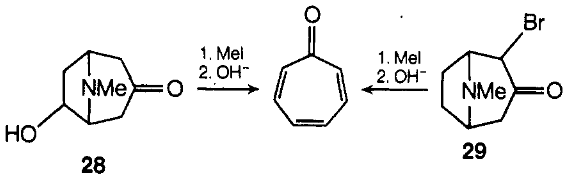
expansion of the cyclohexenone derivative **24**, obtained from 3,5-dihydroxybenzoic acid, gave only **22**.[28b,c]

The mixture **22** + **25** has been transformed into tropone either by bromine[27b] or SeO_2[28b] or into tropolone by perbenzoic or peroxytrifluoroacetic acid.[28c]

Pure **22** has been until recently very difficult to obtain.[28b,c] An efficient synthesis of **22**, starting from the readily available **25** (section V.C), has now been devised.[29] Dissolution of **25** into FSO_2H at −78° gave the conjugate acid **26** which isomerized to **27** on raising the temperature to −10°. Treatment of **27** with $NaHCO_3$ at low temperature finally gave pure **22**.[29]

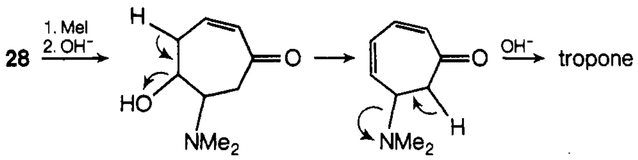


With tropane derivatives that, like **28** or **29**, bear a displaceable substituent, Hofmann degradation leads directly to tropone (80% yield from **28** and a lower yield from **29**).[30] In the case of **28** it has been tentatively proposed that the product of the first β-elimination dehydrates to a 2,4-cycloheptadienone derivative which undergoes further β-elimination under the reaction conditions.[30] This may be a plausible mechanism, in spite of the fact that hydroxyl is a bad leaving group under basic conditions, owing to the gain of conjugation during the process from **28** to tropone (Scheme VI). With tropane derivatives like **30–33**, Hofmann degradation leads to 4-hydroxy- or 4-methoxytropone in 50–100% yields (Scheme VII).[31] As above, these processes too can be conceived to involve cycloheptadienones as intermediates.

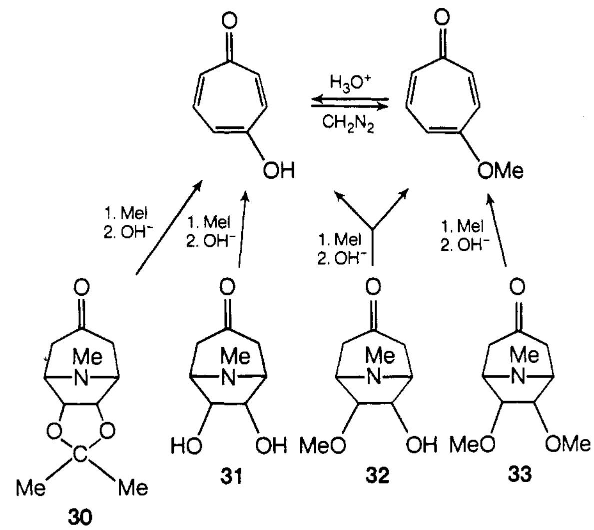


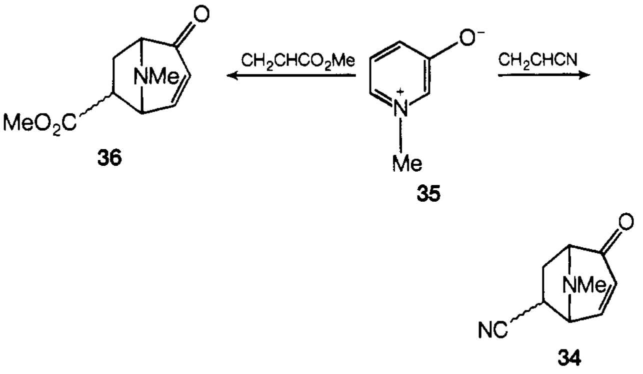
The importance of syntheses of troponoids from tropane-type compounds has greatly increased after the discovery of two smooth routes to bicyclic systems which, like **28–33**, can be transformed into troponoids. The first case concerns anhydro-3-hydroxy-1-methylpyridinium hydroxide (**35**) which possesses substantial 1,3-dipolar reactivity toward either acrylonitrile or methyl acrylate to give **34** or **36** (*ca.* 70%), respectively.[32a]

SCHEME VI



SCHEME VII





Hofmann degradation of either **34** or **36** leads to a mixture of **38** and **39** in *ca.* 30% overall yield.[32a] The expected (see above) path a (Scheme VIII) is not followed. It has been tentatively suggested[32a] that formation of **39** and **38** (the second being a hydrolysis product of the first) involves (Scheme VIII, path b) hydride abstraction from the enolate of **37** by **37** itself. This method[32a] has been adapted, starting from 2-methyl-3-oxidoisoquinolinium, to the synthesis of benzotropones.[32b]

The other novel route to bicyclic systems related to those above is dealt with in section II.B.7 and concerns the synthesis of 4,5-trimethylenetropone and 4,5-homotropone.

A special case which is conveniently treated here concerns the synthesis of the quinoidal, unstable, 2,3:5,6-

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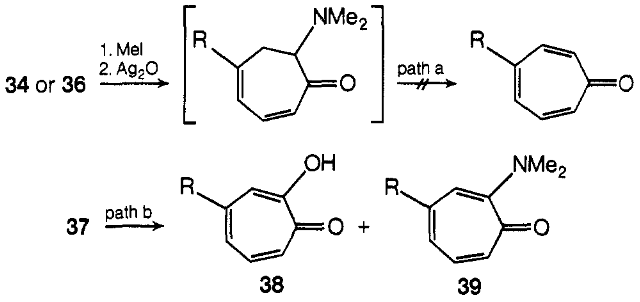
[29] K. E. Hine and R. F. Childs, *J. Chem. Soc., Chem. Commun.*, 144 (1972).

[30] E. E. van Tamelen, P. Barth, and F. Lornitzo, *J. Amer. Chem. Soc.*, **78**, 5442 (1956).

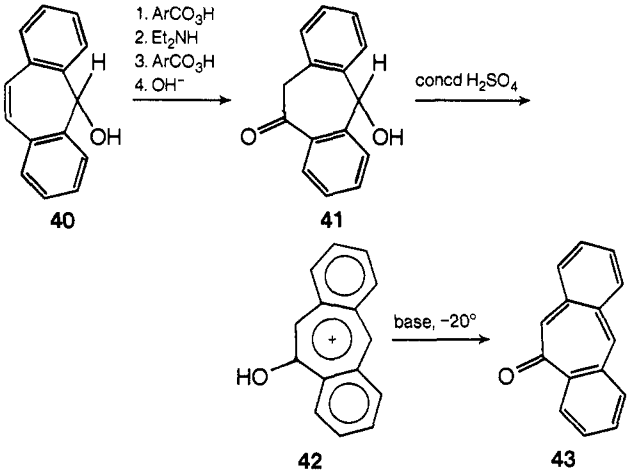
[31] J. Meinwald and O. L. Chapmann, *J. Amer. Chem. Soc.*, **78**, 4816 (1956); **80**, 633 (1958).

[32] (a) A. R. Katritzky and Y. Takeuchi, *J. Amer. Chem. Soc.*, **92**, 4134 (1970); *J. Chem. Soc. C*, 878 (1971); (b) N. Dennis, A. R. Katritzky, and Y. Takeuki, *J. Chem. Soc., Perkin Trans. 1*, 2054 (1972).

SCHEME VIII



dibenzotropone (**43**) by alkali treatment of the tropenylium cation **42**.[33] This was obtained by the treatment of **41** with concentrated sulfuric acid.



Rapid dimerization of **43**, even in solution at low temperature, prevented collection of any physical data.[33] Commercially available **40** was converted into **41** in three steps.[33]

Efforts to synthesize stable, substituted, 2,3:5,6-dibenzotropones were unsuccessful.[33]

2. By Aldol-Type and Other Inter- or Intramolecular Cyclizations

a. By Aldol-Type Cyclizations

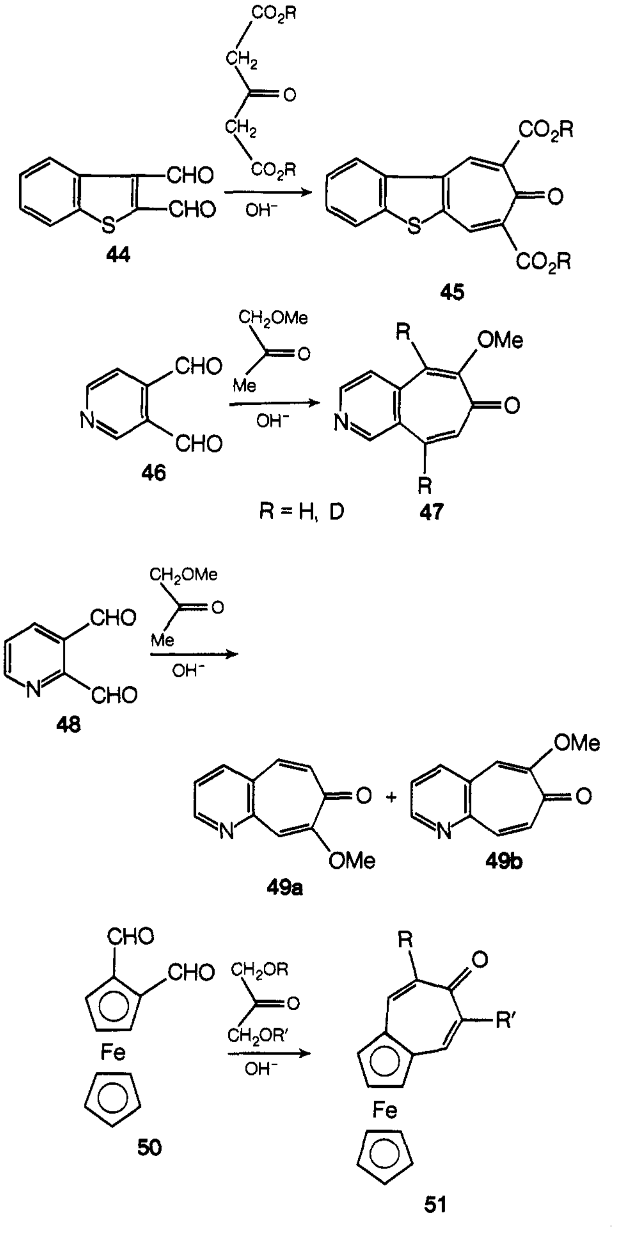
Phthalaldehyde has been condensed with both acyclic and cyclic ketones as well as with cyclic diketones. Thus, 1,3-(2-keto) esters gave the esters of 2,6-dicarboxy-4,5-benzotropone which can be hydrolyzed to dicarboxylic acid and then decarboxylated to 4,5-benzotropone[34a] (Scheme IX). Yields rarely exceed 50% because these tropone derivatives undergo Michael additions by the acetone derivatives under the basic conditions used.[34b] Better yields can be obtained carrying out these cyclizations under strongly acidic conditions.[34]

With alkyl- or 1,3-dialkylacetones, various alkyl-4,5-benzotropones have been synthesized,[34] and with hydroxy- or aryloxyacetone, 4,5-benzotropolone or 2-aryloxy-4,5-benzotropones were obtained, respectively[35] (Scheme IX).

With cyclic ketones, condensation to 2,7-polymethylene-4,5-benzotropones (Scheme IX) was obtained in a single step for n = 7–13, whereas for n = 4–8 dehydration of the aldol adduct had to be completed by treatment with P_2O_5.[36]

With cyclic diketones, condensation to 2,7-polymethylenebis-4,5-benzotropones was obtained[37] in 41–83% yield for n = 4, 5, 8 (Scheme IX).

Aldol-type condensations have been successfully applied to other diformyl compounds such as 2,3-diformylbenzothiophene (**44**),[38] 3,4- (**46**)[39a] and 2,3-diformylpyridine (**48**),[39b] the ferrocene derivative **50**,[40] the furan



R = R' = H, Me, Ph, CO_2Et
R = H; R' = Et

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(33) N. L. Bauld and Y. S. Rim, *J. Amer. Chem. Soc.*, **89**, 179 (1967).

(34) (a) J. Thiele and E. Weitz, *Justus Liebigs Ann. Chem.*, **377**, 1 (1910); (b) B. Föhlish, *Synthesis*, **4**, 1564 (1972).

(35) H. Fernholz, E. Hartwig, and J. C. Salfeld, *Justus Liebigs Ann. Chem.*, **576**, 131 (1952); D. S. Tarbell, G. P. Scott, and A. D. Kemp, *J. Amer. Chem. Soc.*, **72**, 379 (1950); D. S. Tarbell and J. C. Bill, *ibid.*, **74**, 1234 (1952).

(36) E. Kloster-Jensen, N. Tarkoy, A. Eschenmoser, and E. Heilbronner, *Helv. Chim. Acta*, **39**, 786 (1956).

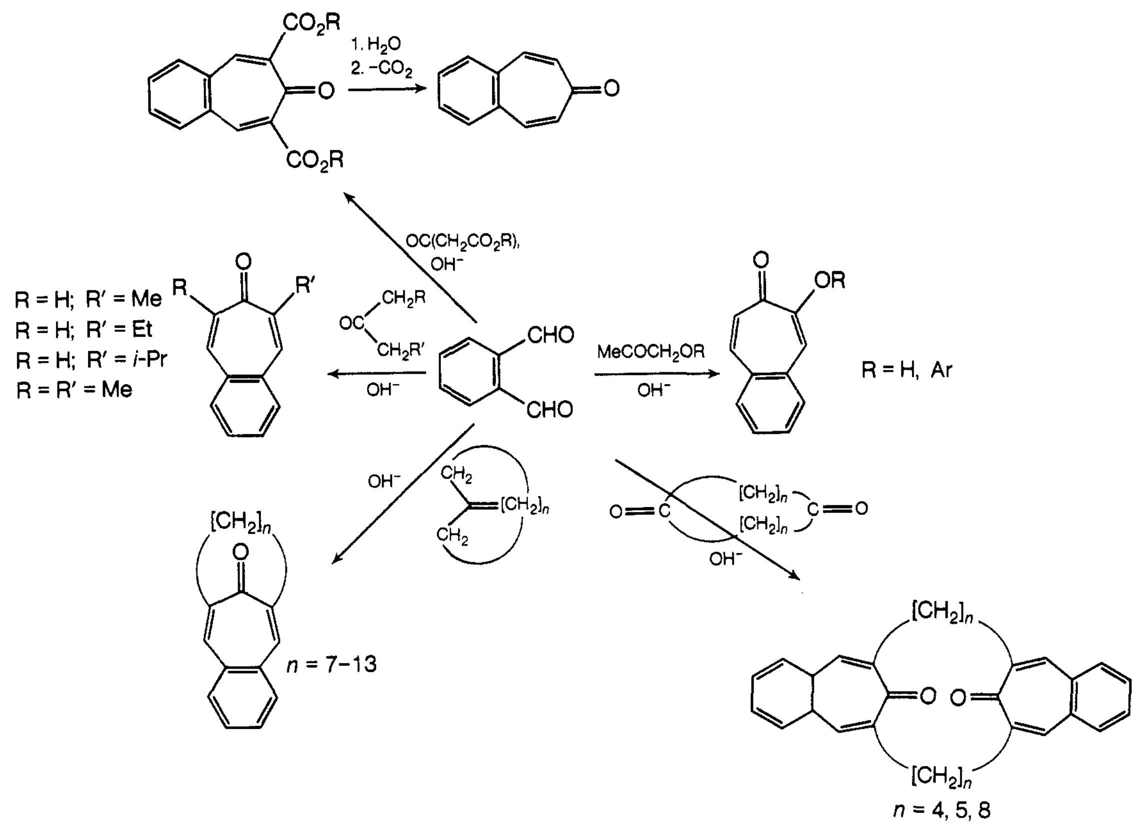
(37) R. E. Harmon, R. Suder, and S. K. Gupta, *Chem. Commun.*, 1170 (1969); *J. Chem. Soc., Perkin Trans. 1*, 1746 (1972).

(38) W. Ried and H. Bender, *Chem. Ber.*, **89**, 1574 (1956).

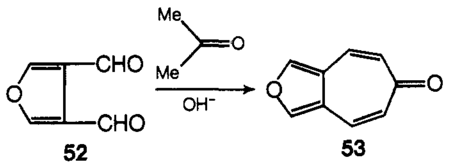
(39) (a) G. Queguiner, C. Fugier, and P. Pastour, *C. R. Acad. Sci., Ser. C*, **270**, 551 (1970); (b) G. Queguiner, C. Fugier, and P. Pastour, *Bull. Soc. Chim. Fr.*, 3636 (1970).

(40) C. Moïse, J. Tirouflet, and H. Singer, *Bull. Soc. Chim. Fr.*, 1182 (1969).

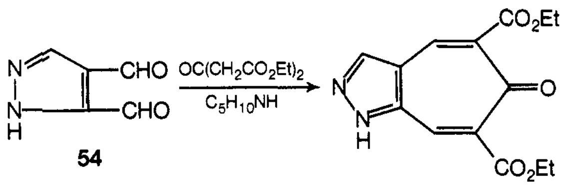
SCHEME IX



52,[41] and pyrazole-3(5),4-dicarboxaldehyde (**54**)[42] to give, respectively, **45**, **47**, a 90:10 mixture of **49a** and **49b**, **51**, **53**, and **55**.



52 **53**



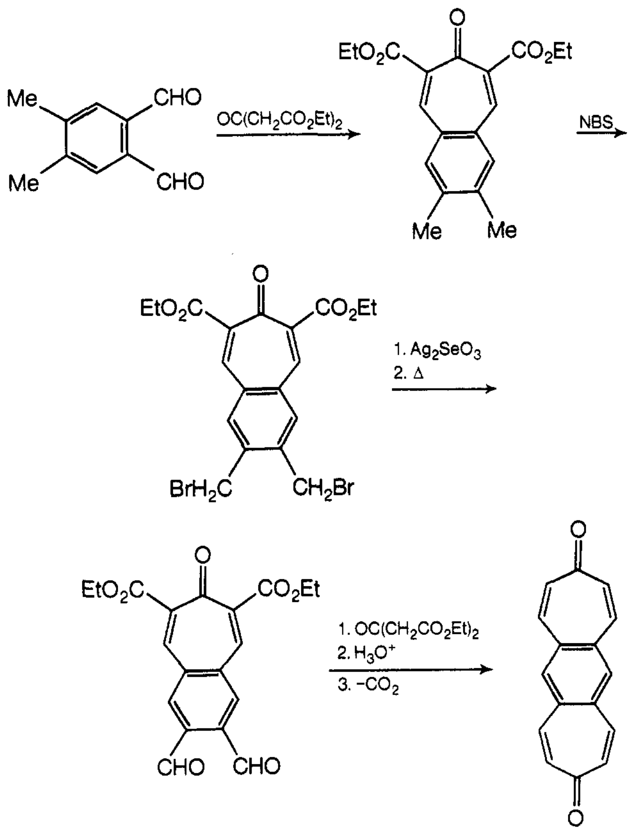
54 **55**

Aldol-type condensations of diformyl compounds have also been applied to the synthesis of the benzoditropone **56** (Scheme X)[43] and to the synthesis of deuterium-labeled derivatives of 2-phenoxy-4,5-benzotropone.[44]

Attempts to condense in this way maleic dialdehyde (**57**) with either methoxy- or hydroxyacetone failed, however, *m*-hydroxybenzaldehyde being the only condensation product isolated in very low yield.[45]

Examples of synthesis of troponoids by intramolecular aldol-type condensations, such as **58** → **59**,[46] **60a** → **60b**,[39a] and **61** → **49b**,[39b] have also been reported.

SCHEME X



56

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[41] M. J. Cook and E. J. Forbes, *Tetrahedron*, **24**, 4501 (1968).

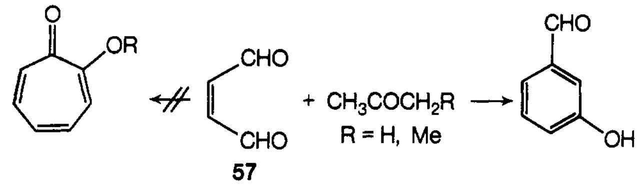
[42] C. V. Greco and M. Pesce, *J. Org. Chem.*, **37**, 676 (1972).

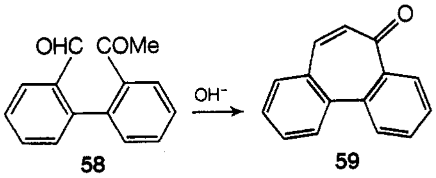
[43] B. Föhlisch and E. Widman, *Z. Naturforsch. B*, **24**, 464 (1969).

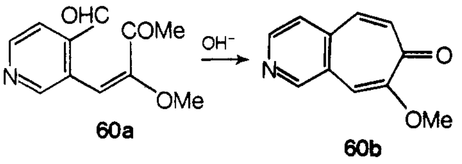
[44] T. H. Kinstle, O. L. Chapman, and M. Sung, *J. Amer. Chem. Soc.*, **90**, 1227 (1968).

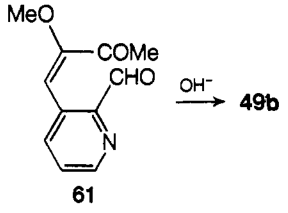
[45] D. L. Hufford, D. S. Tarbell, and T. R. Koszalka, *J. Amer. Chem. Soc.*, **74**, 3014 (1952).

[46] W. Borsche and A. Herbert, *Justus Liebigs Ann. Chem.*, **546**, 293 (1941); J. W. Cook, G. T. Dickson, and J. D. Loudon, *J. Chem. Soc.*, 746 (1947); J. W. Cook, J. Jack, J. D. Loudon, G. L. Buchanan, and J. McMillan, *ibid.*, 1397 (1951).



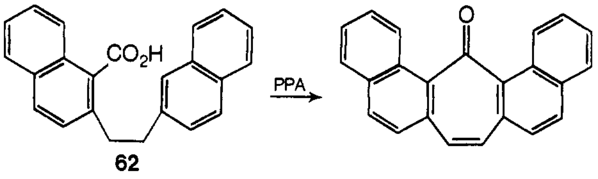




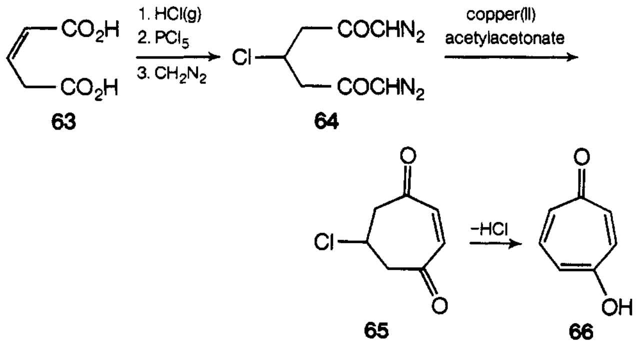


b. By Other Cyclizations

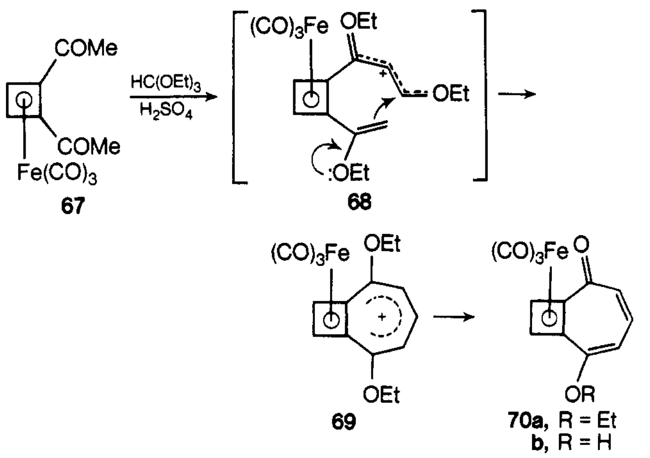
Cyclodehydrations, as in the case of **62**,[47] have been extensively used to synthesize troponoids.



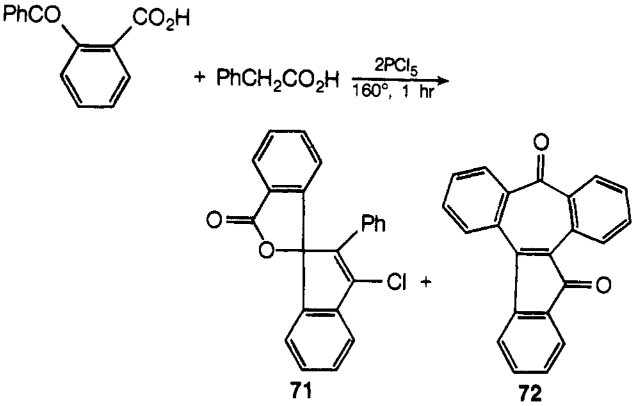
The long tried[48a] intramolecular "dimerization" of α-keto carbenes has recently been reported.[48b] In the case of 1,7-bisdiazo-4-chloroheptane-2,6-dione (**64**), obtained from glutaconic acid (**63**) in three steps, decomposition under high dilution conditions with copper acetylacetonate led to 6-chlorocyclohept-2-ene-1,4-dione (**65**) which, either spontaneously *in vacuo* or under the influence of triethylamine, was dehydrochlorinated and enolized to 4-hydroxytropone (**66**) in *ca.* 27% overall yield.[48b]



The tricarbonyliron complex of 1,2-diacylbutadiene (**67**), which failed to undergo intramolecular aldol cyclization, condensed with ethyl orthoformate in 95% sulfuric acid to give **70a** in 72% yield.[49] Hydrolysis of **70a** afforded the 4-hydroxytropone derivative **70b**.[49] It has been suggested[49] that condensation of an enol ether of **67** with ethyl orthoformate gives, after elimination of ethanol, **68**. Cyclization of the latter in the manner shown should then give **69** which then transforms into **70a** in the work-up.[49]



Heating equimolar 2-benzoylbenzoic acid and phenylacetic acid with the double molar quantity of PCl_5 at 160° for 1 hr led, after separation by recrystallizations from **71**, to **72** in 40% yield.[50]



3. By Carbene Cycloadditions

Cycloaddition of a carbene to a double bond embodied in a six-membered carbocyclic ring may lead, either directly or by subsequent transformation, to troponoids. No distinction is made here between carbene and carbenoid species.[51] Also included here are noncarbene cycloadditions by compounds which, like diazoalkanes, often give carbenes.

Dihalocarbenes proved to be most useful reagents. However, they only add to strongly nucleophilic double bonds, *i.e.*, those which are activated by electron-donating substituents such as alkoxy groups. Thus, to insert dibromocarbene into anisole (**73a**) or veratrole (**73b**), Birch reduction to give **74** was required.[52] Dibromocar-

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(47) E. D. Bergmann and I. Agranat, *J. Chem. Soc. C*, 3532 (1971).

(48) (a) Y. Ernest and J. Hofman, *Chem. Listy*, **45**, 261 (1951); (b) J. Font, F. Serratosa, and J. Valls, *Chem. Commun.*, 721 (1970).

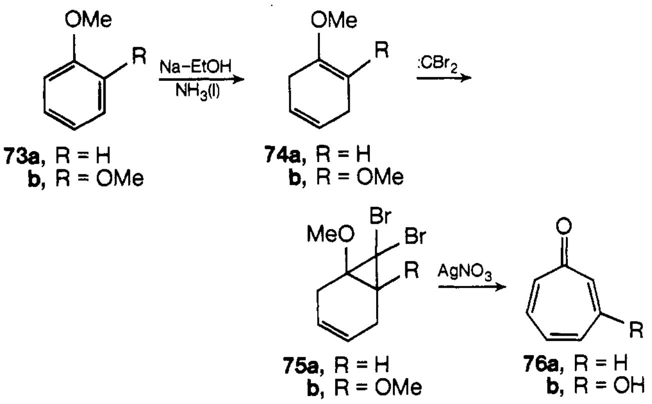
(49) B. W. Roberts and A. Wissner, *J. Amer. Chem. Soc.*, **92**, 6382 (1970).

(50) A. Marsili and M. Isola, *Tetrahedron*, **23**, 1037 (1967).

(51) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes and Arynes," Nelson, London, 1969.

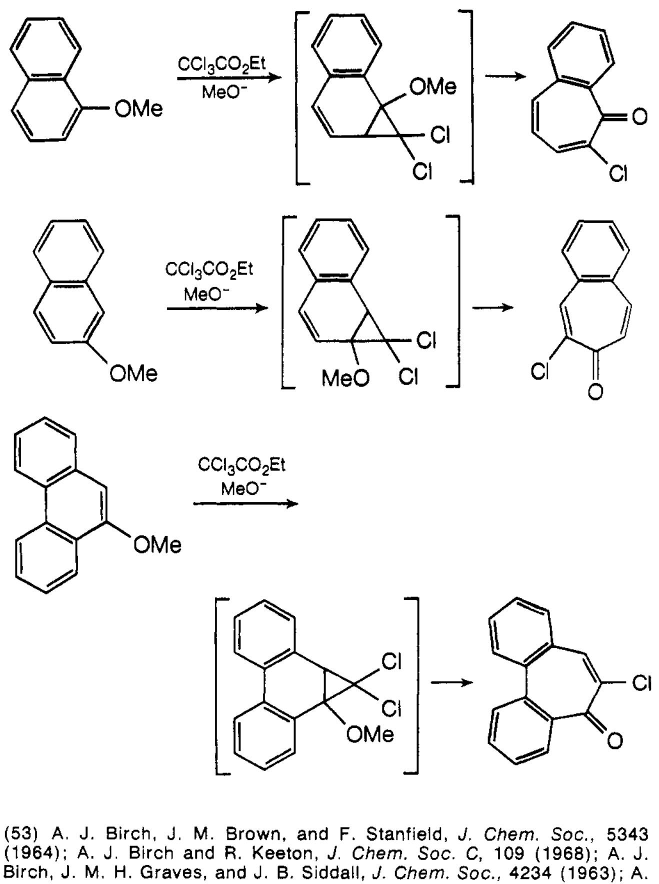
(52) A. J. Birch, J. M. H. Graves, and F. Stanfield, *Proc. Chem. Soc., London*, 282 (1962); A. J. Birch and R. Keeton, *Aust. J. Chem.*, **24**, 331 (1971).

bene addition to **74** was followed by treatment with hot aqueous silver nitrate to obtain tropone (**76a**) or 3-hydroxytropone (**76b**) from, respectively, **73a** or **73b**.[52] However, while Birch reduction worked quite well, only a much lower yield of **76b** than that (60% overall) claimed[52] was obtained in the present author's laboratory during repeated trials. Other tropones have been synthesized along similar lines.[53]



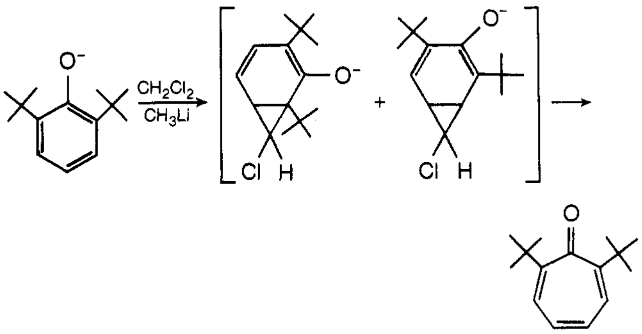
The 1,2 bond of 1- or 2-methoxynaphthalene and the 9,10 bond of 9-methoxyphenanthrene are nucleophilic enough to add to dichlorocarbene.[54] Only 9-methoxyphenanthrene gives an isolable adduct, while those from methoxynaphthalenes lose methyl chloride under the reaction conditions (20°) (Scheme XI).[54] Overall yields range from 11 to 50%.[54]

SCHEME XI



Dichlorocarbene was also added to 1-ethoxycyclohexene, and, by further transformations, a mixture containing tropone (38%) as the only troponoid was obtained.[55] This is erroneously reported as a ready direct access to tropolone in a reference book.[56] Really, 2-hydroxytropones are not accessible by these dihalocarbene routes.

If a strong nucleophilic benzene derivative, such as the metal salt of a phenol, is allowed to react with dihalocarbenes, no ring enlargment results because of the intervention of the Reimer-Tieman reaction. However, changing to chlorocarbene, ring enlargment was obtained. This is the case of 2,6-di-*tert*-butylphenol which gives 2,6-di-*tert*-butyltropone (**77**) in good yield.[57]



77

By this method, phenol or *o*-cresol gave tropone or 2-methyltropone, respectively, in very poor yield. Main products were 2-methyl- or 2,6-dimethylcyclohepta-3,5-dien-1-one, from which the corresponding tropone derivatives were obtained by treatment with bromine.[57] All evidence indicates that tropone or 2-methyltropone, respectively, do indeed form, but they rapidly add methyllithium at C(2).[57] Addition of methyllithium at the carbonyl carbon was also observed albeit at a much lower rate.[57]

Diazoalkanes and α-carbalkoxydiazoalkanes have also been used. Starting from benzene or benzene derivatives, tropenylium salts or cycloheptatrienes were obtained which are suitable for transformation into troponoids. Thus, benzene reacts with diazomethane in the presence of cuprous bromide to give cycloheptatriene which has been recovered as tropenylium perchlorate (**79**) in 85% yield[58] (Scheme XII).

Cycloheptatriene (**78**) was obtained by sodium borohydride reduction of **79**.[58a] By this method, methylene insertion in the aromatic ring of a variety of substituted benzenes has also been achieved.[59] This method[58a] is definitely superior to the photochemical one[58b] which gives large percentages of products of methylene insertion into either aliphatic or aromatic C–H bonds.

Both tropenylium salts and cycloheptatrienes may be transformed into troponoids. Thus, ditropenyl ether (**80**), obtained by alkali treatment of tropenylium salts, is converted by acids into tropone (**76a**) (Scheme XII).[60] Also,

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(53) A. J. Birch, J. M. Brown, and F. Stanfield, *J. Chem. Soc.*, 5343 (1964); A. J. Birch and R. Keeton, *J. Chem. Soc. C*, 109 (1968); A. J. Birch, J. M. H. Graves, and J. B. Siddall, *J. Chem. Soc.*, 4234 (1963); A. J. Birch, and G. S. R. Subba Rao, *Tetrahedron, Suppl.*, **No. 7**, 391 (1966).

(54) W. E. Parham, D. A. Bolon, and E. E. Schweizer, *J. Amer. Chem. Soc.*, **83**, 603 (1961).

(55) W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *J. Amer. Chem. Soc.*, **87**, 321 (1965).

(56) M. Fieser and L. Fieser, "Reagents for Organic Synthesis," Vol. 2, Wiley-Interscience, New York, N. Y., 1969, p 350.

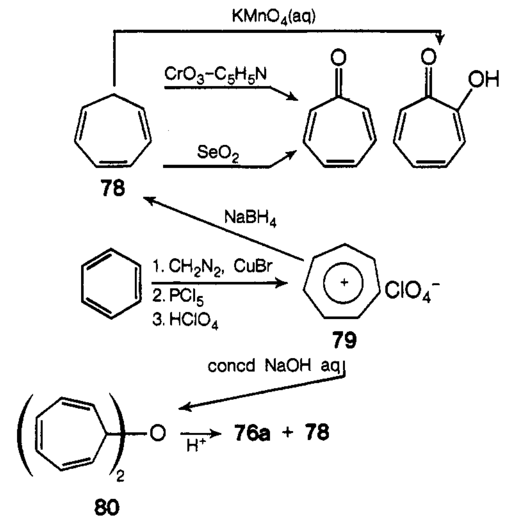
(57) G. L. Closs and L. E. Closs, *J. Amer. Chem. Soc.*, **83**, 599 (1961).

(58) (a) E. Müller and H. Fricke, *Justus Liebigs Ann. Chem.*, **661**, 38 (1963); E. Müller, H. Fricke, and H. Kessler, *Tetrahedron Lett.*, 1501 (1963); (b) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **72**, 2305 (1950); H. Meerwein, quoted in *Chem. Ber.*, **86**, 1528 (1953), footnote 12.

(59) E. Müller, H. Kessler, H. Fricke, and W. Kiedaish, *Justus Liebigs Ann. Chem.*, **675**, 63 (1964), and previous references therein.

(60) A. P. Ter Borg, R. van Helden, and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **81**, 177 (1962); A. P. Ter Borg, R. van Helden, W. Renold, and A. S. Dreiding, *Helv. Chim Acta*, **43**, 457 (1960).

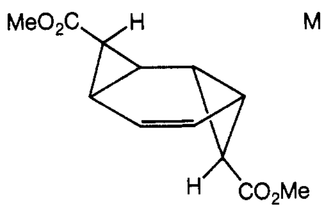
SCHEME XII



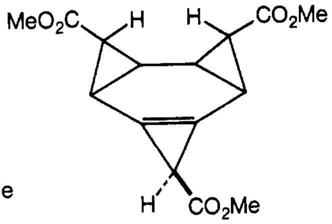
bromotropenylium ion,[61a,b] as well as halo- or methoxytropenylium ions,[61b,c] undergo acid hydrolysis to tropone.

Cycloheptatriene can be oxidized to tropone (either by chromium trioxide in pyridine[62] or by selenium dioxide[63]) or (albeit in very poor yield) to tropolone by potassium permanganate[64] (Scheme XII).

Recently it has been discovered that benzene, on treatment with methyl diazoacetate in the presence of copper–bronze, produces bis (**81**) and tris adducts (**82**) only.[65] The causes of this unusual behavior are not clear, though it is possible that the norcaradiene-cycloheptatriene equilibrium is strongly affected by the heterogeneous catalyst surface.[65]



81



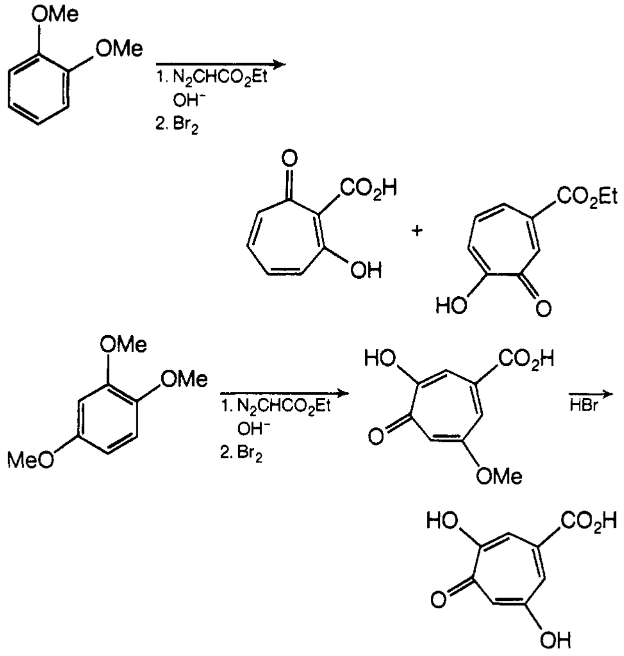
82

Other insertion reactions of diazomethane occur with *o*-benzoquinol acetate (to give tropone and 2,3,5-trialkyltropones),[66] and with some *p*-benzoquinones[67] (to give 2,6-di-*tert*-butyl-4-hydroxytropone[67a] or 2-methoxy-4-hydroxy-5-acetyl-6-alkyltropones[67b]). Usually, however, these products were obtained in mixtures which proved difficult to separate.

Benzene reacts also with diazoacetic ester to give cycloheptatrienecarboxylic acid which is also suitable for transformation into troponoids.[68] However, alkaline hydrolysis of the readily available 7-cyanocycloheptatriene is an easier route to cycloheptatrienecarboxylic acids.[69]

A more direct entry to troponoids by means of diazoacetic ester is from arenes carrying methoxyl substituents at strategic positions (Scheme XIII).[70] However, although starting materials are readily available, yields by these routes (Scheme XIII) are usually poor.[70] Competing, undesired, reactions limit the utility of this method. Such competing reactions include C–H insertions at alkyl groups, such as with durene,[71a] C–Cl insertion, such as with benzal chloride,[71b] C–O insertion between alkyl-oxygen ethereal bonds, such as with anisole,[71c] and enolization of carbonyl compounds followed by alkylation at the enol oxygen, such as with benzosuberone.[71b]

SCHEME XIII



4. *By Cycloadditions of Haloketenes or Olefins*

Ketenes give $[_\pi 2_s + {}_\pi 2_a]$ cycloadditions with dienes, giving solely cyclobutane derivatives.[72] Cycloadditions of this type between cyclopentadienes or fulvenes and haloketenes generated *in situ* have been utilized to produce adducts that can be ring expanded to troponoids. These reactions have been recently reviewed.[73]

In Scheme XIV examples for dichloroketene generated *in situ* from dichloroacetyl chloride and triethylamine are reported. Thus, with cyclopentadiene or fulvene good overall yields of tropolone (**83**) (35%)[74] or dolabrin (**84**) (85%)[75] were obtained. Details for 4-*tert*-butyltropone

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(61) (a) W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956); (b) M. E. Vol'pin, I. S. Akhrem, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 760 (1957); (c) H. J. Dauben, F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Amer. Chem. Soc.*, **79**, 4557 (1957).

(62) T. Nozoe, *Progr. Org. Chem.*, **5**, 141 (1961).

(63) P. Radlick, *J. Org. Chem.*, **29**, 960 (1964).

(64) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **73**, 828 (1951); **75**, 297 (1953).

(65) D. L. Dalrymple and S. P. B. Taylor, *J. Amer. Chem. Soc.*, **93**, 7098 (1971).

(66) (a) E. Zbiral, F. Takacs, and F. Wessely, *Monatsh. Chem.*, **95**, 402 (1964).

(67) (a) W. Rundel and P. Kastner, *Tetrahedron Lett.*, 3947 (1965); *Justus Liebigs Ann. Chem.*, **737**, 87 (1970); (b) F. M. Dean, P. G. Jones, R. B. Morton, and P. Sidisunthorn, *J. Chem. Soc.*, 411 (1964).

(68) J. R. Bartels-Keith, A. W. Johnson, and W. I. Taylor, *J. Chem. Soc.*, 2352 (1951); R. B. Johns, A. W. Johnson, and M. Tišler, *ibid.*, 4605 (1954).

(69) P. L. Pauson and K. H. Todd, *J. Chem. Soc. C*, 2636 (1970).

(70) A. W. Johnson, *J. Chem. Soc.*, 1331 (1954).

(71) (a) L. I. Smith and P. D. Tawney, *J. Amer. Chem. Soc.*, **56**, 2167 (1934); (b) C. D. Gutsche and M. Hillman, *ibid.*, **76**, 2236 (1954); (c) G. B. R. De Graaff, J. H. van Dijck-Rothuis, and G. van de Kolk, *Recl. Trav. Chim. Pays-Bas*, **74**, 143 (1955).

(72) H. Staudinger, "Die Ketene," Enke, Stuttgart, 1912.

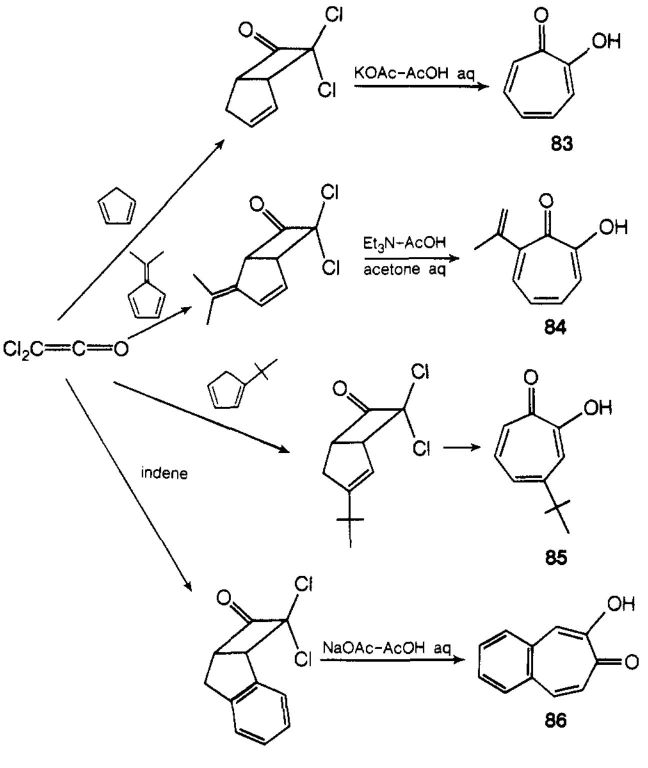
(73) W. T. Brady, *Synthesis*, **3**, 415 (1971).

(74) H. C. Stevens, D. A. Keich, D. R. Brandt, K. R. Fountain, and E. J. Gaughan, *J. Amer. Chem. Soc.*, **87**, 5257 (1965).

(75) T. Asao, T. Machiguchi, T. Kitamura, and Y. Kitahara, *Chem. Commun.*, 89 (1970).

(**85**) were not reported,[76] while in the case of indene only poor yields of 4,5-benzotropolone (**86**) were obtained.[77]

SCHEME XIV

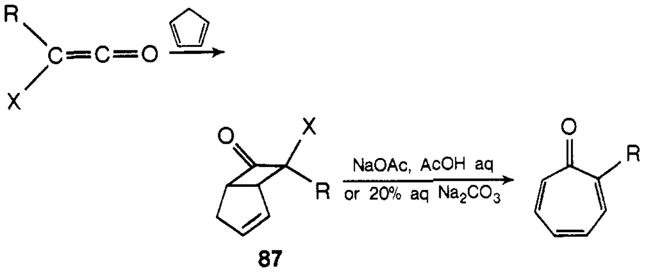


Results in Scheme XIV for **84** and **85** clearly indicate that in the solvolysis of the respective bicyclic precursors the new oxygen which is incorporated becomes attached to the bridgehead carbon adjacent to the carbonyl group. Two views have been expressed concerning detailed mechanisms for the ring expansion of the bicyclic systems of Scheme XIV.[75,76,78] The stereochemical assignment of protons of such adducts has been made possible from nmr spectroscopy by the use of shift reagents.[79]

The method of Scheme XIV has also been adapted to the preparation of 4-methyltropolone from 1-methylcyclopentadiene[73,76] and of a mixture of 4- and 5-isopropyltropolone from a mixture of isopropylcyclopentadienes.[80]

Dibromoketene has been used, with similar results, in the place of dichloroketene. It can be prepared *in situ* from dibromoacetyl chloride and triethylamine or from tribromoacetyl bromide and copper-activated zinc.[73] The latter method can also be adapted to generate dichloroketene from trichloroacetyl chloride.[73]

Alkylhaloketenes have also been used. These can be generated *in situ* from α-halo-α-alkylacetyl chloride and triethylamine and react with cyclopentadiene to give a cycloadduct (**87**) which can be rearranged to 2-alkyltropones by standard methods.[73,81] This method appears to be simpler than those from cycloheptanones or from halocarbenes and phenols discussed in previous sections. However, it failed for 2-phenyltropone.[81] Moreover, Favorskii-type ring contraction was observed to compete with ring enlargment of **87** on alkali treatment.[81]

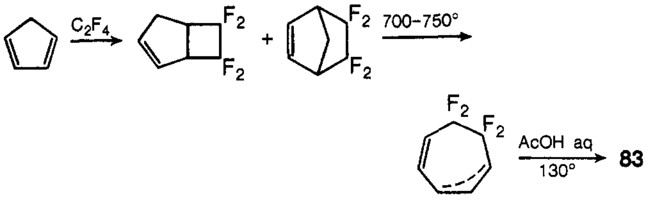


87

X = Cl, Br; R = Me, Et, *i*-Pr,
n-C_4H_9, n-C_8H_{17}, c-C_6H_{11}-,
c-$C_6H_{11}CH_2$-, c-$C_6H_{11}(CH_2)_2$-

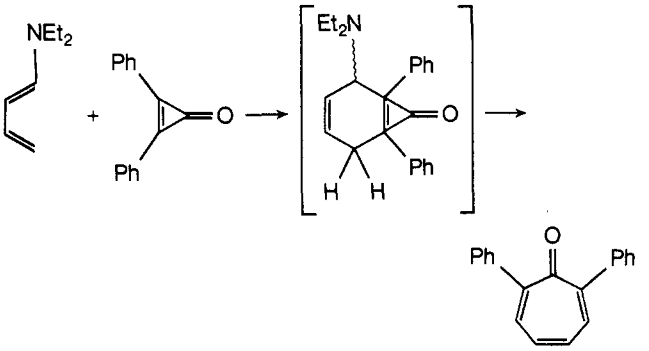
It must also be noticed that with **87** conversion into the cycloheptatrienone is faster using 20% aqueous Na_2CO_3 than aqueous KOAc–AcOH.[81] In contrast, with the dichloroketene adduct of cyclopentadiene, the use of aqueous carbonate was reported to induce ring cleavage of the cyclobutanone ring.[74]

Cycloadditions between olefins (or compounds embodying carbon–carbon double bonds, just to group these reactions together here) have also been used to synthesize troponoids. Thus, cyclopentadiene reacts with tetrafluoroethylene to give a mixture of [2 + 2] and [4 + 2] cycloadducts that on pyrolysis give tetrafluorocycloheptadienes **88**.[82] These, on acid hydrolysis, give tropolone (**83**).[82] The overall yield was 20%.[82]



88

Diphenylcyclopropenone has been treated with 1-diethylamino-1,3-butadiene to give 2,6-diphenyltropone (**89**) in 68% yield by what can be viewed as a [4 + 2] cycloaddition followed by ring enlargment.[83] This method has not been extended notwithstanding its potential versatility.



89

Photocycloaddition of cyclopentane-1,3-dione enol acetate (**90**) with olefins has also been used to produce [2

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(76) P. D. Bartlett and T. Ando, *J. Amer. Chem. Soc.*, **92**, 7518 (1970).

(77) R. W. Turner and T. Seden, *Chem. Commun.*, 399 (1966).

(78) T. Asao, T. Machiguchi, and Y. Kitahara, *Bull. Chem. Soc. Jap.*, **43**, 2662 (1970).

(79) R. M. Cory and A. Hassner, *Tetrahedron Lett.*, 1245 (1972).

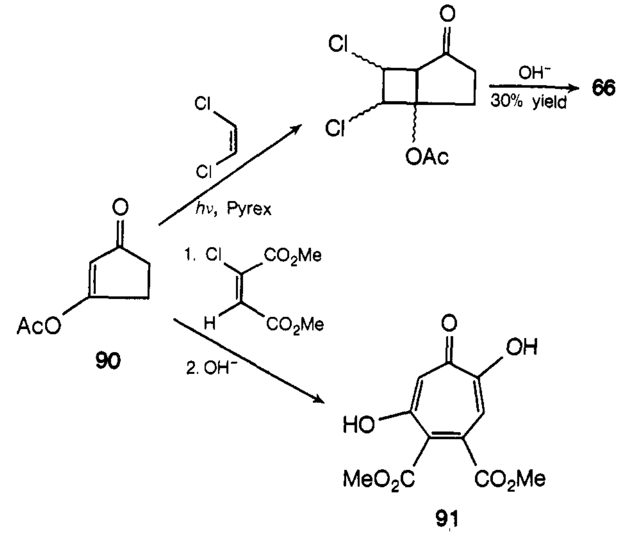
(80) K. Tanaka and A. Yoshikoshi, *Tetrahedron*, **27**, 4889 (1971).

(81) W. T. Brady and J. P. Hieble, *J. Amer. Chem. Soc.*, **94**, 4278 (1972).

(82) J. J. Drysdale, W. W. Gilbert, H. K. Sinclair, and W. H. Sharkey, *J. Amer. Chem. Soc.*, **80**, 3672 (1958).

(83) J. Ciabattoni and G. A. Berchtold, *J. Amer. Chem. Soc.*, **87**, 1404 (1965); *J. Org. Chem.*, **31**, 1336 (1966).

+ 2] cycloadducts that can be ring expanded by alkali into 4-hydroxytropones. Thus, the photocycloadduct with *cis*-1,2-dichloroethylene gave 4-hydroxytropone (**66**) in 30% yield.[84] However, **66** had to be separated from other photochemical products by preparative glpc and the yield has not been reported.[84] Photocycloaddition of **90** to chloromaleic acid dimethyl ester and alkali treatment of the resulting cycloadduct gave **91**.[84] Compound **91** was then transformed into the mold metabolite stipitatonic acid (4% yield from **90**).[84]



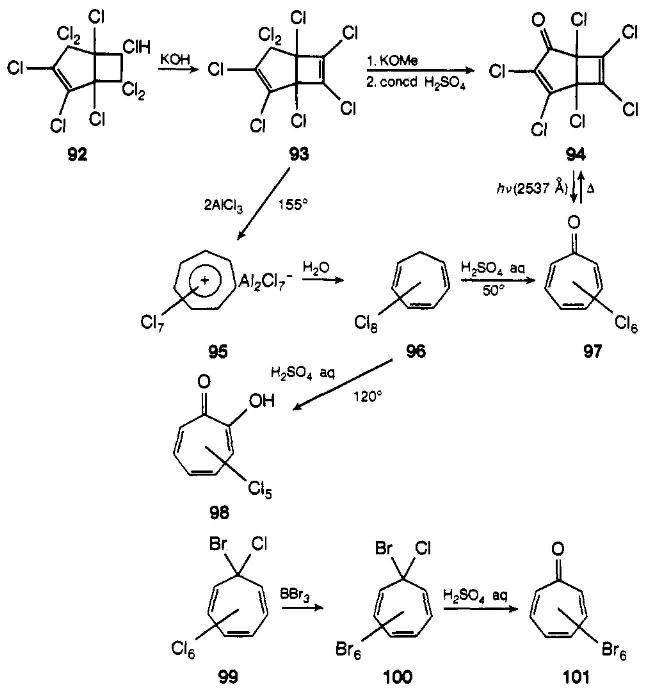
Reaction of hexachlorocyclopentadiene with trichloroethylene in the presence of $AlCl_3$ gave cycloadduct **92** from which **93** and **94** could be obtained in successive steps as shown in Scheme XV.[85] Both **93** and **94** are precursors of very interesting fully halogenated compounds. Thus, treatment of **93** with 2 equiv of $AlCl_3$ at 155° (the temperature is critical) gave perchlorotropenylium heptachlorodialuminate (**95**).[86] On the treatment of **95** with water the seven-membered ring adds a chloride ion to give **96**.[86] Perchlorotropone (**97**) was obtained either by acid hydrolysis of **96** or by irradiation of dilute (1-2%) solutions of **94** in a quartz vessel with a low-pressure mercury lamp.[87] The latter is an equilibrium reaction and **97** was isolated in 30-40% yield by high-vacuum fractional sublimation followed by recrystallization from hexane.[87] Clearly, the first route[86] is superior but, owing to the drastic conditions required, might be inapplicable to related cases.

Acid hydrolysis of **96** under more drastic conditions gave pentachlorotropolone (**98**).[88]

Perbromotropone (**101**) was obtained either by direct halogen exchange between **97** and BBr_3 or by halogen exchange of **96** and BBr_3 (which gave **99** or **100** according to reaction conditions) followed by acid hydrolysis of **100** (Scheme XV).[86]

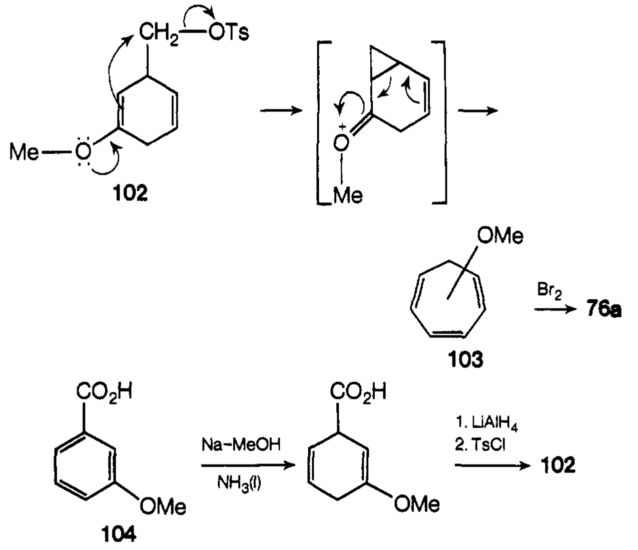
Also the interesting synthesis of **356b**-type compounds probably involves ketene intermediates.

SCHEME XV



5. By Wagner-Meerwein and Other Ring Expansion Reactions

One of the most versatile (though not of high yield) synthesis of troponoids so far devised involves ring expansion, in pyridine solution, of methoxy-substituted 2,4-cyclohexadienyl-1-carbinyl tosylates.[89] In the case of **102**, the mixture of methoxycycloheptatrienes **103** so obtained was oxidized with bromine to tropone (**76a**).[89] Tosylate **102** was obtained from 3-methoxybenzoic acid (**104**) by successive Birch reduction, lithium aluminum reduction, and tosylation.[55]



Along similar routes, tropolone (**83**) as well as 3- (**76b**) and 4-hydroxytropone (**66**) were obtained starting from 2,3- (**105**), 3,5- (**106**), or 2,5-dimethoxybenzoic acid (**107**), respectively.[89]

Success in alkylating cyclohexadiene intermediates gave further flexibility to the above methods. Thus, **109**,

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(84) H. Hikino and P. de Mayo, *J. Amer. Chem. Soc.*, **86**, 3582 (1964); B. D. Challand, H. Hikino, and G. Kornis, G. Lange, and P. de Mayo, *J. Org. Chem.*, **34**, 794 (1969).

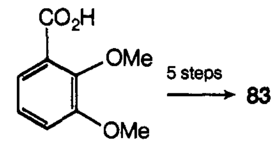
(85) A. Roedig and L. Hörnig, *Justus Liebigs Ann. Chem.*, **598**, 208 (1956).

(86) (a) K. Kusuda, R. West, and V. N. Mallikarjuna Rao, *J. Amer. Chem. Soc.*, **93**, 3627 (1971); (b) R. West in "Aromaticity, Pseudo-Aromaticity, Anti-Aromaticity," (Proceedings of the 3rd Jerusalem Symposium on Quantum Chemistry and Biochemistry), E. D. Bergmann and B. Pullman, Ed., Israel Academy of Sciences and Humanities, Jerusalem, 1971, pp 363-374.

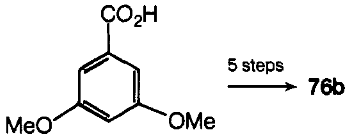
(87) K. V. Scherer, Jr., *J. Amer. Chem. Soc.*, **90**, 7352 (1968).

(88) K. V. Scherer, University of Southern California, unpublished results quoted in ref 86b, p 368.

(89) O. L. Chapman and P. Fitton, *J. Amer. Chem. Soc.*, **85**, 41 (1963).



105



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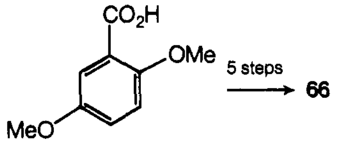
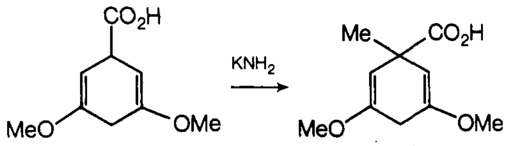


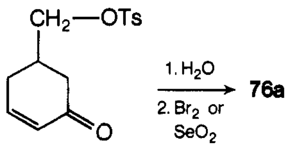
107

obtained by methylation of **108** with methyl iodide and potassium amide, gave 3-hydroxy-5-methyltropone along routes similar to those above.[89]



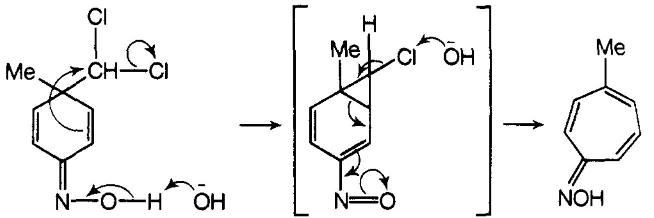
108 **109**

Ring expansion under solvolytic conditions of some compounds not derived from Birch reduction have also been found to lead to troponoids. Thus, **110** (obtained from resorcinol-5-carboxylic acid by successive catalytic reduction, esterification to the enol ether, $LiAlH_4$ reduction, acid hydrolysis, and, finally, tosylation[90]) under solvolytic conditions gave a mixture of cycloheptadienones which was subsequently oxidized to tropone (**76a**) with bromine or selenium dioxide.[90]



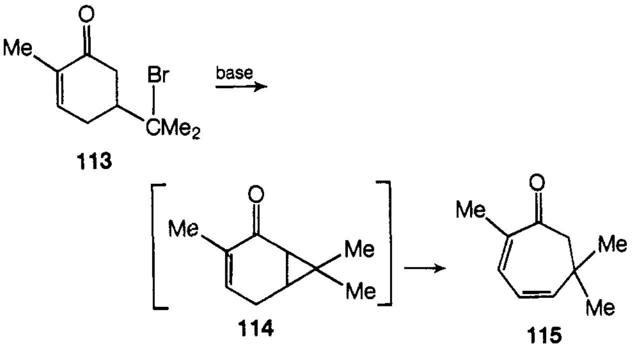
110

Also known is the ring expansion of **111** to 4-methyltropone oxime (**112**) which is hydrolyzable to 4-methyltropone.[91] Here, **111** was derived from *p*-cresol by the Reimer–Tiemann reaction.[91]



111 **112**

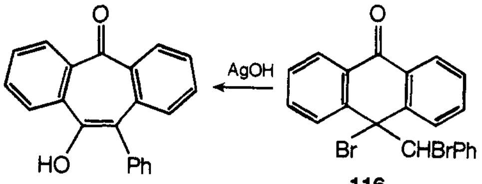
Another ring expansion that has found some use for the synthesis of troponoids has been patterned on the synthesis of eucarvone (**115**) from carvone hydrobromide (**113**)[92] (which may be viewed as an intramolecular nucleophilic substitution of bromine by the enolate carbon in the enol form of **113**). When one of the geminal methyl groups is replaced by hydrogen, the resulting cycloheptadienone may, in fact, be oxidized to the corresponding troponoid.[91] Such a procedure has been used in the synthesis of colchicine.[91]



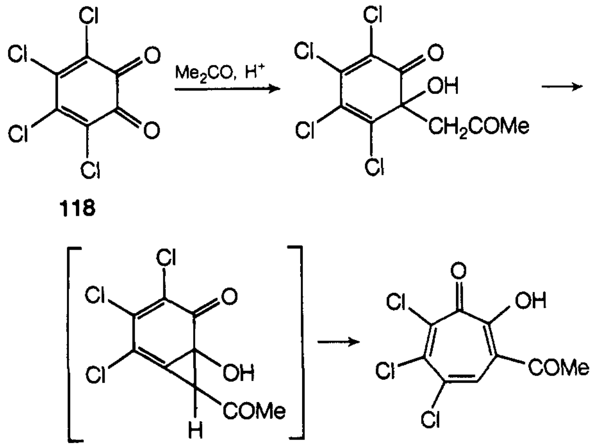
113 **114** **115**

Under carefully controlled conditions, intermediates of the type **114** may sometimes be isolated.[93]

Other, though not very versatile, ring expansions to troponoids are also available. That of **116** into **117** has long been known.[94] Another one occurs when tetrachloro-*o*-benzoquinone (**118**) is treated with acetone in an acidic medium to give **119**.[95] It is believed[95] that aldol condensation occurs, followed by dehydrochlorination and ring expansion. Finally, ring expansion of the diketo- (**120a,b**) or ketobromohydrins (**120c**) during treatment with zinc in acetic acid gave 2,3-benzotropolones **121** in yields ranging from 55 to 70%.[96] Quinols were also obtained as byproducts. The mechanism should be quite complex, and it has been suggested[96] that electrons are transferred from the metal surface to **120** in the first step.



117 **116**



118 **119**

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[90] E. E. van Tamelen and G. T. Hildahl, *J. Amer. Chem. Soc.*, **78**, 4405 (1956).

[91] J. Schreiber, M. Pesaro, W. Leimgruber, and A. Eschenmoser, *Helv. Chim. Acta*, **41**, 2103 (1958).

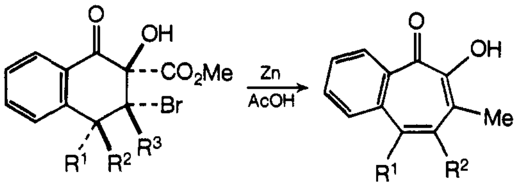
[92] A. von Bayer, *Ber.*, **27**, 810 (1894); **31**, 2067 (1898); E. J. Corey, H. J. Burke, and W. H. Remers, *J. Amer. Chem. Soc.*, **78**, 180 (1956).

[93] E. E. van Tamelen, J. McNary, and F. A. Lornitzo, *J. Amer. Chem. Soc.*, **79**, 1231 (1957).

[94] J. W. Cook, *J. Chem. Soc.*, 2160 (1926); 58 (1928).

[95] G. O. Schenck, B. Brahler, and M. Cziesla, *Angew. Chem.*, **68**, 247 (1956).

[96] G. Read and V. M. Ruiz, *Chem. Commun.*, 735 (1969).



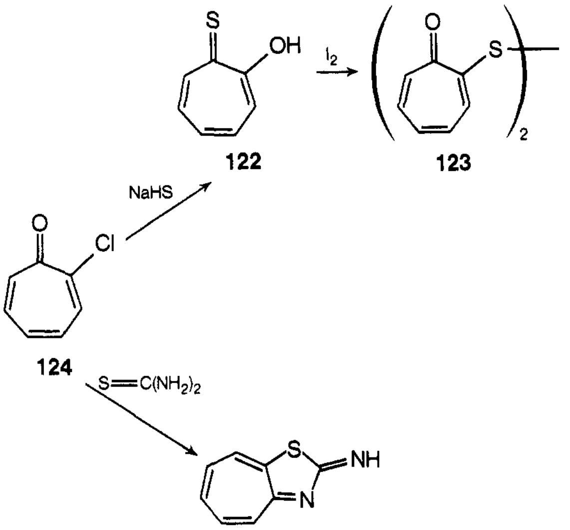
120 **121**

a, $R^1,R^2 = O$; $R^3 = H$
b, $R^1,R^2 = O$; $R^3 = Me$
c, $R^1 = H$; $R^2 = OH$; $R^3 = Me$

B. Other Species

1. Cycloheptatrienethiones and Cycloheptatrieneselenones

2-Mercaptotropone (**122**) (shown here in the thiono form, while a discussion of tautomerism in such compounds is delayed to section IV.B.1) has long been known. It can be easily obtained by the treatment of a tropone derivative carrying a displaceable substituent at C(2), such as 2-chlorotropone (**124**), with sodium hydrogen sulfide.[97a]



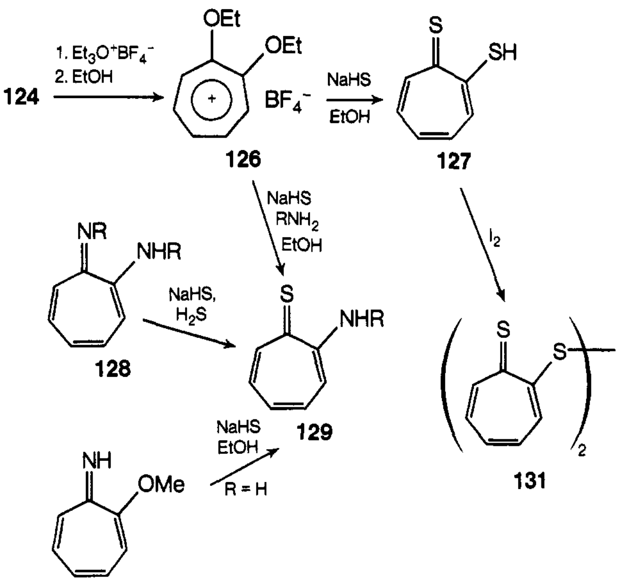
122 **123** **124** **125**

Ditroponyl disulfide (**123**) was obtained from **122** by the standard procedure for the oxidation of thiols, *i.e.*, treatment with iodine.[97a] By this route 2-mercaptoisopropyltropones were also obtained.[97b]

When thiourea is used, **124** gives **125**.[97c] Reactions of this type will be treated in detail in section V.A.2.

A variety of aminothiotropones (**129**) have been prepared along the routes indicated in Scheme XVI. The one from 1,2-diethoxytropenylium ion (**126**), which is readily obtained from 2-chlorotropone and triethyloxonium fluoborate followed by treatment with ethanol,[98] is distinctly simpler than the other ones which require less easily available compounds such as aminotroponeimines (**128**)[99] or 2-methoxytroponeimine (**130**).[100]

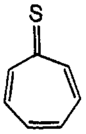
SCHEME XVI



126 **127** **128** **129** **130** **131**

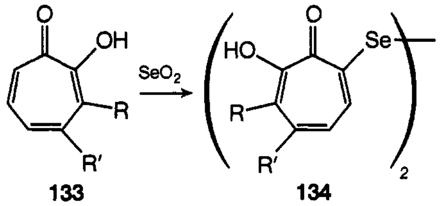
Dithiotropolone (**127**) has been obtained from **126** and sodium hydrogen sulfide.[98] Working under nitrogen, **127** may be oxidized to the disulfide **131** with iodine.[98] Small amounts of **127** have also been obtained by reacting tropolone with P_4S_{10} alone or in the presence of metal ions.[101]

2,3:6,7-Dibenzothiotropone is stable,[101b] while thiotropone (**132**) has been described as an extremely unstable liquid which has been only poorly characterized.[101c] Thiotropone has been recently trapped as a stable palladium complex on treatment of methylene chloride solutions of thiotropone with palladium dichlorodibenzonitrile.[101d] Thiotropone has also been shown to undergo facile [8 + 2] cycloadditions, involving the sulfur atom, with several typical dienophiles.[101d]



132

As regards cycloheptatrieneselenones, it has only been reported that some tropolone derivatives (**133**) react with selenium dioxide to give diselenides (**134**).[102]



133 **134**

R = H, Me, *i*-Pr; R' = H or Br

Ditropenyl selenide has been prepared.[103] This compound might be a precursor for the synthesis of selenotropone.

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[97] (a) T. Nozoe, M. Sato, and K. Matsui, *Proc. Jap. Acad.*, **29**, 22 (1953); *Sci. Rep. Tohoku Univ., Ser. 1*, **37**, 211 (1953); (b) T. Nozoe and K. Matsui, *Bull. Chem. Soc. Jap.*, **34**, 616 (1961); (c) T. Nozoe, *Fortschr. Chem. Org. Naturst.*, **13**, 287 (1955).

[98] (a) C. E. Forbes and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 6884 (1968); (b) **92**, 2297 (1970).

[99] W. R. Brasen and R. E. Benson, *J. Amer. Chem. Soc.*, **83**, 3135 (1961).

[100] N. Soma, J. Nakazawa, T. Watanabe, Y. Sato, and G. Sunagawa, *Chem. Pharm. Bull.*, **13**, 819 (1965); *Chem. Abstr.*, **63**, 13143d (1965).

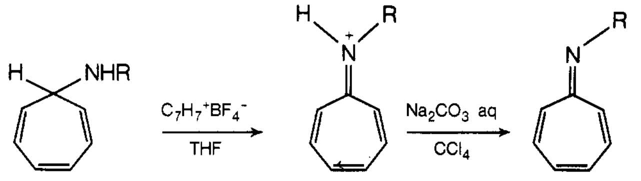
[101] (a) J. P. Fackler and E. L. Muetterties, unpublished, quoted in ref 98b; (b) A. Schönberg and E. Frese, *Chem. Ber.*, **101**, 701 (1968); (c) H. Hartmann and R. Mayer, German (East) Patent 73753 (1970); *Chem. Abstr.*, **74**, P533025 (1971); (d) R. Cabrino, G. Biggi, and F. Pietra, to be published.

[102] E. Ebe and S. Matsumoto, *Sci. Rep. Tohoku Univ., Ser. 1*, **38**, 308 (1954).

[103] A. E. Kemppaineu and E. L. Comper, Jr., *J. Chem. Eng. Data*, **11**, 588 (1966).

2. Cycloheptatrienimines and Cycloheptatrienaminoimines

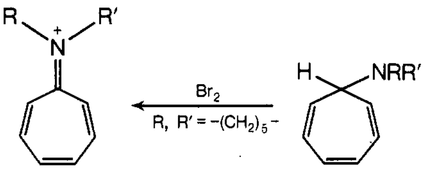
N-*n*-Propyltropenylidenimine (**137**, R = *n*-Pr) has been obtained in CCl_4 solution *via* hydride abstraction by tropenylium tetrafluoborate from the tropylideneamine **135** followed by careful treatment with a base of the intermediate *N*-*n*-propyltropenylidenimmonium fluoborate **136**.[104] Evaporation of the solvent led to immediate polymerization of the imine **137** (R = *n*-Pr). Similar immonium salts, like **136** (R = H, C_7H_7, Me) and **138** (R = R′ = Me, Et, $-(CH_2)_5-$), have been prepared by substantially the same method from the appropriate amines **139**.[104,105] It was thus possible to obtain in solution the parent compound **137** (R = H).[105]



135 **136** **137**

R = *n*-Pr

Also, **139** (R, R′ = $-(CH_2)_5-$) has been oxidized to **138** (R, R′ = $-(CH_2)_5-$) with bromine in 50% yield.[106]



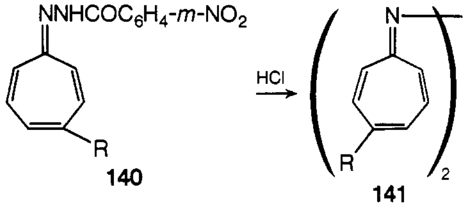
138 **139**

Amines of the types **135** and **139** can be easily obtained in high yield from the reaction of tropenylium salts with primary or secondary amines, respectively.[106] When the tropenylium salt carries a substituent that, like chlorine, is easily displaced as an anion, secondary amines lead to immonium salts of the type **138**, usually in excellent yield.[107,108] An immonium salt of type **136** (R = C_7H_7) was also obtained, albeit in a very low yield, by photolysis of tropenyl azide.[109]

Here may be included also tropone oximes,[110] semicarbazones,[111] and arylhydrazones.[110b,111] These can often, though not always (see section V.A.1.c), be obtained by treating a tropone with the appropriate ketone reagent.

The reaction of tropones with a number of strongly electrophilic isocyanates is a good synthetic entry to cycloheptatrienimines **137** in which R is an electron-attracting group.[112] This method has been utilized with trichloroacetyl isocyanate and chlorosulfonyl isocyanate with 60% yields.[112] These reactions are believed to proceed by nucleophilic attack of the tropone oxygen on the carbon of the isocyanate group.[112] The use of excess isocyanate led sometimes to further reaction of the cycloheptatrienimine.[112]

Also tropone azines (**141**), which have been synthesized from the *m*-nitrobenzoylhydrazones 140,[113] are of the structural type **137**.



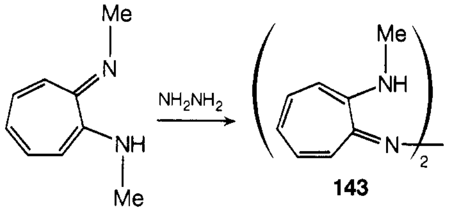
140 **141**

R = H, Ph

Aminotroponeimines (**128**) have already been mentioned in the preceding section. They can be generally obtained by the treatment of either diethoxytropenylium fluoborate (**126**)[98] or the tetrafluoro compound **88**[114] with amines. The former route[98] is generally preferable because **126** is easier to obtain than **88**.

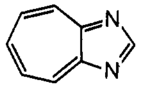
Reduction of oximes also gave aminotroponeimines in some cases.[115]

Reaction of **142** with hydrazine gave **143**[114] which is also closely related structurally to aminotroponeimines. This is a general method for the synthesis of compounds of the type **143** and works well also with diamines in the place of hydrazine.[114]

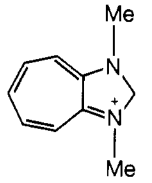


142 **143**

Formally related to aminotroponeimines are also 1,3-diazaazulenes (**144**) and 1,3-diazaazulenium ions, such as **145**.[114] General methods for the synthesis of 1,3-diazaazulenes will be discussed in section V.A.2.



144



145

3. Heptafulvenes

Two recent reviews dealing in part with heptafulvenes have appeared.[116]

The parent compound, heptafulvene (**147**), has been obtained by several methods such as Hofmann elimination at room temperature *in vacuo* from the ammonium

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(104) N. L. Bauld and Y. S. Rim, *J. Amer. Chem. Soc.*, **89**, 6763 (1967).

(105) H. J. Dauben, Jr., and D. F. Rhoades, *J. Amer. Chem. Soc.*, **89**, 6764 (1967).

(106) C. Jutz, *Chem. Ber.*, **97**, 2050 (1964).

(107) E. Haug and B. Föhlisch, *Z. Naturforsch. B*, **24**, 1353 (1969).

(108) A. Krebs, *Tetrahedron Lett.*, 1901 (1971).

(109) D. S. Wulfman, L. N. McCullagh, and J. J. Ward, *Chem. Commun.*, 220 (1970).

(110) (a) T. Nozoe, T. Mukai, J. Minegishi, and T. Fujisawa, *Sci. Rep. Tohoku Univ., Ser. 1*, **37**, 388 (1953); (b) T. Mukai, *Bull. Chem. Soc. Jap.*, **33**, 238 (1960).

(111) T. Nozoe, T. Mukai, K. Takase, and T. Nagase, *Proc. Jap. Acad.*, **28**, 477 (1952); T. Nozoe, T. Mukai, and J. Minegishi, *ibid.*, **27**, 419 (1951).

(112) L. A. Paquette and N. Horton, *Tetrahedron Lett.*, 2289 (1968).

(113) G. Sunagawa and N. Soma, Japan Patent 12674 (1962); *Chem. Abstr.*, **60**, 4064h (1964).

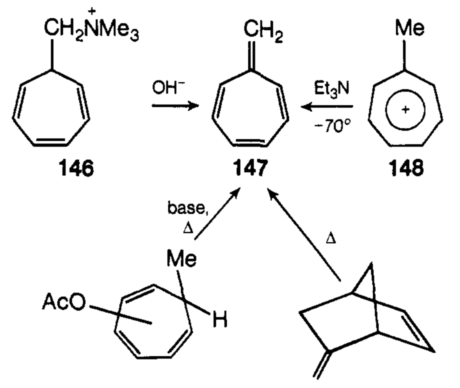
(114) W. R. Brasen, H. E. Holmquist, and R. E. Benson, *J. Amer. Chem. Soc.*, **83**, 3125 (1961).

(115) T. Nozoe, M. Sata, R. Matsui, and T. Masuda, *Proc. Jap. Acad.*, **29**, 565 (1953).

(116) E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968); H. Prinzbach, *Pure Appl. Chem.*, **28**, 287 (1971).

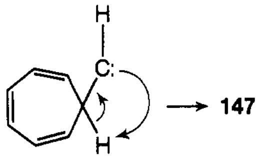
compound **146**,[117] proton abstraction by triethylamine from methyltropenylium ion **148**,[118] pyrolysis, in very poor yield, of **149**,[119a] and pyrolysis in the gas phase in the presence of bases of a mixture of the three isomeric acetoxymethylcycloheptatrienes shown in Scheme XVII.[119b]

SCHEME XVII



149

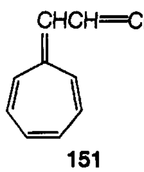
Heptafulvene is also formed, together with benzene, acetylene, and cyclooctatetraene, in the thermal or photochemical decomposition of cycloheptatrienyldiazomethane.[120] A reasonable mechanism for this reaction is decomposition of the diazoalkane to give the carbene **150** which then rearranges to **147**.[120]



150

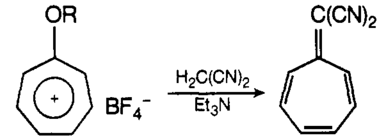
Heptafulvene is a very labile compound which easily polymerizes, even at −80°, in concentrated solutions.[117] Recently, however, the above-mentioned pyrolysis of the mixture of acetoxymethylcycloheptatrienes (Scheme XVII), with collection of the pyrolyzates at −70° followed by purifications at low temperature, allowed the preparation of deep-red crystalline **147** which is stable at −70° but polymerizes in a few minutes at 20°.[119b] At moderately low temperatures it was possible to obtain nmr and ir spectra[119b] (section IV.B.3). Less labile, or even stable, heptafulvenes were obtained by either replacing the methylene hydrogens with strongly electron-attracting groups or inserting the methylene carbon into a conjugated chain or cycle as shown by subsequent examples.

General synthetic entries to heptafulvenes and related compounds can be appropriately divided according to the nature of the starting key compound. Tropenylium salts are important starting materials. Besides the method of Scheme XVII (which has been adapted also to the synthesis of the unstable 8-vinylheptafulvene **151**[121]), the electrophilicity of the seven-membered ring of tropenylium ions has been successfully exploited in this direction.



151

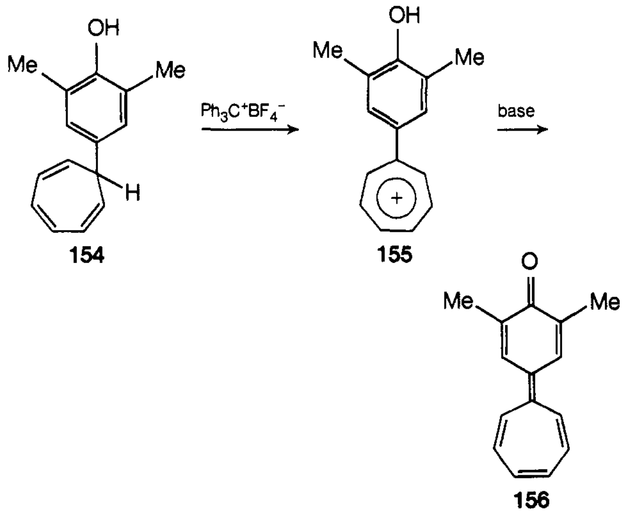
Both active hydrogen compounds and electron-rich aromatics have been used as nucleophiles. Thus, ethoxy[122a] (**152a**) and a methoxytropenylium fluoborate[122b] (**152b**) (which are easily obtained by the O-alkylation of tropone with the appropriate trialkyloxonium fluoborate[122]) react with 1 equiv of dicyanomethane and triethylamine to give the stable 8,8-dicyanoheptafulvene (**153**) in 60% yield. A number of different solvents, such as 1,2-dichloroethane,[122a] dichloromethane,[122b] or acetonitrile[122b] are appropriate when working at reflux.[122b] If the reagents are mixed together at 0°, products of the addition of the carbanion to the tropenylium ion are obtained instead.[122b] However, if the mixture is refluxed, such addition products change into **153**.[122b]



152a, R = Et
b, R = Me

153

Turning to aromatic compounds as nucleophiles, 2,6-dimethylphenol has been treated with tropenylium ion to give **154**.[123] Deprotonation with trityl fluoborate gave **155** which, upon action of a base gave **156**.[123] At least formally, **156** may be considered an heptafulvene derivative. Other similar cases have also been reported.[124] Similar methods were also used to synthesize several heptanonafulvalenes.[124d] This method has also been adapted to the synthesis of the furan derivative **160**.[124a] Thus, compound **157**, obtained from 2-methylresorcinol and tropen-



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(117) W. von E. Doering and D. W. Wiley, *Tetrahedron*, **11**, 183 (1960).

(118) C. Jutz, *Chem. Ber.*, **97**, 2050 (1964).

(119) (a) D. S. Matteson, J. J. Drysdale, and W. H. Sharkey, *J. Amer. Chem. Soc.*, **82**, 2853 (1960); (b) M. Neuenschwander and W. K. Schenk, *Chimia*, **26**, 194 (1972).

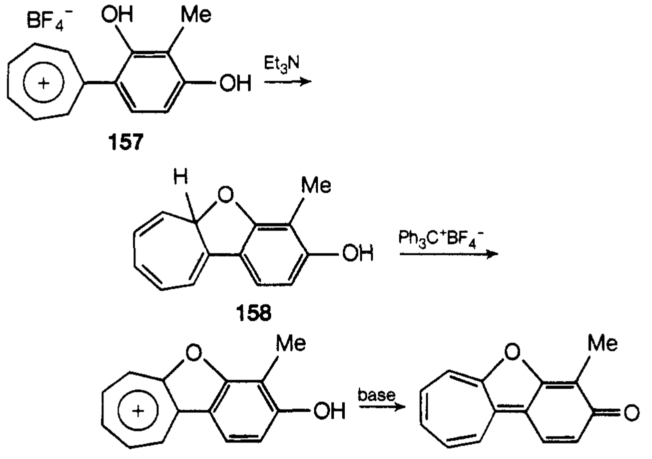
(120) H. E. Zimmerman and L. R. Sousa, *J. Amer. Chem. Soc.*, **94**, 834 (1972).

(121) D. J. Bertelli, C. Golino, and D. L. Dreyer, *J. Amer. Chem. Soc.*, **86**, 3329 (1964).

(122) (a) K. Hafner, H. W. Riedel, and M. Danielisz, *Angew. Chem.*, **75**, **344** (1963); (b) E. Haug and B. Fölish, *Chem. Ber.*, **104**, 2670 (1971); (c) E. Haug and B. Fölish, *ibid.*, **104**, 2338 (1971).

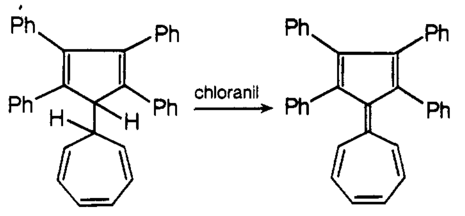
(123) R. van Helden, A. P. ter Borg, and A. F. Bickel, *Recl. Trav. Chim. Pays-Bas*, **81**, 599 (1962).

(124) (a) P. L. Pauson, G. R. Proctor, and R. Watson, *J. Chem. Soc. C*, 2399 (1971); (b) K. Takahashi, N. Nirata, and K. Takase, *Tetrahedron Lett.*, 1285 (1970); (c) R. West, K. Kusuda, and V. N. M. Rao, *Synthesis*, **4**, 553 (1972); (d) P. J. Garratt and K. A. Knapp, *Chem. Commun.*, 1084 (1971); M. Rabinovitz and A. Gazit, *Tetrahedron Lett.*, 3523 (1972).



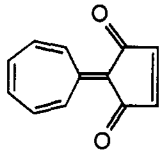
157 158 159 160

ylium ion, was cyclized to **158** with Et_3N. Treatment of **158** with trityl fluoborate led to the tropenylium ion derivative **159** which, finally, gave the desired compound **160** upon action of a base.[124a] In other cases the transformation of a cycloheptatriene into an heptafulvene derivative was effected with an oxidizing agent such as chloranil. For example, compound **161**, obtained by addition of tetraphenylcyclopentadienylsodium) to tropenylium ion, was oxidized with chloranil to the sesquifulvalene derivative **162**.[125]

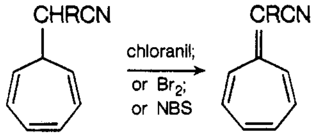


161 162

The heptafulvalene derivative **163** was synthesized along similar lines from cyclopentene-3,5-dione and tropenylium ion.[126] Bromine or *N*-bromosuccinimide have also been used to dehydrogenate cycloheptatrienes as shown here for the transformation of **164** into **165**.[122]



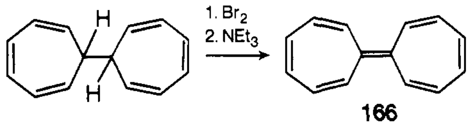
163



164 165

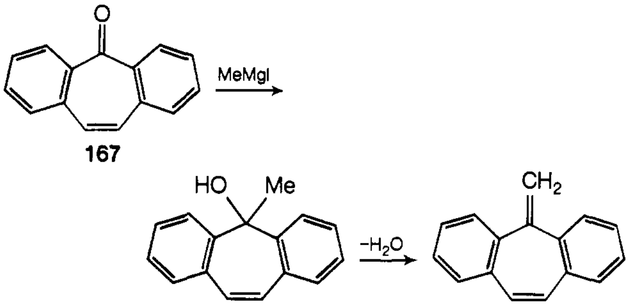
These methods failed with the adduct from cyclopentadienylsodium and tropenylium ion.[127] The desired sesquifulvalene was later obtained by gas-phase pyrolysis in the presence of bases of acetoxycyclopentadienylcycloheptatrienes[119b] by the method used (Scheme XVII) for heptafulvene. Purification gave crystalline sesquifulvalene which is thermally less labile than heptafulvene.[119b]

Reduction of tropenylium ions to cycloheptatriene dimers, followed by dehydrogenation, is another general synthetic entry to heptafulvalenes. This is illustrated here for heptafulvalene itself (**166**).[117,128]

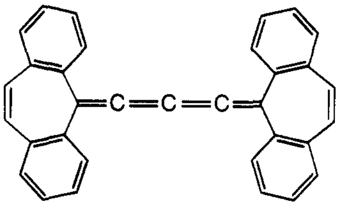


166

Heptafulvenes are accessible from certain tropones. A widely used method involves the addition of a suitable organomagnesium compound to the carbonyl group followed by dehydration. This is the case of 2,3:6,7-dibenzotropone (**167**) and methylmagnesium iodide. The alcohol **168** was easily dehydrated to 2,3:5,6-dibenzoheptafulvene (**169**).[129] This method was adapted to obtain dibenzo analogs of compound **156**[124a] and cumulenes, like **170**.[130] As a final remark about this method, it must be mentioned that dehydration is sometimes difficult to accomplish and may require resource to pyrolysis of the acetate derivative of the alcohol.[116]

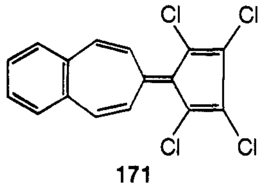


167 168 169



170

Tropones can also be condensed with certain carbanions to give heptafulvene derivatives. Such is the case of compound **171** which was obtained from tetrachlorocyclopentadiene and 4,5-benzotropone.[131] With this carbanion tropone gave only fulvenes,[126b] but with tetramethyl cyclopentadiene-1,2,3,4-tetracarboxylate condensation to the sesquifulvalene **172** took place.[132] Condensation of tribenzocycloheptatrienone with the optically active phosphonium ylide **173** afforded optically active **174**.[133]



171

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(125) H. Prinzbach, *Angew. Chem.*, **73**, 169 (1961).

(126) (a) Y. Kitahara, I. Murata, and T. Azano, *Bull. Chem. Soc. Jap.*, **37**, 924 (1964); (b) *ibid.*, **37**, 1399 (1964).

(127) H. Prinzbach and W. Rosswog, *Angew Chem.*, **73**, 543 (1961).

(128) W. von E. Doering, *Chem. Abstr.*, **59**, 3828 (1963).

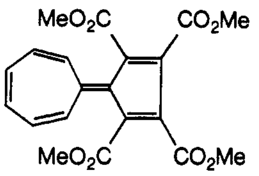
(129) E. D. Bergmann and R. Ikan, *J. Org. Chem.*, **28**, 3341 (1963).

(130) W. Ried, W. Schlegelmilch, and St. Piesch, *Chem. Ber.*, **96**, 1221 (1963).

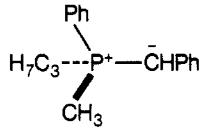
(131) Y. Kitahara, I. Murata, and S. Katagiri, *Angew. Chem., Int. Ed. Engl.*, **4**, 353 (1965).

(132) G. Seitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 82 (1967).

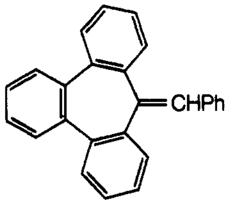
(133) H. J. Bestmann and J. Lienert, *Angew. Chem., Int. Ed. Engl.*, **8**, 763 (1969).



172

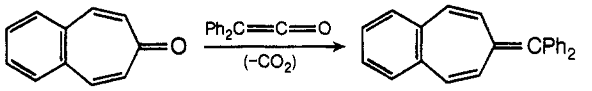


173



174

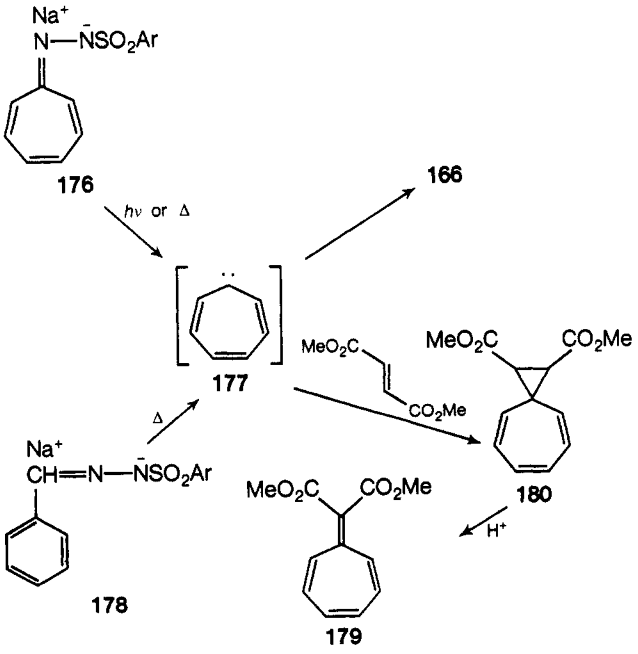
Some tropone derivatives react with diphenylketene to give heptafulvene derivatives. This is the case of **175**.[134] With tropone itself cycloaddition reactions are obtained instead (see section V).



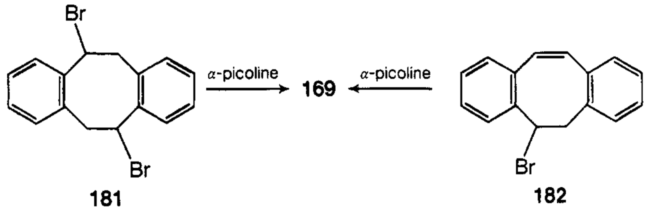
175

Heptafulvalene (**166**) or heptafulvene derivatives were also obtained *via* cycloheptatrienylidene (**177**) (generated by either photolysis or pyrolysis of the sodium salt of tropone tosylhydrazone (**176**) or by flash pyrolysis of the sodium salt of benzaldehyde tosylhydrazone (**178**).[135] Thus, when **177** was generated in the presence of a carbene trap like methyl fumarate, **180** was obtained. Treatment of **180** with acids gave the heptafulvene derivative **179**.[135] In the absence of methyl fumarate, the product of formal dimerization of **177**, heptafulvalene (**166**), was obtained instead.

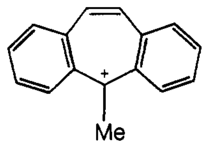
SCHEME XVIII



A further synthetic entry into heptafulvene derivatives, which is probably of limited scope, however, is *via* ring contraction during base-induced dehydrobromination of either **181**[136a] or **182**[136b] whereby **169** was obtained.[136]

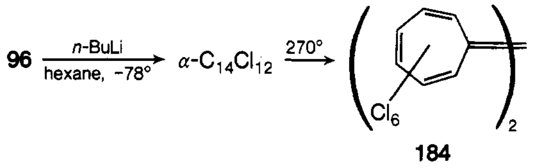


Among various plausible routes for such rearrangements, an appealing one is *via* the tropenylium-type ion **183**. Also of limited use, but interesting conceptually, is the synthesis of some heptafulvene derivatives by photorearrangement of some (7-propenylidene)norbornenes or -norbornadienes.[136c]

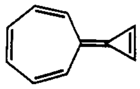


183

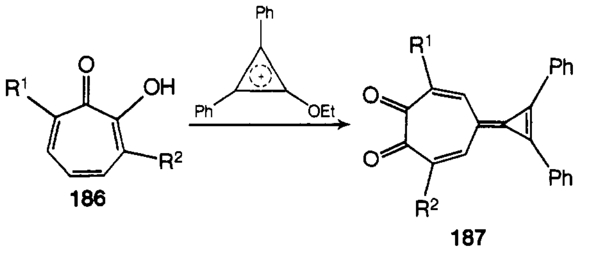
Perchloroheptafulvalene (**184**), which is quite stable in contrast with heptafulvalene (**166**), has been synthesized from perchlorocycloheptatriene (**96**) along the route indicated here.[137a] The structure of the isomer α-$C_{14}Cl_{12}$ has not been reported.[137a] Perchloroheptafulvene is also stable, in contrast with heptafulvene.[137b]



Finally, in an effort to approach the structure of heptatriafulvalene (**185**), some tropolones (**186**) have been allowed to react with diphenylethoxycyclopropenium ion. The unsubstituted[138a] and halogen-substituted[138b] di-



185



$R^1 = R^2 = H, Br, I$
$R^1 = H; R^2 = Br$
$R^1 = H; R^2 = I$

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[134] C. Jutz, I. Rommel, I. Lengyel, and J. Feeney, *Tetrahedron*, **22**, 1809 (1966).

[135] W. M. Jones and C. L. Ennis, *J. Amer. Chem. Soc.*, **89**, 3069 (1967); **91**, 6391 (1969); R. C. Joines, A. B. Turner, and W. M. Jones, *ibid.*, **91**, 7754 (1969); T. Mukai, T. Nakazawa, and K. Isobe, *Tetrahedron Lett.*, 565 (1968).

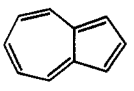
[136] (a) A. C. Cope and S. W. Fenton, *J. Amer. Chem. Soc.*, **73**, 1673 (1951); (b) A. C. Cope and R. D. Smith, *ibid.*, **77**, 4596 (1955); (c) H. Prinzbach, H. J. Herr, and W. Regel, *Angew. Chem.*, **84**, 113 (1972); H. Prinzbach and H. Sauter, *ibid.*, **84**, 115 (1972).

[137] (a) M. Ishimori, R. West, B. K. Teo, and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 7101 (1971); (b) A. Roedig, M. Försch, B. Haveaux, and D. Scheutzov, *Tetrahedron Lett.*, 2613 (1972).

[138] (a) K. Takahashi and K. Takase, *Tetrahedron Lett.*, 2227 (1972); (b) K. Takahashi, T. Fujita, and K. Takase, *ibid.*, 4507 (1971).

phenylheptatriafulvalene-3,4-diones **187** have been so obtained.

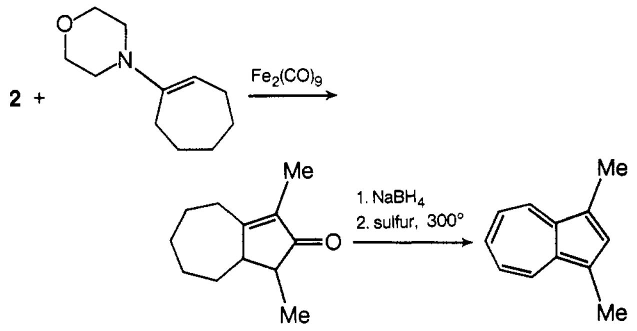
Azulene (**188**) and its derivatives may be discussed here as special heptafulvene derivatives. Admittedly, this is a purely formal analogy.



188

Synthetic methods for azulenes have been reviewed some time ago.[139] A new important synthesis of azulenes *via* dibromo ketones **2** and cycloheptanone enamines in the presence of $Fe_2(CO)_9$ has been recently reported (Scheme XIX).[140a] The first stage occurs with practically quantitative yield. The second stage has been accomplished by standard procedures (Scheme XIX).[140a]

SCHEME XIX

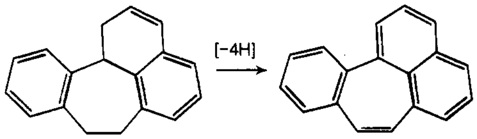


Some azulene derivatives are obtainable by photorearrangement of (7-propenylidene)norbornadienes followed by chemical oxidation of the photoproducts.[140b]

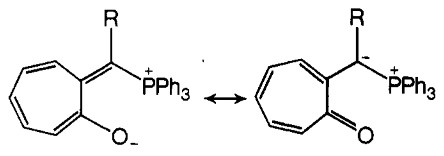
Formation of azulenes as minor by-products has been recently observed in the rearrangement of bicyclo-[1.1.0]butanes induced by transition metal complexes.[141a]

Recent attempts to synthesize 1,2-diazaazulenes failed.[141b] Moreover, it has been said[141b] that previous claims for the preparation of such compounds[141c] are not supported by structural proofs.

Within the same formalism utilized above, both compound **190**, which was obtained by dehydrogenation of **189** with dicyanodichlorobenzoquinone,[142] and compound **191**, obtained by the reaction of 2-chlorotropone with phosphonium ylides,[143] may be included here. Some cycloadditions of 8-oxoheptafulvene, which also is formally related to heptafulvene, will be discussed in section V.F.



189 **190**



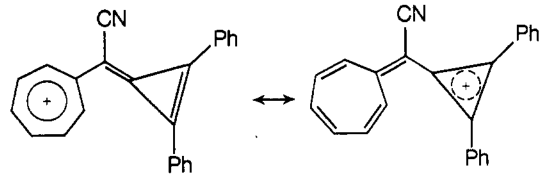
191

R = H, Me, CO_2Et, CN

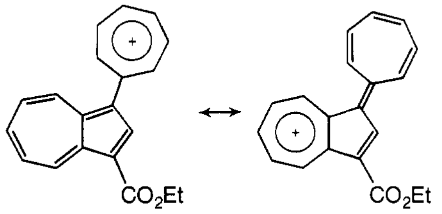
4. Tropenylium Salts

Tropenylium salts can be conveniently arranged into three classes:[144] (1) the halides, which are colored, sublimable, and unstable to moisture; (2) the perchlorates, tetrafluoborates, and all other tropenylium salts of nonnucleophilic anions which sublime with difficulty, if at all, and are stable to air; (3) the tribromides, triiodides, triiodomercurates, and other similar stable salts which derive their color from the anion.[144]

Classification of a compound as a tropenylium species may be ambiguous sometimes. This is the case, for example, of compounds **138** and **192**.[145a] In the last case, it has been reported that the three-membered ring has appreciable positive character.[145a] X-Ray diffraction data show that the molecule is planar, both forms shown in **192** contributing equally.[145b] A similar ambiguity exists with **193**.[146]



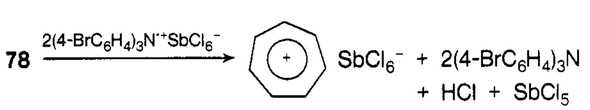
192



193

A relatively recent review on tropenylium salts is available[147] so that only more recent material is reviewed here, placed in perspective, however. Hydride abstraction from tropenylidenes by a variety of reagents is one of the most common routes to tropenylium salts. The standard route to tropenylium ion from cycloheptatriene and phosphorus pentachloride[58] has been described previously (Scheme XII), and various other cases have been dealt with in the last section. Such routes to tropenylium salts continue to be used.

In what is perhaps the most interesting recent synthesis of tropenylium ions, cycloheptatriene (**78**) or bitropenyl has been oxidized to tropenylium hexachloroantimomate (**194**) with the cation radical tris(*p*-bromophenyl)-



194

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(139) W. Keller-Schierlein and E. Heilbronner, ref 1b, pp 277–338.

(140) (a) R. Noyori, K. Yokoyama, S. Makino, and Y. Hayakawa, *J. Amer. Chem. Soc.*, **94**, 1772 (1972); (b) H. Prinzbach and H. J. Herr, *Angew. Chem.*, **84**, 117 (1972).

(141) (a) P. G. Gassmann and T. Nakai, *J. Amer. Chem. Soc.*, **93**, 5897 (1971); (b) C. V. Greco, F. C. Pellegrini, and H. A. Pesce, *J. Chem. Soc., Perkin Trans. 1*, 1623 (1972); (c) ref 1b, p 443.

(142) J. F. Muller, D. Cagniant, and P. Cagniant, *Tetrahedron Lett.*, 45 (1971).

(143) I. Kawamoto, T. Hata, Y. Kishida, and C. Tamura, *Tetrahedron Lett.*, 2417 (1971).

(144) K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *J. Amer. Chem. Soc.*, **84**, 3349 (1962).

(145) (a) M. Oda, K. Tamate, and Y. Kitahara, *Chem. Commun.*, 347 (1971); (b) C. Kabuto, M. Oda, and Y. Kitahara, *Tetrahedron Lett.*, 4851 (1972).

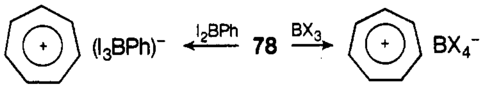
(146) T. Nozoe, T. Toda, and A. Yamamouchi, *Chem. Commun.*, 1675 (1968).

(147) G. D. Kolomnikova and Z. N. Parnes, *Russ. Chem. Rev.*, **36**, 735 (1967).

amminium hexachloroantimomate.[148] These results parallel those for the anodic oxidation of bitropenyl.[149] To the contrary, oxidation of cycloheptatriene (**78**) with PCl_5 gave mainly bitropenylium ion, $C_7H_7^+{-}C_7H_7^+$.[150]

Oxidation of cycloheptatriene with ceric ammonium nitrate gives a mixture of benzaldehyde, benzene, and carbon monoxide through tropenylium ion as an intermediate.[151] Tropenylium ion formation must occur *via* attack by the oxidizing agent at double bonds rather than at carbon–hydrogen bonds of cycloheptatriene. In fact, there is no kinetic primary deuterium isotope effect with deuterated cycloheptatriene.[152a] Also the oxidation of cycloheptatriene to tropenylium ion with 2,3-dichloro-5,6-dicyanobenzoquinone has been studied in detail.[152b]

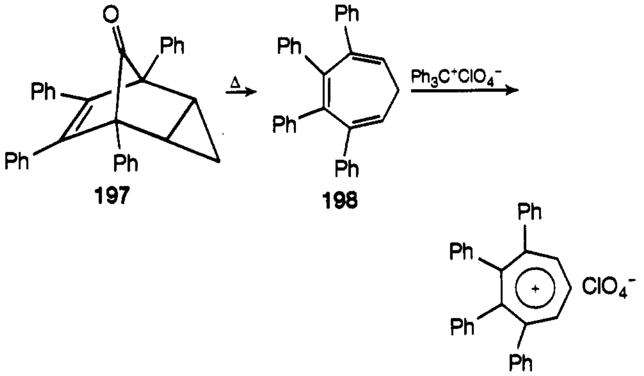
Boron compounds have been recently employed to abstract hydride from tropenylidene. Thus, with boron halides the corresponding tropenylium tetrahaloborates (**196**) have been obtained.[153] With diiodophenylborane, tropenylium triiodophenylborate (**195**) has been obtained.[154] Considerable interest was aroused from these complex anions.[153,154]



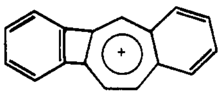
195 **196**

X = Cl, Br, I

The popular method of hydride abstraction from cycloheptatrienes by triphenylmethyl salts such as the perchlorate,[155] tetratrafluoborate, or hexachloroantimonate[156a] [there is evidence that with perchlorotriphenylcarbonium hexachloroantimoniate and cycloheptatriene a two-step process is involved;[156b] the first step is viewed as an electron transfer, and the second as a hydrogen shift: (1) $(C_6Cl_5)_3C^+ + C_7H_7 \rightarrow (C_6Cl_5)_3C\cdot + C_7H_7\cdot^+$; (2) $(C_6Cl_5)_3C\cdot + C_7H_7\cdot^+ \rightarrow (C_6Cl_5)_3CH + C_7H_6^+$] has found several interesting applications. One such case is the synthesis of 1,2,3,4-tetraphenyltropenylium perchlorate (**199**) from 2,3,4,5-tetraphenyl-7-tropenylidene (**198**).[157a] The latter compound was synthesized by Diels–Alder cycloaddition of tetraphenylcyclopentadienone with cyclopropene followed by thermal decarbonylation of the resulting cycloadduct **197**.[157a] The hydride abstraction method has also been adapted to synthesize compound **200** which may be regarded as a homobiphenylene cation in which one of the phenyl rings of biphenylene is replaced by tropenylium ions.[158a] A similar compound, lacking the benzene ring fused to the seven-membered cycle, has also been prepared along similar lines.[158b] By the same principle, dithienotropenylium ions **201** and **202**[159] and benzoyltropenylium ion[160] also have been synthesized.



197 **198** **199**



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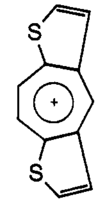

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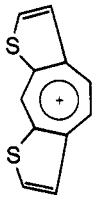
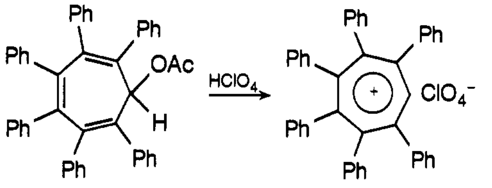


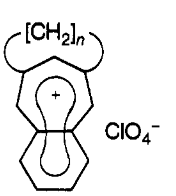
202

Tropenylidenes carrying a substituent that, like chlorine or hydroxyl, can leave with its bonding electrons by the aid of an acid constitute another common source of tropenylium ions. This method has been used to prepare the interesting heptachlorotropenylium ion (**95**) from octachlorocycloheptatriene (**96**) and aluminum trichloride in methylene chloride.[86] Even Brønsted acids have been used sometimes. This is the case of the preparation of hexaphenyltropenylium ion (**204**) from hexaphenyltropylidene acetate (**203**) and concentrated perchloric acid[157a]

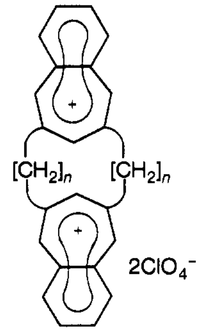


203 **204**

and of some dibenzotropenylium salts.[157b] The synthesis of **203** involved cycloaddition of tetraphenylcyclopentadienone with 2,3-diphenylcyclopropenecarboxylic acid to give hexaphenylcycloheptatrienecarboxylic acid followed by decarboxylation of the latter with lead acetate.[157] This method was also adapted to the preparation of 2,7-polymethylene-4,5-benzotropenylium perchlorate **205**[161] and



205, *n* = 10, 12



206, *n* = 4, 5, 8

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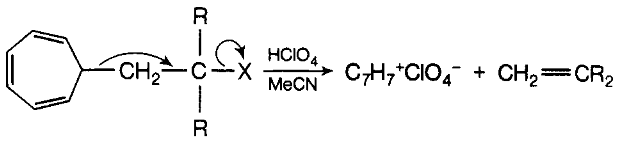
2,7-polymethylenebis-4,5-benzotropenylium perchlorates **206**[37] from the carbinols derived by hydride reduction of the appropriate polymethylene tropones shown in Scheme IX.

Usually,[147] compounds of type **207** dissociate to give tropenylium ions, as shown here, under solvolytic conditions.[162] Compound **208** is an exception, its acetolysis leading only to benzenoid compounds owing to contraction of the seven-membered ring.[163]



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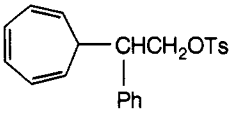


208

An important method for the preparation of substituted tropenylium ions consists of the alkylation of tropone or tropone derivatives with trialkyloxonium fluoborate. This method has already been mentioned before in two occasions: the preparation of 1,2-diethoxytropenylium (**126**)[98] and of methoxy- (**152b**)[122b] or ethoxytropenylium ions (**152a**).[122a] Also chlorotropenylium ions are versatile intermediates owing to the mobility of the halogen. Even this case has been already mentioned before when dealing with the preparation of cyclopeptatrienimmonium salts **138**.[104,105] Also alcohols, mercaptans, and active methylene compounds are able to replace chlorine from chlorotropenylium salts to give the corresponding tropenylium salts derivatives.[107]

In order to study the role of a very stable carbonium ion as a reaction intermediate in hydrolysis of ketals, the hydrolysis of tropone diethyl ketal has been kinetically investigated.[164]

Cycloheptatrienylidene (**177**) might also be classified here because there is evidence that it has largely tropenylium ion character.[165]

Perhaps the most interesting results of recent research concerning tropenylium ions have been obtained in mass spectrometry. Generation of tropenylium ions from a variety of compounds under electron impact classifies, in fact, among the most intriguing and exciting reactions found in mass spectrometry. To the list[147] of compounds giving tropenylium ion under electron impact, heterocyclic organoboron compounds,[166] and, perhaps, also chloroprene dimers[167] have to be added.

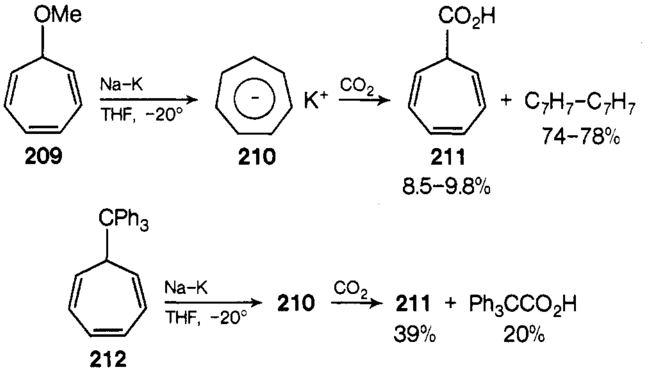
Many studies of both mass spectrometry on labeled compounds[168] or of the application of the quasi-equilibrium theory[169] and ion cyclotron spectrometry[170] have been reported. They deal with detailed mechanistic questions about formation of tropenylium ion.

It must be noticed, however, that benzyl derivatives do not always ring expand to give tropenylium ion under electron impact. For example, the $NH_2C_7H_6^+$ ion, generated by electron impact from either benzylamine or *p*-aminotoluene, was observed to lose first a proton and then HCN with preservation of the six-membered ring.[171]

Formation of tropenylium ion from toluene[172a] or ethylbenzene[172b] have been observed in gas-phase radiolysis experiments.

5. Tropenide Salts

The synthesis of potassium tropenide (**210**) has been accomplished along two different routes.[173] The first one involves cleavage of either 7-methoxy- (**209**) or 7-triphenylmethyl-1,3,5-cycloheptatriene (**212**) by Na-K alloy in tetrahydrofuran at −20°. Thus, a deep-blue solution (broad absorption centered at 750 nm) due to **210** has been obtained.[173] Structural proofs for **210** mainly rest on the results of discharging the color with carbon dioxide, **211** (8.5–9.8%), cycloheptatriene dimer (74–78%), and a trace of a neutral polymer having been obtained.[173] As C_7H_7–C_7H_7 should result from reaction between **209** and **210**, it is implied that **210** must have been formed in 75–80% yield.[173] In the case of **212**, addition of carbon dioxide led to **210** (39%), tritylcarboxylic acid (20%), a neutral polymer (different from that arising from **209**) in appreciable quantity, and some acidic polymer. The higher yield of **210** in this case has been attributed to the lack of a good leaving group on the starting material.[173]



The other route involves hydride abstraction from cycloheptatriene (**78**) by potassium benzyl suspended in toluene.[173] After carbonation, **211** (30%), $PhCH_2COOH$ (20%), and a considerable amount of polymeric materials (40%) have been obtained.[173] Competing polymerization of **78** always occurs and can only be minimized by slow addition of **78** to the base.[173]

The nmr spectrum of **210** has not yet been reported. However, as a further piece of evidence for the structure of **210**, it can be mentioned that prolonged reduction of **209** with sodium in tetrahydrofuran led to cycloheptatrienide dianion radical (see section II.C) which is thought to have arisen *via* **210** as an intermediate.[174]

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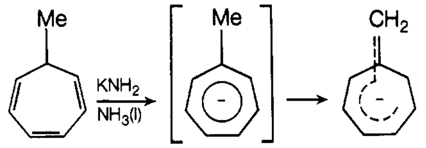
Cycloheptatriene randomly exchanges deuterium with potassium triethoxide in triethylcarbinol-*O-d*.[175] That tropenide anion (**210**) is involved in the exchange is suggested by the observation that 7,7-dideuteriocycloheptatriene exchanges deuterium in anhydrous dimethyl sulfoxide containing potassium triethoxide and triethylcarbinol at essentially the same rate as the uptake of hydrogen from the solvent by C(7) (predicted 6:7).[175]

Methyltropenide anion **213a** has been suggested as an intermediate in the transformation, induced by potassium amide, of 7-methylcycloheptatriene into **213b**.[176]

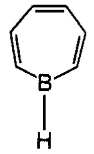


213a **213b**

The resonance energy of the tropenide anion has been estimated to be 0.8–1.1 β units (*i.e.*, about 22–27 kcal mol^{-1}, taking for β the value for benzenoid hydrocarbons) greater than in the case of cycloheptatriene.[173]

6. Heterocyclic Analogs

Comparatively little is known about the seven-membered heterocyclic analogs of the carbocyclic compounds dealt with in this review. Achieved syntheses concern boron and nitrogen heterocyclics. Although borepin (**214**), which is isolectronic with tropenylium ion, remains unknown,[177] some related compounds have been synthesized. Thus, the borinic acid **215**, obtained from *o,o*-dilithiobibenzyl and butyl borate, gave an anhydride which was dehydrogenated to the dibenzoborepinol (**216a**) by bromination with *N*-bromosuccinimide followed by treatment with sodium methoxide.[178] Lithium aluminum reduction of **216a** led to what is thought[178] to be **216b** as judged by the unstable complex with pyridine which has been isolated. This complex undergoes acid-catalyzed reversion to **216a**.[178]



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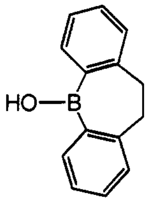

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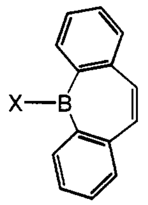
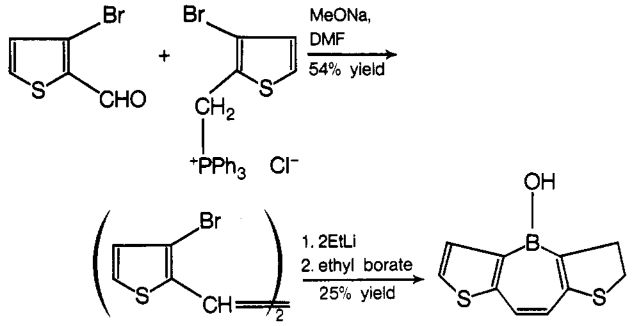


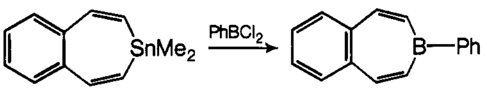
216a, X = OH
b, X = H

The dithienoborepinol **218** (which is more stable than **216a**) has also been synthesized.[179] 3-Bromo-2-thiophenaldehyde was allowed to react with 3-bromo-2-thenyltriphenylphosphonium chloride to give mainly the cis olefin **217**. This was separated from the trans isomer and then converted into **218** by the treatment with 2 equiv of ethyllithium followed by ethyl borate.[179]

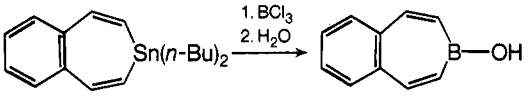


217 **218**

A potentially versatile synthesis of these boron compounds is from stannepins. Thus, 3,3-dimethyl-3-benzostannepin (**219**), obtained from *o*-diethynylbenzene and dimethyltin hydride, gave 3-phenyl-3-benzoborepin (**220**) in 50% yield on the treatment with phenylboron dichloride.[180] Use of boron trichloride in the place of phenylboron dichloride led to borepinols, however. This is the case of **221** which gave **222** by this procedure.[181]

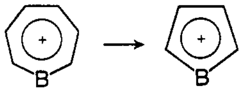


219 **220**



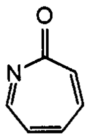
221 **222**

It has also been suggested that boratropenylium ion (**223**) is formed in the mass spectrometer under electron impact from either bis(dimethylamino)phenylborane,[182a] or other aminoboranes,[182b] and 2-phenyl-1,3,2-oxazaborolidines.[182c] Evidence for the decomposition of boratropenylium ion into **224** (a process analogous to the known decomposition of tropenylium ion into cyclopentadienyl cation[182d]) has also been presented.[182b]



223 **224**

A variety of azatropones with base structures **225** and **226** have been synthesized, whereas **227** is unknown. Its 4,5-benzo derivative dimerized on formation.[183b] The synthetic approach consisted of inserting a nitrogen atom into a *p*-quinone ring under Schmidt conditions followed by O-alkylation of the intermediate **228** with a trialkylox-



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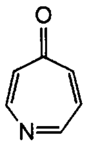

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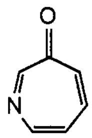

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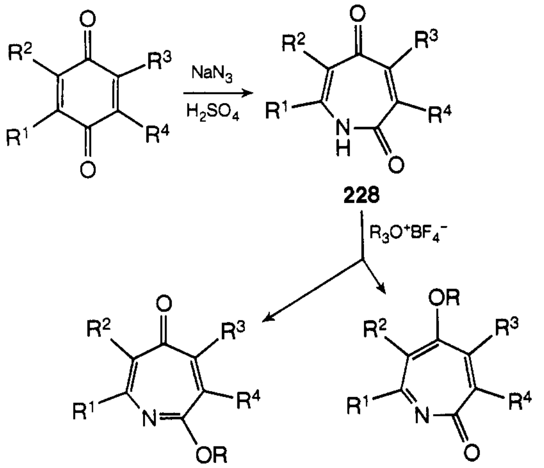
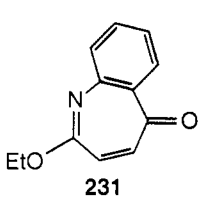
onium fluoborate.[183] Thus, starting from the appropriate *p*-quinone derivative, the series of azatropones **229** and **230** have been synthesized.[183] Benzo- (**231**) and dibenzoazatropones (**232**) have also been obtained along similar lines.[183] The syntheses of dibenzoazatropones **233**[184] and **234**[185] of the dimer **235**,[184,185] as well as of (2,3-dibromobenzo)-4-aza-7-bromotropone[183b] have also been reported.



228

229, $R^1 = R^3 = Me$; $R^4 = H$; $R = Et$

230a, $R^1 = R^2 = R^3 = Me$; $R^4 = H$; $R = Et$ or Me
b, $R^1 = R^2 = R^3 = R^4 = Me$; $R = Et$ or Me



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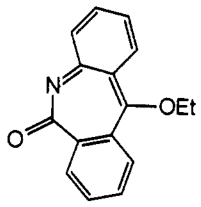

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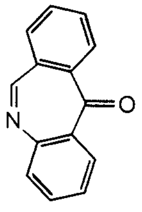

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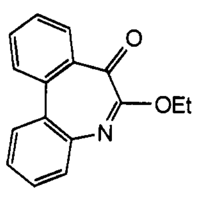

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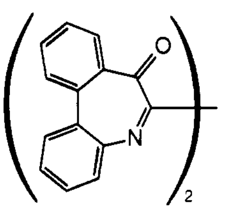
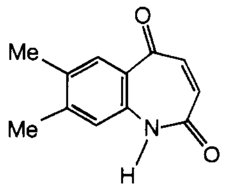


235

No decisive proof for the existence of azatropolones has been so far produced. Thus, though no thorough experimentation is available, both **236**[186] and **237**[183,186] do not seem to exist in their enol form.



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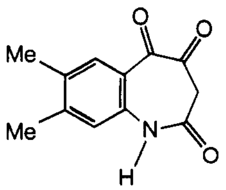
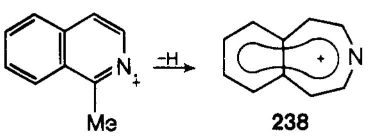


237

Intermediacy of the benzoazatropenylium ion **238** and of azatropenylium ions (**239**) has been suggested for the fragmentation of 1-methylisoquinoline[187] or of various mono- or disubstituted phenyl azides,[188] respectively, under electron impact in the mass spectrometer.



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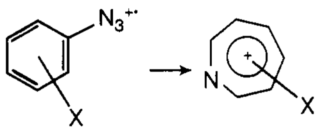
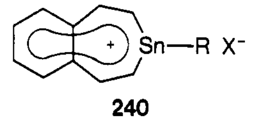


239

$X = o$-, m-, p-Cl; o-, m-, p-CN; m-, p-NO$_2$

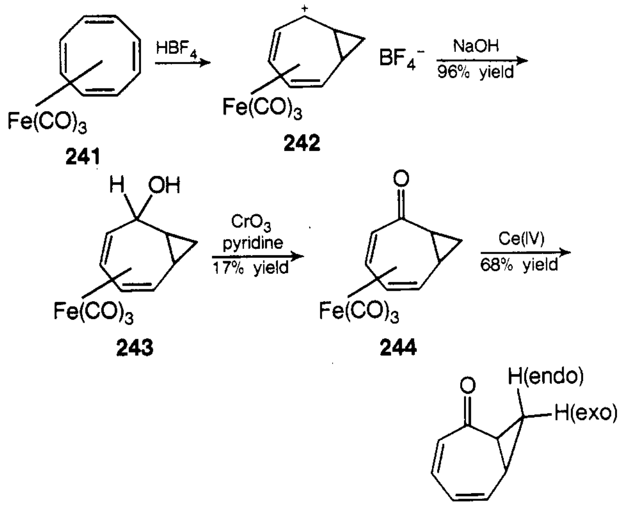
All attempts to demonstrate the occurrence of tin compounds of this class, such as the benzostannatropenylium ion **240**, failed.[180]



240

7. Homo- and Polyhomoconjugated Species

2,3-Homotropone (**245**), which is intrinsically unstable, has been synthesized starting from bicyclo[5.1.0]octa-2,4-dienyliron tricarbonyl fluoborate (**242**) which was already available[189] from the reaction of cyclooctatetraeneiron tricarbonyl (**241**) and an ethereal solution of fluoboric acid. On the treatment of **242** with sodium hydroxide in aqueous acetone at low temperature, **243** was obtained and then oxidized, albeit in a low yield, to **244** with chromic acid.[190] 2,3-Homotropone (**245**), a pale yellow liquid of bp 55-56° (0.15 mm),[190b] was liberated by oxidative degradation of **244** with ceric ammonium nitrate.[190]



241 **242** **243** **244** **245**

4,5-Homotropone (**247**) has also been reported.[191] The synthesis is an adaptation of the degradation route (section II.A.1.d) of tropane-type compounds into cycloheptatrienones. Thus, *cis*-cyclopropane-1,2-dicarboxaldehyde

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(184) R. G. Cooke and I. M. Russell, *Tetrahedron Lett.*, 4587 (1968).

(185) W. G. Peaston and G. R. Proctor, *J. Chem. Soc. C*, 2481 (1968).

(186) A. H. Rees, *J. Chem. Soc.*, 3111 (1959).

(187) M. Marx and C. Djerassi, *J. Amer. Chem. Soc.*, **90**, 678 (1968).

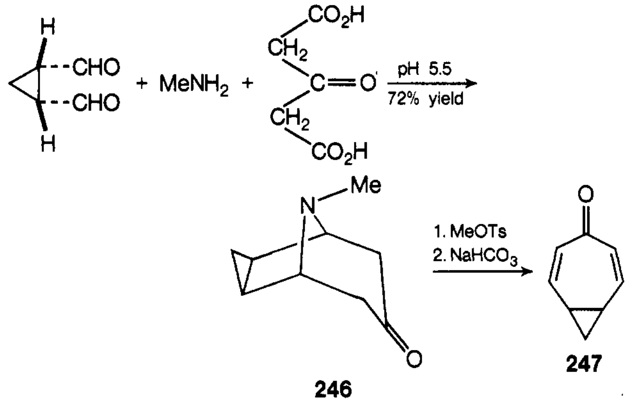
(188) R. A. Abramovitch, E. P. Kyba, and E. F. V. Scriven, *J. Org. Chem.*, **36**, 3796 (1971).

(189) G. N. Schrauzer, *J. Amer. Chem. Soc.*, **83**, 2966 (1961).

(190) (a) J. D. Holmes and R. Pettit, *J. Amer. Chem. Soc.*, **85**, 2531 (1963); (b) L. A. Paquette and O. Cox, *ibid.*, **89**, 5633 (1967).

(191) O. L. Chapman and R. A. Fugiel, *J. Amer. Chem. Soc.*, **91**, 215 (1969).

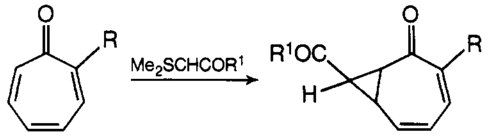
was condensed with acetone-1,3-dicarboxylic acid and methylamine to give **246**.[191] Quaternization of **246** followed by steam distillations of the resultant alkaline solution gave **247** in good yield.[191]



246 **247**

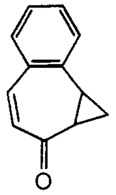
By an adaptation of this route 4,5-trimethylenetropone was also obtained.[192]

Homoconjugated species of the above type have also been obtained on the treatment of the parent conjugate species with sulfur ylides[193] or diazomethane (see section V.F). Thus, 2,3-homotropones **248** were obtained in 30–80% yield by the reactions of appropriate tropones and sulfur ylides in tetrahydrofuran.[193a] 2,3-Homotropones **248** can be further treated with sulfur ylides to give the corresponding 2,3:4,5-dihomotropones.[193a]



248a, R = H; R^1 = OEt
b, R = H; R^1 = Ph
c, R = H; R^1 = p-BrC_6H_4
d, R = Me; R^1 = Ph
e, R = Ph; R^1 = Ph
f, R = Ph; R^1 = p-BrC_6H_4
g, R = Cl; R^1 = Ph

Dimethyloxosulfonium methylide has also been used successfully to synthesize both 4,5-benzohomotropone (**249**) (from 4,5-benzotropone[193b]) and the polymethylenehomobenzotropone **250** (from the corresponding 2,7-polymethylene-4,5-benzotropone[194]). Derivatives of **249** as well as the benzobishomotropone **251** have also been synthesized along similar lines.[193b]



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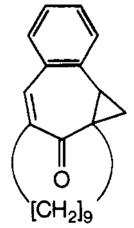

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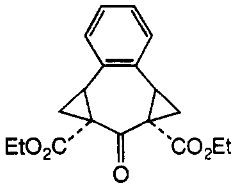
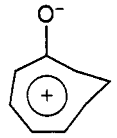


251

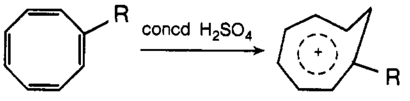
The term homotropone originated[190a] from the concept of homoaromaticity.[195] Thus, 2,3-homotropone is homoaromatic to the extent that its structure is contributed by **252**. We will go back to this point when dealing with structural problems (section IV).



252

A variety of homo- and bishomotropenylium salts, as well as benzo- and dibenzohomotropenylium salts, have been obtained in solution. Some homotropenylium salts have also been isolated and are stable at room temperature provided they are kept out of moist air. In all cases shown below, all evidence (see section IV) points to aromatic character for these ions.

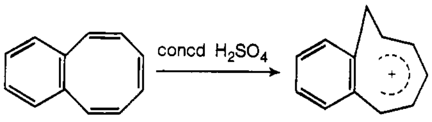
Synthetic entries to these salts in solution include protonation of cyclooctatetraenes **253** in concentrated sulfuric acid. Thus, from cyclooctatetraene itself (**253a**) homotropenylium ion (**254a**) has been obtained.[196] It is notable that when this method was applied to either methyl- (**253b**) or phenylcyclooctatetraene (**253c**), only 1-methyl- (**254b**) or 1-phenylhomotropenylium ion (**254c**) was obtained.[197]



253 **254**

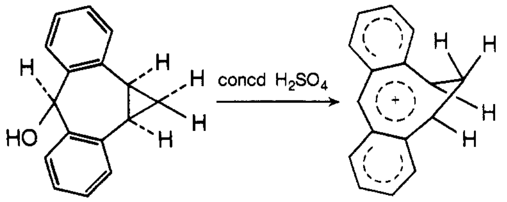
a, R = H
b, R = Me
c, R = Ph

Benzocyclooctatetraene (**255**) is protonated exclusively at C(3) in concentrated sulfuric acid to give the benzohomotropenylium ion **256**.[198] Position of attack was confirmed by carrying out the reaction on 4,5,6,7-tetradeuteriobenzocyclooctatetraene.[198]

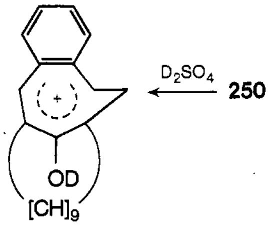


255 **256**

The dibenzohomotropenylium ion **258** was obtained by the treatment of **257** with either concentrated sulfuric



257 **258**



259

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(192) O. L. Chapman and T. H. Koch, *J. Org. Chem.*, **31**, 1042 (1966).

(193) (a) Y. Sugimura and N. Soma, *Tetrahedron Lett.*, 1721 (1970); (b) Y. Sugimura, N. Soma, and Y. Kishida, *ibid.*, 91 (1971).

(194) R. E. Harmon, R. Suder, and S. K. Gupta, *J. Chem. Soc., Chem. Commun.*, 472 (1972); *J. Chem. Soc., Perkin Trans. 1*, 1746 (1972).

(195) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969).

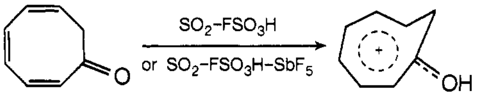
(196) J. E. Mahler and R. Pettit, *J. Amer. Chem. Soc.*, **84**, 2842 (1962).

(197) C. E. Keller and R. Pettit, *J. Amer. Chem. Soc.*, **88**, 604 (1966).

(198) W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, **90**, 814 (1968).

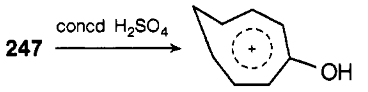
acid or fluorosulfonic acid.[199] Along similar lines **259** has been obtained from **250**.[194]

Strongly acidic mixtures, like SO_2–FSO_3H, SO_2–FSO_3H–SbF_5, or FSO_3H–SO_2ClF have also been utilized, for example, in the case of **260**, which is protonated in such media at low temperature to give exclusively 1-hydroxyhomotropenylium ion (**261**).[200a] Under similar conditions 1-methoxyhomotropenylium ion was obtained from methoxycyclooctatetraene.[200b]

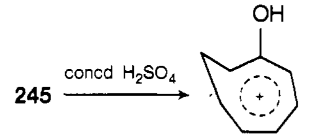


260 **261**

The two isomers, **262** and **263**, of **261** have also been obtained in solution by the treatment with concentrated sulfuric acid of respectively 4,5-homo- (**247**) or 2,3-homotropone (**245**).[191,198]

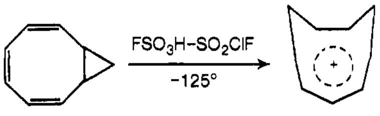


262

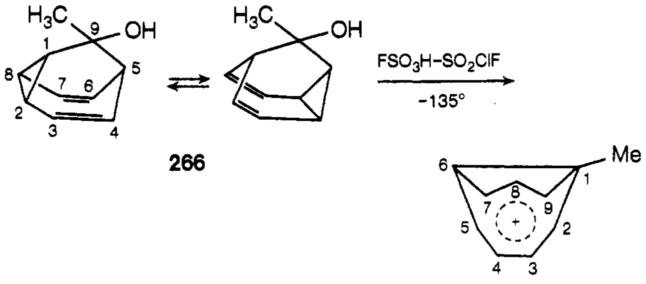


263

The mixture FSO_3H–SO_2ClF has also been utilized to protonate **264** and **266** at very low temperatures. Carbonium ions are observable reaction intermediates which rearrange exclusively into 1,3-bishomotropenylium ion (**265**)[201] and the bridgehead 1,4-bishomotropenylium ion (**267**) in the two cases, respectively.[202] Other bridgehead 1,4-bishomotropenylium salts have also been prepared along similar routes.[202,203]

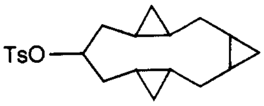


264 **265**

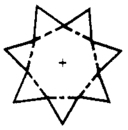


267

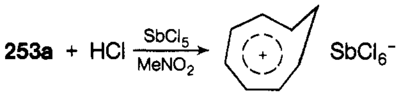
Compound **268** has been proposed as a potential precursor of the hypothetical heptahomotropenylium ion (**269**).[204]



268


269

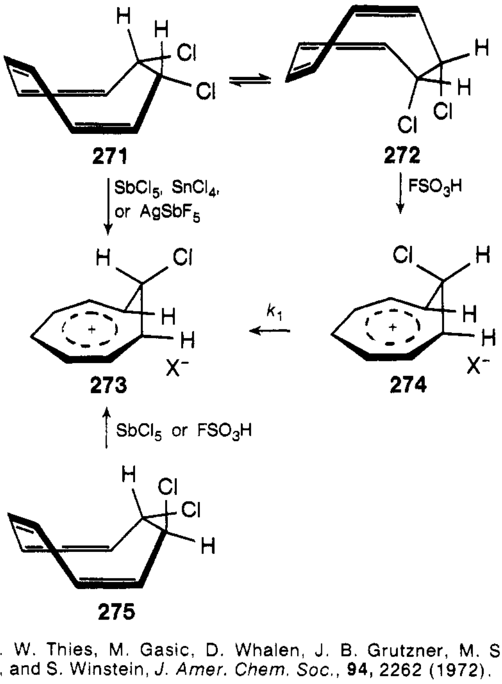
As regards the isolation of homotropenylium salts, addition of antimony pentachloride to equimolar amounts of hydrogen chloride and cyclooctatetraene (**253a**) in nitromethane, followed by dilution with benzene, gave homotropenylium hexachloroantimonate (**270**) in almost quantitative yield.[196] The bromopentachloroantimonate analog of **270** was also obtained on the treatment of **253a** with $SbCl_5$ and hydrogen bromide in benzene.[196]



270

Also *exo*-8-chlorohomotropenylium salts **273** have been isolated on the treatment of *cis*-7,8-dichlorocycloocta-1,3,5-triene (**271** and **272**) with either $SbCl_5$ in dichloromethane or sulfur dioxide ($X^- = SbCl_6^-$) at −15°, $SnCl_4$ in dichloromethane ($X^- = SnCl_5^-$), or $AgSbF_6$ in sulfur dioxide or trideuterionitromethane.[205a] At this temperature **271** and **272** exist in a 46:54 ratio (Scheme XX). In contrast, **271**–**272** with FSO_3, either neat below 0° or dissolved in liquid SO_2, gave the endo isomer **274** (Scheme XX). On warming the FSO_3H solution to 30.4°, **274** isomerizes to **273** (Scheme XX). Ionization of **271** ⇄ **272**, induced by FSO_3, involves chloride removal from the endo side. In fact, the exo isomer **273** was obtained on the treatment of *trans*-7,8-dichlorocycloocta-1,3,5-triene (**275**) with FSO_3H. With $SbCl_5$, the more stable isomer **273** was obtained in any case (Scheme XX). These and related reactions have been

SCHEME XX



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(199) R. F. Childs and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6348 (1967); R. F. Childs, M. A. Brown, F. A. L. Anet, and S. Winstein, *ibid.*, **94**, 2175 (1972).

(200) (a) M. S. Brookhart, M. Ogliaruso, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 1965 (1967); (b) M. S. Brookhart and M. A. Monroe Atwater, *Tetrahedron Lett.*, 4399 (1972).

(201) P. Warner and S. Winstein, *J. Amer. Chem. Soc.*, **93**, 1284 (1971).

(202) P. Ahlberg, D. L. Harris, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 2146, 4454 (1970); M. Roberts, H. Hamberg, and S. Winstein, *ibid.*, **92**, 6346 (1970); P. Ahlberg, D. L. Harris, M. Roberts, P. Warner, P. Seidl, M. Sakai, D. Cook, A. Diaz, J. P. Dirlam, H. Hamberger, and S. Winstein, *ibid.*, **94**, 7063 (1972).

(203) (a) G. Schröder, U. Prange, B. Putze, J. Thio, and J. F. M. Oth, *Chem. Ber.*, **104**, 3406 (1971); H. P. Löffler, *Tetrahedron Lett.*, 4893 (1971); (b) H. A. Corver and R. F. Childs, *J. Amer. Chem. Soc.*, **94**, 6201 (1972).

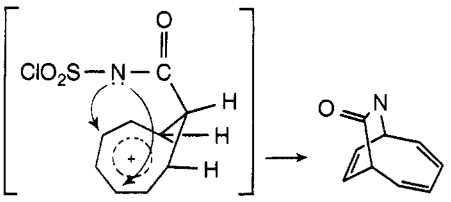
(204) R. W. Thies, M. Gasic, D. Whalen, J. B. Grutzner, M. Sakai, B. Johnson, and S. Winstein, *J. Amer. Chem. Soc.*, **94**, 2262 (1972).

(205) (a) G. Boche, W. Hechtl, H. Huber, and R. Huisgen, *J. Amer. Chem. Soc.*, **89**, 3344 (1967); (b) R. Huisgen and J. Gasteiger, *Tetrahedron Lett.*, 3661 (1972); J. Gasteiger and R. Huisgen, *ibid.*, 3665 (1972); (c) J. Gasteiger and R. Huisgen, *J. Amer. Chem. Soc.*, **94**, 6541 (1972); (d) R. Huisgen and J. Gasteiger, *Angew. Chem.*, **84**, 1187 (1972).

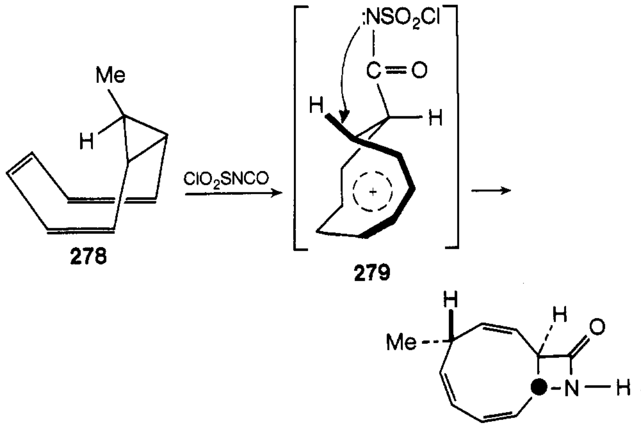
further studied.[205b] Similar inversions have also been detected for the 8-substituted homotropenylium ion obtained by SbF_5-induced ring opening of the 1,4-cycloadduct of cyclooctatetraene and SO_2.[205c]

Cyclooctatetraene, on treatment with $SbCl_5$ in methylene chloride at −60°, gave the crystalline endo isomer **274** ($X^- = SbCl_4^-$).[205d]

Homotropenylium ions have been proposed as transient intermediates in certain reactions. This is the case of 8-chlorohomotropenylium ion in the chlorination of cyclooctatetraene[206] or of the homotropenylium species **276** which has been proposed to rationalize formation of **277** on the treatment of cyclooctatetraene (**253a**) with chlorosulfonyl isocyanate.[207] Moreover, 8-acetoxyhomotropenylium ions have been tentatively suggested as intermediates in the electrochemical oxidation of cyclooctatetraene in acetic acid–acetate.[208] Also, the intermediacy of bishomotropenylium ions has been suggested for the reactions of *cis*-bicyclo[6.1.0]nonatriene with electrophiles such as chlorosulfonyl isocyanate or tetracyanoethylene.[209] It was, in fact, proposed that **278** reacts in the folded conformation shown here with chlorosulfonyl isocyanate to give **280** through the *trans*-1,3-bishomotropenylium ion **279**.[209] The driving force for this reaction has been identified in the "aromaticity" of the trans species **279**.[209] This contrasts with ^1H nmr data for benzo-1,4-bishomotropenylim ions[203b] (discussed in section IV.B.6) which suggest that the cis species is bishomoaromatic while the trans isomer is devoid of homoaromaticity. Finally, the intermediacy of a 8-substituted homotropenylium species seems to be formed in the first step of the SbF_5-catalyzed cycloaddition of SO_2 to cyclooctatetraene.[205c]



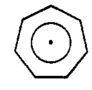
276 **277**



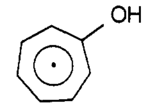
278 **279** **280**

C. Radicals and Ion Radicals

Tropenyl radical (**281**) has been generated from bitropenyl either at 350° in a silica capillary tube directly joined to a mass spectrometer[210a] or, as a neat liquid, at 80–120° in a tube placed directly into the cavity of an esr spectrometer.[210b] In the first case, rearrangement of **281** led to bibenzyl too.[210a] The second method[210b] was adapted also to generate methyltropenyl,[211a] cyclopropyltropenyl,[211a] and (2-cyclopropyl-1-ethynyl)tropenyl radicals.[211b]



281



282

Tropenyl free radicals can also be obtained by photolysis of bitropenyls.[210b,212]

Mass spectral evidence for hydroxytropenyl radical **282** during the pyrolysis of 7-methoxycycloheptatriene (**209**) has been obtained. End products are benzene and carbon monoxide formed by the intermediacy of tropone.[210a] However, most cycloheptatriene derivatives do not pyrolyze to tropenyl radicals. For example, 7-methylcycloheptatriene gives ethylbenzene on pyrolysis, no tropenyl radical being involved.[210a]

Electrochemical reduction of tropenylium ion in methylene dichloride gives ditropenyl in 50–65% yield under preparative conditions.[213] All evidence points to tropenyl radical as an intermediate which dimerizes to give ditropenyl.[213b] Recombination must be very fast ($t_{1/2} < 10^{-3}$ sec) because no esr signal could be detected during electrolysis carried out directly into the spectrometer cavity in the temperature range from 25 to 100°.[213a]

It has also been reported that for various tropenylium ions the rate of the one-electron reduction by the chromous ion parallels the ease of electron acceptance of a couple of electrons by nucleophiles.[213b] One wonders whether this might rather constitute evidence that the latter process also involves a one-electron transfer in the rate-limiting step.

Further examples of the generation of tropenyl radicals will be reported in section IV.C.

A wider variety of anion radicals than radicals is known. They have been prepared from tropone[214,215] and 2,6-dimethyl-[215] and 2,6-di-*tert*-butyltropone[215] by electrolytic reduction. Tropone was reduced to the anion radical also by DMSO solutions of potassium *tert*-butoxide.[216]

The alkali metal technique for the generation of anion radicals was unsuccessful with tropone[214] but worked well in other cases such as the reduction of heptafulvalene (**166**) to the anion radical.[217] A particularly interesting case in which this technique was employed has

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(206) R. Huisgen, F. Boche, and H. Huber, *J. Amer. Chem. Soc.*, **89**, 3345 (1967).

(207) L. A. Paquette, J. R. Malpass, and T. J. Barton, *J. Amer. Chem. Soc.*, **91**, 4714 (1969).

(208) L. Eberson and H. Schäfer, *Fortschr. Chem. Forsch.*, **21**, 43, 86 (1971).

(209) L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *J. Amer. Chem. Soc.*, **94**, 630 (1972); L. A. Paquette and M. J. Broadhurst, *ibid.*, **94**, 632 (1972).

(210) (a) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Amer. Chem. Soc.*, **82**, 5593 (1960); (b) G. Vincow, M. L. Morrell, W. V. Volland, H. J. Dauben, Jr., and F. R. Hunter, *ibid.*, **87**, 3527 (1965).

(211) (a) F. Farr, Y. S. Rim, and N. L. Bauld, *J. Amer. Chem. Soc.*, **93**, 6888 (1971); (b) C. E. Hudson and N. L. Bauld, *ibid.*, **94**, 1158 (1972).

(212) G. Vincow, M. L. Morrell, F. R. Hunter, and H. J. Dauben, Jr., *J. Chem. Phys.*, **48**, 2876 (1968).

(213) (a) P. H. Plesh and S. Stasko, *J. Chem. Soc. B*, 2052 (1971); (b) K. Okamoto, K. Komatsu, O. Murai, and O. Sakaguki, *Tetrahedron Lett.*, 4989 (1972).

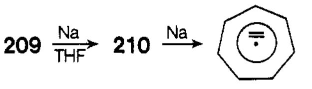
(214) Y. Ikegami and S. Seto, *Bull. Chem. Soc. Jap.*, **41**, 2225 (1968).

(215) G. A. Russell and G. R. Stevens, *J. Amer. Chem. Soc.*, **93**, 2432 (1971).

(216) G. A. Russell and R. L. Blankespoor, *Tetrahedron Lett.*, 4573 (1971).

(217) M. D. Sevilla, S. H. Flajser, G. Vincow, and H. J. Dauben, Jr., *J. Amer. Chem. Soc.*, **91**, 4139 (1969).

already been mentioned in section II.B.5. Thus, prolonged reduction of 7-methoxy-1,3,5-cycloheptatriene (**209**) with sodium in tetrahydrofuran gave cycloheptatrienide dianion radical **283** through tropenide anion

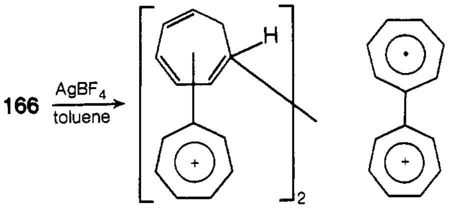


283

210.[174] Analogous benzo-[174] or dibenzo dianion radicals,[174] as well as methyl-,[211a] cyclopropyl-,[211a] propynyl-,[211a] and (2-cyclopropyl-1-ethynyl)tropenyl radicals,[211b] have been prepared along similar routes.

The anion radical of azulene has been recently observed during the reduction of 1,6-methylamino[10]annulene with sodium.[218] Electrolytic reduction has also been employed to generate anion radicals of azulene and azulene derivatives.[219]

Heptafulvalene (**166**), on the treatment with $AgBF_4$ in dry toluene, gave the dimer **284**. This is in a thermal equilibrium with the cation radical of heptafulvalene (**284a**).[217]

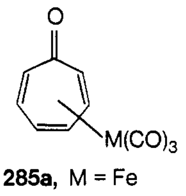


284 **284a**

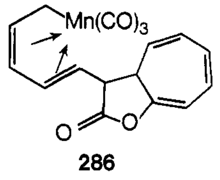
D. Metal π Complexes

1. Cycloheptatrienone Metal π Complexes

Direct ligand replacement has been successfully employed for the synthesis of troponeiron tricarbonyl (**285a**) (which exists in at least two crystalline modifications of mp 63.5–64.5 and 83–84°) and tropenechromium tricarbonyl (**285b**). The first was obtained by reaction of tropone with $Fe_3(CO)_{12}$,[220] while the latter was obtained from tropone and $Cr(MeCN)_3(CO)_3$ utilizing the ready replaceability of the weakly bound acetonitrile.[221]



285a, M = Fe
b, M = Cr
c, M = Mo

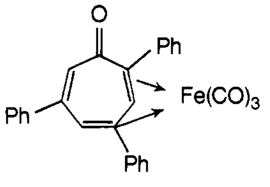


286

The claimed[222] synthesis of **285c** from tropone and $Mo(CO)_6$ could not be repeated, however.[221] Also the use of $Mn_2(CO)_{10}$ failed to give a **285**-type complex, **286** being obtained instead.[223]

The chromium complex **285b** was obtained from methoxy- or ethoxy-cycloheptatriene. On their treatment with $Cr(MeCN)_3(CO)_3$ the corresponding alkoxy tricarbonyl complexes were obtained. These were deprotonated to the alkoxytropenylium complexes with trityl tetrafluoborate. Finally, hydrolysis gave **285b**.[221]

Also the iron complex **285a** has been obtained by an alternative route, *i.e.*, from acetylene and iron carbonyls under pressure.[220a] With phenylacetylene in the place of acetylene, two isomeric 2,4,6-triphenyltroponeiron tricarbonyls (**287** and **288**) were obtained.[224] These two isomers equilibrate in boiling benzene giving a **287**:**288** ratio of 1:2.[224] The existence of two isomers indicates that each one must exist as a *d,l* pair. However, efforts to separate them were unsuccessful.[224]



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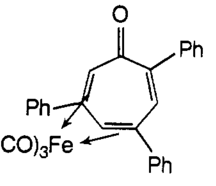


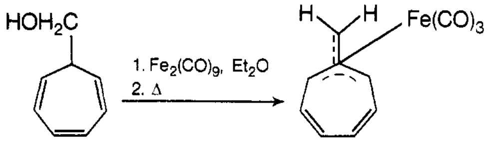
288

Free tropone can be obtained, together with little troponeiron dicarbonyl triphenylphosphine, on the treatment of **285a** with triphenylphosphine.[224] Also 2,4,6-triphenyltropone was liberated, in high yield, from either **287** or **288** with triphenylphosphine.[224]

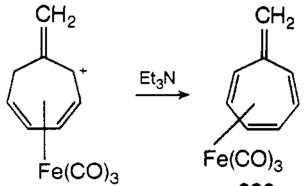
As concerns fused arenetropones, a tricarbonylchromium complex of 2,3:5,6-dibenzotropone was obtained.[124] Here, however, the metal is bound to a phenyl unit.[124]

2. Metal π Complexes of Heptafulvenes and Related Compounds

A number of iron tricarbonyl complexes of heptafulvenes have been prepared. Two isomers of heptafulveneiron tricarbonyl have been described (see section IV.D.2 for structural evidence). In fact, on attempted distillation of the mixture obtained from the reaction of 7-hydroxymethylcycloheptatriene (**289**) with a large excess of $Fe_2(CO)_9$ in ethyl ether, **290**, mp 37–41°, has been obtained in 25% yield.[225] The π-complex **292** (a liquid) was obtained by deprotonation of **291** with triethylamine.[226]



289 **290**



291 **292**

Another heptafulvene metal complex, **293**, has been described.[227a] However, this seems to have the tropenyl-

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(218) F. Gerson, J. Heinzer, and E. Vogel, *Helv. Chim. Acta*, **53**, 95, 103 (1970).

(219) Y. Ikegami and S. Seto, *Bull. Chem. Soc. Jap.*, **44**, 1905 (1971).

(220) (a) E. Weiss and W. Hübel, *Chem. Ber.*, **95**, 1179 (1962); (b) R. B. King, *Inorg. Chem.*, **2**, 807 (1963).

(221) P. L. Pauson and K. H. Todd, *J. Chem. Soc. C*, 2315 (1970).

(222) G. Wilkinson, U. S. Patent 3064021 (1962); *Chem. Abstr.*, **59**, 10118b (1963).

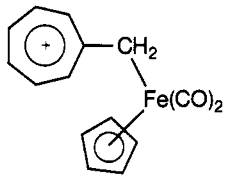
(223) M. J. Barrow, O. S. Mills, F. Haque, and P. L. Pauson, *Chem. Commun.*, 1239 (1971).

(224) E. H. Braye and W. Hübel, *J. Organometal. Chem.*, **3**, 25 (1965).

(225) D. J. Ehnthold and R. C. Kerber, *Chem. Commun.*, 1451 (1970).

(226) G. T. Rodeheaver, G. C. Farrant, and D. F. Hunt, *J. Organometal. Chem.*, **30**, C22 (1971).

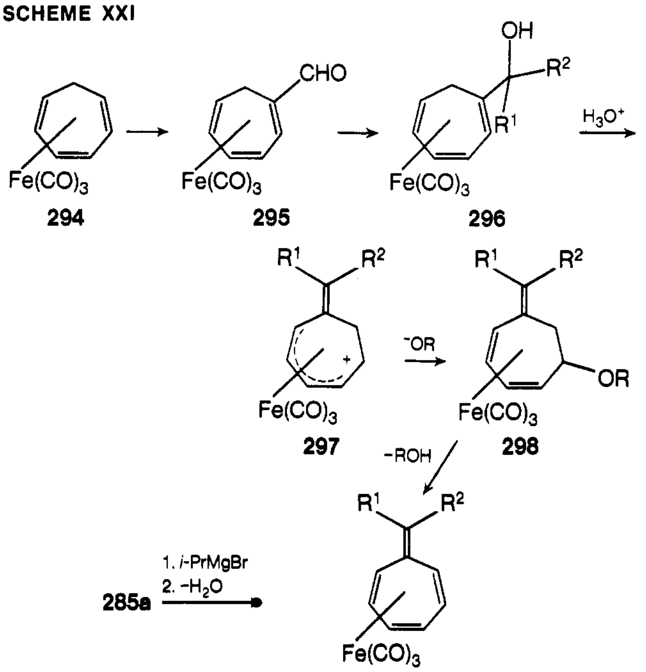
ium structure indicated here (**293**) due to a σ bond between the metal and the methylene.[227b]



293

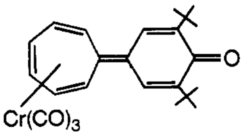
Two rather general routes to iron tricarbonyl complexes of heptafulvene derivatives, **299**, but not of heptafulvene itself, have been described.[228a] One follows the lines indicated in Scheme XXI which is self-explanatory. The other one involves reaction of troponeiron tricarbonyl (**285a**) with isopropylmagnesium bromide to give the corresponding carbinol which, on dehydration, finally gave **299** (Scheme XXI).[228a] This notable reaction of the organomagnesium compound will be commented on in section V.L.

SCHEME XXI



299a, $R^1 = H$; $R^2 = Ph$
b, $R^1 = H$; $R^2 = PhCH_2$
c, $R^1 = R^2 = Ph$
d, $R^1 = R^2 = Me$

The fact that heptafulvene and its simple derivatives are known as extremely unstable compounds (see section II.B.3), whereas nearly all complexes described above are sublimable and nicely crystalline compounds, shows the effectiveness of the iron tricarbonyl group as a stabilizing unit. In contrast, **300** could not be synthesized from the free organic ligand and $Cr(MeCN)_3(CO)_3$.[124a] A longer route through the tropenylium salt corresponding to **300** was taken.[124a] When the preparation of the analogs of **300** with either methyl or methoxyl groups in the place of the *tert*-butyl groups was attempted, only gummy tars were obtained.[124a]



300

8,8'-Dimethyl- and 8,8'-diphenylheptafulvenechromium tricarbonyl have been prepared by proton abstraction from the corresponding tropenylium salts.[228b]

Little has been reported on the use of heptafulvene π complexes to obtain free heptafulvenes. One such attempt from the σ-complex **293** failed.[225] Chromium complexes seem to be promising, however, which is in line with previous success to obtain free tropylidenes from chromium, but not from iron, complexes.[228b]

Various metal carbonyl complexes of azulene or azulene derivatives have been described. Detailed reference to such complexes as $C_{10}H_8Fe_2(CO)_5$, $[C_{10}H_8Mo(CO)_3CH_3]_2$, $C_{10}H_8Mn_2(CO)_6$, $(CH_3)_3C_{10}H_5Ru_4(CO)_9$, and $(C_{10}H_8)_2Fe_4(CO)_{10}$ is available in a recent paper dealing with guaiazulenedimanganese hexacarbonyl $(i\text{-}C_3H_7)(CH_3)_2C_{10}H_5Mo_2(CO)_6$.[229]

3. Metal π Complexes of Tropenylium Ions

There are many reports about simple metal π complexes of tropenylium ions. A versatile synthetic entry to metal-carbonyl complexes is by hydride abstraction from cycloheptatrienemetal carbonyls (**301**) with trityl fluoborate. Complexes **302** (M = Cr, Mo), which are remarkably stable, have been obtained in this way.[230]

$$\underset{\mathbf{301}}{C_7H_8{\cdot}M(CO)_3} \xrightarrow{PhC^+BF_4^-} \underset{\mathbf{302}}{[C_7H_7{\cdot}M(CO)_3]BF_4}$$

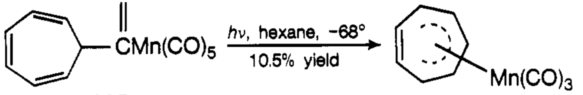
M = Cr, Mo

By an adaptation of this route, both alkoxy- and carbomethoxytropenylchromium tricarbonyls[69] and tropenyldiiron hexacarbonyl[231] have also been prepared. However, this method failed for both $C_7H_8PtBr_2$ and $C_7H_8PtCl_2$.[232]

On the treatment with $Fe_2(CO)_9$, 7-methoxycycloheptatriene (**209**) gave the iron tricarbonyl complex **303**. This gave the tropenylium complex **304** on treatment with fluoboric acid.[232] The fact that complex **304** is less stable than the corresponding chromium or molybdenum complexes[232] contrasts with the case of heptafulvene complexes where, as already stated above, iron tricarbonyl is a better stabilizing unit than chromium tricarbonyl.

$$\mathbf{209} \xrightarrow{Fe_2(CO)_9} \underset{\mathbf{303}}{C_7H_7OMe{\cdot}Fe(CO)_3} \xrightarrow{HBF_4} \underset{\mathbf{304}}{[C_7H_7{\cdot}Fe(CO)_3]BF_4}$$

A photochemical method has been employed to synthesize **306** which was inaccessible by other routes.[233]



305 **306**

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(227) (a) D. J. Ehntholt, G. F. Emerson, and R. C. Kerber, *J. Amer. Chem. Soc.*, **91**, 7547 (1969); (b) M. R. Churchill and J. P. Fennessey, *Chem. Commun.*, 1056 (1970).

(228) (a) B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, *Chem. Commun.*, 177 (1971); *J. Chem. Soc., Dalton Trans.*, 2076 (1972); (b) J. A. S. Howell, B. F. G. Johnson, and J. Lewis, *J. Organometal. Chem.*, **42**, C54 (1972).

(229) M. R. Churchill and P. H. Bird, *Inorg. Chem.*, **7**, 1545 (1968).

(230) H. J. Dauben, Jr., and L. R. Honnen, *J. Amer. Chem. Soc.*, **80**, 5570 (1958); J. D. Munro and P. L. Pauson, *Proc. Chem. Soc., London*, 267 (1959).

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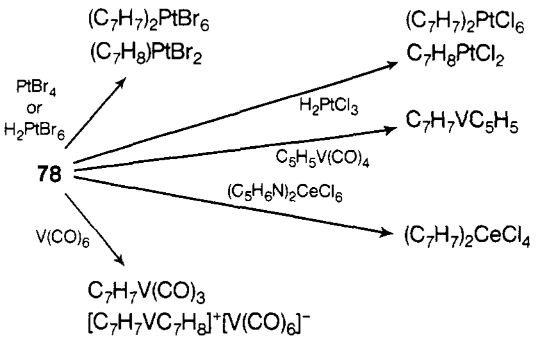
(233) T. H. Whitesides and R. A. Budnik, *Chem. Commun.*, 1514 (1971).

Thus, **305**, obtained from C_7H_7COCl and $Mn(CO)_5$, underwent photolysis to give **306** in hexane at −68°.[233]

Tropenylium metal π complexes containing a second organic ligand (which may also be a second tropenylium unit) are also known. They have been obtained, though generally in mixtures, from cycloheptatriene (**78**) by a number of different routes (Scheme XXII). Thus, on the treatment of **78** with $PtBr_4$ or H_2PtBr_6, the tropenylium salt of Pt(VI), together with $C_7H_8PtBr_2$, was obtained.[234] In the case of H_2PtCl_3 the analogous chlorine complexes were obtained.[234] In contrast, reaction of **78** with (dipyridinium)cerium(IV) hexachloride gave the tropenide complex $(C_7H_7)_2CeCl_2$.[235] Finally, reaction with $C_5H_5V(CO)_4$ gave $C_7H_7VC_5H_5$.[236] A number of substituted tropenylium complexes have been prepared by adaptations of this method.[237]

SCHEME XXII

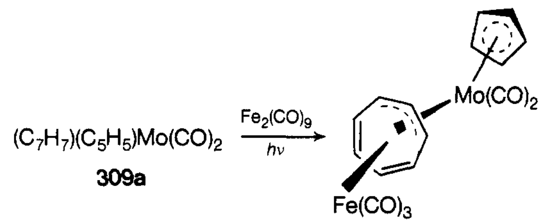


Complexes of this type have also been obtained from mixed metal π complexes of both cycloheptatriene and a second organic ligand. Thus, starting from $(C_7H_8)Cr(C_5H_5)$, catalytic dehydrogenation on platinum gave $(C_7H_7)Cr(C_5H_5)$ whereas oxidation with atmospheric oxygen gave $[(C_7H_7)Cr(C_5H_5)]^+$ instead.[238]

Insertion reactions in the carbon-carbon bond of benzene has been observed under Friedel-Crafts conditions for chromium and manganese benzene-cyclopentadienyl complexes. Thus, on the treatment of **307** with acetyl chloride and aluminum chloride **308** was obtained.[239,240] A similar reaction course was observed also with benzoyl chloride and the manganese complex analogous to **307**.[240] Under these conditions acylation of free benzene does not occur.[240]

$$\underset{\mathbf{307}}{C_6H_6CrC_5H_5} \xrightarrow{AcCl,\ AlCl_3,\ CS_2,\ -40°} \underset{\mathbf{308}}{[(C_7H_6CH_3)Cr(C_5H_5)]^+}$$

A tropenylium ion complex containing two different transition metals and a second organic ligand (**309b**) has been obtained by uv irradiation of **309a** in the presence of $Fe_2(CO)_9$ (alone or in mixture with $Fe(CO)_5$).[241a]

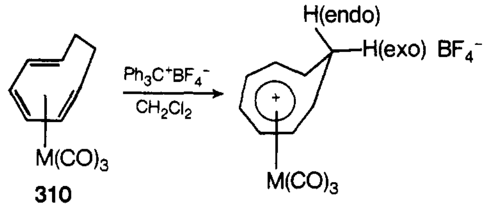


309a **309b**

It was suggested that an intermediate complex $C_7H_7M(H)(CO)_3$ of tropenylium ion with a transition metal (M) tricarbonyl is responsible for the observed scrambling of the hydrogen at the saturated carbon of cycloheptatriene.[241b] This suggestion has been now refuted.[241c] The scrambling, which is faster with the uncomplexed cycloheptatriene, has been attributed to a sequence of [1,5] hydrogen migrations.[241c]

4. *Miscellaneous Metal π Complexes*

Crystalline homotropenylium metal tricarbonyl tetrafluoborates (**311**, M = Cr, Mo, W) have been obtained by hydride abstraction from the corresponding 1,3,5-cyclooctatriene tricarbonyl complexes (**310**) with trityl fluoborate in methylene dichloride.[242]

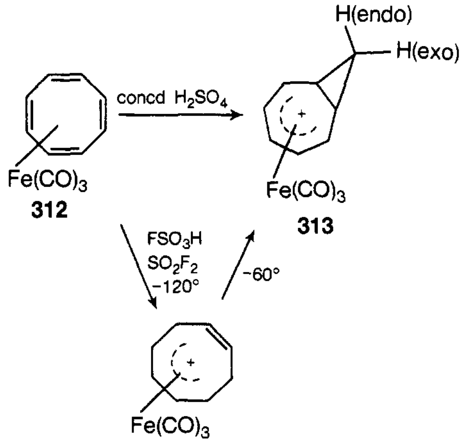


310 **311**

M = Cr, Mo, W

Complexes analogous to **311** (M = Mo, W) have also been obtained in solution by protonation with sulfuric acid of the corresponding cyclooctatetraenemetal tricarbonyl complexes or by protonation, with loss of carbon monoxide, of the corresponding cyclooctatetraenemetal tetracarbonyl complexes.[242,243]

Protonation of cyclooctatetraeneiron tricarbonyl (**312**) in concentrated sulfuric acid was found to give bicyclo[5.1.0]octadienyliron tricarbonyl (**313**),[244] whereas in



312 **313** **314**

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(243) S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Amer. Chem. Soc.*, **87**, 3267 (1965); H. D. Kaesz, S. Winstein, and C. G. Kreiter, *ibid.*, **88**, 1319 (1966).

(244) A. Davidson, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962).

$FSO_3H-SO_2F_2$ at −120° cyclooctatrienyliron tricarbonyl (314) was obtained.[245] On raising the temperature to −60°, **314** was observed to isomerize to **313** in a first-order electrocyclic reaction.[245]

Of great theoretical interest is a communication concerning tropenideiron tricarbonyllithium (**315**) which is claimed[246] to have been obtained as a deep red viscous oil on the treatment of cycloheptatrieneiron tricarbonyl (**294**) with *n*-butyllithium in tetrahydrofuran at −78°.[246] No heavy cation salt of **315** has yet been reported.

$$\mathbf{294} \xrightarrow[\text{THF, }-78^\circ]{n\text{-BuLi}} (C_7H_7)Fe(CO_3)^- \quad \underset{}{\mathbf{315}}$$

The complexes $(C_7H_7)_2CeCl_2$, $(C_7H_7)_2MCl_2$ (M = Ti, Zr), $(C_7H_7)_2MOCl_2$ (M = Mo, W), and $(C_7H_7)_2TaCl_3$ have been described also.[237]

E. Chelate Complexes

Tropolone (**83**), thiotropolone (**122**), dithiotropolone (**127**), aminotroponeimines (**128**), aminothiotropones (**129**), and their ring-substituted derivatives possess potential chelating structures through their electronegative atoms. In fact, extraction from reaction mixtures and purification of tropolones through their copper(II) chelate complexes has found extensive use.[9] Chelate complexes of these ligands with transition metals are stable in both neutral and acid solutions, whereas in alkaline solutions the organic ligand is liberated. Moreover, the thermal stability of these complexes correlates well with electronic spectral properties. Thus, whereas colorless chelates of tetravalent thorium, hafnium, and zirconium cations possess very high thermal stability, the intensely colored chelates of Ca(IV) and Pb(IV) are thermally unstable.[247] This has been attributed to facile electron transfers with the latter.

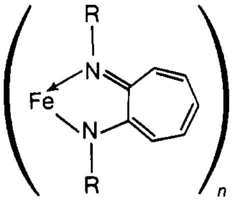
Complexes of the above ligands with a large variety of transition metals have been synthesized. These studies appear to have been stimulated to a large extent by the often fulfilled expectation[248,249] that such ligands, owing to their low resultant charge and relatively small "bite" as bidentate ligands, should be especially well adapted to give stable complexes which utilize the higher coordination numbers (>6).

With all the ligands mentioned above, metal chelates are usually obtained by simple treatment of the ligand with an inorganic metal salt. As regards tropolone or simple alkyl tropolones, stable complexes with a wide variety of cations have been so obtained.[248] They have been studied both in solution[248] and in the solid state[249] and these studies have been recently reviewed.[248,249] Briefly, in solution species of such high coordination number as ten, $Th(C_7H_5O_2)^-$, nine, $(Me_2SO)Th(C_6H_5O_2)_4$, eight, $(C_7H_5O_2)_4Ta^+$, $Sn(C_7H_5O_2)_4$, $Ln(C_7H_5O_2)_4^-$ (Ln = lanthanide), and seven, $(C_7H_5O_2)SnCl$, $(C_7H_5O_2)_3SnOH$, have been observed.[248] Some of these complexes have also been studied in the crystalline state.[249]

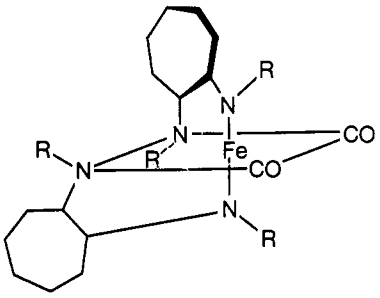
New complexes have been obtained sometimes during attempted recrystallizations. This is the case of the crystalline complex $(HCONMe_2)Th(C_7H_5O_2)_4$ which has been obtained on attempted recrystallization of $NaTh(C_7H_5O_2)_5$ from dimethylformamide.[249]

A variety of chelate complexes with thiotropolone,[250] dithiotropolone,[98] or 2-aminothiotropones[99] have also been prepared by the treatment of the appropriate ligand with an inorganic metal salt.

With aminotroponeimines this simple method worked well for the preparation of nickel(II) complexes.[114] However, in the case of iron(III) it gave good results in certain instances[114,251] while, for example, with iron(II) it failed.[251] Two other methods have been developed for iron(II) complexes. The first one involves treatment of the aminotroponeimine with $Fe(CO)_5$ in an open vessel.[114] Thus, with aminotroponeimines **128** (R = Et, *t*-Bu, Ph, or *p*-tolyl), the corresponding iron(II) complexes **316a** have been obtained.[114] With R = Me the iron(III) chelate complex **316b** was obtained instead.[114,251] Also, working under pressure, complexes **316c** (where the position of mobile electrons in the seven-membered rings is not indicated), instead of **316a**, were obtained.[251] Complexes **316c** have also been obtained from **316a** by carbon monoxide absorption.[251]



316a, *n* = 2
b, *n* = 3



316c

The second method, which is usually preferable to the one just described,[251] involves generation of the conjugate base of the aminotroponeimine with *n*-butyllithium in tetrahydrofuran and then addition of the desired metal chloride.[251] This method worked well for all **316a** complexes above, and it has been later applied to the preparation of bis(*N*,*N*-dimethylaminotroponeiminato)zinc(II).[98]

Chelate complexes of tropolone with boron have also been synthesized. Thus, reaction of 2-alkoxy-1,3,2-benzodioxaboroles with tropolones gave yellow crystalline compounds to which structures of the type **317** have been assigned.[252] Analogous compounds have been obtained from tropolones and diarylborinic esters.[253]

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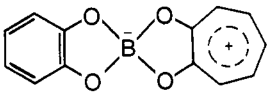
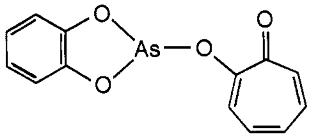


317

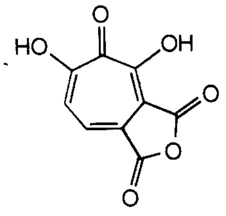
Arsenic seems to prefer nonchelated structures. Thus, on the treatment of tropolone with *o*-phenylene arsenite in benzene at reflux, a crystalline compound precipitated to which structure **318**, rather than a chelated structure of type **317**, was assigned.[254]



318

III. Biosynthesis

A large variety of tropolone derivatives have been found in nature as secondary vegetable metabolites.[255] They include stipitatonic (**330**),[256] stipitatic (**331**),[256] puberulonic (**319**),[257] and puberulic (**320**)[257] acids, as well as sepedonin (**321**).[258]



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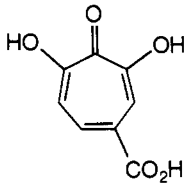

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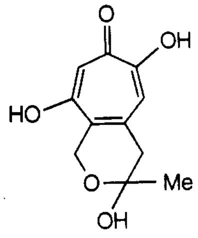
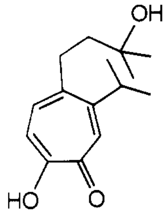


321

Various alkyl tropolones (such as all the isomeric isopropyl tropolones and 5-ethyltropolone[259]), alkyl hydroxyalkyltropolones (such as nookatinol (**322**)[260]), alkenyl tropolones (such as β-dolabrin (**323**) and nootkatin (**324**)), hydroxy alkenyl tropolones (like **325**[261]), and, which is remarkable in view of the general instability of simple tropones, 4-isopropyltropone (nezukone (**326**)[262]) have been found in the heartwood of various *Cupressales*.[263]



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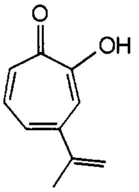

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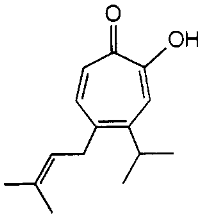

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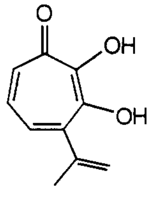

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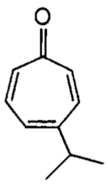


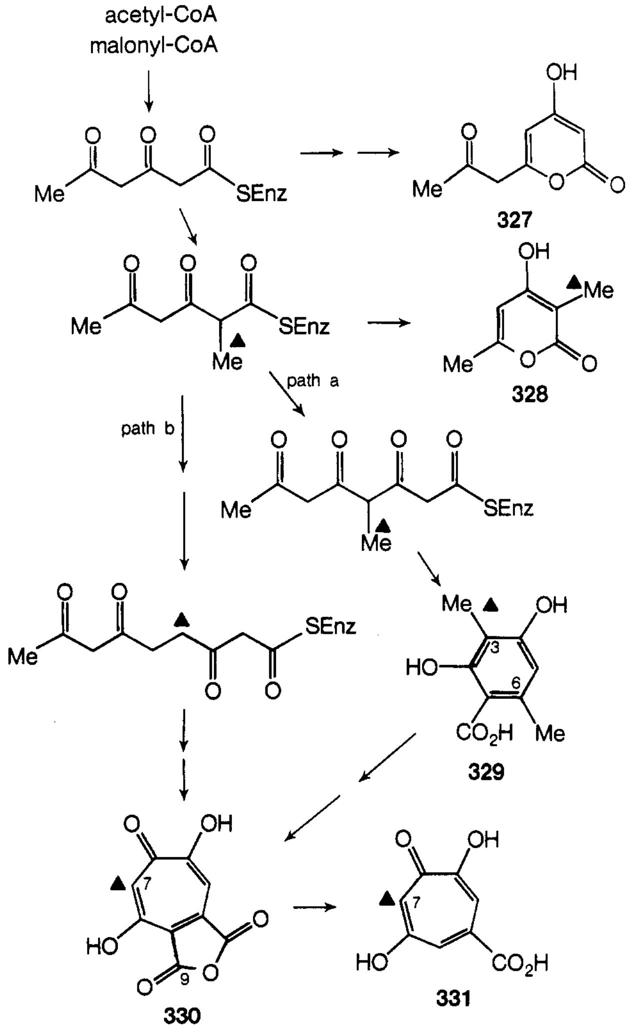
326

Alkaloidal tropolone derivatives, notably colchicine (**334**),[264] have been found in plants of the *Liliacee*. Arene-fused tropolones, such as theaflavins[265] and isotheaflavins,[266] have been found in various galls as well as in black tea.

Hydroazulenes and azulene have also been found in nature.[267]

Biogenesis of **330** and **331** (Scheme XXIII) in *Penicillium stipitatum* cultures has been the subject of much

SCHEME XXIII



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(259) Y. T. Lin, K. T. Lin, K. T. Wang, and B. Weinstein, *Experientia*, **22**, 140 (1966).

(260) Y. Hirose, *Agr. Biol. Chem.*, 795 (1963); *Chem. Abstr.*, **60**, 5561a (1964).

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(264) A. R. Battersby, R. B. Herbert, E. McDonald, R. Ramage, and J. H. Clements, *J. Chem. Soc., Perkin Trans. 1*, 1741 (1972).

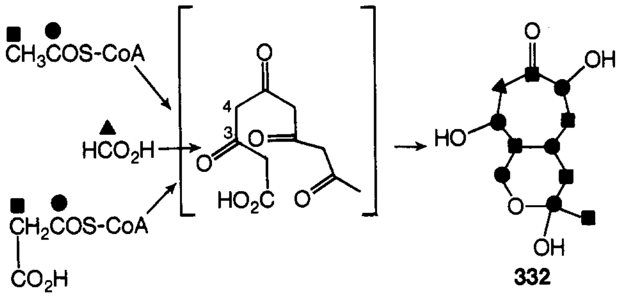
(265) D. T. Coxon, A. Holmes, W. D. Ollis, and V. C. Vora, *Tetrahedron Lett.*, 5237 (1970); T. Bryce, P. D. Collier, R. Mallows, P. E. Thomas, D. J. Frost, and C. K. Wilins, *ibid.*, 463 (1972).

(266) D. T. Coxon, A. Holmes, and W. D. Ollis, *Tetrahedron Lett.*, 5241 (1970).

(267) T. Nozoe and S. Ito, *Fortschr. Chem. Org. Naturst.*, **19**, 33 (1961).

work.[256a] Compound **330** was found to be a precursor of **331** and 3,6-dimethyl-4-hydroxy-2-pyrene (methyl triacetic lactone (**328**)) has also been isolated from such cultures. Tracing experiments with the appropriate ^{14}C-labeled materials indicate that poly-β-ketides, formed from acetyl-CoA and malonyl-CoA, are mutual progenitors of both **329** and **330** and that the aromatic path a is preferred to the nonaromatic path b (Scheme XXIII). Addition of ethionine to these cultures was found to inhibit the formation of **331** and to favor that of tetracetic lactone (**327**). The formate-derived C(1) moiety corresponds to the methyl group at C(3) in **329** and at C(7) in both **330** and **331**. Experiments of incubation of *P. Stipitatum* under an atmosphere enriched with ^{18}O–^{18}O showed that a single ^{18}O is incorporated into stipitatonic acid (**330**). This indicates that a monooxygenase mechanism is operative in the ring expansion of **329** to **330**.[256c] The biosynthesis of another mold tropolone derivative, sepedonin (**321**), has been investigated by feeding [1-^{13}C]acetate, [2-^{13}C]acetate or [^{13}C]formate to cultures of *Sepedonium chrysospermum*.[258] Examination of sepedonin isolated from such cultures indicates that sepedonin is formed by insertion of the formate carbon atom between C(3) and C(4) carbon atoms of a β-polyketide chain of ten carbon atoms built from acetyl-CoA and malonyl-CoA as in the previous case (Scheme XXIV).[258]

SCHEME XXIV

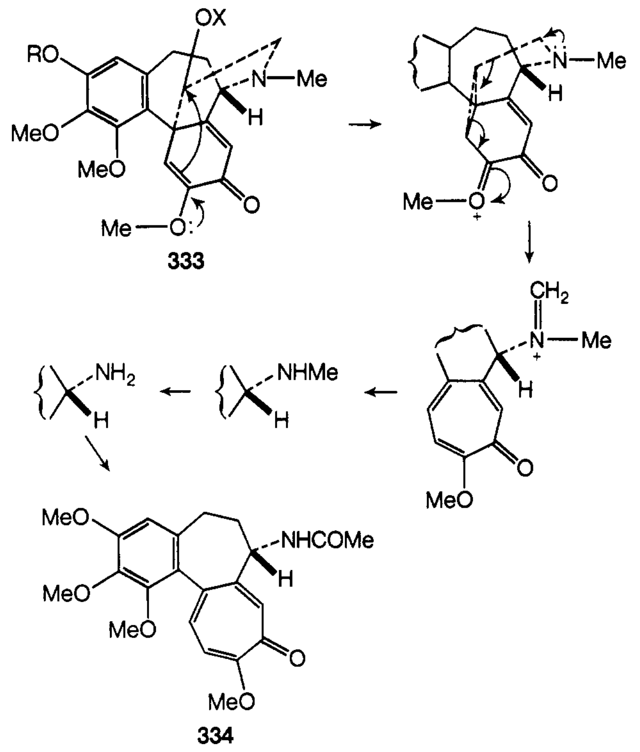


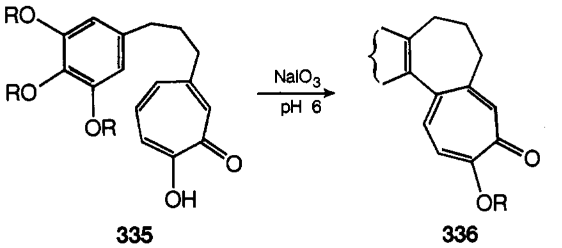
It seems also that the biogenesis of puberulonic and puberulic acids follows the lines of other fungal tropolones.[256b]

The relative merits of the ^{14}C-labeling (requiring degradation) and the ^{13}C-labeling (not requiring degradation but simply ^{13}C nmr examination of the isolated compounds) techniques for biosynthetic studies have been briefly discussed.[268]

The biosynthesis of colchicine (**334**) in *Colchicum autumnale* and *C. byzanthinum* has also been studied by feeding experiments with ^{14}C- and ^{3}H-labeled compounds.[264,269] The results obtained support the hypothesis that 3β-hydroxy-*O*-methylandrocymbine (**333**, X = H; R = Me) is the precursor which undergoes the tropolone ring-forming step[264] (Scheme XXV). The phosphate **333** (X = phosphate) was postulated to undergo enlargement of the dienone ring by homoallylic assistance to ionization (formally similar to the nonenzymatic case **102** → **103**) to give colchicine through the intermediates shown in Scheme XXV.[264] These results do not conform to an earlier hypothesis[270] according to which ring B of cochicine (**334**) might result from oxidative coupling between the benzene and tropolone rings. However, a nonenzymatic oxidative ring closure of this type (**335** → **336**) is a key step in a convenient total synthesis of colchicine.[271]

SCHEME XXV

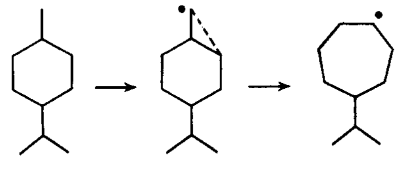




However, in this regard it must be noticed that **333** (R = H, OX = H) derives by oxidative coupling from a phenolic precursor (autumnaline).[264] This allows one to envisage a isoquinoline origin for colchicine.[264]

There has been much speculation about possible biogenetic routes for *Cupressaceae* tropolones.[262b,263] The frequent cooccurrence of several tropolones, such as the three isomeric thujaplicins, with terpenes in *Cupressaceae* trees has generated the idea[263] that *Cupressaceae* tropolones are modified terpenes formed by a ring-enlargement reaction of the type sketched in Scheme XXVI. The isolation of terpenoidal tropolones, such as nootkatin (**324**) (the biogenesis of which has been suggested to occur via a sesquisterpene of an abnormal, bicyclic type[263] (Scheme XXVII), reinforces somewhat this idea.[263] This awaits experimentation, and the case of nezukone (**326**) is particularly interesting for the reasons stated above.

SCHEME XXVI



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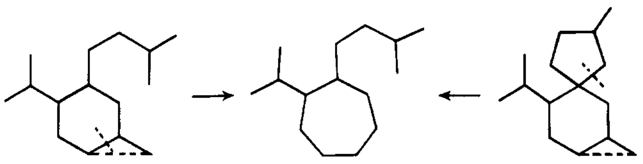
SCHEME XXVII



The interesting possibility of an enzymic approach to synthetic problems in the field of troponoids has received sporadic attention. For example, purpurogallin-4-carboxylic acid has been obtained, albeit in low yield, from the oxidation of gallic acid with a phenol oxidase obtained from potatoes.[272]

Troponoidal products frequently show interesting biological activity. Perhaps the most impressive cases are those of the fungicidal activity of the tropolones of the *Thuja* trees, which effectively preserve their wood,[263] and the antimitotic activity of colchicine and some of its derivatives.[263,273]

IV. Physical Data and Structure

The problem of the aromaticity of the compounds dealt with here has greatly stimulated their investigation. The experimental approach to this problem varied in parallel with the change of the criteria adopted to establish the degree of aromaticity, and there is still no general agreement beyond the general belief that aromatic compounds are unusually stable and typically undergo electrophilic substitution.

There has been much discussion in recent years about the relative merits of the various physical approaches to establish the extent of aromaticity of a given compound, and various prefixes, such as pseudo, quasi, anti, homo, . . ., etc., have been joined to the word aromaticity just to denote extent and origin of aromaticity. This has originated some confusion which led, in certain areas,[274a] to the proposal of abolishing the term aromaticity and its derivatives. Other relevant discussion also appeared.[274b] This is not the place to comment in detail on these problems which are still more appropriately treated in specialized papers. However, this author finds it unnecessary at present to introduce any drastic change in the existing terminology, although further proliferation of prefixes for aromaticity it is hoped will be avoided.

In this section an effort has been made both to illustrate structural features and to present a source of physical data, particularly spectroscopic, for the compounds dealt with in previous sections. To this end these compounds have been grouped together, according to their similarity from drawing on the paper (following the classification criteria illustrated in the Introduction), in various subgroups where their physical data and structural features have been discussed.

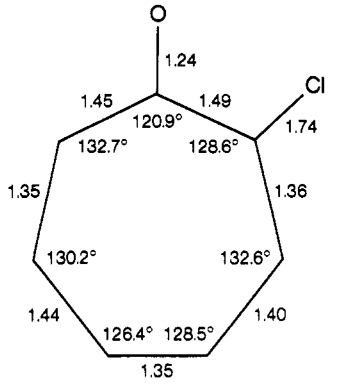
The order in which physical data are presented for each class of compounds is: X-ray crystallographic analysis and other diffraction techniques, nmr (chemical shifts, δ, are relative to TMS as an internal standard, if not otherwise stated) and esr spectra, ir and Raman spectra, uv spectra, and dipole moments, followed by less common experimental techniques, semiempirical calculations, and, finally, mass spectra. Each of these items is printed in italics the first time it appears along the discussion to aid localization. However, for cycloheptatrienethiones (section IV.B.1), cycloheptatrienimines and cycloheptatrienaminoimines (section IV.B.2), heterocyclic analogous (section IV.B.5) homo species (section IV.B.6), and radicals and ion radicals (section IV.C), physical data are presented for each specific compound or group of compounds which are printed in italics the first time they appear along the discussion.

Tropenide salts are not discussed here. The scarce physical data available for them may be found in section II.B.5.

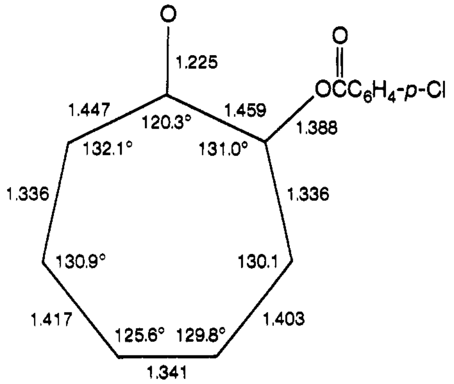
A. Cycloheptatrienones

1. Monocyclic Tropones

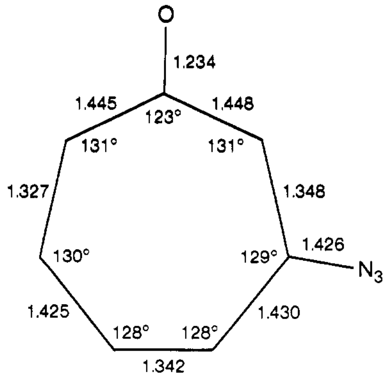
X-Ray crystallographic analysis of 2-chloro- (**337**),[275] 2-(*p*-chlorocarbobenzoxy)- (**338**),[276] and 3-azidotropone



337



338



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(**339**)[277] shows that the seven-membered ring is planar. The chlorine, C(2)-bound oxygen, and carbon-bound nitrogen in **337**, **338**, and **339**, respectively, lie close to the plane of the ring while the carbonyl oxygen is displaced out of the plane of the seven-membered ring by 0.07, 0.136, and 0.06 Å in **337**, **338**, and **339**, respectively. Carbon–carbon bond lengths around the seven-membered ring show a marked alternation. With **339** (in which, probably, perturbation by the substituent is smaller than in the other two cases) the bonds C(1)–C(2), C(3)–C(4), C(5)–C(6), and C(1)–C(7) are slightly shorter than a single C(sp^2)–C(sp^2) bond (1.48–1.50 Å)[278] while C(2)–C(3), C(4)–C(5) and C(6)–C(7) bonds are slightly longer than the pure carbon–carbon double bond (1.335 Å)[279] (esd 0.009 Å).

With **337** and **338** the C(1)–C(2) bond is longer than C(3)–C(4), C(5)–C(6), and C(1)–C(7) bonds. The C(1)–O bond is slightly longer than the normal C═O double bond length (1.215 Å).[279] The bonds between the substituent and the seven-membered ring have the lengths found for bonds with a typical sp^2-hybridized carbon. Therefore, localized resonance structures with alternate bonds seem to have a greater weight than aromatic, tropenylium-type, resonance structures. For both **337** and **338** the C(1)–C(2) bond represents a joint of special insulation.

For tropone itself no X-ray crystallographic study has been so far reported. On the basis of the *electron diffraction* spectrum, taken in the vapor phase, it was not possible to decide between a planar regular heptagonal structure (with C–C = 1.405, C–O = 1.26, and C–H = 1.09 Å) and a planar heptagonal structure with slight bond alternation.[280]

A strikingly different situation has been encountered with perchlorotropone (**97**) which preliminary single-crystal X-ray diffraction data indicate to be boat shaped,[281a] probably to release repulsive interactions among bulky atoms at the periphery of the ring. Perbromotropone (**101**) is expected to have a similar conformation. Perfluorotropone[281b] is likely to have a planar, or nearly so, structure owing to the smallness of fluorine. While the results of the X-ray crystal examination, which is being done,[281b] must be awaited, our suggestion above is supported by the fact that perfluorotropone has no tendency to rearrange and gives substitution products with sodium methoxide.[281b]

The proton *nmr spectrum* of tropone in a nematic solvent has been studied.[282] The spectrum can be accurately reproduced on the basis of a planar model with bond alternation.[282] These results definitely rule out a regular heptagonal structure for tropone but show that the extent of bond fixation is not high. Rapid, on the nmr time scale, flipping between two puckered structures cannot be excluded, but it has been argued[282] that the results allow only very little deviation from planarity, if any.

Proton nmr spectra of some simple tropones and of tropone itself in usual media have also been carefully examined.[283] Ring proton resonances appear at benzenoid field and, as for arenes, are markedly solvent dependent. Carbon tetrachloride produces the least spread (broad singlet at *ca.* δ 7 ppm), and aromatic solvents produce the largest spread of the absorptions. However, even in aromatic solvents nmr spectra of either tropone or monosubstituted tropones are highly complex. The values of the coupling constants are independent of the solvent used and, for the typical case of tropone and 2-chlorotropone in C_6D_6, they are listed in Table I.[283] The fact that the coupling constants of tropone are related to the parameters observed for cyclic polyenones also points to bond alternation in this molecule.

TABLE I. Coupling Constants for Protons of Tropone or 2-Chlorotropone[283]

Tropone		2-Chlorotropone	
$J_{23} = J_{67}$	12.0	J_{34}	9.5
$J_{24} = J_{57}$	1.1	J_{35}	0.8
$J_{25} = J_{47}$	0.7	J_{36}	0.1
$J_{26} = J_{37}$	−0.3	J_{37}	−0.3
J_{27}	3.2	J_{45}	11.1
$J_{34} = J_{56}$	8.2	J_{46}	1.1
$J_{35} = J_{46}$	1.1	J_{47}	0.7
J_{36}	0.1	J_{56}	8.3
J_{45}	11.0	J_{67}	12.4

Proton nmr spectra of tri- or more heavily substituted tropones are much simpler, actually often interpretable by direct inspection. Therefore, they can be used to locate substituents at the ring.[284] Special such cases are those of cycloheptatrienones labeled with two or three deuterium atoms at the ring. On deuterium decoupling easily interpretable spectra are obtained[285] which have been of invaluable help in defining reaction courses of these substrates with nucleophilic reagents (section V).

Simplification of the nmr spectra of C(2)-substituted tropones has been also possible by the use of Eu(dpm)$_3$ as a shift reagent.[286] Complete spectral assignment was possible in some cases, and a set of rules has been proposed to aid in location of substituents at the seven-membered ring.[286]

Tropone shows the following principal *ir absorption* bands in solution (in CCl$_4$ when not otherwise stated). In parentheses are reported approximate relative intensities, when available:[287] 3028 (2, CS$_2$), 1643 (8), 1632, 1609 (sh), 1594 (10), 1522 (4), 1474 (4), 1251 (3), 1212 (4), 888 (3), 831 (2, CS$_2$), 776 (6, CS$_2$), 570 cm^{-1} (CS$_2$, 7). The 1594-cm^{-1} band was observed to shift to 1570 cm^{-1} changing to [^{18}O]tropone and was therefore unequivocally assigned to C═O stretching.[287] All other bands are only very little affected by isotopic substitution, and most of them have been tentatively assigned.[287] The low C═O stretching frequency value indicates that this group is involved in conjugation with the carbon–carbon double bonds to a nonnegligible extent.

It is important to note that a single band, instead of the two bands at 1643 and 1632 cm^{-1}, was previously reported and erroneously assigned to the C═O stretching mode.[1b] It is therefore likely that other previous band assignments for C═O stretching of other tropones are also erroneous.

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(284) See, for example, S. Seto, K. Ogura, H. Toda, Y. Ikegami, and T. Ikenoue, *Bull. Chem. Soc. Jap.*, **41**, 2696 (1968).

(285) G. Biggi, A. de Hoog, F. Del Cima, and F. Pietra, to be published.

(286) H. Tanida, T. Tsushima, and Y. Terni, *Tetrahedron Lett.*, 399 (1972).

(287) A. Krebs and B. Schrader, *Justus Liebigs Ann. Chem.*, **709**, 46 (1967); H. Junge, *Spectrochim. Acta, Part A*, **24**, 1951 (1968).

The Raman spectrum of tropone has also been reported.[288]

The case of 2,6-di-*tert*-butyltropone is interesting because a strong absorption at 1635 cm^{-1} and only weak absorptions at 1610 and 1590 cm^{-1} appear.[57] Clearly, in this spectral region intensities are reversed with respect to tropone, and it has been suggested that this reflects an unusual structure for this compound.[57] This is also indicated by both the observed low basicity with respect to tropone[57] and by the uv spectral data discussed below, as well as by esr spectra of the radical anion (section IV.C).

Ir absorptions for perchlorotropone have also been reported.[86,87] The nonplanar structure of this compound[281] would suggest that the 1695-cm^{-1} band may be attributed to the C=O stretching though no specific experimental evidence is available.

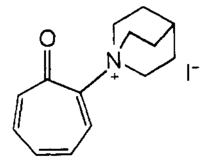
Tropone in solution shows two broad absorptions in the *uv region* at λ_{max}(isooctane) 225 and 305 nm (log ϵ 4.37 and 3.7).[289] There is general agreement[290] that the 305-nm band is due to two different π-π^* transitions, and it has been suggested that also the 225-nm band cannot be attributed to a single transition.[291,292]

Alkyl-substituted tropones show much the same pattern, but the case of 2,6-di-*tert*-butyltropone is unusual, showing two broad absorption bands at 237 and 286 nm (log ϵ 4.18 and 3.81).[57] It is seen that the long wave band is displaced by 20 nm to shorter wavelength with respect to tropone, again suggesting an unusual structure for this compound.[57]

Perchlorotropone, which is definitely nonplanar,[281] presents two main absorptions at 269 and 362 nm (log ϵ 4.16 and 3.40).[86,87]

Other substituents may strongly influence the tropone uv spectrum. Amino groups at C(2) displace the absorptions toward the visible region. Thus, 2-piperidinotropone[293] in ethanol shows four strong absorptions at 225, 257, 358, and 400 nm (which are typical also of other 2-piperidinotropones substituted at the piperidino moiety[293]), and 2-aminotropone shows absorptions at 268 (log ϵ 3.97), 340 (3.94), 375 (3.84), 385 (3.76), 395 nm (3.89) in cyclohexane.[294] When the amino nitrogen is bound to C(4) or C(3), the longest wavelength absorption appears at appreciably shorter wavelength. This effect is more marked for substitution at C(3). Values are 362 and 313 nm for 4- and 3-aminotropone,[295,296] respectively (although there is considerable discrepancy as regards values of the extinction coefficient for 3-aminotropone at 313 nm among different authors[295,296] and even among different papers by the same authors[296a,b]).

When nonbonded electrons are not available at nitrogen for conjugation with the cycloheptatrienone moiety, such as in the case of **340**, the spectrum is nearly identical with that of tropone.[293]



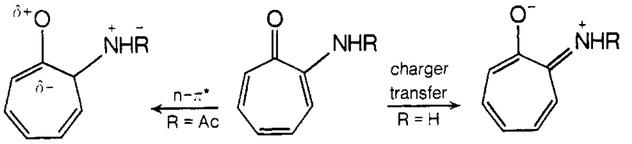
340

Oxygen, sulfur, and, to a much lesser extent, halogen substituents also displace tropone uv absorptions toward longer wavelengths. Thus, 2-methoxytropone shows broad absorptions with absorption maxima at 322 and 368 nm and shoulders at longer wavelengths,[293] whereas the longest wavelength band for 2-halotropones has a maximum around 315 nm.

Phenyl substituents also induce a red shift. Thus, for 2,4,6-triphenyltropone the long wavelength absorption band occurs at *ca.* 370 nm (log ϵ *ca.* 3.9).[224]

Both empirical[297] and semiempirical approaches[290] to the interpretation of the uv absorption spectra of cycloheptatrienones have been attempted. Thus, from the observation of a red shift in a protic solvent for the longest wavelength absorption band of 2-aminotropone, this has been assigned to a transition to a lowest lying charge-transfer state (Scheme XXVIII).[297] Conversely, the blue shift in a protic solvent of the absorptions (320–385 nm) of 2-acetylaminotropone has been taken as an indication that a transition of the n-π^* type is involved (Scheme XXVIII).[297] These empirical correlations help very much the understanding of the photochemical behavior of cycloheptatrienones (section V).

SCHEME XXVIII



The *dipole moment* of tropone is 4.30 D.[298] This is definitely higher than the value, 3.04 D, found for cycloheptanone[299] but of the same order of that, 4.04 D, found for 2,6-cycloheptadienone. It has been concluded that this indicates only a very modest contribution of the tropenylium ion type structure for tropone.[298] The evidence is convincing as 2,6-cycloheptadienone is certainly a better model than cycloheptanone. Enhanced dipole moment of tropone with respect to the latter has been attributed, in accordance with the whole body of evidence summarized above, to polyenone-type delocalization.[298] The value (4.72 D) of the dipole moment of 2-methoxytropone is also consistent with this view.[298] Dipole moments for a number of other tropones have been also reported.[300]

In the case of tropone, values of both the experimental *diamagnetic susceptibility* (recent recalculations lead to only a modest exaltation[298]) and the experimental *stabilization energy* (11.9 kcal mol^{-1}, *i.e.*, only 3 kcal mol^{-1} greater than that of cycloheptatriene[298]) are also in accord with lack of aromatic character. Also the relatively high *basicity* of tropone, which in the past was taken as evidence for the dominance of the tropenylium ion type structure, finds its origin in the high stability of the prod-

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(288) Y. Ikegami, *Bull. Chem. Soc. Jap.*, **35**, 967 (1962).

(289) W. von E. Doering and F. L. Detert, *J. Amer. Chem. Soc.*, **73**, 876 (1951).

(290) Z. Yoshida and T. Kobayashi, *Theor. Chim. Acta*, **20**, 216 (1971).

(291) E. Weltin, E. Heilbronner, and H. Labhart, *Helv. Chim. Acta*, **46**, 2041 (1963).

(292) T. Hoshi and Y. Tanizaki, *Z. Phys. Chem. (Frankfurt am Main)*, **71**, 230 (1970).

(293) F. Pietra, G. Biggi, and F. Del Cima, *J. Chem. Soc. C*, 3626 (1971).

(294) T. Nozoe, S. Seto, H. Takeda, S. Morosawa, and K. Matsumoto, *Sci. Rep. Tohoku Univ., Ser. 1*, **36**, 126 (1952); *Chem. Abstr.*, **48**, 4497 (1954).

(295) J. D. Hobson and J. R. Malpass, *J. Chem. Soc. C*, 1499 (1969).

(296) (a) S. Seto, H. Sugiyama, and H. Foda, *Chem. Commun.*, 562 (1968); (b) H. Toda, H. Sugiyama, and S. Seto, *Chem. Pharm. Bull.*, **17**, 2548 (1969).

(297) T. Mukai and M. Kimura, *Tetrahedron Lett.*, 717 (1970).

(298) D. J. Bertelli and T. G. Andrews, Jr., *J. Amer. Chem. Soc.*, **91**, 5280 (1969).

(299) H. H. Gunthard and T. Gaumann, *Helv. Chim. Acta*, **34**, 39 (1951).

(300) Reference 1b, p 377.

uct, hydroxytropenylium ion, of protonation of tropone.[298,301,302]

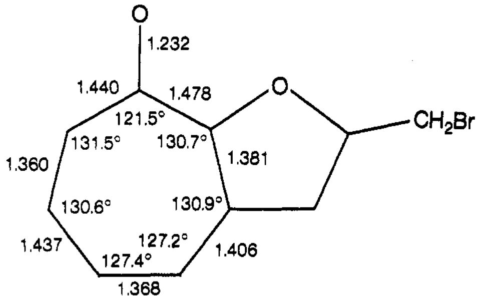
Various *semiempirical calculations* concerned with the structure of simple tropones[292,303] also point to alternate bond type structures in agreement with all evidence above. Calculations by CNDO/2 suggest that planarity of the tropone molecule is not due to π-electron energy factors but rather to alleviation of coulombic repulsive interaction in the planar model.[304]

Studies of electron impact *mass spectra* of simple tropones have been reviewed.[305] Although the molecular ion peak is well pronounced, the most intense peak corresponds to loss of carbon monoxide $(M - 28)^+$. At lower masses the spectrum is often similar to that of the corresponding benzene derivative of M − 28 mass. In the case of 2-methoxytropone, the carbonyl carbon is extruded to give a formyl radical.[306]

2. Polycyclic Tropones

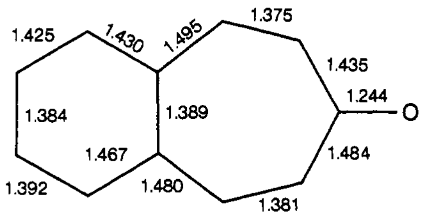
X-Ray crystallographic analysis has been reported for the following fused tropones: 2-bromomethyl-2,3-dihydrofuro[2,3-*b*]tropone (**341**),[307] 4,5-benzotropone (**342**),[308] 5-chloro- (**343**)[309] and 5,7-dibromo-2,3-benzotropone (**344**),[309] and 2,3:6,7-dibenzotropone (**345**).[310a]

All carbons of the seven-membered ring of **341** lie in a plane. However, the carbonyl oxygen is appreciably (0.069 Å) out of this plane owing to intermolecular interactions in the crystal.[307] Clear alternation of carbon–carbon bond lengths is also seen.



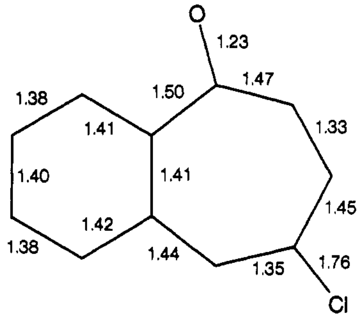
341

The tropone ring in 4,5-benzotropone (**342**) is not exactly planar, the carbonyl carbon and the carbonyl oxygen being displaced by 0.1 and 0.2 Å, respectively, from the mean plane of the heptaatomic ring.[308] As the intermolecular contacts are normal, these displacements seem to be due to intrinsic molecular properties rather than to interactions in the crystal.[308]



342

The seven-membered ring in both **343** and **344** takes a shallow boat form and clear bond alternation is seen.[309]



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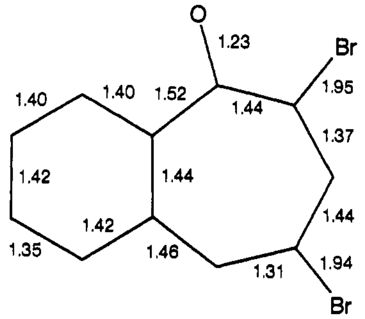
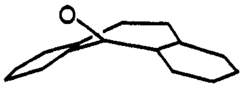


344

Finally, deviation from planarity of the cycloheptatrienone ring is most pronounced in 2,3:6,7-dibenzotropone (**345**).[310a] Preliminary results[310a] indicate that the tropone ring is boat shaped in this molecule, owing to repulsions between oxygen and the peri hydrogens.[308] The tropone ring shows bond alternation.[310a] Also colchicine has been examined by X-ray crystal diffraction.[310b]



345

Proton *nmr spectra* of fused tropones differ markedly from those of tropone. While the latter under usual experimental conditions shows a broad singlet, chemical shift differences for protons of fused tropones are usually so large that coupling constants can be often directly obtained by inspection of the spectra.[311] All evidence from nmr studies points to bond alternation for the cycloheptatrienone ring of fused tropones.[311a] These studies[311a] also indicate that 2,3-benzotropone is fully planar. A tribenzotropone flattened by either methylene or carbonyl bridges between arene units has also been reported.[311b] Studies of lesser scope for colchicine and isocolchicine have been reported.[312]

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(301) H. J. Dauben and K. M. Harmon, unpublished, quoted in ref 200.

(302) G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, 3586 (1959).

(303) (a) M. J. S. Dewar, A. J. Harget, and N. Trinajstić, *J. Amer. Chem. Soc.*, **91**, 6321 (1969); N. Trinajstić, *Bull. Chem. Soc. Jap.*, **44**, 3208 (1971); (b) M. J. S. Dewar and N. Trinajstić, *Croat. Chem. Acta*, **42**, 1 (1970); (c) R. Zahradnik and J. Koutecky, *Collect. Czech. Chem. Commun.*, **28**, 1117 (1963); (d) C. A. Coulson and A. Stretwieser, "Dictionary of π-Electron Calculations," Pergamon Press, Oxford, 1965, p 168.

(304) D. J. Bertelli in ref 86b, pp 326–333.

(305) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass-Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 18; J. M. Wilson, M. Ohashi, H. Budziklewicz, C. Dierassi, S. Ito, and T. Nozoe, *Tetrahedron*, **19**, 2247 (1963).

(306) J. C. L. Wright, W. D. Jamieson, S. Safe, and L. C. Vining, *Can. J. Chem.*, **50**, 821 (1972).

(307) H. Shimanouchi, T. Ashida, Y. Sasada, M. Kakudo, I. Murata, and Y. Kitahara, *Bull. Chem. Soc. Jap.*, **40**, 779 (1967).

(308) T. Hata, H. Shimanouchi, and Y. Sasada, *Tetrahedron Lett.*, 753 (1969).

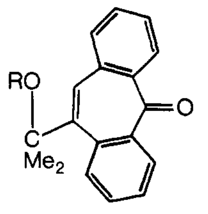
(309) K. Ibata, T. Hata, H. Shimanouchi, and Y. Sasada, *J. Chem. Soc., Chem. Commun.*, 339 (1972).

(310) (a) H. Shimanouchi, T. Hata, and Y. Sasada, *Tetrahedron Lett.*, 3573 (1968); (b) M. V. King, J. L. De Vries, and R. Pepinsky, *Acta Crystallogr.*, **5**, 437 (1952).

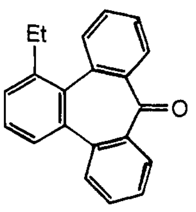
(311) (a) D. J. Bertelli, J. T. Gerig, and J. M. Herbelin, *J. Amer. Chem. Soc.*, **90**, 107 (1968); (b) W. Tochtermann, C. Degel, and G. H. Schmidt, *Chem. Ber.*, **105**, 1431 (1972).

(312) G. Severini and B. Danieli, *Gazz. Chim. Ital.*, **99**, 133 (1969).

Energy barriers to conformational inversion of the nonplanar cycloheptatrienone ring in the 2,3:6,7-dibenzotropone derivatives **346a,b** and in the tribenzotropone **347** have been obtained by proton nmr spectroscopy.[313] Energy barriers of less than 9 kcal mol^{-1} for both **346a** and **346b**, and of 20.0 kcal mol^{-1} for **347**, have been found.[313] The fact that, like for tropone, no appreciable aromaticity could be detected for **347** (from the difference between estimated and experimental inversion barriers)[313] is not surprising to this reviewer in view of the expected bond localizing effect of the arene groups.



346a, R = H
b, R = Me



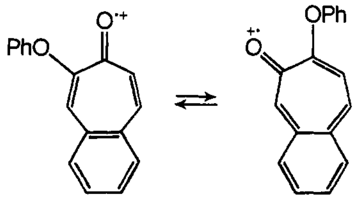
347

No other physical property of fused tropones received such detailed attention as X-ray diffraction or proton nmr spectra. To make some generalization, both *ir and uv spectra* or benzo-,[1b] dibenzo-,[1b] tribenzo-,[314] and furotropones[1b] show the characteristic absorptions of tropone.

Dipole moments for some benzotropones are also available.[300] Recent data, and their use for locating substituents at the ring, have been recently reported.[315]

Semiempirical calculations for several arene-fused tropones[303b] and furotropones[316] support bond alternate structures and, in agreement with naive chemical intuition, indicate[303b] lessened stabilization for compounds of quinoidal structure like 3,4-benzotropone. One such quinoidal tropone (**43**) has been recently obtained, but it is so unstable that it proved impossible to obtain any physical data.[33]

Mass spectra of fused tropones are similar to those of monocyclic tropones.[305,317] An interesting case is offered by 2-phenoxy-4,5-benzotropone. Here, besides $[M - CO]^+$, a prominent fragment ion is $[M - OH]^+$.[318] Labeling experiments revealed that the oxygen of these fragment ions comes from both oxygen atoms of the molecular ion while the hydrogen comes only from the ortho position in the phenyl group.[318] Therefore, the 1,4-aryl migration **348** ⇄ **349** must be involved in the molecular ion before fragmentation.[318]



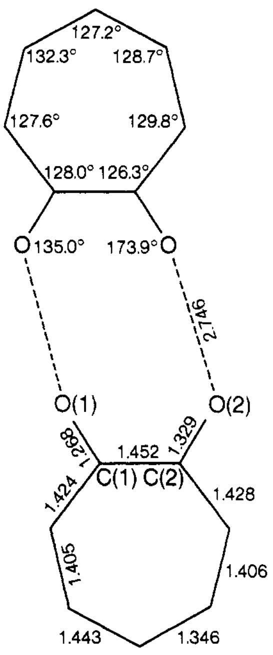
348 **349**

Mass spectral fragmentation patterns of alkaloids related to colchicine[319] and of anhydrosepedonin dimethyl ether[306] have also been discussed.

3. Mono- and Polycyclic Tropolones

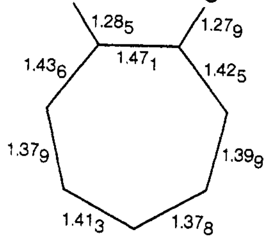
Structural studies are much more abundant for tropolones than for 3- and 4-hydroxytropones. Available data for compounds of the last two types are reviewed here in parallel with those for tropolones, and data collected in Table II allow a comparison of the physical properties of the three parent compounds.

X-Ray diffraction examination of tropolone reveals an almost planar dimeric structure (**350**).[320a] The C(1)-C(2) bond is definitely longer than all other C-C bonds. However, within the estimated standard deviation of 0.08 Å, the typical bond alternation of tropones is not observed. Another interesting point is that the acidic hydrogen is mainly bonded to O(2) as judged from C-O bond lengths and O. . . O-C angles.



350

A similar situation, with the C(1)-C(2) bond being even more markedly longer than all other C-C bonds, has been encountered with sodium tropolonate (**351**).[321] The ring deviates from planarity slightly, owing to some effect of the crystalline field.[321] In contrast, the hydrochloride salt of tropolone in the crystal shows a completely planar structure with substantially identical C-C bond lengths



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(313) M. Nógrádi, W. D. Ollis, and I. O. Sutherland, *Chem. Commun.*, 158 (1970).

(314) M. Stiles and A. J. Libbey, *J. Org. Chem.*, **22**, 1243 (1957).

(315) T. Shimozawa, S. Kumakura, M. Hoshino, and S. Ebine, *Bull. Chem. Soc. Jap.*, **44**, 565 (1971).

(316) N. Zambelli and N. Trinajstic, *Z. Naturforsch. B*, **26**, 1007 (1971).

(317) O. L. Chapman and T. H. Hoch, *J. Org. Chem.*, **31**, 1042 (1966).

(318) T. H. Kinstle, O. L. Chapman, and M. Sung, *J. Amer. Chem. Soc.*, **90**, 1227 (1968).

(319) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 1, Holden-Day, San Francisco, Calif., 1964, Chapter 13.

(320) (a) H. Shimanouchi and Y. Sasada, *Tetrahedron Lett.*, 2421 (1970); (b) J. E. Derry and T. A. Hamor, *J. Chem. Soc., Perkin Trans. 2*, 694 (1972).

(321) Y. Sasada and I. Nitta, *Acta Crystallogr.*, **9**, 205 (1956); R. Shiono, *ibid.*, **14**, 42 (1961).

TABLE II. Physical Properties for Tropolone (83) and 3- (76b) and 4-Hydroxytropone (66)

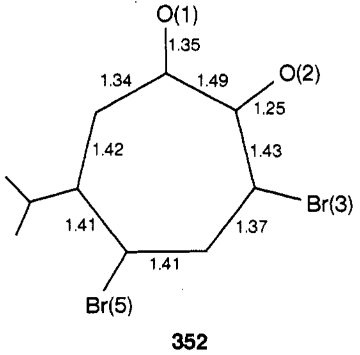
	Tropolone	3-Hydroxytropone (β-tropolone)	4-Hydroxytropone (γ-tropolone)
Mp, °C	49[64]	183–183.5[89]	212[a]
Picrate mp, °C	83.5–84[64]	165 dec[b]	85–87 dec[a,c]
pK_a	6.7[64]	5.4	5.6[a]
Volatility	Sublimes at 150 mm, 100°[64]	Sublimes slowly with dec at 0.1 mm, 140°[b]	Sublimes slowly at 0.1 mm, 170°[d]
$FeCl_3$ test	Green color[64]	Negative[b]	Negative[a]
Solubility	Sol in nonpolar and polar solvents[64]	Sol in MeOH, EtOH, and, less, in water; insol in CCl_4, CS_2, and $CHCl_3$[b]	Sol in water, alcohols, acetone, dioxane, AcOH; insol in C_6H_6, $CHCl_3$, pet. ether[d]
λ_{max}^{EtOH}, nm (log ϵ)	(In isooctane) 200–240, (~4.2–4.3), 300–380 (~3.5–3.7)[64]	247 (4.49), 254 (4.42), 270 (3.84), 297 (3.68), 307 (3.59)[89]	226 (4.28), 333 (4.14)
$\lambda_{max}^{NaOH\,(concd)}$, nm (log ϵ)	(0.01 *M*) 234 (~4.5), 330 (~4.1), 393 (~4)[64]	(0.05 *M*) 256 (4.62), 266 (4.58), 294 (3.88), 303 (3.88)[89]	(0.1 *M*) 227 (4.30), 360 (4.34)[a,d]
ν_{max}, cm^{-1}	Broad band at 3100 (dilute in (CCl_4), 1615, 1553, 1475, 1440, 1255 (Nujol mull)[64,e]	No distinct OH str, 1647, 1587, 1550, 1515, 1477, 1443, 1258, 1230, 1196, 996, 985, 881, 872, 826, 819, 786, 763, 722 (Nujol mull)[b]	2440 (broad), 1645, 1621, 1600, 1529, 1439, 1399, 1282, 1212 (Nujol mull);[a] 2460 (broad); 1640 w, 1597, 1440, 1400, 1285[48b]
Dipole moment (benzene), D	3.53[f]		5.9
X-Ray diffraction molecular structure	**350**[320a]		
Electron diffraction molecular structure	Regular heptagon or slight bond alternation[324]		
Proton nmr spectra	CH at about benzene field,[283] OH at very low field (δ 9.51,[41] independent of concn[325a] in $CDCl_3$)		(In aq NaOH) δ 7.40, 7.23, 7.19 and 7.12 (1 H, d, J = 9.4 Hz), 7.06 (2 H, s), 6.54 (2 H, unsym d, J = 9.4 Hz)[48b]
Mass spectrum (electron impact)	M^+ 100%; $(M - CO)^+$ 97%[305]		M^+ 45%; $(M - CO)^+$ 100%[305]

[a] R. S. Coffey and A. W. Johnson, *J. Chem. Soc.*, 1741 (1958). [b] R. B. Johns, A. W. Johnson, and M. Tisler, *J. Chem. Soc.*, 4605 (1954). [c] On rapid heating; decomposition to free components tends to occur below the melting point: footnote *a*. [d] B. D. Challand, H. Hikino, G. Kornis, G. Lange, and M. De Mayo, *J. Org. Chem.*, **34**, 794 (1969). [e] H. P. Koch, *J. Chem. Soc.*, 512 (1951). [f] Y. Kurita, S. Seto, T. Nozoe, and M. Kubo, *Sci. Rept. Res. Inst., Tohoku Univ., Ser. A*, **38**, 85 (1954).

(1.40 Å),[322] suggesting a dihydroxytropenylium ion structure.

4-Isopropyltropolone has a planar structure with the C(1)–C(2) bond distance (1.469 Å) being typical of a single bond.[320b] The remaining bonds around the ring alternate as expected for the classical bond-alternate structure,[320b] in contrast with the results for tropolone (**350**).[320b]

3,5-Dibromo-6-isopropyltropolone (**352**) also possesses a planar ring structure as revealed by X-ray diffraction studies in the crystal.[323a] Here, however, not only is the C(1)–C(2) bond longer than all other C–C bonds, but the C(1)–C(7) and C(3)–C(4) bonds have marked double bond character. There is no full double bond fixation, however, because the C(5)–C(6) bond has little double bond character (esd ±0.02 Å).[323a]



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3,7-Dibromo- and 3,5,7-tribromo-6-isopropyltropolone have also been examined by X-ray diffraction in the crystal.[323a] Owing to strong repulsions among ring substituents, both compounds have nonplanar, twisted boat, conformation in the crystal, and there is considerable bond fixation.[323a] Also purpurogallin[323b] and colchiceine[323c] have been examined by X-ray crystal diffraction.

The *electron diffraction spectrum* of tropolone (vapor) has also been examined.[324] The most plausible (mean) model seemed to be a regular heptagon[324] with C–C 1.39, C–H 1.10, C–O 1.34, and C–O 1.26 Å bond lengths.[324b] This was interpreted in terms of a mobile unsymmetrical tautomeric system (**353**) with the acidic hydrogen not occupying a position midway between the two oxygen atoms. This view is in accord with recent proton *nmr spectra*.[283] In fact, both vicinal and long-range

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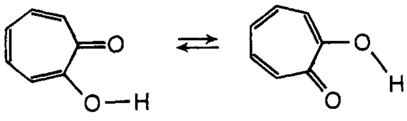
(322) Y. Sasada and I. Nitta, *Acta Crystallogr.*, **9**, 205 (1956).

(323) (a) S. Ito, Y. Fukazawa, and Y. Iitaka, *Tetrahedron Lett.*, 741, 745 (1972); (b) J. D. Dunitz, *Nature (London)*, **169**, 1088 (1952); C. Taylor, *ibid.*, **169**, 1087 (1952); (c) J. D. Morrison, *Acta Crystallogr.*, **4**, 69 (1951).

(324) (a) E. Heilbronner and K. Hedberg, *J. Amer. Chem. Soc.*, **73**, 1386 (1951); (b) M. Kimura and M. Kubo, *Bull. Chem. Soc. Jap.*, **26**, 250 (1953).

coupling constants are average values of their corresponding components in tropolone methyl ether.[283] This implies that instantaneous species should have bond alternation as shown by structural formulas **353a** and **353b**.



353a **353b**

That this is in contrast with the X-ray analysis in the crystal, according to which all C–C bonds, except the C(1)–C(2), have substantially the same length (**350**),[320a] passed unnoticed in the original literature.[320a] Origin of different molecular structures in the crystal and in solution is not immediately clear and the problem deserves further attention.

Proton nmr data also point to intramolecularly hydrogen-bonded structures for tropolone. In fact, the OH resonance appears at very low field, δ 9.51 ppm,[41] independent of the concentration[325a] (0.1–2 mol %) in $CDCl_3$ (Table II). Proton nmr studies of lesser scope have been reported for 4-hydroxytropone[48b] (Table II).

The ^{13}C nmr spectrum of ^{13}C-labeled sepedonin (**332**) has been studied to locate the label for biosynthetic purposes.[268]

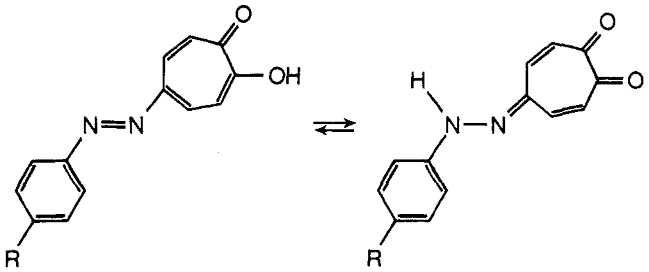
Ir spectral data for all three parent tropolones are compared in Table II. Only for tropolone has a detailed study been carried out, with limited success, however.[325b] In fact, ^{18}O-labeling led to such small displacements of absorptions that it was not even possible to assign the C=O stretching vibration.[325b] The fact that no distinct OH stretching band is observed for 3-hydroxytropone in a Nujol mull (Table II) has been taken as an indication of extensive aggregation by intermolecular hydrogen bonding.

Uv spectral data for all three parent tropolones, and their conjugate bases, are also collected in Table II. It can be noticed that on going from α- to γ- to β-tropolonato the long-wavelength band undergoes a blue shift, and the same is true for their conjugate acids. A similar trend has already been noticed for the corresponding aminotropolones (section IV.A.1). The long-wavelength absorptions for the couples α-tropolonato-2-aminotropone and γ-tropolonato-4-aminotropone appear at the same position, and for the first couple the whole absorption pattern is also identical.[291] This has been taken as an indication that the conjugative effects of the oxyanion and amino groups are the same and that the negative charge must be mainly localized on one-sided oxygen atom in α-tropolonato.[292] The last conclusion[292] is surprising because the great stability of tropolonato ion requires a great deal of conjugation energy. It is not apparent how this system may acquire so much conjugation energy without involving both oxygen atoms.

In contrast, the long-wavelength absorption band occurs at shorter wavelength (303 nm, Table II) for β-tropolonate than for 3-aminotropone (313 nm).[295,296] It is also notable that, contrary to the case of both α- and γ-tropolone, where change to the corresponding tropolonate leads to considerable red shift for the long wavelength absorption band, with β-tropolone little shift, and just in the reverse direction, is observed (Table II).

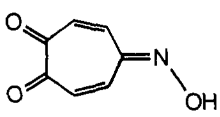
Assignment of the electronic transitions for tropolone has also been attempted on a semiempirical basis[290,326] and on rotational analysis.[325c] The latter[325c] indicates that equilibrium structure is midway between **353a** and **353b**.

The uv and visible spectra of 5-phenylazotropolones **354** have also been studied.[327] No evidence for hydrazone tautomerization has been found.[327] However, tautomerization to hydrazones has been discovered with 5-nitrosotropolones whose predominant form is represented by **355**.[328] Connected to this problem is the isolation of the diketone-type tautomer **356a**[329a] and of the tropoquinones **356b**.[329b] Unusual stability of the diketone **356a** has been attributed to strong repulsions between bulky substituents preventing planarity of the ring[323] in the tropolone tautomer.



354

R = H, Me, OMe, F, Cl, I, NO_2, Ac, CN



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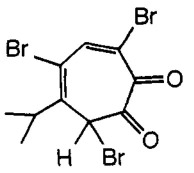
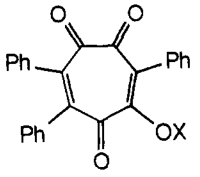


356a



356b, R = Ph, $PhCH_2$; X = COR, H

The tropoquinones **356b**[329b] are interesting because many attempts to synthesize tropoquinone itself failed.[329c] This seems to have escaped the attention of the original authors.[329b] The one with R = Ph and X = $COCH_3$ was obtained in fair yield by the treatment of phenylmalonyl chloride with sodium acetate in benzene at reflux, and the other ones were obtained by an adaptation of this route.[329b] Saponification led to **356b** (X = H).[329b] A ketene mechanism has been proposed for this important route to seven-membered carbocyclic rings. However, structural proofs for compounds **356b** relies only on mass spectrometry.[329b]

Whether 1,3- or 1,4-diketone-type tautomerism exists in respectively β- or γ-tropolones does not appear to have been studied, although this type of problem has been raised for the case of 4,5-benzo-β-tropolone.[330]

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(325) (a) N. N. Shapet'ko and D. N. Shigorin, *Zh. Strukt. Khim.*, **8**, 538 (1967); *Chem. Abstr.*, **67**, 103798d (1967); (b) H. Junge, *Spectrochim. Acta, Part A*, **24**, 1957 (1968); (c) A. C. P. Alves and J. M. Hollas, *Mol. Phys.*, **23**, 927 (1972).

(326) (a) H. Kuroda and T. Kunii, *Theor. Chim. Acta*, **7**, 220 (1967); (b) H. Hosoya, J. Tanaka, and S. Nagakura, *Tetrahedron*, **18**, 859 (1962).

(327) J. Griffiths, *J. Chem. Soc. B*, 801 (1971).

(328) T. Nozoe and S. Seto, *Proc. Jap. Acad.*, **27**, 188 (1951).

(329) (a) M. Yasunami, K. Takase, and T. Nozoe, *Tetrahedron Lett.*, 4327 (1970); (b) H. Wittmann, V. Illi, H. Rathmayr, H. Sterk, and E. Ziegler, *Z. Naturforsch. B*, **27**, 524 (1972); H. Wittmann, and N. Rathmayr, *ibid.*, **27**, 528 (1972); (c) ref 1b, pp 434–436.

(330) S. Ebine, M. Hoshino, and K. Takahashi, *Bull. Chem. Soc. Jap.*, **41**, 2942 (1968); M. Hoshino and S. Ebine, *ibid.*, **41**, 2949 (1968).

The extent of the red shift of the long-wavelength absorptions observed on going to the conjugate base of **354** correlates well with the Hammett ρ values of the substituents R.[327]

Annelation induces a red shift of the electronic absorption bands. Thus, 3,4-benzotropolone and 2,3-benzo-4-hydroxytropone show absorptions at λ_{max} (log ϵ) 390 (3.8) and 440 (3.8), respectively, in ethanol.[331]

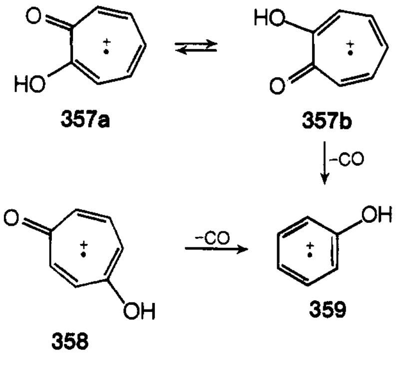
From the *acid–base* data of Table II it can be seen that acid strengths of all three tropolones have intermediate values between those of phenols and carboxylic acids. Also, both 3- and 4-hydroxytropone are stronger acids than tropolone. All three compounds are also basic enough to give picrates, that of tropolone being thermally the most stable.

Volatility is much higher for tropolone than for either β- or γ-tropolone (Table II). This reflects more extensive aggregation in the last two cases in agreement with other data discussed above. *Solubility* data are also consistent with this view as both 3- and 4-hydroxytropone are insoluble in nonpolar solvents in which, in contrast, tropolone dissolves readily (Table II).

The *dipole moment* is higher for 4-hydroxytropone than for tropolone (Table II).

Semiempirical calculations gave[326] a value for the dipole moment of tropolone which is considerably higher than the experimental value. Resonance energies[303a] and bond lengths[303b] have also been calculated for all three compounds of Table II, bond alternate structures being favored.[303b]

The molecular ion peak is the prominent peak in the *mass spectrum* of tropolone while the $[M - CO]^+$ peak has a relative intensity of *ca.* 97%.[305] This has been rationalized in terms of stabilization of the positive charge on the molecular ion by hydrogen transfer (**357a** ⇄ **357b**) between the two ortho oxygens.[305] This extra stabilization is not possible in the case of either tropone or γ-tropolone where the base peak is given by the $[M - CO]^+$ ion.[305] Mass spectra of substituted tropolones have also been discussed.[305,306]



B. Other Species

1. Cycloheptatrienethiones

Spectra, solubility, and p*K* data for 2-mercaptotropone have been rationalized in terms of preponderance of the thionoform (**122**).[97b] However, strong intramolecular hydrogen bonding, as in the case of tropolone,[325a] is suggested by the low-field resonance (δ 9.95 ppm in $CDCl_3$) of the acidic proton.[98] The fact that 2-mercaptotropone is alkylated exclusively at sulfur[97b] should not be surprising. In fact, as a rule valid at least for reactions in hydrogen-bonding solvents, sulfur nucleophiles are much more rapidly alkylated than oxygen nucleophiles.[332]

In the mass spectrum of 2-mercaptotropone the molecular ion is the base peak and prominent fragmentation peaks correspond to loss of CO or CS, respectively.[305]

The proton nmr spectrum of *dithiotropolone* (**127**) shows that the SH proton is markedly deshielded (δ 9.24 ppm in $CDCl_3$) again pointing to the existence of a strong intramolecular hydrogen bond.[98] The part of the spectrum due to the ring protons is surprisingly simple for a system of five adjacent protons bonded to unsaturated carbons.[98] The spectrum has not been fully interpreted, however.

In the mass spectrum (70 eV) of dithiotropolone the molecular ion is the base peak and prominent fragmentation peaks correspond to $C_7H_5S_2^+$, $C_7H_5S^+$, $C_6H_6S^+$, $C_7H_6^+$, and $C_7H_5^+$, for loss of H, SH, CS, S_2, and S_2H, respectively, from the molecular ion.[98] Infrared and ultraviolet absorption spectra have been also reported for dithiotropolone.[98]

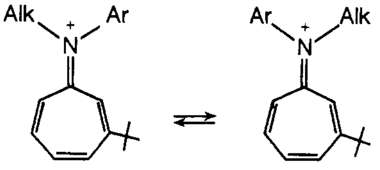
2-Aminothiotropones (**129**) are characterized by the absence of the tautomeric imino form even in alkaline solution.[99] These compounds are, in fact, easily soluble in dilute acid but insoluble in strong base.[99] This is confirmed by the proton nmr spectrum of **129** (R = Me) where the methyl group shows up as a doublet.[99] The ring protons of 2-aminothiotropones give rise to an extremely complex nmr absorption pattern.[99] The electronic absorption spectrum of 2-aminothiotropones is characterized by two strong bands at *ca.* 450 and 280 nm.[99]

Thiotropone (**132**) has been calculated to have delocalization energy of intermediate value between heptafulvene and tropone.[303c]

2. Cycloheptatrienimines and Cycloheptatrienaminoimines

Both *cycloheptatrienimines* (**137**) and their conjugate acids (**136**) show ir and uv absorption spectra similar to those of tropone.[104,105] Also, the protons bound to ring carbons show up as a structured nmr single peak at slightly higher (δ 7.7 ppm for **136**, R = C_3H_7) or at slightly lower field (δ 6.3 ppm for **137**, R = C_3H_7) than the tropone signal (δ 6.9 ppm).[104,105] Their conjugate acids (**136**) cannot be further protonated as shown by the fact that both uv and nmr spectra are unchanged in concentrated sulfuric acid. Uv absorption bands for troponeimine (**137**, R = H) have been assigned to specific transitions.[326]

The problem of the resonance between the immonium (**138**) and the tropenylium ion structure has been attacked by the variable-temperature nmr method on a series of hexachloroantimoniate salts of type **360**.[108] Coalescence temperatures of the *tert*-butyl signal due to **360a** and **360b** range from −28 to +70° corresponding to free energy barriers of 12–18 kcal mol^{-1}.[108] These are lower than those found for either true immonium salts or cyclopropenylidenimmonium salts.[108] This points to the important contribution of tropenylium structures.[108]



360a **360b**

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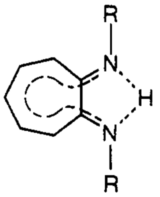
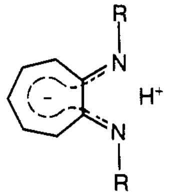
(331) G. L. Buchanan, *J. Chem. Soc.*, 1060 (1954).

(332) E. P. Grimsrud and J. W. Taylor, *J. Amer. Chem. Soc.*, **92**, 739 (1970).

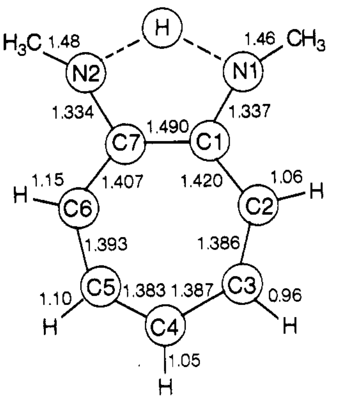
Aminotroponeimines **128** can be best described, on the basis of available data, in terms of structures of type **361a** with possibly some contribution from no-bond structures **361b**, the ten π electrons encompassing the seven-membered ring and the two nitrogen atoms.[114] In fact, accurate tridimensional crystallographic analysis of 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (**362**) showed that this molecule possesses C_2 symmetry including the methyl groups which are staggered with respect to the nearest C(6)-H and C(2)-H hydrogen atoms.[333] The C(1)-C(7) bond is practically a single bond as in the case of sodium tropolonate (**351**). All other evidence is in accord with this view. Thus, equivalence of the two R (alkyl or aryl) groups was proved by nmr spectroscopy, and the dipole moment was found to be directed toward the heptaatomic ring (whereas the reverse direction was found for both cycloheptatrienones and cycloheptatrienethiones).[114] Reactivity data for reactions with electrophilic reagents, to be considered in section V, also support this view.



361a



361b



362

3. Heptafulvenes

X-Ray crystal structures of a number of heptafulvene derivatives have been reported. Thus, 8,8-dicyanoheptafulvene (**153**) deviates only slightly from planarity and shows marked bond alternation as indicated by the structural representation **363**.[334] The exocyclic C–C bond is unusually long (1.422 Å) for a double bond and suggests considerable tropenylium ion character.[334]

Such an analysis has been carried out for the benzosesquifulvalene system **171** as well.[335] In this case, the component ring systems are nearly planar while the whole molecule deviates from planarity. The five-membered and the seven-membered rings are twisted by 31° around the bond interconnecting them. Moreover, the planes of the seven-membered and the six-membered rings make a dihedral angle of 5°. Marked alternation in the seven-membered ring is also apparent (**364**).[335]

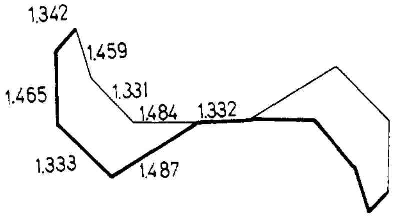
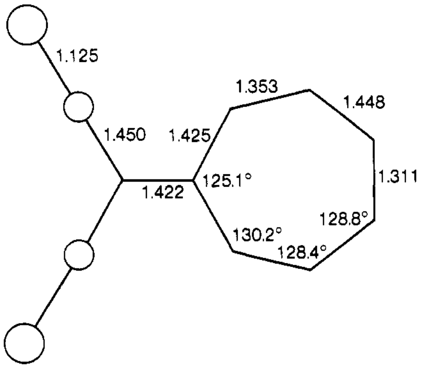


Figure 1. Configuration of the perchloroheptafulvene molecule, $C_{14}Cl_{12}$, of crystallographic site symmetry C_i-$\bar{1}$; its geometry closely conforms to C_{2h}-$2/m$ symmetry.



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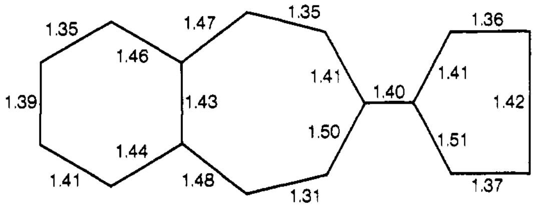

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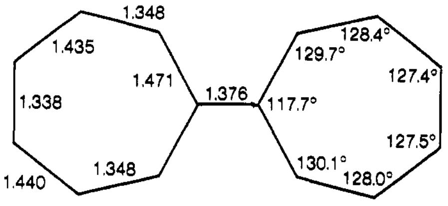

365

Crystal X-ray diffraction of heptafulvalene revealed that, owing to severe strain in the ring, the molecule is not fully planar.[336] Alternation of nearly pure single and nearly pure double bonds is observed (**365**).[336]

A single-crystal X-ray diffraction analysis of perchloroheptafulvalene (**184**) has revealed that the molecule is not planar and that there is marked bond alternation.[137a] Molecular parameters are shown in Figure 1.

X-Ray crystallographic examination of **191** (R = CN) revealed that the P···O distance (2.36 Å) is greater than for a true bond between these two atoms (**366**).[143] The heptafulvene system is nearly planar and, clearly, no marked bond alternation is seen in the seven-membered ring.[143] In the case of **191** (R = CO_2Et) the P···O bond distance is shorter, 2.14 Å, than with **191** (R = CN) but still longer than for a full P–O bond.[337]

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(333) P. Goldstein and K. N. Trueblood, *Acta Crystallogr.*, **23**, 148 (1967).

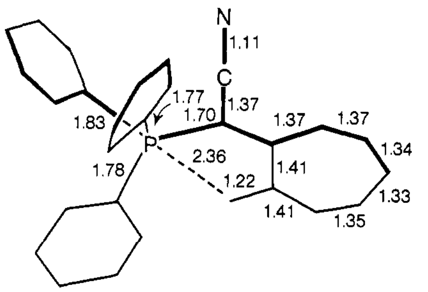
(334) H. Shimanouchi, T. Ashida, Y. Sasada, M. Kakudo, I. Murata, and Y. Kitahara, *Bull. Chem. Soc. Jap.*, **39**, 2322 (1966).

(335) Y. Nishi, Y. Sasada, T. Ashida, and M. Kakudo, *Bull. Chem. Soc. Jap.*, **39**, 818 (1966).

(336) R. Thomas and P. Coppens, quoted by P. Coppens, *Mol. Cryst. Liquid Cryst.*, **9**, 25 (1969).

(337) I. Kawamoto, T. Hata, Y. Kishida, and C. Tamura, *Tetrahedron Lett.*, 1611 (1972).

In contrast, X-ray crystal diffraction examination of both 1-oxoazulenone (**367**)[338] and its derivative **286**[223] revealed clear alternation of bonds in the seven-membered ring.



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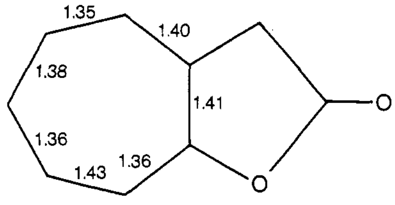
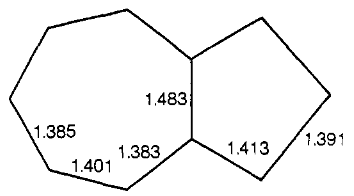


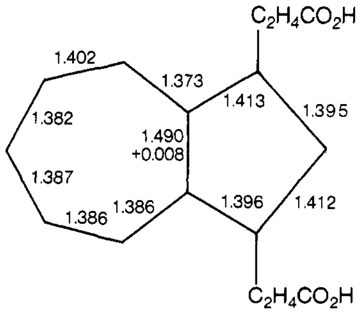
367

Similar studies have been reported for azulene itself (**368**).[339] Azulene crystallizes in a disordered manner so that no accurate data were obtained. However, the transannular C–C bond is clearly longer than all other carbon-carbon bonds. The same pattern of bond lengths was obtained for 2-aminoazulene[340] and 2-phenylazulene.[341]



368

Refined data could be obtained for azulene-1,3-dipropionic acid, which crystallizes orderly.[342] Molecular parameters are reported here (**369**).[342] Again, the transannular bond length (1.490 ± 0.008 Å) suggests a transannular C–C single bond. The average value of the peripheral bonds, 1.393 ± 0.005 Å, is in agreement with the benzene carbon–carbon bond length and points to the importance of valence bond structures **370**.[342]



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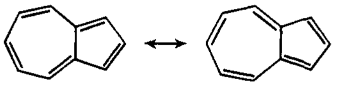

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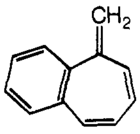
The *proton nmr spectrum* of the parent compound, heptafulvene (**147**), which is extremely unstable, has been obtained in acid-free $CDCl_3$ at −10°.[119b] It consists of a complex multiplet at δ 5.1–6.2 due to the ring protons and of a singlet at δ 4.45 due to the exocyclic methylene group.[119b]

Detailed proton nmr spectral studies of 8,8-dicyanoheptafulvene (**153**) revealed[283] unequal coupling constants, thus indicating bond alternation, in agreement with the crystal structure (**363**).[334] The proton nmr spectrum of the unstable sesquifulvalene has recently been obtained.[119b] Other proton nmr studies have also been reported. They revealed that **371** is rapidly inverting between two nonplanar forms.[311] Also, tetrabenzoheptafulvalene[343a] (**372**) and tetrabenzopentafulvalenes[343b] have a nonplanar, transoid, conformation. A similar analysis of tetrabenzo[5,7]fulvalene (**373**) uncovered[344a] a structural analogy with 9-diphenylmethylenefluorene[345] rather than with **372**. Planarity of the fluorene moiety prevents geometrical isomerism and forces the dibenzocycloheptene unit out of this plane, thus placing the aromatic rings above (or below) C(8)–H and C(1)–H as well as C(2)–H and C(7)–H.[344a] In parallel with these studies[344a] it would be interesting to investigate the conformation of some tetrabenzoheptafulvalenes which have been recently synthesized by the dehydration method[129] (section II.B.3) of carbinol precursors.[344b]



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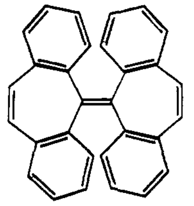

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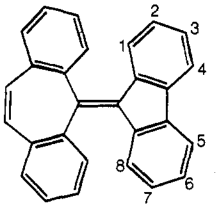

373

The ${}^{35}Cl$ *nuclear quadrupolar resonance spectrum* of perchloroheptafulvene (**184**) at 77°K reveals[137] the presence of three different types of vinylic chlorine atoms, being consistent with the results of the X-ray diffraction study which indicate the nonplanar structure of Figure 1.[137]

The *ir absorption spectrum* of heptafulvene (**147**), obtained[119b] in CCl_4–CS_2 at 20°, consists of only a few bands at 3020 (m), 1583 (s), 853 (s), 830 (m), 741 (s), and 530 (s) cm^{-1} which have been attributed, in the order of decreasing wave number, to C—H str, C=C str, and to various bending modes.[119b] The ir spectrum of sesquifulvalene has also been reported.[119b] Ir data are also available for a variety of stable heptafulvene derivatives such as 8,8-dicyanoheptafulvene (**153**) which shows absorptions at 2205 (CN), 1633, 1585, 1520, 1490, 1406, 1269, 885, 830, and 763 cm^{-1} in a KBr pellet.[122b] Ir data indicate that **156** is better represented by

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(338) Y. Sasada, *Bull. Chem. Soc. Jap.*, **32**, 171 (1959).

(339) J. M. Robertson, H. M. M. Shearer, G. A. Sim, and D. G. Watson, *Acta Crystallogr.*, **15**, 1 (1962).

(340) Y. Takaki, Y. Sasada, and I. Nitta, *J. Phys. Soc. Jap.*, **14**, 771 (1959).

(341) B. D. Sharma and J. Donohue, *Nature (London)*, **192**, 863 (1961); J. Donohue and B. D. Sharma, *ibid.*, **198**, 878 (1963).

(342) H. L. Ammon and M. Sundaralingam, *J. Amer. Chem. Soc.*, **88**, 4794 (1966).

(343) (a) E. D. Bergmann, M. Rabinovitz, and I. Agranat, *Chem. Commun.*, 334 (1968); (b) I. Agranat, M. Rabinovitz, A. Weitzen-Dagan, and I. Gosnay, *ibid.*, 732 (1972).

(344) (a) I. Agranat, M. Rabinovitz, and M. Weissmann, *Tetrahedron Lett.*, 273 (1972); (b) P. J. Garratt and K. A. Knapp, *Chem. Commun.*, 1084 (1971).

(345) M. Rabinovitz, I. Agranat, and E. D. Bergmann, *J. Chem. Soc. B*, 1281 (1967).

a tropenylium-type structure than by the tropoquinone structure indicated.[124c] However, full chlorination of the seven-membered ring imparts greater stability to these compounds and gives rise to two absorptions in the 1600 and 2850 cm^{-1} regions consistent with a tropoquinone structure.[124c]

The *electronic absorption spectrum* of heptafulvene (**147**) in *n*-hexane is composed of three broad bands at 209, 279, and 400–423 nm.[119b] Because of the large uncertainty in the concentration values, it was difficult to estimate extinction coefficients. However, the extinction coefficient at 400–423 nm should not be too different from 300 l. mol^{-1} cm^{-1}.[117] All these data point to extensive conjugation.

The electronic absorption spectra of several heptafulvene derivatives have also been reported. Thus, for 8,8-dicyanoheptafulvene (**153**) the following absorptions, λ_{max} (log ϵ) 252 (3.98), 368 (4.26), 374 (4.27), and 381 (4.27), have been observed in *n*-hexane.[122a] Uv data for sesquifulvalene have also been reported.[119a]

Experimental values for the *dipole moment* of the parent member of this family, heptafulvene (**147**), are unavailable. That (0.7 D) reported recently in a symposium as the experimental value[346a] really is only an estimated value.[346b] An earlier estimate (3.07 D) for the dipole moment of heptafulvene[347] has been criticized[348] as based on a theoretically unsound basis. Experimental values of the dipole moment for stable heptafulvene derivatives have been reported.[347] Thus 8,8-dicyanoheptafulvene (**153**) gave 7.49 D in dioxane at 25° while 8-cyano-8-carbethoxyheptafulvene gave 4.40 D in benzene at 25°.[347]

The *diamagnetic susceptibility exaltation* criterion,[349] applied to heptafulvene, reveals no exaltation in accord with predictions from the localized-bond model **166**.[349]

Semiempirical calculations have been carried out for both heptafulvenes[350] and azulenes or azulenoids.[351] Thus, by the LCAO-MO method, dipole moments of 2.35[350a] or 4.6D,[350b] with the negative end of the dipole directed toward the methylene group, have been calculated for heptafulvene. Self-consistent MO calculations gave both a much lower value, 0.14 D, and the reverse orientation of the dipole.[352]

According to some MO calculations, delocalization energy for heptafulvene (**147**) is predicted to be even lower than that for thiotropone.[303c,d] Other semiempirical calculations also suggest that both heptafulvene and heptafulvalene are nonaromatic.[353]

CNDO/2 calculations predict that heptafulvene should be planar[304] in accord with its uv spectrum.[177,119b] Such calculations[304] indicate also that planarity originates from mitigation of coulombic repulsions in the planar model rather than from π-electron factors.

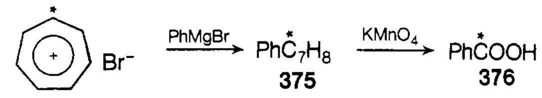
Refined Hückel MO calculations have been recently extended to nonalternant hydrocarbons.[354] Calculations for the π-electron transitions energies of heptafulvene have also been carried out.[355] Finally, it is worth mentioning that *ab initio* calculation using molecular fragments have been done for azulene.[356]

Mass spectra for both heptafulvene (**147**) and sesquifulvalene show the respective molecular ions.[119b]

4. Tropenylium Ions

X-Ray single crystal diffraction studies revealed that both C_7H_7I and $C_7H_7ClO_4$ are ionic.[357] These systems are planar, the C–C distance amounting to 1.47 Å. In both cases, $C_7H_7^+$ occupies a statistically disordered position rotating about an axis which is perpendicular to the plane of the ring.[357]

That the ring carbons and hydrogens of tropenylium ion are equivalent was demonstrated by treating tropenylium bromide mono-^{14}C-labeled (**374**) (obtained from benzene and $^{14}CH_2N_2$) with phenylmagnesium bromide to give labeled phenylcycloheptatriene (**375**). Degradation of the latter gave benzoic acid labeled at the carboxyl group (**376**) whose specific radioactivity was just one-seventh that of **374**.[358]



374 **375** **376**

Complete delocalization of the positive charge on tropenylium ion is also indicated by the *photoelectron spectrum* of tropenylium hexafluoroantimonate which gives a single 1s line (E_b = 284.7 eV).[359]

Proton nmr spectra of tropenylium salts have been extensively studied. Tropenylium ion itself shows a single narrow signal at extremely low field. Thus, for tropenylium hexachloroantimonate values of δ 9.44, 9.33, and 9.38 ppm have been found in nitromethane, acetonitrile, or sulfolane, respectively.[360] Data for a wider variety of solvents are available for tropenylium tetrafluoborate.[361] The very low field position of the nmr signal is consistent with the presence of a delocalized positive charge in the ion. Whereas ditropenylium ion also shows a single signal,[360] substituted tropenylium ions generally show complex multiplets for the ring protons whose exact position depends markedly on the nature of the substituent. For example, hydroxytropenylium ion shows a complex multiplet at δ 7.72 ppm in SO_2–FSO_3H.[362]

^{13}C nmr spectra of both tropenylium and ditropenylium ion have been reported.[360] Proton decoupled spectra in CD_3NO_2 show a single signal at 160.62 ppm for tropenyl-

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(346) (a) H. Kuroda and T. Ohta in ref 86b, p 243; (b) personal communication from the authors in (a) above.

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(361) T. G. Beaumont and K. M. C. Davis, *J. Chem. Soc. B*, **592** (1970).

(362) H. J. Dauben and K. M. Harmon, unpublished material quoted in ref 200.

ium ion and a couple of signals at 161.17 and 163.05 ppm for ditropenylium ion.[360]

When dealing with a carbonium ion, even as stable as tropenylium ion, *equilibrium addition of bases,* such as the anion of the salt itself, added bases, or the solvent, must always be taken into account. For example, in water there is an equilibrium between tropenylium ion and the carbinol. The high pK_a value of this carbonium ion (4.75)[363] reflects its high stability and is such that at pH 5 half of the carbonium ion is converted into the carbinol. Consequently, only salts of nonnucleophilic anions, like perchlorate or tetrafluoborate, are largely dissociated in solution. Salts of nucleophilic anions, like cyanide, exist in solution as cycloheptatriene derivatives. Fusion to benzene rings decreases the stability of the ion, as indicated by the fact that pK_a values for benzo- and dibenzotropenylium ion are lower than for tropenylium ion.[147]

Ir[363,364] *and Raman*[364] *spectra* of tropenylium ion have been examined. In HBr solution tropenylium bromide showed[364] the following: ir 3080 (w), 3020 (s), 2060 (w), 1477 (vs), 1278 (w), 1222 (w), 992 (mw), 658 (m), 633 (s) cm^{-1}; Raman 3045-3085 (s), 1594 (m), 1210 (mw), 925 (w), 868 (vs), and 433 (m) cm^{-1}. Both the paucity of the bands and the lack of coincidence of the two spectra are consistent with the highly symmetrical structure assigned to tropenylium ion.

Electronic absorption spectra of tropenylium salts have been studied in detail. When the anion is a nonnucleophilic one, like tetrafluoborate or perchlorate, two characteristic broad absorptions with maxima at 217 and 273 nm (log ϵ 4.61 and 3.63) are observed.[155] The long-wavelength band ($^1E_{3u}$)[365] is unchanged in such a wide variety of solvents as water, 96% sulfuric acid, acetonitrile, and methylene chloride.[366]

For tropenylium halides, new absorption bands are found in the visible region in the less polar solvents only.[366] These absorptions have been assigned to charge transfer between the halide anion and tropenylium ion.[366] It has also been suggested that the color displayed by these salts in the solid state has a similar origin.[366]

Fragmentation of tropenylium ion in the *mass spectrometer*[182d] has already been mentioned in section II.B.4.

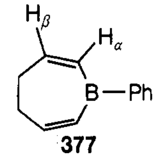
Studies of *optical activity* of chiral tropenylium ions indicate that tribenzotropenylium ion is boat shaped and that rapid inversion between the two boat forms occurs at room temperature.[367]

It would be very interesting to look at the structure of perchlorotropenylium ion (**95**, or changing to a suitable anion) as it should be nonplanar owing to repulsions between chlorine atoms.

5. Heterocyclic Analogs

Borepin Derivatives. Proton nmr spectra of **218**,[179] **220**,[180] and **222**[181] have been reported. In CS_2 solution **218** shows a sharp signal at δ 7.32 ppm and a couple of AB doublets at δ 7.53 and 6.70 ppm (J = 5.0 Hz).[179]

The heterocyclic H_α and H_β protons of **220** in CCl_4 solution show up at δ 8.22 and 7.72 ppm, respectively (J = 14 Hz).[180] The fact that these signals appear at appreciably lower field than for model compounds, like **377**, is taken as evidence for ring currents in the seven-membered ring of **220**.[180] However, in view of the complexity of the factors determining chemical shifts, this cannot be considered as definitive evidence.



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The corresponding H_α and H_β protons of **222** in $CDCl_3$ solution appear at δ 6.68(d), and 8.02(d) ppm (J = 14 Hz).[181]

In the ir region, the pyridine complex of **216b** shows an absorption band at 2315 cm^{-1} which has been attributed to the B-H bond stretching.[178] In the case of **222** in $CHCl_3$, absorptions appear at 3650, 3012, 1600, 1541, 1447, 1274, 1256, 1189, 992, and 817 cm^{-1}.[181]

The electronic spectrum of **216** (X = $OCH_2CH_2NH_2$) consists of two absorptions bands with maxima (EtOH) at 227 and 298 nm (log ϵ 4.204 and 3.915).[178] In the case of **222** in C_7H_{16} the following maxima (log ϵ) have been observed:[181] 235 (4.6), 244 (4.7), 257 (4.7), 268 (4.1), 275 (5.0), 286 (3.5), 307 (2.6), 319 (2.6), and 335 nm (2.9).

The mass spectrum of **222** shows a feeble molecular ion: 156 (10%), 128 (100), 115 (10%), and 102 (13%).[181]

Azatropones. The proton nmr spectra of 4-azatropones **229**, 4-azabenzotropones **231**, and 2-azatropones **230a** show that the heterocyclic ring protons are in the vinyl region (δ 6.13–6.81 ppm).[183] This observation, coupled with the observed easy reduction of these compounds, indicates little stabilization.[183] The ir absorption band at 1610–1660 cm^{-1} for these compounds has been attributed to the C=O stretching vibration.[183]

The electronic spectra (EtOH) of 4-azatropones **229** and 2-azatropones **230a** consist of two broad absorption bands at 225–230 and 300–320 nm (log ϵ 4.3–4.4 and 3.7–3.9), while for 4-azabenzotropones the two bands are shifted toward the blue and are more intense [**218** and **265** nm (log ϵ 4.57 and 4.02)].[183]

Azatropenylium Ions. Benzoazatropenylium ion (**238**) fragments in the mass spectrometer losing HCN.[187]

6. Homo- and Polyhomoconjugated Species

Homotropones. Proton nmr spectra clearly indicate the absence of ring currents for 2,3-homotropone (**245**).[368] In fact, the chemical shift difference between endo and exo methylene protons is only *ca.* 0.5 ppm.[368] This has to be compared with the large chemical shift difference between similar protons of homotropenylium ion which sustains large ring currents (see below).

Detailed nmr data ($CDCl_3$, 100 MHz) have been reported for **248a**.[193a] Chemical shifts (δ, ppm) and coupling patterns are indicated in structure **378** which is also

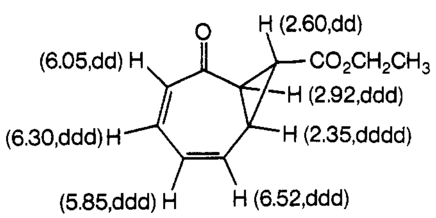

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TABLE III. Physical Properties for 2,3- (245) and 4,5-Homotropone (247)

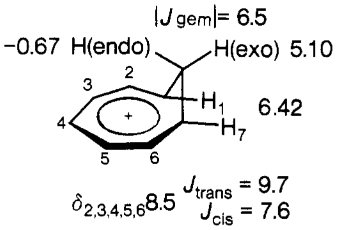
	2,3-Homotropone[190a]	4,5-Homotropone[191]
ν_{max} (neat), cm^{-1}	C=O str 1650	1650 (C=O), 1603 (C=C), 751.9 (*cis*-HC=CH-), 709.2 (*cis*-HC=CH-)
λ_{max}^{EtOH}, nm (log ϵ)	293 (3.65), 340 (3.15)	264 (3.88), 290 (sh 3.66)
pK_{BH^+}	−2.8	
Nmr	(Neat) unresolved multiplet centered at δ 6.5 (2 H), 5.8 (2 H), 2.4 (1 H), 2.0 (2 H), and 1.5 (1 H), unchanged down to −100°	(CS_2) multiplets at δ 6.64 (2 H), 5.75 (2 H), 1.9 (3 H), and 0.45 (1 H), unchanged in the temp range +40 to −50°
Bp, °C	55-56 (0.15 nm)	Can be distilled at reduced pressure
Solubility	43 g $l.^{-1}$ in H_2O at room temp; very sol in acids	Very sol in H_2O or in acids

supported by the high-field resonances found for the two bridgehead protons.

Molecular models indicate that 4,5- (**247**) and 2,3-homotropone (**245**) are capable of cis-trans isomerism. However, no change in the nmr spectrum with the temperature (down to −100° for **245** (racemate)[190b] and in the range from +40 to −55° for **247**[191]) has been observed. Therefore, barriers to interconversion are either too low or too high for observation of separate isomers in such ranges of temperature. The first alternative has been preferred for 2,3-homotropone, low energy of the planar form for the interconversion of the isomers having been attributed to substantial contribution by homotropenylium ion-type delocalized structures (**252**).[190b] This view is not supported by the nmr spectra which, as said above, rule out structure **252** for 2,3-homotropone. However, uv and ir spectra (Table III) seem to indicate some contribution of the cyclopropane ring to electron delocalization for 2,3-homotropone. This is also suggested (Table III) by the low basicity of 2,3-homotropone which is lower than that of 2,4,6-trimethylcyclohepta-2,4-dienone by 2.1 p*K* units.[190a]

As regards 4,5-homotropone, data of Table III suggest that the cyclopropane system does not take part in the electron delocalization. It is also surprising that this compound does not undergo the easy Cope rearrangement expected for a *cis*-1,2-divinylcyclopropane.[191] Its mass spectrum shows M^+ (17.4%), $[M - CO]^+$ (100%), and an intense (70.2%) peak at *m/e* 91.[191]

Homo- and Bishomotropenylium Ions. Proton nmr data (δ, ppm) for homotropenylium ion (**254a**) in concentrated sulfuric acid fully support the homoaromatic structure (**379**).[369] They do not conform to either the classical structure **380**, with an intact cyclopropane ring,[368-370] or the planar cyclooctatrienyl structure **381**.[369,370] Structure **381** is immediately excluded because, contrary to what has been observed, the two geminal protons shown in the display should be magnetically equivalent. According to structure **380** protons H_1 and H_7 should appear at a definitely higher field than was found. Moreover, the large chemical shift difference between endo and exo protons and the assignment[368] of the signal at higher field to the endo proton strongly support ring currents as in **379**.[368] Finally, the fact that trans coupling constants (with H(endo)) are larger than cis coupling constants (with H(exo)) also supports structure **379**. The reverse pattern of the coupling constants should have been observed for a fully formed cyclopropane ring as in **380**.[369]



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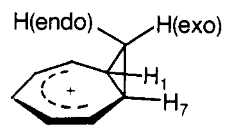

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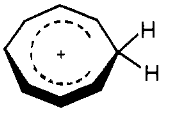

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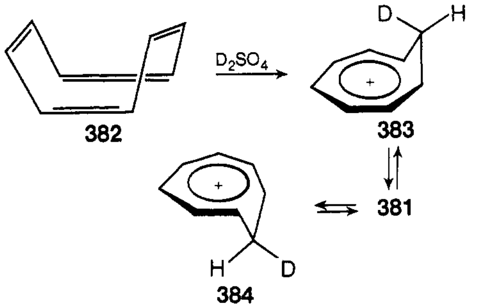
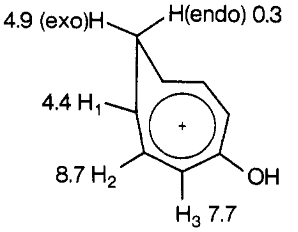
Deuteration of cyclooctatetraene **382** with D_2SO_4 at −15° is highly stereospecific, 80% of the deuterium appearing in the endo position (**383**).[371] Equilibrium of **383** with **384** can be established, and it has been calculated that, if it takes place through **381**, the free energy of the planar form **381** is 22.3 kcal mol^{-1} higher than the homoaromatic structure.[371]

Similar analysis of the nmr spectra of 1-methyl- (**254b**), 1-phenyl- (**254c**), 1-hydroxy- (**261**), and 2-hydroxyhomotropenylium ion (**263**),[368] as well as of 8-chlorotropenylium ions (**273, 274**) and of benzo- (**256**) and dibenzohomotropenylium ions (**258**), supports the nonclassical structures displayed here.[195]



The same conclusion holds for 4-hydroxyhomotropenylium ion (**262**). Here, the H_1 and H_7 protons appear[191] (**385**) at higher field (δ 4.4 ppm) than for homotropenylium ion (**379**). However, for a fully formed cyclopropane ring they would be expected at considerably higher field (δ ~3 ppm, or above). Moreover, the two methylene protons are distinctly dissimilar indicating ring currents.



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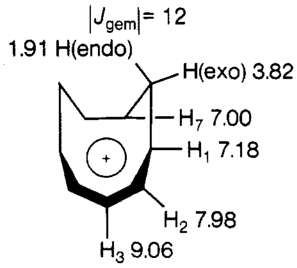

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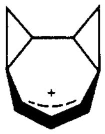
As for bishomotropenylium ions, proton nmr spectra support the nonclassical structure **265**.[201] Some relevant data are shown in the structural representation **386** which is compared with the other two conceivable structures **387** and **388**.[201] Structure **387** is ruled out because the value of $|J_{\text{gem}}|$ is too high for a fully formed cyclopropane ring.[201,370] Structure **388** is also discounted on the basis of the following considerations.[201] Taking **389** as a model, it is seen that the C(1)–H and C(5)–H protons in **386** are shifted to higher field, by *ca.* 2 ppm, with respect to the corresponding protons in **389**. This upfield shift has been attributed[201] to charge removal from the pentadienyl unit of the hypothetical **388** with consequent downfield shift of the C(6)–H and C(7)–H protons (in fact, vinyl protons in, say, cyclohexene appear at δ 5.59 ppm). Moreover, the fact that $J_{1\text{-endo}}$ (J_{trans}) is higher than $J_{1\text{-exo}}$ (J_{cis}) is in accord with structure **386** but not with **387** for the same reasons stated above for the case of **379**.[201] Finally, calculations from models like **386** gave $\Delta\delta$ 3.4 ppm between endo and exo protons of such ion.[201] It has been argued[201] that the $\Delta\delta$ 1.9 ppm evaluated directly from the spectra does not reflect accurately the extent of ring currents.



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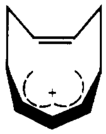

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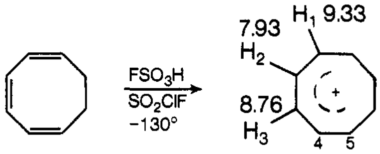

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Analysis of proton nmr spectra for 1,4-bishomotropenylium ions also supports nonclassical structures.[202,203a] The stereochemical requirements for bishomoaromaticity have also been studied on protonated *cis-* and *trans*-4,5-benzo-2,3:6,7-bishomotropone.[203b] The cis species appears to be homoaromatic, as judged from the fact that inside methylene protons appear at higher field than outside methylene protons in the ^{1}H nmr spectrum. In contrast, inside and outside methylene protons for the trans species appear at substantially the same field. On this basis, the trans species lacks homoaromaticity.[203b]

The homotropenylium ion (produced from C_8H_8 in H_2SO_4) shows two absorptions in the uv region ($\lambda_{\max}$ 232.5 (log ϵ 4.52) and 313 nm (3.48)[371]) at higher wavelengths than tropenylium ion (section IV.B.4).

Studies of diamagnetic susceptibility also support the presence of ring currents in homotropenylium ions.[195]

C. Radicals and Ion Radicals

Tropenyl radicals have been extensively studied by esr spectroscopy. Samples of neat bitropenyl, sealed under nitrogen, gave a detectable (from 80° upwards) esr signal, the intensity of which increased with the temperature.[210b] The planar symmetrical structure **281** is fully supported by the esr spectrum which consists of eight equally spaced absorptions with relative intensities in accord with hyperfine interactions from seven equivalent protons.[210b]

A similar spectrum was also obtained at room temperature for tropenyl radical obtained either by photolysis of bitropenyl in hydrocarbons[210b] or (in a flow apparatus) by hydrogen abstraction from cycloheptatriene with hydroxyl radical.[372] The proton hyperfine splitting decreases with decreasing temperature from 3.95 ± 0.01 G at −50 to 90°[373] to 3.62 ± 0.015 G at 196°,[210] with a notable 3.5% change over 100°.

Similar results were obtained using hydrocarbon radicals (obtained by hydrogen abstraction from the parent hydrocarbon by photochemically generated *tert*-butoxy radicals) to abstract hydrogen from cycloheptatriene in a solution of the hydrocarbon itself.[374]

A similar esr spectrum was also obtained by irradiation of a crystal of naphthalene containing cycloheptatriene with 50-kV X-rays.[375]

Less well defined esr spectra of tropenyl radicals were obtained either by reducing tropenylium bromide in dimethoxyethane at −80° with K-Na alloy[376] or by electron bombardment of cycloheptatriene at −196°.[377]

The ^{13}C hyperfine constant for tropenyl radical is 2.24 ± 0.025 G at 139°.[210b]

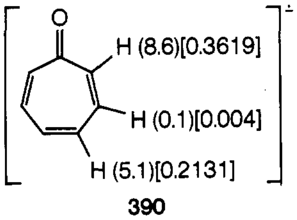
Esr spectral studies of tropenyl radical generated in polycrystalline perdeuterionaphthalene and the temperature dependence of both the dipolar proton hyperfine splitting[378] and spectral line widths for a sample thermally generated from neat bitropenyl[379] have also been reported.

Proton hyperfine splitting constants for all the protons of methyl- and cyclopropyltropenyl radicals show a satisfactory agreement with HMO-calculated values.[211]

From the temperature dependence of the intensity of the hyperfine components of tropenyl radical (generated by homolytic thermal cleavage of bitropenyl), the enthalpy of dissociation of bitropenyl, 35 ± 1 kcal mol^{-1}, has been obtained.[380a] This allowed calculation of both the total empirical resonance, 31 kcal mol^{-1}, and the "extra" resonance energy, 21 kcal mol^{-1} (obtained by the delocalization of the unpaired electron).[380a] The fact that tropenyl radical is one of the most stabilized (by resonance) radicals gives further support to the planar structure **281**.[380a]

The tropenyl radical has also been obtained from pulse radiolysis of aqueous solutions containing tropenylium ion.[380b] This is interpreted as a reduction of tropenylium ion by the hydrogen atom.[380b]

Radical anions of tropones have also been carefully investigated. Proton hfsc (within parentheses) for tropone radical anion (**390**) and experimental spin densities



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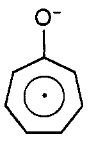
(379) R. G. Kooser, W. V. Volland, and J. H. Freed, *J. Chem. Phys.*, **50**, 5243 (1969).

(380) (a) G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *J. Amer. Chem. Soc.*, **91**, 2823 (1969); (b) M. Schöneshöfer, *Z. Naturforsch. B*, **26**, 1120 (1971).

(within square brackets) have been reported.[214] Spin densities agree with the values obtained[214] by McLachlan calculations.[381] The structure of tropone ketyl should be influenced substantially by the resonance form **391** because proton hfsc are definitely higher than for cyclopentadienone ketyl for which the structure **392** should possess the highest aromatic character.[216]



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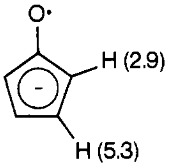
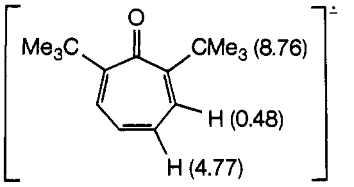


392

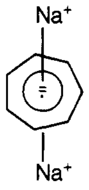
Similar studies for 2-methyl- and 2,6-di-*tert*-butyltropone radical anions have also been reported.[215] The latter (**393**) gave only a triplet of broadened lines, with pro-



393

ton a_H of 2.14 G, which has been attributed to the γ proton.[215] It has been thus concluded that the conformation of 2,6-di-*tert*-butyltropone must be quite different from that of tropone, in agreement with conclusions[57] from uv and ir spectra of 2,6-di-*tert*-butyltropone (section IV.A.1).

Cycloheptatrienide dianion radicals have also been studied. Thus, disodium tropenide (**394**) exists as inti-



394

mate ion triplets, or higher ion clusters, under the conditions used to generate them in ethereal solvents (section II.C).[174] In fact, a very large sodium splitting was observed in the range from −100° to room temperature.[174] The esr spectrum consists of an octet (a_H = −3.52 G) which is further splitted into septets (a_{2Na^+} ± 1.76 G).[174] With potassium as cation the spectrum is much simpler, consisting of an octet with the same splitting as in the previous case.[174] Lack of potassium splitting has been attributed to rapid exchange of the potassium ion.

Proton hfsc for both benzo- and dibenzotropenide dianion radicals are in accordance with values obtained by McLachlan[381] semiempirical calculations.[174]

With both methyl- and cyclopropyltropenide dianions, metal splittings were observed for both sodium and potassium.[211] Calculations indicate that it is the symmetrical tropenyl-type molecular orbital which is occupied by the odd electron in these dianion radicals.[211]

Solutions of tropenide dianion radical are blue-green (λ_{max} (THF) 570 nm; λ_{max} (dimethyl ether) 566 nm).[174]

For the heptafulvalene anion radical esr spectra indicate that the counterion (potassium) jumps from one ring to another, intramolecularly, with concomitant reverse jump of the spin.[217]

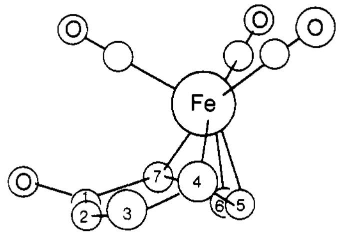
Both anion and cation radicals of heptafulvalene show considerable resonance stabilization and thus differ from heptafulvalene itself which shows the localized structure **166**.[217]

The esr spectrum of the azulene radical anion,[218] 2- and 6-methoxyazulene radical anions.[382] and of 1,1′- and 2,2′-biazulenyl radical anions[383] have also been obtained.

D. Metal π Complexes

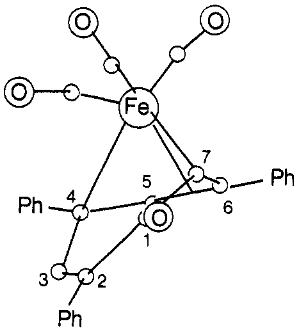
1. Cycloheptatrienone Metal π Complexes

X-Ray crystal studies have been reported for troponeiron tricarbonyl (**285a**) (crystalline modification of mp 63.5–64.5°),[384] one isomer (**287**) of 2,4,6-triphenyltroponeiron tricarbonyl,[385] and troponechromium tricarbonyl (**285b**).[386] In both iron complexes above, only a planar *syn*-butadiene group of the tropone ligand is bonded to the iron tricarbonyl unit as a four-electron donor as shown in **395**[384] and **396**.[385] The seven-membered rings therefore assume a bent conformation. These studies[384,385] suggest that iron is attached to the diene unit by three points. However, a different bonding pattern is suggested by the electronic spectra discussed below for the complexes in solution.



395

C_1–C_2	1.45	C_5–C_6	1.40
C_2–C_3	1.34	C_6–C_7	1.44
C_3–C_4	1.45	C_7–C_1	1.49
C_4–C_5	1.44		



396

C_2–C_3	1.34	C_1–C_2	1.44 (av)
C_4–C_5	1.45	C_3–C_4	
C_5–C_6	1.38	C_7–C_1	
C_6–C_7	1.49		

The chromium complex **285b** possesses a mirror plane of symmetry as shown by **397**. The ring is not planar, and there is bond length alternation. The Cr—C(1) distance (2.64 Å) is probably too long for effective bonding, and the C=O bond length (1.23 Å) is typical for a carbonyl

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(381) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(382) Y. Ikegami and S. Seto, *Bull. Chem. Soc. Jap.*, **44**, 1905 (1971).

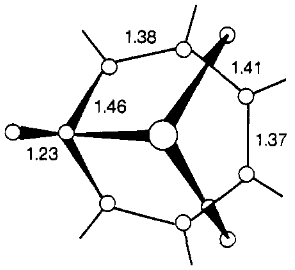
(383) Y. Ikegami and S. Seto, *Bull. Chem. Soc. Jap.*, **43**, 2409 (1970).

(384) R. P. Dodge, *J. Amer. Chem. Soc.*, **86**, 5429 (1964).

(385) D. L. Smith and L. F. Dahl, *J. Amer. Chem. Soc.*, **84**, 1743 (1962).

(386) M. J. Barrow and O. S. Mills, *Chem. Commun.*, 119 (1971).

compound. Therefore C(1) cannot be involved at any great extent, if at all, in the conjugation.



397

The last point is also supported by the *ir spectrum*.[221] In fact, the carbonyl stretching frequency for **285b** (1632 cm^{-1} in CCl_4 and 1623 cm^{-1} in CH_3CN)[221] is higher than for tropone itself (1594 cm^{-1} in CCl_4[287]). Three metal carbonyl frequencies (Nujol mull), 1905, 1940, 1995 cm^{-1}, are also characteristic.[221]

Also for the other complexes mentioned above the carbonyl stretching frequencies are higher than for tropone, being 1637 (CCl_4), 1623 (KBr) and 1629 cm^{-1} (KBr) for **395**,[220a], **288**,[224] and **396**,[224] respectively.

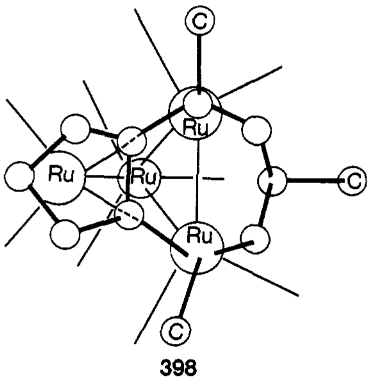
The *electronic spectrum* of the isomeric 2,4,6-triphenyltricarbonyls **287** and **288** is similar to that of 2,4,6-triphenyltropone itself.[224] This favors structures of types **287** and **288** with linkage of the metal to two double bonds[224] in contrast with X-ray analysis of the crystal which favored structure **396**.[385]

The dipole moment of **285a** (4.30 D) has been tentatively dissected into the components for the irontricarbonyl and the ligand moieties.[220a] Thus, the part (3.6 D) attributed[220a] to the ligand is smaller than for free tropone (4.30 D[298]).

2. *Metal π Complexes of Heptafulvenes and Related Compounds*

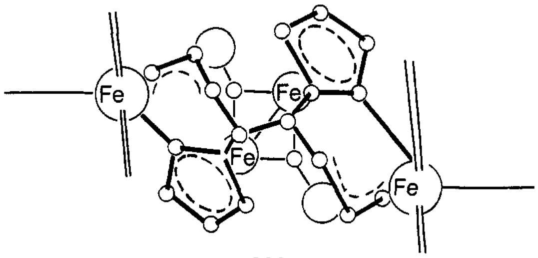
X-Ray crystal studies have been focused on metal carbonyl complexes of azulene and azulene derivatives. Because azulene is only formally related to the principal categories of compounds examined in this review, such studies are not reviewed comprehensively here. Exhaustive references to such studies may be found in a recent paper dealing with the crystal and molecular structure of guaiazulenedimolybdenum hexacarbonyl complex.[229]

A variety of azulene-metal bonding schemes have been observed. Generally, for Fe_2 or Mo_2 complexes, both metal atoms lie on the same side of the azulene unit, one linked to the seven-membered ring and the other to the five-membered ring. In the case of $(CH_3)_3C_{10}H_5Ru_4(CO)_9$, the organic ligand is bonded to the metal cluster of the four, tetrahedrally arranged, ruthenium atoms *per se*, rather than to individual metal atoms (**398**).[387]



398

The azulene C–C bond distances are generally altered with respect to the free ligand,[229] and in the case of diazulenetetrairon decacarbonyl (**399**) the azulene ligand is severely distorted from planarity.[388]



399

Proton nmr spectra of heptafulvene tricarbonyliron complexes **290**,[225] **292**,[226] and **299a**[228] support the structures drawn here. Thus, **290** shows absorptions (CS_2) at δ 1.40 (2 H, s), 3.70 (2 H, dd), and 5.87 ppm (4 H, centrosymmetric multiplet).[225] The signal at very high field supports the trimethylene–methane-type structure **290.** No signal at such high field appears for either **292** [(CS_2) δ 2.93 (1 H, t), 3.63 (1 H, d), 4.89 (1 H, s), 5.19 (1 H, s), and 5.44 ppm (4 H, multiplet)][226] or **299a** [δ 2.9 (1 H, t), 4.0 (1 H, dd), 5.2–5.9 (4 H, multiplet), 6.5 (1 H, d), and 7.2 ppm (5 H, multiplet)].[228]

The two complexes **290** and **292** cannot be easily equilibrated since the nmr spectrum of the latter is unchanged from −60 to +140°.[225]

The ir absorption spectra of complexes **299** in n-C_6H_{14} show three sharp metal carbonyl bands being, in this respect, typical of diene–iron tricarbonyl complexes.[220] Two metal carbonyl bands (2040 and 1980 cm^{-1}, in $CHCl_3$) are observed for **292**[226] and **290** (2050 and 1980 cm^{-1}, in CH_2Cl_2).[225] Three metal carbonyl bands (1995, 1938, and 1915 cm^{-1}, in C_6H_6) are observed for **300.**[124]

Mass spectra of **299**,[228] **290**,[225] and **292**[226] have been reported. Molecular ions are observed for **299** and **290** under electron impact. In the latter case a fragmentation pattern is also observed (intense peaks at m/e 104, 103, 91, 78, 77, 52, 51, 50, 40, and 39, which can be probably attributed to free heptafulvene).[225] The molecular ion for **292** was observed only under chemical ionization conditions.[226] Under electron impact only peaks at m/e 104, 77, and 56 have been observed.[226]

Electronic spectra of these heptafulvene complexes have not been reported.

3. *Metal π Complexes of Tropenylium Ions*

X-Ray crystal diffraction studies have been reported for $C_7H_7Mo(CO)_3{}^+BF_4{}^-$,[389] $C_7H_7VC_5H_5$,[390] and $C_7H_7V(CO)_3$.[390a] In all these complexes the tropenylium unit is a planar regular heptagon in the center of which the metal has its projection.

The tropenylium cyclopentadienyl complex is a real sandwich compound possessing a mirror plane of symmetry (**400**).[390] It is interesting that the average carbon–carbon bond length in the metal-coordinated tropenylium unit is definitely shorter (1.401 and 1.403 Å for the molybdenum[389] and the sandwich compound **400**,[390] re-

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(387) M. R. Churchill and P. H. Burd, *J. Amer. Chem. Soc.*, **90**, 800 (1968).

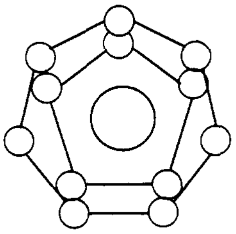
(388) M. D. Rausch, A. K. Ignatowicz, M. R. Churchill, and T. A. O'Brien, *J. Amer. Chem. Soc.*, **90**, 3242 (1968).

(389) G. R. Clark and G. J. Palenik, *Chem. Commun.*, 667 (1969).

(390) G. Engebretson and R. E. Rundle, *J. Amer. Chem. Soc.*, **85**, 481 (1963).

(390a) G. Allegra and G. Perego, *Ric. Sci., Part 2, Ser. A*, 362 (1961).

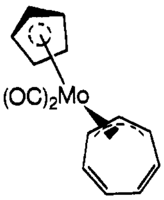
spectively; accuracy is insufficient for the other complexes[390a] to have a comparison) than in the free tropenylium ion (1.47 Å).[357] Moreover, the Mo–C(carbonyl) bond distance (2.035 Å) is greater than with typical olefin-$Mo(CO)_3$ complexes (1.94 Å).[389] This suggests a different type of bonding of molybdenum to the organic ligand in the two cases.[389]



400

Proton nmr spectra of certain tropenylium metal complexes change with the temperature.[241,391] Thus, at temperatures below −50° a nmr spectrum (Figure 2) consistent with the instantaneous structure **309b** was obtained.[241] In fact, the spectrum at −71° shows four multiplets A, C, D, E and a singlet, B, with relative intensities 2, 1, 2, 2, 5. The singlet B may be attributed to the cyclopentadienyl protons and the various multiplets to the inner protons of the butadiene system (A), the central proton of the allylic system bound to Mo(C), the outer protons of the allyl system (D), and the outer protons of the butadiene system (E).[241] This spectrum can be nicely reproduced (Figure 2, bottom) by the computer with 1-sec residence time for the species involved assuming that only 1,2-shifts occur.[241] Thus, **309b** is an instantaneous structure, frozen at the low temperature used. As the temperature is raised up to −50°, the spectrum broadens (this is shown for 0° in Figure 2). At +50° the spectrum consists of two sharp signals, that at δ 4.57 ± 0.01 ppm being attributable to C_7H_7. Clearly, rapid averaging of the positions of the C_7H_7 unit which are bound to the metals occurs at this temperature.

Less detailed studies of the temperature dependence of the proton nmr spectrum have indicated that **401** is also fluxional.[392] However, the instantaneous structure **401** can be frozen only at much lower temperatures than **309b**.



401

Fluxional behaviors of **306** and **403** have been compared.[233] Both complexes show a single sharp nmr absorption at 88 and 10°, respectively. Broadening of the signals was observed on going to lower temperatures, and at −47° for **306** or −80° for **403** the spectra are consistent with the structures drawn here. The coalescence temperature is 27 ± 10 and −50 ± 10° for **306** and **403**, respectively, an increase in the nuclear charge having the effect of speeding up the process. This has been connected with a lower degree of back-bonding in the iron complex.[233]

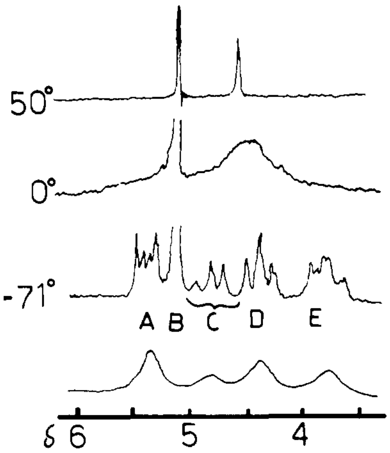
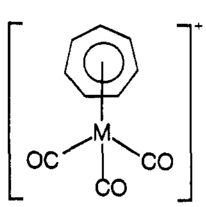


Figure 2. Proton nmr spectra of compound **309b** in a 4:1 $CDCl_3$-$C_6D_5CD_3$ mixture at various temperatures.[241] Bottom: spectrum computed for 1-sec residence time assuming rearrangement exclusively by a sequence of 1,2 shifts.[241]

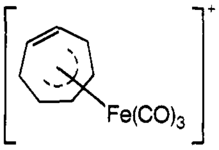
The case of $C_7H_7V(CO)_3$ is peculiar. Thus, in toluene solution at low temperatures a single sharp absorption is observed, whereas at room temperature the spectrum is more complex, indicating lessened symmetry of the C_7H_7 unit.[393] Possibly, this has changed into a system of three delocalized double bonds and a carbonium C atom.[393] In contrast, the X-ray diffraction studies discussed above indicate that in the crystal the C_3H_7 group is symmetrically bonded to the metal.[390a]

Ir absorption spectra of $[C_7H_7M(CO)_3]^+$ complexes show a single strong absorption in the C–H stretching region for M = Cr, Mo, and W whereas in the case of M = Fe there are three strong bands, indicating a lower symmetry than in the other cases.[232] This has been interpreted[232] in terms of the symmetrical structures **402** for M = Cr, Mo, and W and of the 4 π 5C structure **403** for the iron complex.[232] In further support of this interpretation, these Cr, Mo, and W complexes are transparent in the spectral region 650–800 cm⁻¹, while the iron complex, in accordance with the presence of a cis double bond, strongly absorbs at 731 cm⁻¹.[232]



M = Cr, Mo, W

402



403

4. *Miscellaneous Metal π Complexes*

Proton nmr spectroscopy proved to be a powerful tool in the investigation of the electronic structure of $C_8H_9^+$ metal π complexes. Exactly as in the case of uncoordinated homoconjugated species (section IV.B.6), the homoaromatic structure **311** for the $C_8H_9M(CO)_3^+$ (M = Cr, Mo, W) complexes is fully supported by both the large chemical shift difference between endo and exo protons and the low-field appearance of the other protons.[243,368]

In the case of the corresponding iron complex (**313**), both exo and endo methylene protons appear at much the same field strength, thus supporting the bicyclic

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(391) F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

(392) R. B. King and A. Fronzaglia, *J. Amer. Chem. Soc.*, **88**, 709 (1966).

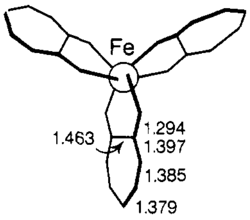
(393) H. P. Fritz and C. G. Kreiter, *Chem. Ber.*, **97**, 1398 (1964).

nonaromatic structure proposed.[243,368] These discussions parallel those for the free species (section IV.B.6) and, therefore, need not to be further detailed here.

In the case of $C_7H_7Fe(CO)_3^-$ (**315**), the observation of only one sharp absorption (δ 4.65 ppm, in perdeuteriotetrahydrofuran), from room temperature to −65°, points to a fluxional structure.[246] The ir absorption spectrum of **315** shows two absorptions (in THF) at 1942 and 1868 cm^{-1}, consistent with an $Fe(CO)_3$ anion.[246] Enhanced stability of the complexed tropenide anion **315**[246] has been attributed to either removal of 4 π electrons from $C_7H_7^-$ by $Fe(CO)_3$ or to some interaction of $Fe(CO)_3$ with all 8 π electrons of $C_7H_7^-$.[246]

E. Chelate Complexes

X-Ray diffraction crystal analysis of a number of tropolonato transition metal chelate complexes have been reported. The structure of iron(III) tristropolonate (**404**) is propeller-like with planar seven-membered rings and considerable distortion from the ideal octahedral configuration.[394] The C_1–C_7 bond length (1.463 Å) is practically that expected for a $C(sp^2)$–$C(sp^2)$ single bond whereas all other C–C bond lengths are close to the aromatic value. Thus, there is extensive peripheral conjugation which involves also the oxygen atoms but excludes the bridge bond C(1)–C(7). Although the remote possibility that the real pattern of bond lengths is somewhat masked by crystal disorder[394] cannot be rigorously excluded, the structure of the tropolonato units of **404** is remarkably similar to that observed for both sodium tropolonate (**351**)[321] and 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (**362**).[333]



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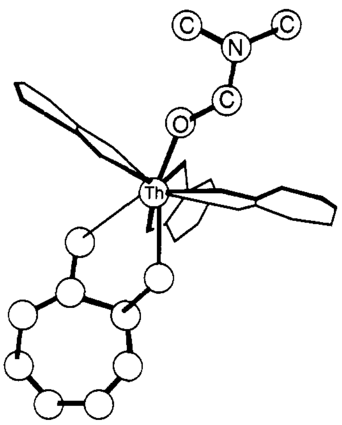
A similar structure for the tropolonato units has also been observed for (DMF)Th(tropolonato)$_4$ (**405**),[249] (tropolonato)$_3$SnCl (**406**),[249b] (tropolonato)$_3$SnOH (**407**),[249b] and (tropolonato)$_3$Al(III).[249c] This close structural similarity of the tropolonato unit for chelates of such various coordination number, and even for a nonchelate structure such as sodium tropolonate, has been taken as an indication of difficulty for the tropolonato unit to adjust itself internally for maximum overlap with metal ion orbitals.[249c] However, the structure of the tropolonato units in Cu(tropolonato)$_2$ (**408**) is very different, carbon–carbon bond alternation being apparent.[395]

It has also been found that the plane of the seven-membered ring makes an angle of 4.9° with the plane of the copper and oxygen atoms.[395] Departure from planarity of the molecule allows more effective van der Waals bonding between successive molecules.[395]

A rough X-ray crystal examination of the copper complex of nootkatin, aimed only at locating substituents at the seven-membered ring, has also been carried out.[396]



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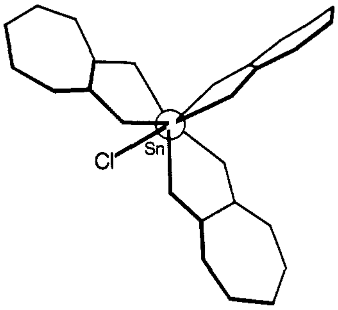

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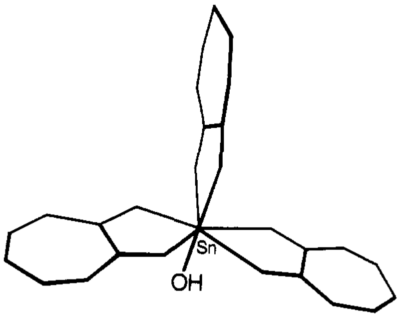

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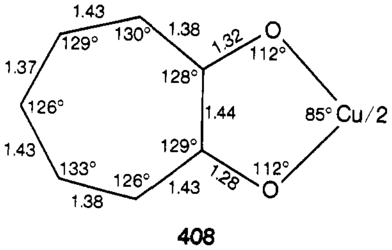

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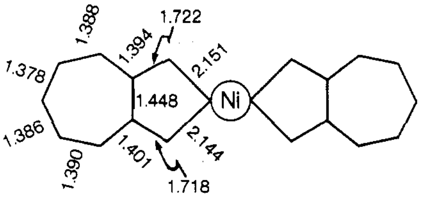

409

Crystal X-ray diffraction analysis of Ni(dithiotropolonato)$_2$[98] has also been reported (**409**).[397] The coordination geometry around the metal is planar and the seven-membered rings are also planar. Moreover, whereas the bond length (1.448 Å) for the bridge C(1)–C(7) bond is by merely 0.05 Å shorter than that expected for a pure

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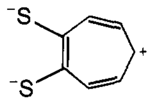
(394) T. A. Hamor and D. J. Watkin, *Chem. Commun.*, 440 (1969).

(395) W. M. Macintyre, J. M. Robertson, and R. F. Zahrobsky, *Proc. Roy. Soc., Ser. A*, **289**, 161 (1966).

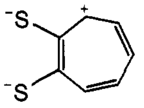
(396) R. B. Campbell and J. M. Robertson, *Chem. Ind. (London)*, 1266 (1952).

(397) G. P. Khare, A. J. Schultz, and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 3597 (1971).

$C(sp^2)$-$C(sp^2)$ single bond, all other C–C bond lengths are close to the benzene value. This indicates extensive peripheral conjugation which, as the C–S mean distance, 1.720 Å, is significantly smaller than the value, 1.81 Å, expected for a C–S single bond, must involve also the sulfur atoms. These findings show that this ligand has a closely similar structure to that found for the ligands in sodium tropolonate (**351**),[321] Fe(tropolonate)$_3$ (**404**),[394] (DMF)Th(tropolonato)$_4$ (**405**),[249a] (tropolonato)$_3$SnCl (**406**),[249b] (tropolonato)$_3$SnOH (**407**),[249b] and for the noncoordinated 1-methylamino-7-methylimino-1,3,5-cycloheptatriene (**362**).[333] These results,[397] allowing only a minor contribution by the resonance structures **410a** and **410b**, account for the lack of dithiolene character[398] for these complexes.[98]



410a



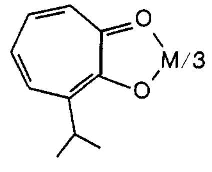
410b

A comprehensive account of the properties of these chelate complexes (which should be subdivided according to the ligand nature and the coordination number for each ligand type) in solution is well beyond the scope of this review. We will limit ourselves to a brief discussion of the points of major current interest.

As concerns tropolonato complexes, it is to be noticed that, in solution, several of them are polymeric, presumably through bridging oxygen atoms, *i.e.*, three-coordinated chelate oxygen atoms.[399] As the solubility of neutral tropolone metal chelates is generally too low for accurate *molecular weight determination*, the corresponding chelates of γ-thuyaplicin, which are generally soluble enough, have been systematically studied.[399] Intra- and intermolecular exchange of polytopal[400] and stereoisomeric forms of these chelates, as well as stability constants, have been extensively studied.[248,399]

The ir absorption spectrum of [$^{18}O_2$] tropolonato Cu(II) chelate, showing only one stretching frequency, 1357 cm^{-1}, for the carbon–oxygen bonds, indicates that both C=O groups vibrate independently from one another.[325b]

Recently it has been found that cis and trans forms of 3-isopropyltropolone chelates of Co(III) or Al(III) (**411**) undergo intramolecular isomerization faster than the corresponding β-diketonates.[401a] The possibility for a cis and a trans form for **411** is apparent when, viewing the complex in the space (with the aid of **404**), it is recognized that the two methyl groups, which are magnetically equivalent in the cis form, should be magnetically nonequivalent in the trans form. In accord with this, low-temperature *proton nmr spectra* of **411** show four methyl signals which coalesce into a single signal at higher temperature.[401a] A mechanism for the isomerization, which does not involve bond breaking, is envisaged[401a] as a twist around the pseudo-threefold axis of the trans isomer.[401b] These studies have been extended to include also 3-isopropyltropone as ligand and rhodium(III) as metal.[401c]



411

M = Co(III) or Al(III)

Proton nmr spectra of aminotroponeiminate chelate complexes revealed very distinctive features. The marked dependence of the position of the signals on the temperature, solvent, and structure of the ligand is best explained (in accordance with other physical data) in terms of an intramolecular diamagnetic (planar form) $\rightleftarrows$ paramagnetic (tetrahedral form) equilibrium.[402] Only very narrow signals were observed because of the short electronic relaxation times of the paramagnetic form.[403] Moreover, because of the varied (with respect to the free ligand) magnetic field at the proton (as the result of a fractional unpaired electron on carbon), signals for the paramagnetic species cover a frequency range up to 50 times as great as for either the diamagnetic chelate complex or the free ligand.[404] This allows the determination of both unpaired electron distributions in the π-electron system and the conjugating, or hyperconjugating, abilities of substituents.[404]

Also ^{13}C isotropic shifts have been studied in these paramagnetic species from *^{13}C nmr spectra*.[405] It seems that propagation of spin density occurs principally through σ bonds.[405]

Electrochemical studies[98] showed that dithiotropolone metal chelates fail to undergo the easy and reversible electron transfer reactions characteristic[398] of the analogous bis(dithiolene) systems. This is in accord with the results of X-ray crystal diffraction analysis of the nickel(II) chelate **409** according to which the resonance forms **410a** and **410b**, which would be required for dithiolene character, have negligible weight.[397]

V. Reactivity

The pattern of the reactivity of the compounds dealt with in this review is generally extremely complex. This is usually true also when a single class of these compounds is considered. Following our aim to arrive at a unified picture of the behavior of these compounds, we classify their reactions according to reaction types rather to compound classes. Such a grouping together of the various reactions is based on their formal appearance (such as the type of the bonds made or broken during the reaction and the nature of the reagents utilized) rather than on detailed mechanistic information. This offers an easy reference to the various reaction modes of these compounds which, as regards synthetic problems, is complementary to the material of section II.

Because of the scanty data available, and to emphasize the different behavior with respect to the non-complexed ligands, reactivity of metal complexes will be treated in a separate section.

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A. Nucleophilic Substitution Reactions at the Conjugated Ring

1. Nucleophilic Substitution Reactions at the Conjugated Ring without Rearrangement

These are reactions in which a charged or neutral nucleophilic species replaces an atom or group (leaving group), taking the position originally occupied by this, from a ring position of the conjugated compound (substrate). To prove this, a label at the ring is required. Such information is available only in certain cases, and, therefore, all other cases are included here for analogy. Superimposition with material (discussed in later sections) concerning rearrangement reactions cannot be entirely avoided, however.

Typical condensation processes, such as those leading to semicarbazones from cycloheptatrienones, are included here because, formally, they are nucleophilic substitutions (of oxygen).

a. Replacement of Halogen

Halogens may be replaced by a large variety of nucleophilic reagents. Most examples concern halocycloheptatrienones or halotropolones, but such reactions occur also with halotropenylium salts and, although our knowledge is very scanty, with halocycloheptatrienimines.

As concerns halocycloheptatrienones, recently in the author's laboratory fluorine has been extensively used as a leaving group.[406] Often, though not always, fluorine is in fact much more easily replaceable than the other halogens.[406]

Replacement of halogens by aromatic compounds under Friedel-Crafts conditions did not succeed, however. Thus, neither 2-chloro- nor 2,7-dichlorotropone reacts with benzene in the presence of $AlCl_3$.[407]

i. By Halide Ions. Halogen exchange at the seven-membered ring positions has been reported only for cycloheptatrienone derivatives and is synthetically important, being the only known route to iodo derivatives and the only general one to bromo derivatives. Such exchanges are generally very slow even in dipolar aprotic solvents like acetone (DMSO or DMF have not yet been tried as solvents). However, exchange of chlorine with either bromine or iodine or of bromine with chlorine is very much accelerated by added acids. Thus, 2-chlorotropone remains unchanged after 3 hr at 100° in acetone in the presence of sodium iodide, whereas in acetic acid at reflux in the presence of potassium iodide complete exchange of halogen occurs in 5 hr.[408] Also, chlorine-bromine exchange with 2-chlorotropone is very rapid with hydrogen bromide in acetic acid but very slow with potassium bromide in acetic acid.[408] Tetraalkylammonium halides have also been used in the place of alkali halides or hydrogen halides.[408]

In the presence of water competitive substitution of halogen by hydroxyl was also observed. This is the case of 4-bromotropone which gives both 4-chlorotropone and γ-tropolone when heated in acetic acid with added concentrated aqueous hydrogen chloride.[409]

2-Bromotropone, 2-chloro-3-bromotropone, and 2,5-dichlorotropone have been subjected to the same treatment.[409] The first gave both 2-chlorotropone and tropolone, albeit more slowly than in the above case of 4-bromotropone.[409] The second gave 2,3-dichlorotropone and 2-chloro-3-hydroxytropone.[409] Finally, the third gave 2-chloro-5-hydroxytropone as the major product accompanied by 5-chlorotropolone.[409] Thus, under acidic conditions, the C(2) nuclear position seems to be less susceptible than the other nuclear positions to nucleophilic substitution.

Conclusions above seem to be in contrast with the results of a similar treatment of 2,4,7-tribromotropone.[409] In fact, after 1 hr at 100°, a dichlorobromotropone (possibly, 2,4-dichloro-7-bromotropone) was obtained, whereas after 10 hr at 135° 4-hydroxy-7-chlorotropolone and 4,7-dichlorotropolone were obtained in 70 and 10% yields, respectively.[409] However, it cannot be excluded that under milder conditions only reaction at C(4) would have been observed.

Acid catalysis of these reactions, though it has never been studied in mechanistic detail, can be reasonably attributed to protonation of the cycloheptatrienone oxygen at some reaction stage with stabilization of the negative charge accepted by the oxygen atom. Catalysis of the removal of halides ions does not appear to be important because silver ion in no way facilitates the hydrolysis of 2-chlorotropone.[408]

ii. By Hydroxide Ion or Water. Generally, 2-chlorotropones rearrange to benzenoid derivatives under alkaline conditions. 2-Fluorotropone is an exception, its alkaline hydrolysis leading to tropolone.[410] Such behavior probably reflects the high mobility of fluorine as found for other nucleophilic substitutions of 2-fluorotropone.[406] Both 3-chloro- and 4-chlorotropone gave only tars on alkaline treatment.[411]

Halotropolones are much more resistant than halotropones to benzenoid rearrangement under alkaline conditions provided they do not bear such strongly electron-attracting groups as nitro groups. However, the negative charge on oxygen renders halotropolones less reactive than halotropones toward nucleophilic substitution of the halide. Presumably, as a consequence of this, alkaline treatment of halotropolones often led, under the rather severe conditions required, to products of cine-substitution accompanied by products of replacement of halogen without rearrangement. Thus, alkaline fusion of 3-bromotropolone gave mainly 4-hydroxytropolone together with some 3-hydroxytropolone.[412] Alkaline fusion at 200° for 15 min of 4-carboxy-6-hydroxy-7-bromotropolone (bromostipitatic acid) led to replacement of bromine with hydroxyl (puberulic acid) in 58% yield.[413] Drastic alkaline fusion was required to observe rearrangement of halotropolones to benzenoid compounds[412,413] which contrasts with the extreme ease of such rearrangements with halotropones as shown in later sections.

Halotropenylium salts undergo facile hydrolysis, with halogen replacement, to give tropone.[414]

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(406) F. Pietra and F. Del Cima, *J. Chem. Soc. B*, 2224 (1971).

(407) B. J. Abadir, J. W. Cook, J. D. Loudon, and D. K. V. Steel, *J. Chem. Soc.*, 2350 (1952).

(408) W. von E. Doering and C. F. Hiskey, *J. Amer. Chem. Soc.*, **74**, 5688 (1952).

(409) T. Nozoe, T. Asao, E. Takahashi, and K. Takahashi, *Bull. Chem. Soc. Jap.*, **39**, 1310 (1966).

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(411) J. D. Hobson and J. R. Malpass, *J. Chem. Soc. C*, 1499 (1969).

(412) Y. Kitahara, *Sci. Rep. Res. Inst. Tohoku Univ., Ser. A*, **39**, 258 (1956).

(413) R. B. Johns, A. W. Johnson, and J. Murray, *J. Chem. Soc.*, 198 (1954).

(414) H. J. Dauben, F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Amer. Chem. Soc.*, **79**, 4557 (1957); D. N. Kursanov, *Uch. Zap. Kharkovsk. Gos. Univ. Tr. Khim. Fak. i Nauchn.-Issled. Inst. Khim.*, **No. 17, 7** (1961); *Chem. Abstr.*, **58**, 4398 (1963); W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 665 (1956).

Acid hydrolysis is the ideal condition to replace halogen with hydroxyl from halotroponoids. Usually, in fact, these reactions are not attended by rearrangements. It has already been pointed out that in reactions of exchange of halogen under acidic conditions the presence of water leads competitively to halogen replacement by hydroxyl. In aqueous acidic medium this is generally the only reaction observed. Thus, 2-chlorotropone can be hydrolyzed to tropolone in very high yield with dilute hydrochloric acid for 9 hr at 150°.[408] As already pointed out for halogen exchange reactions under acidic conditions, the replacement of halogen with hydroxyl is slower at C(2) than at the other positions. Thus, 2,3-dihalotropones undergo preferential replacement of the 3-halogen atom by hydroxyl,[415] more drastic conditions being required to replace both halogen atoms.[416]

Also 4-bromotropone is effectively hydrolyzed in acid solution, and this constituted a key step in one of the synthetic routes to γ-tropolone (4-bromotropone was obtained as a by-product of the bromination of suberone).[417]

It would be very interesting to investigate if perchlorotropone, which is as labile as polynitro-substituted troponoids, being rearranged to methyl pentachlorobenzoate on simple dissolution in methanol,[87] could be hydrolyzed with preservation of the seven-membered ring in acid solution.

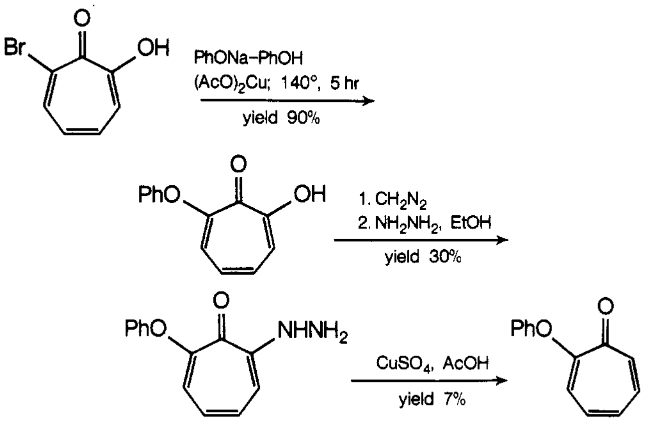
iii. By Alkoxide or Phenoxide Ions. 2-Halotropones were reported to rearrange to benzenoid compounds when treated with alkoxide ions. Synthesis of tropolone ethers was therefore carried out along other routes. Thus, O-alkylation of tropolone was carried out with diazoalkanes, alkyl sulfates, or alcohols plus mineral acid. Otherwise, tropolonato ion was alkylated with alkyl halides as discussed more fully in later sections. Tropolone aryl ethers have been obtained by indirect routes. For example, 2-phenoxytropone was synthesized by the series of reactions shown in Scheme XXIX.[418] It is seen that, in analogy with the behavior toward aqueous alkali discussed in the above section, tropolones carrying a good leaving group undergo substitution, rather than benzenoid rearrangement, by phenoxides. However, the drastic conditions required may lead to products of cine-substitution, as observed with alkoxides as nucleophiles. It is also interesting that copper acetate helps these reactions (Scheme XXIX). In fact, in the absence of the copper salt, the yield of the substitution product dropped to only 49%, whereas 30% of the starting material was recovered.[320]

Nothing is known in regard to the behavior of 3- and 4-halotropones toward alkoxides. Analogy with the behavior toward alkali, where resinification was observed to occur,[411] may be expected.

Very little is known about β- and γ-tropolone ethers. The only known cases are those of the methyl ethers which have been obtained by diazomethane treatment of β-[419] or γ-tropolone.[420]

Chlorotropenylium chloride is so reactive that chlorine is replaced by alkoxyl group on the mere treatment with an anhydrous alcohol.[421]

SCHEME XXIX



iv. By Sulfur Nucleophiles. Negatively charged sulfur nucleophiles generally give clean substitution of halogen with either halotropolones or halotropones. Generally, more drastic conditions are required for halotropolones, whereas for halotropones the reactions are extremely rapid. In all cases so far investigated, sulfur takes the place of the leaving halogen. Thus, for example, treatment of 2-chloro-4-isopropyltropone with *p*-thiocresol in alkali gave 2-*p*-thiocresoxy-4-isopropyltropone.[422]

Alkali metal hydrosulfides replace halogen from either 2-halotropones or halotropolones. Thus 2-chloro- or 2-bromotropone gave 2-mercaptotropone in good yield when treated with sodium hydrosulfite in ethanol.[423] 3-Bromotropolone gave 3-mercaptotropolone under the same conditions.[423]

With sodium sulfide, di(2-troponyl) disulfide or di(3-troponyl) disulfide was obtained from respectively 2-halotropones or 3-halotropones.[423]

2-Chlorotropone reacts with either sodium thioacetate, sodium benzoylacetate, or $HSCH_2CO_2Na$ to give 2-acetylmercaptotropone, 2-benzoylmercaptotropone, or 2-troponylthioacetic acid, respectively.[424] 2-Chlorotropone reacts also with the sodium salt of 2-mercaptotropone to give di(2-troponyl) sulfide.[423,424]

Studies with polyhalogenated tropones and tropolones have also been reported. For the same halogen, C(2) (or C(7)) is the most reactive position. Thus 2,4,7-tribromotropone with *p*-thiocresol in alkali gave 2,7-di-*p*-thiocresoxy-4-bromotropone.[423] Under the same conditions 3,5,7-tribromotropolone gave 3,7-di-*p*-thiocresoxy-5-bromotropolone and 3,5-dibromo-7-*p*-thiocresoxytropolone.[423] Position C(5) also has some reactivity because the last compound gave 3,5,7-tri-*p*-thiocresoxytropolone with *p*-thiocresol in alkali under rather drastic conditions.[425]

When equivalent positions are compared, bromine appears to be more easily substituted than either methoxy or chlorine. Thus, bromine is selectively replaced by sodium hydrosulfide, sodium sulfide, or sodium methyl mercaptide from 2-bromo-7-methoxytropone.[423] Also, bromine is selectively replaced from 2-bromo-7-chlorotropone by sodium hydrosulfide[424] or *p*-thiocresol in an alkaline medium.[426a] However, the behavior of simple 3- or

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(418) K. Takase, *Bull. Chem. Soc. Jap.*, **37**, 1288 (1964).

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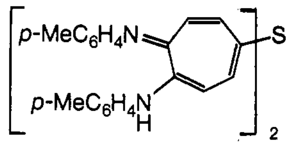
(424) T. Nozoe, M. Sato, and K. Matsui, *Proc. Jap. Acad.*, **29**, 22 (1953); *Chem. Abstr.*, **48**, 5172 (1954).

(425) J. W. Cook, J. D. Loudon, and D. K. V. Steel, *J. Chem. Soc.*, 530 (1954).

4-halotropones toward sulfur nucleophiles has not been investigated so far.

Chlorine is also easily substituted by mercaptans from chlorotropenylium perchlorate to give alkylmercaptotropenylium salts.[421]

The only recorded example of substitution of nuclear halogen from cycloheptatrienaminoimines is also by sulfur nucleophiles. Thus, bromine is substituted from 5-bromo-1-(*p*-tolylimino)-2-(*p*-tolylamino)-1,3,5-cycloheptatriene by either thiourea in DMF or by hydrogen sulfide to give the sulfide **412**.[114] With azulene derivatives, like 6-chloro-1-azaazulen-2-one or 2,6-dichloroazaazulene, *p*-tolylmercaptide succeeded in replacing chloride whereas other nucleophilic reagents, like hydroxide, methoxide, cyanide, liquid ammonia, and *p*-toluidine, proved to be ineffective.[426b] Substitution at the seven-membered ring was faster than at the five-membered ring.[426b] However, photoexcited azulenes proved to be more reactive. Thus, 1-nitroazulene reacted with methoxide or cyanide ions, under uv irradiation, with replacement of the nitro groups in fair yield.[426c]



412

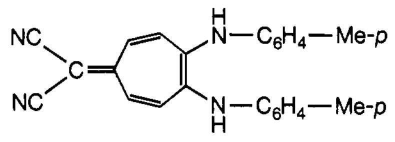
v. By Carbanions or Organometallic Reagents. It is uncertain whether in the reaction of 2-bromo- or 2-chlorotropone with phenylmagnesium bromide[408,427] or phenyllithium,[408] to give 2-phenyltropone, the phenyl group has taken the position originally occupied by the halogen. This holds also for the reaction[143] of 2-chlorotropone with phosphonium ylides to give **191**. Labeling of the ring with the cyano group shows that rearrangement occurs. Thus, reaction of 2-chloro-5-cyanotropone with phenylmagnesium bromide leads to 2-phenyl-4-cyanotropone.[428] However, these findings may have little bearing on those above. In fact, substitution with rearrangement might be primarily a consequence of the strong electronic influence of the cyano group. Direct evidence for directive influence of this type by a quaternary ammonium group as a substituent has been obtained in the reviewer's laboratory as shown in later sections.

That substituents at the ring may exert a delicate balance on the course of these reactions is also shown by the fact that reaction of phenylmagnesium iodide with 2-chloro- (or bromo-) 7-methoxytropone led to products of substitution of methoxide by the phenyl group accompanied by benzenoid rearrangement.[429] The treatment of 2-chloro-7-methoxytropone with the double molar quantity of phenylmagnesium bromide led to 2,7-diphenyltropone in only 1.5% yield.[429]

The nature of the organometallic compound is also an important factor influencing the reaction course. Thus on treatment of 2-chloro-7-methoxytropone with methylmagnesium iodide, only benzenoid products have been obtained.[429]

In all these reactions the organometallic reagent should never be in excess; otherwise the substitution products may undergo further reaction. Therefore, the organometallic reagent must be added slowly to a solution of the substrate. Neither the behavior of 3- nor of 4-halotropones toward these reagents has been investigated so far.

The only reported example of halogen replacement by carbanions from cycloheptatrienaminoimines concerns the reaction of 5-bromo-1-(*p*-tolylimino)-2-(*p*-tolylamino)-1,3,5-cycloheptatriene by malononitrile under basic conditions, **413** having been obtained.[99]



413

vi. By Ammonia or Amines. Reaction of ammonia with 2-chlorotropone is slow and leads, by attack at C(7), to rearranged 2-aminotropone and to benzenoid products. This has been shown by both deuterium[430] or isopropyl[431] labeling of the ring.

Both primary and secondary unhindered amines react much faster than ammonia with 2-halotropones and usually lead only to unrearranged substitution products of the halogen as proved by deuterium labeling of the halotropone.[406,432] In these reactions fluorine is by far the most easily replaceable leaving group.[406] Even nonpolar solvents, like benzene, work well with these reactions, and it is striking that change to a dipolar aprotic solvent, like DMSO, leads to a mere sevenfold increase of the reaction rate.[406] This is in contrast with common experience in nucleophilic substitutions which are normally accelerated by many powers of ten on the change from benzene to DMSO. Also, these reactions do not undergo general base catalysis[406,432] while acidic substances, like phenol, are powerful catalysts.[433] However, because of the fact that one of the reactants, the amine, is a relatively strong base, its effective concentration diminishes on addition of the acid so that there is no practical advantage of adding an acid.[433] The fact that these reactions proceed cleanly at practically their highest rates in hydrocarbon solvents has obvious synthetic advantages.

2-Iodo-substituted substrates constitute an exception, their reaction with protic amines being, in fact, accelerated by added tertiary amines of low steric bulk around nitrogen, such as quinuclidine.[433] Here, however, a mixture of products arising from competitive substitutions at the carbon carrying iodine and at C(7) was obtained.[433] The product of attack at C(7) originates from the quinuclidine catalyzed pathway *via* a quinuclidinium salt of the type **340**.[433] This new mode of catalysis has been termed "nucleophilic catalysis with rearrangement"[433] and should not be forgotten when devising syntheses in this area.

As regards unsubstituted 3- or 4-halotropones, a single example is known concerning the reaction 3-chlorotropone with dimethylamine which gave equal amounts of 3- and 2-dimethylaminotropone in good yield.[411] The reaction of 2-phenyl-4-bromotropone with hydrazine gave 3-phenyl-4-bromo-7-aminotropone.[434] It is peculiar that

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(426) (a) T. Nozoe, M. Sato, S. Ito, K. Matsui, and T. Matsuda, *Proc. Jap. Acad.*, **29**, 565 (1953); (b) T. Toda, S. Seto, and T. Nozoe, *Bull. Chem. Soc. Jap.*, **41**, 2102 (1968); (c) C. M. Lock, J. Lugtenburg, J. Cornelisse, and E. Havinga, *Tetrahedron Lett.*, 4701 (1970).

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(431) T. Nozoe, S. Seto, and T. Sato, *Proc. Jap. Acad.*, **30**, 473 (1954).

(432) F. Pietra, M. Giocasta, and F. Del Cima, *Tetrahedron Lett.*, 5097 (1969).

(433) G. Biggi, F. Del Cima, and F. Pietra, *J. Chem. Soc., Perkin Trans. 2*, 1424 (1972).

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bromine is not replaced and that hydrazine is fragmented. With 2-halotropones hydrazine behaves normally; *i.e.*, the halogen is replaced by hydrazine without fragmentation. Thus, treatment of 2,4,7-tribromotropone with hydrazine in benzene at reflux gave a mixture of 2,4-dibromo-7-hydrazinotropone and 2,5-dibromo-7-hydrazinotropone.[435]

Reactions of 2-halotropones with tertiary amines generally do not stop at the stage of the quaternary salt arising by replacement of the halogen. Further reaction of the quaternary salt with available nucleophiles generally ensues,[293,436] as discussed more fully in a subsequent section. Only in the case of 2-iodo-substituted substrates was it relatively easy to obtain pure quaternary salts in high yield.[293,436] 2-Fluorotropone constitutes a special case. Fluorine substitution by tertiary amines, with concomitant dealkylation, could be obtained only in DMSO.[406] In benzene as solvent no reaction occurs under the conditions used for the other 2-halotropones.[406] Forcing of the conditions led to hydrolysis at an extent which is dependent on the dryness of the reaction mixture.[406] 2-Trimethylammonio-6-methyltropone has been prepared by methylation with methyl iodide of 2-dimethylamino-6-methyltropone.[437]

Chlorotropenylium salts react with either protic aromatic[438] or protic alkyl aryl-amines[421] to give, respectively, arylaminotropenylium salts[438] or *N*-alkyl-*N*-arylaminotropenylium salts[421] under thermodynamic conditions.[421] Under kinetic conditions, addition of the amine to the unsubstituted ring positions of the tropenylium salt obtains instead.[421] In contrast, aliphatic amines give only products of benzenoid rearrangement[421] (see, however, subsection b below for the preparation of *N*-alkyl- or *N*-dialkyltropenylium salts from alkoxytropenylium salts.[122c]).

vii. By Other Nucleophiles. Substitution of bromine by the cyano group has been studied to some extent. It has been concluded that heating of 2-bromotropones with excess cuprous cyanide leads to 2-cyanotropones without rearrangement. Thus, 2-bromo-6-isopropyl- or 2-bromo-4-isopropyltropone gave 2-cyano-6-isopropyl- or 2-cyano-4-isopropyltropone, respectively.[439] It was already known that, on the same treatment, 2-bromotropone leads to 2-cyanotropone.[440] Heating of 3-bromotropolone with cuprous cyanide in pyridine led to 3-cyanotropolone,[407] whereas when potassium cyanide was used 4-cyanotropolone was obtained instead.[441]

The behavior of polybrominated tropolones toward cuprous cyanide has also been investigated. With 3,5,7-tribromotropolone in pyridine 5-bromo-3,7-dicyanotropolone was obtained.[442] In the case of 3,6-dibromotropolone, 3,6-dicyano- and 4-bromotropolone were obtained.[443] These cyano compounds easily undergo hydrolysis to the corresponding carboxy compounds.[439]

Another nucleophile which has been extensively used is the azide anion owing to the easy reduction of azido compounds to the corresponding amino compounds and because azido compounds are potential sources of nitrenes. Thus, 2-, 3-, or 4-chlorotropone was found to react with sodium azide in DMSO at room temperature to give 2-,[444] 3-,[411] or 4-azidotropone,[411] respectively.

b. Replacement of Alkoxy and Aryloxy Groups

Hydrolysis of 2-alkoxytropones to tropolones with C(sp^2)–O bond breaking has been carried out under either acid[445] or dilute alkali[446] conditions. Concentrated alkali may lead to benzenoid rearrangement competitively with alkoxy replacement by OH. Hydrolysis in dilute alkali is described as a process free from any rearrangement.[446]

The 2-methoxy group is hydrolyzed preferentially in polymethoxytropones. It is remarkable that the 2-phenoxy group is removed preferentially to either 2-chlorine, 2-bromine, or, perhaps, 2-tosyloxy from 2,7-disubstituted tropones. Thus, 2-chloro-7-phenoxy- or 2-bromo-7-phenoxytropone undergo hydrolysis in dilute alkali to give 3-chloro- or 3-bromotropolone, respectively.[418] In the case of 2-tosyloxy-7-phenoxytropone it seems that 3-tosyloxytropolone is produced,[418] although some reservation about the validity of the structural assignment of the product must be advanced.

In contrast, transetherification catalyzed by *p*-toluenesulfonic acid gives a mixture of products of both the (formal) replacement of the carbonyl oxygen and the replacement of the alkoxy group. This was observed with colchicine and isocolchicine in ethanol.[447] A similar situation was also found with thiols in the place of ethanol.[448]

2-Methoxytropones were reported to react with thiols in basic solution to give 2-mercaptotropones.[449] However, with 2-methoxytropone other authors obtained clean demethylation by *p*-tolylmercaptide in hexamethylphosphoramide.[450] Moreover, with ethylmercaptide in ethylmercaptan only complex, high molecular weight, materials were obtained, whereas in alcohols untractable tars were obtained.[450] This contrasts with the behavior of 2-halotropones which react with thiols in basic solution to give 2-mercaptotropones in high yield (section V.A.1.a.iv).

It has been also shown in a previous section (V.A.1.a.v) that the alkoxy group is replaced preferentially with respect to either chlorine or bromine from 2-halo-7-methoxytropone by phenylmagnesium bromide.[429]

2-Methoxytropones react smoothly with ammonia or primary or secondary (aliphatic or aromatic) amines to give replacement products of the alkoxy group without rearrangement. This has been established with deuterium-labeled 2-methoxytropone.[406,430,432] The reactivity of 2-methoxytropone toward piperidine in benzene is very similar to that of 2-chloro-, 2-bromo-, and 2-iodotropone in the same medium, an isokinetic relationship being obeyed with the isokinetic temperature near room temperature.[406,432] This clearly contrasts with selective aminodemethoxylations from (i) 2-bromo-7-methoxytropone by

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(435) T. Nozoe, Y. Kitahara, T. Ando, S. Masamune, and H. Abe, *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, **36**, 166 (1952).

(436) F. Pietra and F. Del Cima, *Chem. Commun.*, 297 (1970).

(437) P. Akroyd, R. D. Haworth, and P. R. Jeffries, *J. Chem. Soc.*, 286 (1954).

(438) Y. Kitahara, T. Asao, and M. Funamizu, Japanese Patent 17825 (1964); *Chem. Abstr.*, **62**, 5233 (1965).

(439) T. Asao and M. Kobayashi, *Bull. Chem. Soc. Jap.*, **39**, 2538 (1966).

(440) T. Nozoe, S. Seto, and S. Matsumura, *Proc. Jap. Acad.*, **28**, 483 (1952); *Chem. Abstr.*, **48**, 2679 (1954).

(441) T. Nozoe, Y. Kitahara, and H. Abe, *Proc. Jap. Acad.*, **29**, 347 (1955); *Chem. Abstr.*, **49**, 3035 (1955).

(442) Y. Kitahara, *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, **40**, 74 (1956).

(443) Reference 1b, p 421.

(444) J. D. Hobson and J. R. Malpass, *J. Chem. Soc. C*, 1645 (1967).

(445) T. J. Fitzgerald, Ph.D. Thesis, Ohio State University, 1965, University Microfilm 66.6251.

(446) K. Bowden and M. J. Price, *J. Chem. Soc. B*, 1784 (1971).

(447) R. M. Horowitz and G. E. Ullyot, *J. Amer. Chem. Soc.*, **74**, 587 (1952).

(448) L. Velluz and G. Muller, *Bull. Soc. Chim. Fr.*, 755 (1954); 194, 198 (1955).

(449) Reference 1b, p 420.

(450) G. Biggi, F. Del Cima, and F. Pietra, *Tetrahedron Lett.*, 183 (1973).

either liquid ammonia, *p*-toluidine, or hydrazine,[451] (ii) 2-methoxy-3,5,7-tribromotropone or 2-methoxy-3,7-dibromotropone by ammonia,[451] and (iii) 7-bromo-2-methoxy-4-isopropyltropone by hydrazine.[452]

The phenoxy group is selectively replaced by hydrazine from 2-phenoxy-7-tosyloxytropone.[418] Also, the methoxyl group is replaced preferentially to the methylthio group from 2-methoxy-7-methylthiotropone by hydrazine.[453]

The 2-methoxy group can also be selectively replaced by either ammonia or primary or secondary amines from 2-methoxytropones carrying other replaceable groups at positions different from C(7). Such is the case of 3-bromo-2-methoxytropone (with liquid ammonia or hydrazine),[451] 5-bromo-2-methoxytropone (with ammonia),[451] 3-bromo-2-methoxy-6-isopropyltropone (with hydrazine),[452] 4-bromo-7-methoxy-2-phenyltropone[452] or 2-methoxy-5-nitrotropone[451] (with liquid ammonia), 3,5-dibromo-2-methoxy-7-phenyltropone (with ammonia),[454] and 2-methoxy-5-azidotropone (with ethylamine or diethylamine).[455]

In sharp contrast with the behavior of primary or secondary amines and ammonia, a tertiary amine only little sterically hindered, like quinuclidine, cleanly demethylates 2-methoxytropone in benzene.[450] This is the best procedure so far available to effect alkyl–oxygen bond breaking in tropolone ethers.

2-Methoxytropones react also with organomagnesium reagents although generally in a complex way. Thus, both 2-methoxy-4-methyltropone and 2-methoxy-6-methyltropone react with phenylmagnesium bromide to give 5-methyl-2-phenyltropone and 3-methyl-2-phenyltropone, attack at C(7) being involved in both cases.[437] However, it has also been reported above (section V.A.1.a.v) that 2-chloro- or 2-bromo-7-methoxytropone and phenylmagnesium iodide give the corresponding 2-halo-7-phenyltropone,[429] whereas methylmagnesium iodide induces rearrangement, only benzenoid products being obtained.[429]

As concerns 3- and 4-alkoxytropone, it is known that both 3- and 4-methoxytropone can be easily hydrolyzed under acid catalysis to the corresponding hydroxytropones.[420] 4-Methoxytropone is also reported to hydrolyze to 4-hydroxytropone in alkali,[417] which seems surprising to this author in view of the observed resignification of 4-chlorotropone in alkali.[411] Practically no other information is available concerning reactions of these substrates with nucleophilic reagents.

Alkoxyl groups are replaced by a variety of nucleophilic reagents from alkoxytropenylium ions. The preparation of both 8,8-dicyanoheptafulvene (**153**)[122b] and dithiotropolone (**127**)[98] along such lines has already been mentioned previously. Methoxytropenylium salts react also with primary or secondary amines to give, respectively, alkylamino- or dialkylaminotropenylium salts.[122c]

c. Replacement of Doubly or Singly Bonded Oxygen

Some tropones condense easily with ketonic reagents. This is the case, for example, of both 4,5-furantropone and 4,5-benzotropone which form an oxime or a dinitrophenylhydrazone under standard conditions.[41] Tropone itself forms an oxime but only as a minor product besides much 2-aminotropone.[456]

Tropolones require strongly electron-attracting substituents at the ring to be able to react with ketonic reagents. Thus, whereas tropolone only forms salts with amines, 3,5-dinitro-6-isopropyltropolone condenses with ammonia, aniline, *p*-toluidine, or *p*-chloroaniline to give, respectively, 2-amino-, 2-anilino-, 2-*p*-toluidino- or 2-*p*-chloroanilino-5,7-dinitro-4-isotropyltropone.[457] Also 5-nitro- and 5-nitrosotropolone condense with ammonia to give 5-nitro- and 5-nitroso-2-aminotropone, respectively.[458] Alkyl- or aryllithium reagents are able to replace one oxygen atom from either tropolones[408] or their cupric chelates[459a] to give 2-alkyl- or 2-aryltropones, respectively, in high yield. The cupric chelate of 4-methyltropolone was reported to give exclusively 2-phenyl-6-methyltropone.[459] This behavior parallels that of carboxylic acids toward organolithium compounds. Clearly, owing to complexation to a metal, oxygen becomes a replaceable atom.

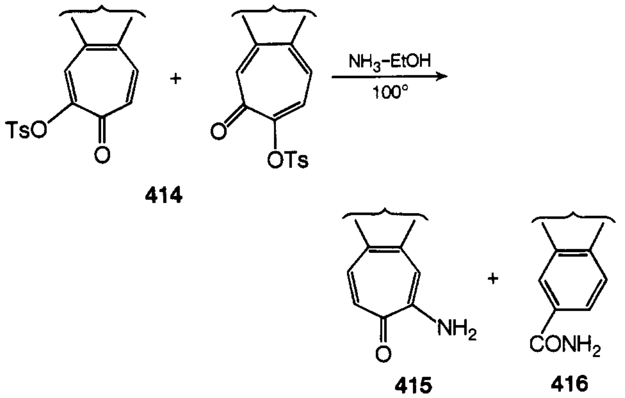
Reaction between 1,2,3,4-tetrachlorocyclopentadiene and 4,5-benzotropone to give a heptafulvalene derivative by loss of the elements of water has also been observed.[459b]

d. Replacement of Sulfonate and Other Ester Groups

Tropolone-*p*-toluenesulfonates are easily obtained from tropolones and *p*-toluenesulfonyl chloride in dry pyridine. The *p*-toluenesulfonate groups can be replaced by ammonia or amines. In the case of 2-tosyloxytropone deuterium labeling of the seven-membered ring showed that reaction by either ammonia or methylamine leads to 2-amino- or 2-methylaminotropone, respectively, by attack at both C(2) and C(7).[430] In contrast, reaction with dimethylamine led to dimethylaminotropone by exclusive attack at C(2).[430]

Products of substitution of the tosyloxy group by attack at C(7) were also observed for the reaction of ammonia with 3-isopropyl-, 3-isopropenyl-, and 6-isopropenyl-2-tosyloxytropone.[460]

A key step in a total synthesis of colchicine utilized this attack at C(7) by ammonia.[461] The mixture of iso-



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415 416

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(451) T. Nozoe, S. Seto, H. Takeda, S. Morosawa, and K. Matsumoto, *Proc. Jap. Acad.*, **28**, 192 (1952); *Chem. Abstr.*, **47**, 6392 (1953).

(452) S. Seto, *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, **37**, 297 (1953).

(453) T. Muroi, quoted in ref 1b, p 417.

(454) T. Nozoe, S. Ito, and K. Sonobe, *Proc. Jap. Acad.*, **29**, 101 (1953).

(455) T. Nozoe, H. Horino, and T. Toda, *Tetrahedron Lett.*, 5349 (1967).

(456) T. Nozoe, T. Mukai, T. Minegishi, and T. Fujisawa, *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, **37**, 380 (1953).

(457) T. Nozoe, S. Seto, H. Takeda, S. Morosawa, and K. Matsumoto, *Proc. Jap. Acad.*, **27**, 556 (1951); *Chem. Abstr.*, **46**, 7559 (1952).

(458) T. Nozoe, S. Seto, H. Takeda, S. Morosawa, and K. Matsumoto, *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, **36**, 126 (1952); *Chem. Abstr.*, **48**, 4497 (1954).

(459) (a) R. D. Haworth and P. B. Tinker, *J. Chem. Soc.*, 911 (1955); (b) Y. Sasada, H. Shimanouchi, I. Murata, A. Tajiri, and Y. Kitahara, *Tetrahedron Lett.*, 1185 (1969).

(460) T. Seto and T. Nozoe, referred to in ref 1b, p 419.

(461) J. Schreiber, W. Leimgruber, M. Pesaro, P. Schudel, and A. Eschenmoser, *Angew. Chem.*, **71**, 637 (1959).

mers **414** was heated with ammonia in ethanol and from the reaction mixture the desired **415** (*ca.* 15% yield) and the product of benzenoid rearrangement **416** were isolated.[461]

It has also been reported in the previous section that the phenoxy group is exclusively replaced by either hydrazine or OH^- from 2-phenoxy-7-tosyloxytropone.[418]

As regards sulfonate esters of β- or γ-tropolone, it is only known that 3-tosyloxytropone reacts with a saturated methanolic solution of ammonia at 40° for 30 min to give 3-aminotropone in 57% yield.[462]

It is also known that the tosyloxy group can be replaced by iodine from 2-tosyloxytropone on the treatment with tetraalkylammonium iodides in acetic acid.[408] 2-Tosyloxytropone can be hydrolyzed to tropolone in either acid or basic solution.[408] Moreover, 2-tosyloxytropone reacts with *p*-tolylmercaptide to give 2-*p*-tolylthiotropone.[425]

It is peculiar that no products of attack at the sulfur atom of tropolone sulfonates have been reported. This contrasts with the situation of the acetate of tropolone which reacts with ammonia to give tropolone and acetamide.[463]

e. Replacement of Amino Groups

The amino group of 2-aminotropones may be replaced by a variety of nucleophilic reagents. Generally, dialkylamine groups are more easily replaceable than monosubstituted, or unsubstituted, nitrogen. Thus, 2-dimethylaminotropone reacts with sodium methoxide in methanol, liquid ammonia, phenylmagnesium bromide, methylmagnesium bromide, or butyllithium to give 2-methoxy-, 2-amino-, 2-phenyl-, 2-methyl-, or 2-butyltropone, respectively.[464] In contrast, both 2-methylamino- and 2-aminotropone remain unchanged with either sodium methoxide at reflux or with neat aniline at 200° for 3 days.[464] 2-Methylaminotropone remained also unchanged after 6 days in liquid ammonia. Such inertness of both amino and dimethylamino compounds has been attributed to the formation, by proton abstraction from nitrogen, of aminotroponates which, being negatively charged, resist nucleophilic attack.[464] In contrast, it was reported, without giving yields, however, that 6-methyl-2-aminotropone reacts with excess aniline at reflux for 2 days to give 6-methyl-2-anilinotropone.[465]

Substitution of a 2-dimethylamino group from 2-dimethylaminotropones by organomagnesium reagents is long known to occur by attack at C(7). For example, 4-methyl- or 6-methyl-2-dimethylaminotropone and phenylmagnesium bromide give 5-methyl- or 3-methyl-2-phenyltropone, respectively.[437,466]

Alkaline hydrolysis of either 2-aminotropones or their *N*-alkyl- or *N*-aryl-substituted derivatives leads to exchange of nitrogen with hydroxyl without rearrangement.[464]

Catalysis by Cu(II) or Fe(III) salts of the replacement of the hydrazino group by chlorine, bromine, or iodine from 2-hydrazinotropones and the appropriate hydrogen halide is long known.[439,467]

Both cycloheptatrienimines[468] and cycloheptatrienaminoimines[114] exchange their nitrogen with amines. In the latter case, benzylamine exchanges both nitrogen atoms, whereas *p*-anisidine is only able to exchange one nitrogen.[114] We have already mentioned (section II.B.1) that cycloheptatrienaminoimines exchange one nitrogen with sulfur (**128** → **129**) on the treatment with $HS^- - H_2S$.[99]

Cycloheptatrienaminoimines can also be hydrolyzed provided the conditions are neither strongly acidic not strongly basic.[114] Thus, 1-(*p*-chlorphenylimino)-2-*p*-chlorophenylamino-1,3,5-cycloheptatriene was hydrolyzed to 2-*p*-chloroanilinotropone in acetic acid containing potassium acetate at reflux.[114]

f. Replacement of Ammonio and Diazonio Groups

The only authenticated example of substitution of an ammonio group without rearrangement is that of the reaction of 2-quinuclidinium tropone (**340**) with either *p*-tolylmercaptide or thiophenoxide to give *p*-tolylthio- or phenylthiotropone.[469] Deuterium labeling of the seven-membered ring proved that sulfur becomes attached to the position vacated by the ammonio group.[469]

2-Quinuclidinium tropone (**340**) reacts with piperidine in anhydrous DMSO to give 2-piperidinotropone in quantitative yield by attack of piperidine at C(7) (as proven by deuterium labeling experiments).[470] The rate is higher than for substitutions *via* attack at C(2) with other 2-X-tropones (X = Cl, Br, I, OCH_3).[406,432] Apparently, the quaternary nitrogen group activates the seven-membered ring toward nucleophilic attack.[470] When **340** and piperidine are mixed in water the reaction takes a different course. Interception of intermediates by water mainly leads to *m*-hydroxybenzaldehyde.[471] With other nucleophilic reagents still other competitive paths were observed. Thus, in alkali **340** gives benzoic acid.[471] whereas either iodide ion and a tertiary amine attack **340** at the bicyclic skeleton giving ring-opened products.[293,436]

It was also observed that 2-trimethylammoniotropone reacts with hydrogen chloride in dioxane to give 2-chlorotropone.[464] Neither 3- nor 4-trialkylammoniotropone is as yet known, but their synthesis is being attempted in the reviewer's laboratory.

Replacement of nitrogen by sodium azide from diazonium salts derived from 5-aminotropolones occurs with ease,[455,472] much more easily, in fact, that the analogous reaction of 5-chlorotropolones.[472] Rearrangements of the diazonium salts derived from 2-aminotropones are also known.[473] However, our knowledge of the chemical behavior of the diazonium salts of aminotropones and -tropolones is comparatively scanty.

g. Miscellaneous Group Replacement

The methylthio group of 2-methylthiotropones has been replaced by amines or alkali. Thus, reaction of hydrazine with 2-methylthio-7-phenyltropone gave 2-hydrazino-7-phenyltropone.[453] A methoxy group at an equivalent position is displaced in preference to a methylthio group. Thus, as noticed in section V.A.1.b, reaction of hydrazine

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(462) S. Seto, H. Sugiyama, and H. Toda, *Chem. Commun.*, 562 (1968); H. Toda, H. Sugiyama, and S. Seto, *Chem. Pharm. Bull.*, **17**, 2548 (1969).

(463) T. Seto, referred to in ref 1b, p 419.

(464) T. Toda, S. Ryu, and T. Nozoe, *Bull. Chem. Soc. Jap.*, **42**, 2028 (1969).

(465) P. Akroyd, R. D. Haworth, and J. D. Hobson, *J. Chem. Soc.*, 3427 (1951).

(466) R. D. Haworth and P. B. Tinker, quoted in ref 1a, p 61.

(467) Reference 1a, p 61.

(468) T. Nozoe, T. Mukai, K. Takase, and T. Nagase, *Proc. Jap. Acad.*, **28**, 477 (1952); *Chem. Abstr.*, **48**, 2678 (1954).

(469) G. Biggi, A. de Hoog, F. Del Cima, and F. Pietra, to be published.

(470) G. Biggi, F. Del Cima, and F. Pietra, *J. Amer. Chem. Soc.*, **94**, 4700 (1972).

(471) G. Biggi, F. Del Cima, and F. Pietra, *Chem. Commun.*, 1627 (1971).

(472) T. Toda, H. Horino, and T. Nozoe, *Bull. Chem. Soc. Jap.*, **45**, 226 (1972).

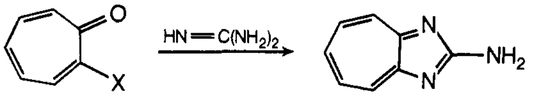
(473) Reference 1b, p 424.

with 2-methoxy-7-methylthiotropone gave 2-hydrazino-7-methylthiotropone only.[453] 2-Methylthio-7-phenyl- and 2,7-di(methylthio)tropone react in alkaline solution to give, respectively, 3-phenyltropolone[453] and a mixture of 3-methylthiotropolone and (2-methylthio)benzoic acid.[423]

Replacement of the nitro group by a halogen atom from nitrotropolones may also be effected.[474]

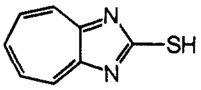
2. *Reactions of Bidentate Nucleophilic Reagents or of Nucleophilic–Electrophilic Reagents with Cyclization to Azulenes or Heteroazulenes*

Reactions of molecules carrying two geminal amino groups, such as thiourea or guanidine, with tropones carrying a good leaving group at C(2) do not usually stop at the stage of replacement of the leaving group. Intramolecular condensation with the carbonyl group often leads to heteroazulenes. This is the case of 2-chloro- or 2-methoxytropone. With guanidine the same product (**417**) was obtained from either substrate.[475a]



X = Cl, OMe **417**

In the case of thiourea, compound **418** was obtained from 2-methoxytropone whereas from 2-chlorotropone compound **419** was obtained.[475a] Problems of tautomerism in these compounds are not touched here. Also, it is not known whether or not these reactions occur with rearrangement.



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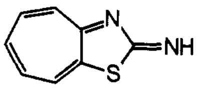
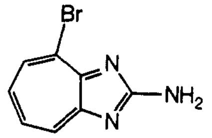


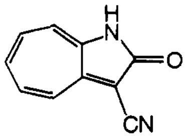
419

In the case of a tropone derivative carrying displaceable groups at both C(2) and C(7), one of these and the carbonyl oxygen are replaced by these bifunctional reagents. In the case of 2-bromo-7-methoxytropone and guanidine the methoxy group was selectively replaced, compound **420** having been obtained.[475a]



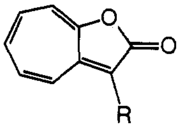
420

Cyanoacetamide is another bifunctional reagent. From 2-chloro- or 2-methoxytropone, in the presence of an alkoxide, **421** was obtained.[475b] The mechanism of these two reactions may not be the same, however. It seems, in fact, that the carbanion attacks 2-methoxytropone at C(2) and 2-chlorotropone at C(7).[475b] When, however, a nondisplaceable group, like an alkyl group, occupies C(7), even 2-chlorotropones are attacked at C(2).[475b]



421

The same substrates may also give heteroazulenes in a different way, *i.e.*, by incorporating the tropone oxygen in the seven-membered ring. This occurs with carbanionic species which, like ethyl malonate or ethyl acetoacetate, possess a displaceable (by nucleophiles) α group. Thus, 2-chloro, 2-bromo-, or 2-methoxytropone reacts with such reagents (under basic or Reformatsky conditions) to give products of type **422**. These processes may be viewed in terms of a nucleophilic attack by the carbanion at either C(2) or C(7), which is unknown, with concomitant or subsequent intramolecular attack by the electron-rich oxygen of the substrate at the C═O ester carbon.[475c]

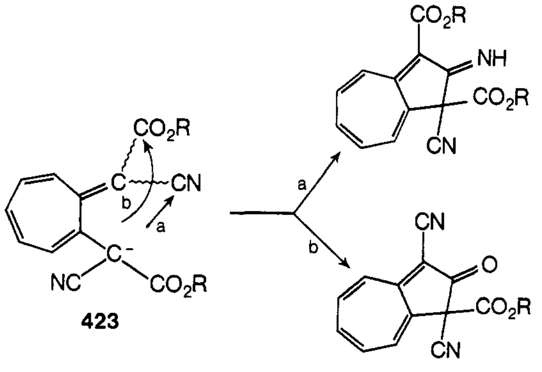


422

In the case of 2,5-dichloro- or 2-methoxy-5-chlorotropone, attack by the carbanion in benzene occurs at C(7). The latter substrate was examined also in benzene–ether mixtures where it gave a mixture of products of both C(7) and C(2) attacks.[475c]

With ethyl cyanoacetate and malonodinitrile, more complex pathways are involved. It is interesting that azulenes, instead of heteroazulenes, were obtained in all the above cases,[476] though usually accompanied by several other by-products. These processes may be tentatively viewed as the attack of two reagent molecules on the troponoid: the first one to replace the leaving group (chlorine,[476] methoxy,[476] or tosyloxy[455]) and the second one to condense with the carbonyl group to give intermediates of type **423** (Scheme XXX). Intramolecular cyclization by carbanion attack at either the nitrile or ester function as indicated by the arrows, and subsequent loss of the nitrile or the ester functions, is thought to lead to the main reaction products (Scheme XXX). Initial replacement of the leaving group may occur by attack at C(2) or C(7).[455,476]

SCHEME XXX



3. *Nucleophilic Substitutions at the Conjugated Ring with Rearrangement*

Many substitutions with rearrangement at the seven-membered ring of troponoids, *i.e.*, those substitution reactions in which the nucleophilic reagent takes a different position on the ring from that vacated by the leaving group, have already been met in sections V.A.1,2. These reactions may be phenomenologically, without any concern about mechanisms, divided into three types accord-

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(474) Reference 1b, p 408; K. Yamane, *J. Chem. Soc. Jap.*, **76**, 787 (1955).

(475) (a) Reference 1b, p 431; (b) *ibid.*, p 428; T. Nozoe, K. Takase, M. Kato, and T. Nogi, *Tetrahedron*, **27**, 6023 (1971); (c) ref 1b, p 427.

(476) Reference 1b, p 432.

ing to whether the nucleophilic reagent becomes attached to C(7) (the leaving group departing from C(2)), to a nuclear position adjacent to that vacated by the leaving group (cine-substitutions) or, finally, to a nuclear position different from the two above.

Rearrangements of this type are practically known only for troponoids. Another potential substitution with rearrangement with these substrates, *i.e.*, attack of the nucleophilic reagent to the carbonyl carbon with shift of the carbonyl oxygen to the adjacent carbon and departure from this of the substituent,[477] has so far received no clear experimental substantiation.

a. Substitution by Attack at C(7) with Leaving-Group Departure from C(2)

We have already encountered above, alongside substitutions free of rearrangements with troponoids, title processes. These are summarized here to bring into focus those circumstances in which they may be expected. One has to be careful in the choice of the label with which to monitor the reaction course. In fact, we show below and in the following sections that the position of attack may be strongly influenced, through either electronic (through bonds), dipolar (through space), or steric effects, by the label nature. The ideal label is deuterium[406,430,432,470,471] whereas the cyano group, which has also been used as a label,[428] is likely to exert strong directing effects on the attack of the nucleophilic reagent.

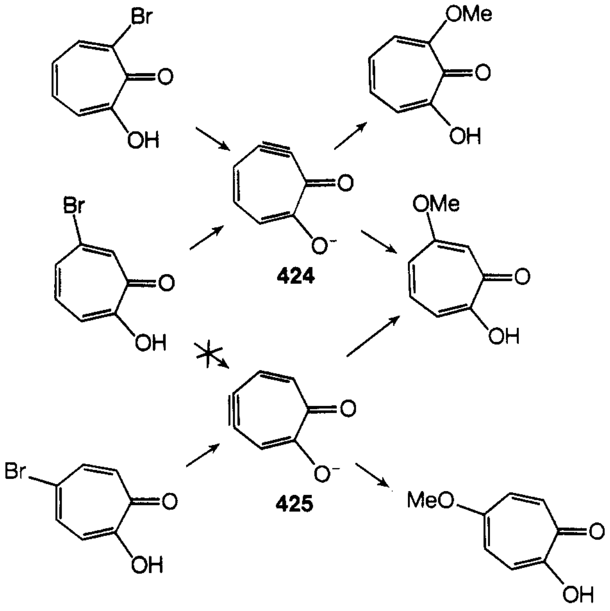
Two types of reagents, ammonia or protic amines and carbanionic species, have been so far observed to give these rearrangements. As regards the first class of reagents, ammonia seems to be much more prone than amines to these rearrangements. With ammonia, besides benzenoid contraction, substitution with exclusive rearrangement has been observed for chlorine[430,431] and substitution at both C(7) and C(2) with tosyloxy[430] as leaving groups. Only the methoxy group has been observed to be replaced without rearrangement by this reagent.[430] In contrast, replacement of the halogens or methoxyl by piperidine[406,432] or of iodine by quinuclidine[293] under a variety of conditions gave clean substitution without rearrangement. From a communication[430] one could conclude that, in the case of 2-chlorotropone, also amines like methylamine or dimethylamine lead to these rearrangements. This is sharply contrasted by the results above and, moreover, it has also been found that a primary amine like *n*-butylamine gives displacement of chlorine without rearrangement.[478] The origin of such different results is difficult to assess because experimental conditions were not specified by the Japanese workers.[430]

When the leaving group at C(2) is a quaternary ammonium group, substitution by protic amines proceeds with quantitative yields by attack at C(7), and the mechanism is known in great detail.[470] With carbanionic species, like arylmagnesium or aryllithium compounds, these rearrangements occur in nearly all cases so far examined (replacement of dialkylamino[437,466] or methoxyl[437] groups and of chlorine or bromine[428]). The only exception is 5-cyanotropolone which reacts with phenylmagnesium bromide to give 5-cyano-2-phenyltropone.[428] However, the last case is subjected to the criticism above concerning the nature of the label (the cyano group). Rearrangements of this type have also been found for carbanionic species which, like cyanoacetamide and a base lead to azulenoids.[475b] Moreover, a mechanism of attack of the (carbonionic) vinyl carbon of enamines to C(7) of 2-chlorotropone has been tentatively proposed to account for the formation of 2-(2-oxocycloalkyl)tropones in such reactions.[479]

b. Cine-Substitutions

Several cases of cine-substitution are known. Thus, on the treatment with sodium methoxide in DMSO at 80°, 3- and 4-bromotropolone gave an almost 1:1 mixture of 3- and 4-methoxytropolone, whereas 5-bromotropolone gave an almost 1:1 mixture of 4- and 5-methoxytropolone.[480] These findings can be explained by the intermediacy of dehydrotropolone species, as shown in Scheme XXXI. These intermediates have, in fact, been trapped with either diphenylisobenzofuran or sodium azide,[480] and it seems likely that they are also on the reaction path to the methoxytropolones.

SCHEME XXXI



No clear evidence, as far as the mechanism is concerned, is available for other cases of cine-substitution.

Michael-type additions[470] followed by elimination is an alternative mechanism which has been proposed for the reaction of 3-iodotropolones with potassium amide in liquid ammonia to give 4-aminotropolones in low yield.[481] Another case concerns the reaction of 3-bromotropolone with alkali which gave 4-hydroxytropolone together with a small amount of 3-hydroxytropolone.[419] Finally, certain 2,3-benzo-7-bromotropones react with hydroxylamine to give 2,3-benzo-6-hydroxylaminotropone.[482]

A case of cine-substitution has been met also with a tropone carrying the replaceable group at C(3), like 3-chlorotropone. It has already been mentioned in section V.A.1.a.vi that 3-chlorotropone and methylamine gave an almost 1:1 mixture of 3- and 4-aminotropone in good yield.[411] In contrast, 3-tosyloxytropone seems to give exclusively 3-aminotropone under similar conditions.[462]

Other cases of cine-substitution, like the intramolecular cyclization of **426** and **427** under the influence of al-

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(477) Reference 1a, p 64.

(478) G. Biggi, F. Del Cima, and F. Pietra, unpublished.

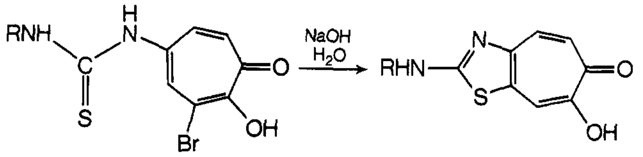
(479) M. Oda and K. Kitahara, *Synthesis*, **3**, 368 (1971).

(480) T. Yamatani, M. Yasunami, and K. Takase, *Tetrahedron Lett.*, 1725 (1970).

(481) K. Doi, *Bull. Chem. Soc. Jap.*, **34**, 497 (1961).

(482) S. Ebine, M. Hoshino, and K. Takahashi, *Bull. Chem. Soc. Jap.*, **41**, 2942 (1968); M. Hoshino and S. Ebine, *ibid.*, **41**, 2949 (1968).

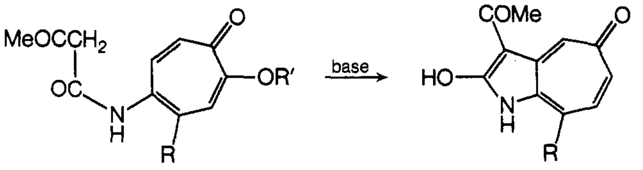
kali,[483a] as well as similar cyclizations,[483b] very likely proceed *via* Michael-type of attack.[470]



426 **427**

c. By Attack at Other Nuclear Positions

Cases of this type are confined to intramolecular cyclizations like that leading, under the influence of a base, from **428** to the azaazulene **429**.[484]



428 **429**

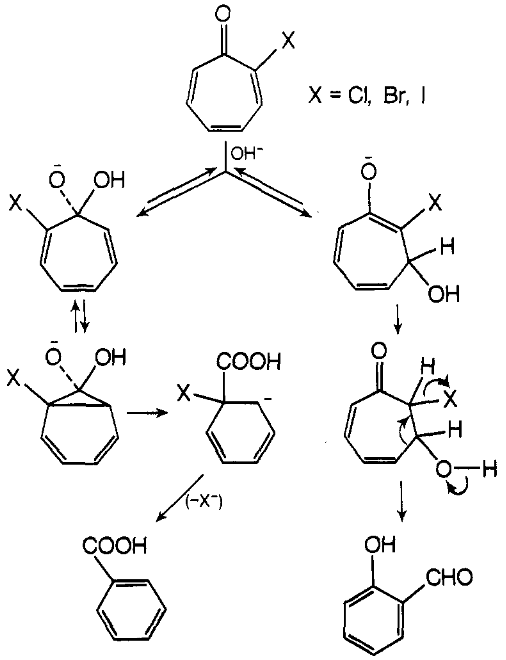
R = *i*-Pr
R′ = Me, MeCO

B. Base-Induced Rearrangements to Benzenoids or Dihydrobenzenoids

We have frequently encountered above cases in which, competitively with substitution, the substrate rearranges to a benzenoid compound. Proneness toward benzenoid rearrangement and the detailed course of this depend on a very delicate balance among a multiplicity of factors concerning both the structure of the reagents and the reaction conditions so that it is not possible to draw broad generalizations. These rearrangements, which are known almost only for cycloheptatrienone derivatives (with a few cases for tropenylium salts), are given by substrates carrying (or not) a good leaving group and are typical of basic conditions. Usually, the first give the cleanest rearrangements while the latter require oxidizing agents or stop at the dihydroarene stage. Electron-attracting groups at the seven-membered ring, other than accelerating the substitution processes above, may even hasten the benzenoid rearrangement. This factor, coupled with the availability of a good leaving group at a strategic ring position, may render a substrate so labile that, as with 2-halopolynitrotropones, rearrangement to benzenoid compounds is observed on the mere dissolution of the compound in an alcoholic solvent. Tropolones lie at the other extreme. Thus, halotropolones are much more resistant than halotropones toward benzenoid rearrangement, whereas tropolone itself requires drastic alkaline fusion to rearrange.

Simple 2-halotropones react with alkali to give both benzoic acid (by extrusion of the carbonyl carbon, as proved by ^{14}C-labeling[485]) and salicylaldehyde (by extrusion of C(3) as proved by deuterium labeling[486]). As the relative percentage of benzaldehyde rises from nearly nil (in concentrated alkali) to 40% in dilute alkali, a protonation step in the pathway to the aldehyde is required.[486] The backbone of plausible mechanisms is shown in Scheme XXXII which is self-explanatory.

SCHEME XXXII



A more general case is offered by cycloheptatrienones which carry mobile substituents at both C(2) and C(7) positions. Which of these leaves is determined more by the directive effects of the substituents at C(3)–C(6) (stabilizing the negative charge developing on the opening of the three-membered ring of the norcaradiene species) rather than by the stability as anions of the mobile groups at C(2) and C(7).[487] Also the observation that alkali treatment of stipitatic acid (**331**) or of its decarboxylated analog leads to specific extrusion of the carbonyl carbon atom has been interpreted in terms of directive effects of the substituents.[488]

Alkoxides (section V.A.1.a.iii) and amines[430,431,461] have also been found to induce benzenoid rearrangements on 2-halo- and 2-tosyloxytropones.

When substituents which, like the nitro[489] or the quaternary ammonium group,[471] have strong electronic influence are present, other ring positions may be attacked to give *m*-hydroxybenzaldehide. This is shown in Scheme XXXIII for 2,4-dinitro-7-chlorotropone.[489] It is seen that the postulated intermediate **430** gives an halogen-free aldehyde by the protonation route or, if oxidizing agents are present, it retains the halogen along the oxidative route.[489]

The case of 2-quinuclidiniumtropone[471] (Scheme XXXIV, NR_3 = quinuclidine) is very interesting. It is seen that alkali, by the attack to both C(1) and, possibly, C(3) leads to benzoic acid and salicylaldehyde, respectively, whereas piperidine, probably attacking C(6) (as indicated by preliminary deuterium labeling experiments[490]), leads to *m*-hydroxybenzaldehyde.[471] All these processes are extremely fast.[471]

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[483] (a) S. Seto, Y. Nishiyama, and K. Ogura, *Bull. Chem. Soc. Jap.*, **35**, 1998 (1962); (b) K. Ogura, *ibid.*, **35**, 808 (1962); **36**, 45 (1963); S. Seto, K. Ogura, and Y. Nishiyama, *ibid.*, **36**, 173 (1963); S. Seto and K. Ogura, *ibid.*, **37**, 1526 (1964).

[484] S. Seto, K. Ogura, and H. Toda, *Bull. Chem. Res. Inst. Non-Aqueous Solutions, Tohoku Univ.*, **17**, 65 (1967); K. Ogura, H. Sasaki, and S. Seto, *Bull. Chem., Soc. Jap.*, **38**, 307 (1965).

[485] W. von E. Doering and D. B. Denney, *J. Amer. Chem. Soc.*, **77**, 4619 (1955).

[486] E. J. Forbes, D. C. Warrell and W. J. Fry, *J. Chem. Soc. C*, 1693 (1967).

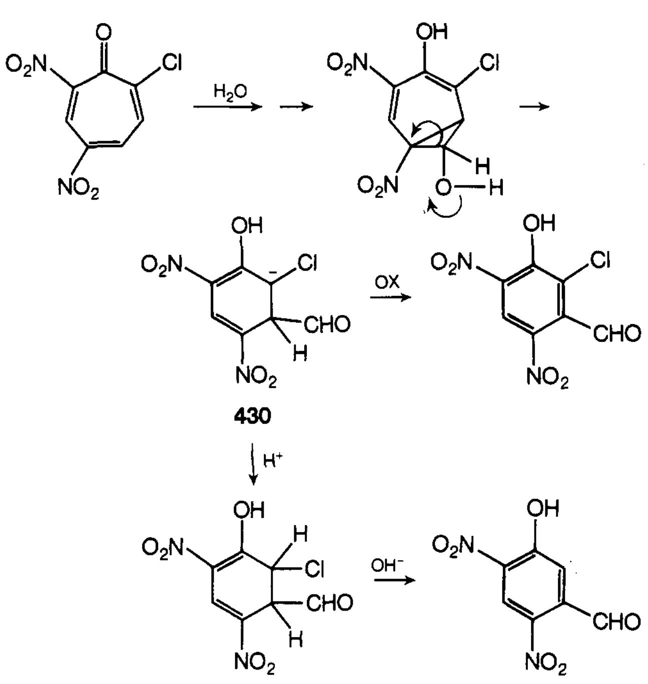
[487] R. M. Magid, C. R. Grayson, and D. R. Cowsar, *Tetrahedron Lett.*, 4819, 4877 (1968).

[488] I. G. Andrew and W. Segal, *J. Chem. Soc.*, 607 (1964).

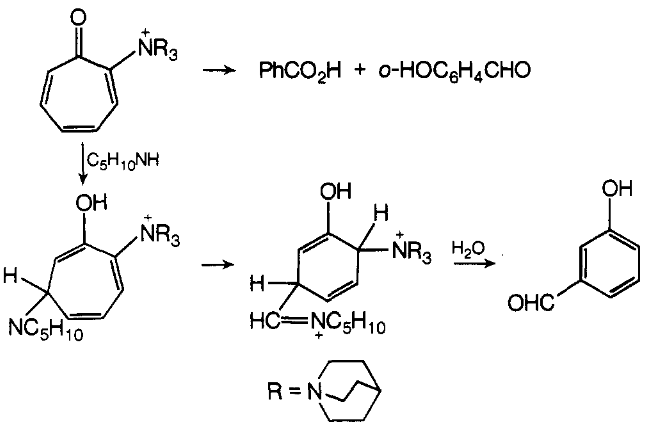
[489] E. J. Forbes, M. J. Gregory, and D. C. Warrell, *J. Chem. Soc. C*, 1969 (1968).

[490] G. Biggi, A. J. de Hoog, F. Del Cima, and F. Pietra, work in progress.

SCHEME XXXIII



SCHEME XXXIV



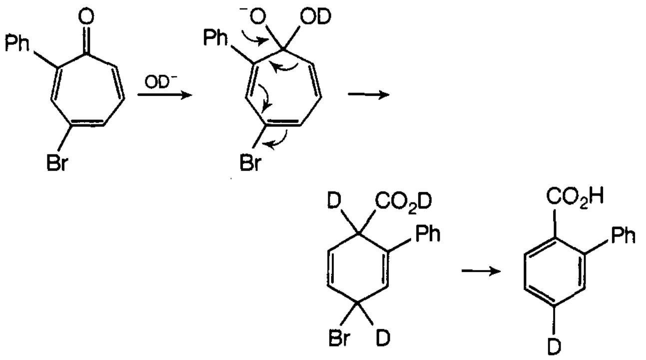
Rearrangement to carboxylic acids, with loss of nitrogen, has also been observed in water for diazonium salts derived from 3-aminotropolone.[491]

Also perchlorotropone (**97**) and perbromotropone (**101**) are very labile, giving methyl pentachloro-[87] or pentabromobenzoate[86a] on the mere dissolution in methanol. Even amines and thiols fail to substitute the halogen in these cases, leading to products of benzenoid rearrangement instead.[87] This behavior has been attributed to the nonplanarity of the ring.[87]

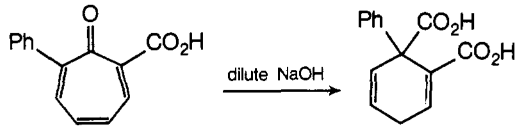
Attack of a carbanion at unsubstituted ring positions of halotropones has been proposed to rationalize benzenoid rearrangements induced by organomagnesium compounds.[492]

To account for the formation of 2-carboxy-5-deuteriobiphenyl on treatment of 2-phenyl-4-bromotropone with alkaline D_2O, the mechanism of Scheme XXXII (left) has been modified to include a protonation stage (Scheme XXXV).[493] A similar mechanism was proposed for the rearrangement of 3-phenyl-4-methoxy-5-bromotropone to 3-phenyl-4-methoxybenzoic acid.[493] In contrast, both 3- and 4-chlorotropone are reported to give only tars on the treatment with alkali.[411] A formal parallelism to this behavior is observed for 2-phenyltropone and tropone. On the treatment with alkali (and air oxidation of intermediates), the first gives 2-carboxybiphenyl, whereas the latter only resinifies.[494] Also, on the treatment with hydrazine, 2-phenyltropones rearrange to benzenoid compounds whereas tropone itself gives 2-aminotropone.[495]

SCHEME XXXV



The dihydroarene **431** has been obtained on the treatment with dilute alkali of 2-carboxy-7-phenyltropone, and a similar behavior was also observed for 2-phenyl-5-carboxytropone and 2-carboxytropone.[494] It seems likely that the rearrangement stops at the dihydroarene stage because neither a mobile group on the substrate nor an oxidizing agent in the medium is available.



431

Besides the cases of Scheme XXXIII,[489] a typical base-induced benzenoid rearrangement which requires oxidizing agents is the transformation of tropone into a mixture of tropolone (14%), salicylaldehyde (3%), and p-hydroxybenzaldehyde (8%) on treatment of tropone with alkali in the presence of potassium ferricyanide or Cu(II)-amine complexes.[496] It has been proposed that these complexes not only act as oxidizing agents but also inhibit, in an unclear way, addition of the base to the carbonyl carbon.[496]

The rearrangement of 5-chlorotropolone into chlorobenzaldehydes with $POCl_3$ in excess is thought to occur with prior halogenation of the carbonyl carbon and subsequent attack by hydroxyl ion at unsubstituted ring positions.[497a]

The aliphatic amine induced rearrangement of chlorotropenylium ion into bis(dialkylamino)phenylmethane has been observed,[421] and it has already been mentioned in section V.A.1.a.v.

Ring contraction of tropenylium ion or of alkoxytropenylium ions to benzenoid compounds on treatment with sulfur ylides has also been observed.[497b] The extruded tropenylium carbon forms a double bond with the carbon bound to sulfur of the ylide. Starting from phenyl-substituted tropenylium ions, this process has been adapted to the synthesis of unsymmetrical biphenyls.[497b]

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(491) R. D. Haworth and P. R. Jefferies, *J. Chem. Soc.*, 2067 (1951).

(492) H. Tsuruta and T. Mukai, *Bull. Chem. Soc. Jap.*, **41**, 2489 (1968).

(493) Y. Kitahara, I. Murata, and T. Muroi, *Bull. Chem. Soc. Jap.*, **38**, 1195 (1965).

(494) K. Kikuchi, *Bull. Chem. Soc. Jap.*, **40**, 355 (1967), and references therein.

(495) T. Mukai, H. Tsuruta, and T. Nozoe, *Tetrahedron Lett.*, 1063 (1966).

(496) K. Kikuchi, *Bull. Chem. Soc. Jap.*, **40**, 385 (1967).

(497) (a) K. Kikuchi, *Bull. Chem. Soc. Jap.*, **41**, 424 (1968); (b) Y. Sugimura, K. Iino, I. Kawamoto, and Y. Kishida, *Tetrahedron Lett.*, 4895 (1972).

C. Nucleophilic Additions and "Hydride" Replacement

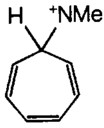
Tropones, as polyenones, are prone to undergo addition reactions. With activating substrates like 2-quinuclidinium tropone (**340**) and protic amines as reagents, Michael-type additions occur at extremely high rates but the addition complexes are usually ephemeral species because of the intervention of subsequent elimination reactions with reconjugation to tropone derivatives[470] or interception of the adducts by nucleophilic species (Scheme XXXIV) to give benzenoid products.[471] Usually, more than one addition species is observable with spectrophotometric techniques.[470] With sulfur nucleophiles still other pathways, like substitution reactions on the free substrate which is in equilibrium with the adducts, may compete.[469] In contrast, tropolones are deactivated toward Michael-type attacks.

Addition of organomagnesium compounds to tropones also occurs, thus trapping tropones arising from the interaction of phenols with organo-lithium-generated carbenes.[57] Usually C(2) and C(7) are attacked by the carbanion much more rapidly than the carbonyl carbon,[57] as discussed in section II.A.3. Addition reactions of organomagnesium compounds to tropones have been utilized to obtain versatile synthetic intermediates.[498a]

Addition of carbanions also occurs with certain stabilized heptafulvene derivatives[124a] and, as discussed in section II.B.4, with tropenylium ions.[122b] Other carbanionic species have been added to tropenylium ions. With organomagnesium compounds and alkyltropenylium ions 1,7-dimethylcycloheptatriene is the major isomer and 1,7-di-*tert*-butylcycloheptatriene is the minor one.[498b] Addition of 8,8-dicyanoheptafulvene to tropenylium fluoborate led to 8-cyano-8-cycloheptatrienylheptafulvenium fluoborate.[498c] Moreover, C-addition to tropenylium ion by enamines and dienamines,[498d] ethyl acetoacetate (as the thermodynamic product),[498e] phenols,[498f] and *N,N*-dialkylarylamines[498g] have been observed.

Addition of hydride to a variety of substrates like tropone[499a] or certain stabilized dibenzoheptafulvenes[124a] also occurs. With tropone, $LiAlH_4$ gives, on short reaction periods, a mixture of 3,5-cycloheptadienone (**25**), 3,5-heptadienol[499a] and, from one report only,[499b] cycloheptatriene. Relative yields depend on the conditions used. Reduction in ether, followed by quenching with glacial acetic acid, gives the best (90%) yields of ketone.[499a] Sodium borohydride gives nearly pure 3,5-cycloheptadienol.[499a] This is the only product of the reduction with dimethylaminoborane.[499c] Thermal isomerization of **25** to give **22** has been described.[499b]

Tropenylium salts typically undergo a variety of nucleophilic additions which have been adequately reviewed.[144,147,499c] Simple addition of trimethylamine to tropenylium ion, to give the easily hydrolyzable **432**, has been observed.[500a] In contrast, with other tertiary amines, like triethylamine, quite complex reactions starting, probably, with hydride abstraction (but, reportedly, not involving carbenes) from the amine by tropenylium ion have been observed[500a] (see, however, section V.L for a related case where a carbene seems to be involved).



432

The competition of tropenylium ion and monosubstituted (with phenyl, *p*-chlorophenyl, *p*-methoxyphenyl, or *p*-dimethylaminophenyl) group toward OH^- and H_2O has been studied by stopped-flow spectrophotometry.[500b] Although the rate increases with substitution along the series in the above order by three powers of ten, the selectivity k_{OH^-}/k_{H_2O} remains approximately constant around unity.[500b] This is in line with previous findings for the competition for the same nucleophilic by other carbonium ions like triphenylcarbonium ion and contrasts with the well-known dependence of selectivity on reactivity in solvolytic reactions.[500b] An argument to explain the lack of reactivity-selectivity has been advanced, and the origin of the reactivity-selectivity in solvolytic reactions is under study.[500b]

A possible case of nucleophilic (intramolecular) addition with a homotropenylium ion (**276** → **277**) has already been mentioned.[206]

Both here and in section V.A.3 we have encountered many cases of formal replacement of hydride. In the reaction of 2-quinuclidinium tropone (**340**) with piperidine,[470] the hydrogen is removed from C(7) as a proton with the aid of a base while quinuclidine leaves with its bonding electrons.[470] This is a general route in these systems to avoid the expulsion of an hydride.[470] In the amination of tropone with hydrazine the electronegative leaving group may arise from the fragmentation of hydrazine in the firstly formed adduct.[22]

Formally related to amination by hydrazine[22] is the reaction of tropone with phenacylpyridinium ylide in the presence of triethylamine to give 2-phenacyltropone.[500c] Fragmentation of the adduct of the ylide to C(2) of tropone with loss of pyridine and generation of an α-hydroxyl substituted heptafulvene derivative may be viewed as the driving force for "hydride" replacement.[500c]

Chemical oxidation of intermediates of addition of the nucleophilic reagent to unsubstituted ring positions is another general route to substitute hydrogen, avoiding its expulsion as hydride. This has been mentioned in previous sections for substitution reactions by bases on tropone which only occur in the presence of strongly oxidizing agents.[496]

D. Electrophilic Substitution and Addition Reactions

Understanding of electrophilic substitutions in this area has not progressed much in recent years so that a previous review[1b] is still satisfactory. We will limit ourselves to illustrate some recent work which either presents new ideas or modifies previous ones.

Electrophilic substitutions have been observed with tropolones,[1b] aminotropones,[501] cycloheptatrienaminoimines,[99] azulenes,[502] and, in a few cases, halotropon-

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(498) (a) C. A. Cupas, W. E. Heyd, and M. S. Kong, *J. Amer. Chem. Soc.*, **93**, 4623 (1971); (b) C. A. Cupas and W. E. Heyd, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, No. ORGN-116; (c) T. Otomo, M. Oda, and Y. Kitahara, *Chem. Commun.*, 114 (1971); (d) T. Watanabe and N. Soma, *Chem. Pharm. Bull.*, **18**, 1595, 1604 (1970); (e) W. J. Le Noble, *Synthesis*, **2**, 1 (1970); (f) K. Takanashi, *Bull. Chem. Soc. Jap.*, **40**, 1462 (1967); (g) J. J. Looner, *J. Org. Chem.*, **30**, 4180 (1965).

(499) (a) D. I. Schuster, B. R. Sckolnick, and F. T. H. Lee, *J. Amer. Chem. Soc.*, **90**, 1300 (1968); (b) A. P. Ter Borg and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **82**, 1189 (1963); (c) W. C. Perkins and D. H. Wadsworth, *J. Org. Chem.*, **37**, 800 (1972); (c) T. Nozoe, K. Takahashi, and H. Yamamoto, *Bull. Chem. Soc. Jap.*, **42**, 3277 (1969).

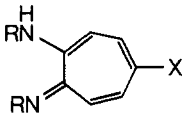
(500) (a) S. G. McGeachin, *Can. J. Chem.*, **47**, 151 (1969); (b) C. D. Ritchie and H. Fleischhauer, *J. Amer. Chem. Soc.*, **94**, 3481 (1972); (c) Y. Sugimura, N. Soma, and Y. Kishida, *Bull. Chem. Soc. Jap.*, **45**, 3175 (1972).

(501) T. Nozoe, S. Ryu, and T. Toda, *Bull. Chem. Soc. Jap.*, **41**, 2978 (1968).

(502) (a) E. Grovenstein, Jr., and F. C. Schmalstieg, *J. Amer. Chem. Soc.*, **89**, 5084 (1967); (b) W. Engewald, M. Scholz, and C. Weiss, *Z. Chem.*, **10**, 446 (1970).

es.[486,489] With tropone a single case, the nitration with nitric acid to give an adduct between tropone and 3,5,7-trinitrotropolone, has been found.[503] Nitric acid, as a strong acid, is generally an unsuitable medium because, like strong Lewis acids, it deactivates typical substrates, like tropolones, toward electrophilic attack. Nitration of 2-chlorotropones with nitric acid has also been tried, but complex benzenoid rearrangements have been observed.[486,489,504] Another related exception is the Friedel-Crafts reaction **186** → **187**.[138] Here, the success stems from the use of a special carbonium ion, cyclopropenium ion.

Cycloheptatrienaminoimines (**128**) undergo rapid bromination (with bromine), chlorination (with chlorine), or diazo coupling to give a single product (**433**) in high yield.[114] This constitutes strong evidence in favor of structure **361**. Reaction of **128** with nitrous acid gave 5-nitrosotropolone.[114]



433

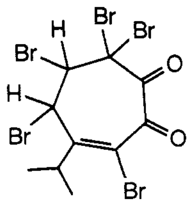
X = Cl, Br, N=NC$_6$H$_4$-*p*-NO$_2$

With tropolone the reactive nuclear positions are C(3), C(5), and C(7). Previous ideas[505] that tropolones substituted at C(5) do not undergo azo coupling have been modified. It has been found, in fact, that tropolones substituted at C(5) with phenyl, chlorine, isopropyl or methoxyl groups undergo azo coupling at C(3) with diazo compounds of a variety of para-substituted anilines.[506]

Other papers have appeared concerning azo coupling or iodination, with I_2, of 4-ethyltropolone (at C(5) or C(7), respectively),[507] azo coupling or nitration (with concentrated nitric acid) of 6-hydroxy-7-bromo-2,3-benzotropone (replacement of bromine),[508] aminomethylation or thiomethylation of 4-methyltropolone (at C(7), whereas with tropolone or 5-isopropyltropolone polysubstitution occurs),[509] and various electrophilic substitutions on 2-amino-, 2-alkylamino-, and 2-dialkylaminotropone.[501]

Reaction of azulene with iodine in the presence of iodide ion or various other bases gives 1-iodoazulene and, at lower rate, diiodoazulene.[502a] This reaction is very interesting because comparison with the reaction of deuterium-labeled azulene revealed a magnification of the primary kinetic deuterium isotope effect with sterically hindered pyridines.[502a] HMO reactivity indexes for 1-substituted azulenes have been calculated.[502b] Also, proton exchange with azulene has been studied in detail.[510]

A basic question with the electrophilic substitution reactions in this area is whether they occur *via* a Wheland-type mechanism or, rather, *via* addition to the double bonds, followed by elimination. While the first mechanism is very likely for reactions like azo coupling, the latter seems to be involved in the bromination of certain tropolones.[329a] Thus, on the treatment of 3,7-dibromo-4-isopropyltropolone with bromine, the addition product **434**



434

was isolated in good yield and then transformed into 3,5,7-tribromo-4-isopropyltropolone.[329a] Whether substitution products arise entirely *via* addition to double bonds is unknown, however. With tropolone, intermediate adducts have not been clearly characterized.[511] With tropone, addition of bromine led to 1,2,5,6-tetrabromocyclohepten-4-one in CCl_4 solution, or, on prolonged reaction times without solvents, to hexabromocycloheptanone.[512] These products partially debrominate either spontaneously or under the action of sodium acetate.[512]

Chlorine also adds to tropone in CCl_4 to give 2,3-dichlorocyclohepta-4,6-dien-1-one.[60]

The behavior of 2-methoxy- and 2-methoxy-5-bromotropone toward bromine is complex, 3,5,7-tribromotropolone (in aqueous solvents) or addition products, besides substitution products (in methanol), having been found.[513]

Related to **434** is the intermediate tentatively proposed for the reaction of 3-bromo-6,7-benzotropolone with thionyl chloride, as will be stated in section V.I.

E. Thermal Rearrangements and Decompositions

The pyrolytic behavior of a variety of cycloheptatrienone derivatives has been investigated, the results obtained paralleling more those for electron-impact mass spectrometry (section IV) than those for photolysis (section V.G) of the same compounds. A rough order of decreasing thermal stability is[86a,514a] 4,5-benzotropones > 2-aminotropone > tropolone > tropone > 2-methoxytropone > perchlorotropone > perbromotropone. The first compound requires temperatures of 700–800° to pyrolyze[514a] whereas the last one starts to pyrolyze at 163°, as shown by differential scanning calorimetry.[86a]

The products formed in these reactions have been accounted for in terms of the mechanisms shown in Scheme XXXVI. The starting troponoid was proved to undergo intramolecular cyclization to give a norcaradienone intermediate species which, either *via* the diradical path A or the cheletropic[515] path B, may either rearrange to give benzoyl derivatives or decompose to give benzene derivatives, by loss of CO, and polymers, by loss of XY.[514] The evidence for norcaradienone intermediates is meager, however. With perbromo- and perchlorotropone differential scanning calorimetry provided no evidence for reaction intermediates[86a] so that a norcaradienone-like transition state, stabilized by aromaticity, rather than a norcaradienone intermediate has been envisaged.[86a] Also the detailed role of the substituents at the cycloheptatrienone ring is not clear. With X and Y groups like H,

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(503) T. Nozoe, M. Oyama, and K. Kikuchi, *Bull. Chem. Soc. Jap.*, **36**, 168 (1963).

(504) T. Nozoe, T. Mukai, and K. Sakai, *Tetrahedron Lett.*, 1041 (1965).

(505) Reference 1b, p 400.

(506) T. Toda, H. Horino, T. Mukai, and T. Nozoe, *Tetrahedron Lett.*, 2387 (1968).

(507) T. Nozoe, K. Takase, and K. Umino, *Bull. Chem. Soc. Jap.*, **38**, 358 (1965).

(508) M. Hoshino and S. Ebine, *Bull. Chem. Soc. Jap.*, **43**, 1778 (1970).

(509) P. L. Pauson, P. B. Kelly, and R. J. Porter, *J. Chem. Soc. C*, 1323 (1970).

(510) L. C. Gruen and F. A. Long, *J. Amer. Chem. Soc.*, **89**, 1287 (1967).

(511) (a) R. A. Haworth and J. D. Hobson, *J. Chem. Soc.*, 561 (1951); (b) J. W. Cook, A. R. M. Gibb, and R. A. Raphael, *ibid.*, 2244 (1951).

(512) T. Mukai, *Bull. Chem. Soc. Jap.*, **31**, 846 (1958).

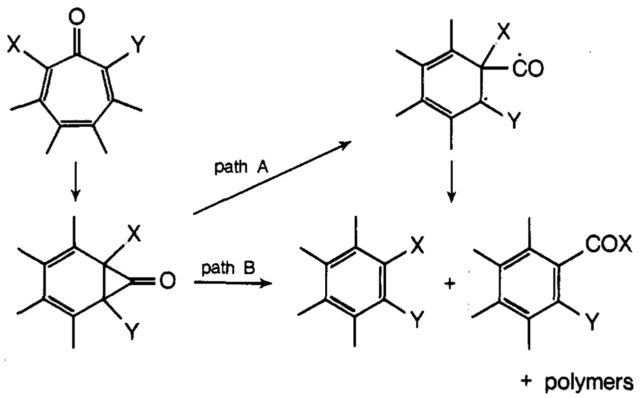
(513) T. Nozoe, K. Takase, and M. Yasunami, *Bull. Chem. Soc. Jap.*, **44**, 2218 (1971).

(514) (a) T. Mukai, T. Nakazawa, and T. Shishida, *Tetrahedron Lett.*, 2465 (1967); (b) T. Mukai, T. Nakazawa, and K. Okayama, *ibid.*, 1695 (1968).

(515) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

OPh, NH_2, Ph, OMe, and SPh, the principal, or exclusive, mode of reaction is loss of CO. With α-branched alkyl chains like the isopropyl group at X or Y, the rearrangement product (an aldehyde in this case, presumably by hydrogen transfer from the methyl to the carbonyl group) forms in fair amounts,[514b] and with X = H, Y = halogen, or X = Y = halogen, it predominates.[86a,514b] In the case of X = OH, Y = Br, the product of rearrangement, salicyloyl bromide, undergoes further pyrolysis under the reaction conditions.[86a]

SCHEME XXXVI



In contrast, when the pyrolysis of 3-bromotropone was carried out in the presence of methanol, and the pyrolyzate was injected into the mass spectrometer, besides phenol and 2-bromophenol, dimethyl dicyclopentadienedicarboxyate has been isolated.[516] The latter has been explained *via* loss of CO and HBr from the starting material to give the phenoxy radical which isomerizes to fulven-6-one. The latter should then add methanol to give methyl cyclopentadienecarboxylate which then dimerizes.[516] No evidence for the intermediacy of salicylyl bromide has been adduced. 3-Cyanotropolone is said to show a similar behavior.[516]

Pyrolysis of 2-hydrazinotropone gave, besides some 2-cyanophenol, 2-aminotropone as the main product. The latter is considered to arise from the fragmentation of the hydrazido group without decarbonylation.[514b]

Pyrolysis of the sodium salt of tropone tosylhydrazone (**176**) *to give cycloheptatrienylidene* (**177**)[135] *has already* been considered above. Thermolysis of tropone oxime, or its benzoate and tosylate, gives benzene and benzonitrile, the latter being the equivalent product of nondecarboxylative routes from tropones.[514b]

Thermolysis of 2-azidotropone occurs under very mild conditions, this product rapidly decomposing in boiling cyclohexane. The primary product seems to be an open-chain ketene which in the absence of trapping agents isomerizes to *o*-cyanophenol.[444] The isomeric 3- and 4-azidotropone are more thermostable, decomposing in inert solvents only above 140° to give mainly tars.[411]

2-Allyloxy-3,5,7-tropone undergoes Claisen-type thermal rearrangement at 160° to give 7-allyl-3,5,7-trimethylcyclohepta-3,5-diene-1,2-dione which then isomerizes to give two tricyclic α-diketones.[517a] Sigmatropic shift[515] to C(5) was not observed.[517] These results[517a] bear some relationship with those for the thermal isomerization of 7-allyloxycycloheptatriene[517b] which gives tricyclic ketones *via* 7-allyl-2,4-cycloheptadienone.

Both 1-hydroxyhomotropenylium ion (**261**)[200a] and the methoxy analog[200b] undergo thermal rearrangement, in *concomitance with ring inversion, to the conjugate acid* of acetophenone or *O*-methylacetophenone ion, respectively. A mechanism for the ring contraction reaction has been suggested.[200b]

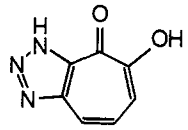
F. Thermal Cycloadditions

Although a few [4 + 2] Diels–Alder and 1,3-dipolar cycloaddition reactions in this area are long known,[1] this whole matter has been actively investigated only after the enunciation of orbital symmetry conservation rules.[515] Any discussion of these principles,and their variants,[518] is avoided here because excellent reviews are available.[515,518] Rather than support orbital symmetry rules, the material here is arranged so as to serve as a quick reference to the behavior of these compounds toward reagents that typically give cycloadditions. To this end, the various reactions are grouped together according to the number of π electrons used by the seven-membered compound in the cycloaddition. As a visual aid, at the beginning of each such group the number of π electron appears in italics. Generally the primary, or what is presumed to be the primary step, is considered in this classification, irrespective of the nature of the end products.

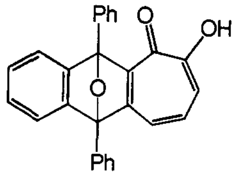
Two π Electrons. Some sulfur ylides are capable of adding a CXY group to a double bond of tropones to give homotropones which are then able to add a second CXY group.[193] Such reactions have already been considered in section II.B.7.

Also diazoalkanes are capable of adding a CXY group to the C(2)–C(3) bond of tropone to give 2,3-homotropone (**245**) in 21% yield together with at least other four compounds.[519] Probably 2,3-homotropone arises from an initial 1,3-dipolar cycloaddition of the diazoalkane to the tropone C(2)–C(3) bond[519,520] (see section V.I for the other products).

The dehydrotropolone **424** is trapped by *either sodium* azide or diphenylisobenzofuran to give **435** or **436**, respectively.[480] With the isomeric dehydrotropolone **425**, the corresponding isomer of **435** was isolated, whereas with diphenylisobenzofuran addition at the C(4)–C(5) triple bond was followed by oxygen loss to give a naphthotropolone.[480]



435



436

Finally, as will be discussed below under 8 π electrons, [2 + 2] cycloadditions with ketenes have been observed.

Four π Electrons. Diels–Alder cycloadditions have been observed for tropenylium ion, tropone imines, 2,3-homotropone, and, most commonly, cycloheptatrienones. Thus, the reaction of tropenylium ion with cyclopentadiene is thought to proceed (with complete perispecificity and high stereospecifity) *via* initial [4 + 2] cycloaddition to give the intermediate cations endo **437a** and exo **437b** (in the ratio 80:2) which give the origin of a multitude of tri- and quadricyclic products.[521] The high endo stereospecificity observed can be attributed to secondary ef-

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(516) H. F. Grützmacher and J. Hübner, *Tetrahedron Lett.*, 1455 (1971).

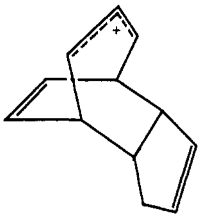
(517) (a) R. M. Harrison, J. D. Hobson, and M. M. Al Holly, *J. Chem. Soc. C*, 3084 (1971), and references therein to other Claisen rearrangements; (b) C. A. Cupas, W. Schumann, and W. E. Heyd, *J. Amer. Chem. Soc.*, **92**, 3237 (1970).

(518) H. E. Zimmerman, *Accounts Chem. Res.*, **4**, 272 (1971); M. J. S. Dewar, *Angew. Chem.*, **83**, 859 (1971).

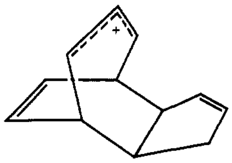
(519) L. J. Luskus and K. N. Houk, *Tetrahedron Lett.*, 1925 (1972).

(520) M. Franck-Neumann, *Tetrahedron Lett.*, 2143 (1970).

fects[515] in the absence of strong steric effects. Real involvement of the tropenylium ion is supported by the observation that the reaction proceeds only at low pH where the tropenylium ion exists and does not occur under otherwise identical conditions with cycloheptatriene species.[521] Cycloadditions of tropenylium ion with enamines or dienamines have also been reported.[522]

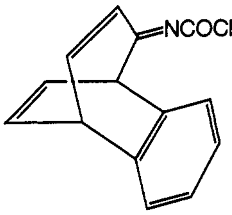


437a



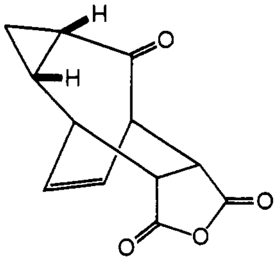
437b

N-Trichloroacetyltroponeimine adds to benzyne to give **438**.[523]



438

2,3-Homotropone, as a conjugated diene, gave cycloadducts with typical dienophiles like maleic anhydride or *N*-phenylmaleimide.[524] The configuration of the cyclopropyl group, as in the anhydride adduct **439**, has been conjectured on the basis of the presumably less crowded transition state from the examination of stereomodels.[524]



439

With cycloheptatrienones the [4 + 2] is the most common cycloaddition mode. However, most often with reactants possessing more than a couple of π electrons suitably situated, the [4 + 2] path competes, often unfavorably, with the [6 + 4] path discussed below. Moreover, with unsymmetrically substituted reagents there is further chance to obtain an even wider variety of products because of the formation of isomers from each ([4 + 2] or [6 + 4]) reaction path. In these cases the separation of the products requires laborious chromatographic work. However, in the absence of large steric crowding, marked stereospecificity, attributable to secondary effects,[515] has been observed in these [4 + 2] cycloadditions. The four-centered nature of the transition state for these [4 + 2] cycloadditions is also supported by kinetic studies of the reactions of maleic anhydride with tropone, tropolone or 2-chloro- or 2-methoxytropone.[521b] [4 + 2] cycloadditions of tropone or tropolone with 7-oxonorbornadienyl compounds have also been reported.[521c]

Only rarely, with certain dienophiles, substitution at the cycloheptatrienone nucleus, rather than cycloaddition, has been observed. This occurred with tropolone and azo-type dienophiles, like diethyl azodicarboxylate[525a] or 4-phenyl-1,2,4-triazoline-3,5-dione.[525b] These reagents which give [4 + 2] cycloaddition with tropone[525] or 2-methoxytropone,[525a] substitute instead, through a nitrogen atom, the hydrogen at C(5) in tropolone.

Dienophiles which add in the normal [4 + 2] way include open-chain olefins like butadiene or isoprene with tropone (where, however, the main product arises from [6 + 4] cycloaddition),[526a] ethylene, acenaphthylene, styrene, or indene with tropone,[526b] acetylenedicarboxylate with tropone, 2-methoxy- or 2-chlorotropone,[527] acrylonitrile with tropone, tropolone, 2-methoxy- or 2-chlorotropone,[528] and enamines with tropone (in competition with [8 + 2] cycloaddition).[529]

A wide variety of cyclic dienophiles has been used as in the reactions of sulfolene with tropone,[526] benzyne with tropone,[523,530] tropolone, 2-chloro-, 2-bromo-, or 2-methoxytropone[523] (with tropone also a small quantity of the symmetry-disallowed[515] product of [6 + 2] cycloaddition was observed),[531] azo dienophiles such as phthalazine-1,4-dione or 4,4-diethylpyrazoline-3,5-dione,[525b] spiro-2,4-hepta-4,6-diene with tropone,[532] cyclopentadiene with 2-chlorotropone (in competition with [6 + 4] cycloaddition),[533] tetrachlorocyclopentadienone acetal with tropone (where a 2:1 adduct to the C(2)-C(3) and C(6)-C(7) bonds of tropone was obtained),[534] 2,5-dimethyl-3,4-diphenylcyclopentadienone with tropone (in competition with [6 + 4] and [8 + 2] cycloaddition),[535] enamines of cyclic ketones,[529] typical highly reactive dienophiles like maleic anhydride with tropone,[536] 2-bromotropone, or tropolones,[1b] and cyclopropene with tropone or tropolone.[536b] Tropone undergoes 1:2 cycloaddition also with 6-methylfulvene[537a] to give **440** or with 6-phenyl-[537a] or 6,6′-dimethylfulvene to give similar products.[537b] Two consecutive [6 + 4] cycloadditions are involved in these cases. Tropone uses 4 π-electrons in the first cycloaddition and 6 π-electrons in the second one. Still another case in which the cycloheptatrienone uses

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(521) (a) S. Ito and I. Itok, *Tetrahedron Lett.*, 2969 (1971); (b) S. Ito, A. Mori, Y. Shoji, and H. Takeshita, *ibid.*, 2685 (1972); (c) T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Chem. Soc., Perkin Trans. 1*, 1951 (1972).

(522) T. Watanabe and N. Soma, *Chem. Pharm. Bull.*, **18**, 1595, 1604 (1970).

(523) M. Kato, Y. Okamoto, and T. Miwa, *Tetrahedron*, **27**, 4013 (1971).

(524) L. A. Paquette and O. Cox, *Chem. Ind. (London)*, 1748 (1967).

(525) (a) Y. Kitahara, I. Murata, and T. Nitta, *Tetrahedron Lett.*, 3003 (1967); (b) T. Sasaki, K. Kanematsu, and K. Hayakawa, *Chem. Commun.*, 82 (1970); T. Sasaki, K. Kanematsu, and K. Hayakawa, *J. Chem. Soc., Perkin Trans. 1*, 783 (1972).

(526) (a) S. Ito, H. Ohtani, S. Narita, and H. Honma, *Tetrahedron Lett.*, 2223 (1972); (b) T. Uyechara and Y. Kitahara, *Chem. Ind. (London)*, 354 (1971).

(527) T. Uyehara, M. Funamizu, and Y. Kitahara, *Chem. Ind. (London)*, 1500 (1970).

(528) S. Ito, H. Takeshita, and Y. Shoji, *Tetrahedron Lett.*, 1815 (1969).

(529) M. Oda, M. Funamizu, and Y. Kitahara, *Chem. Commun.*, 737 (1969); M. Oda and Y. Kitahara, *Synthesis*, **3**, 368 (1971).

(530) J. Ciabattoni, J. E. Crowley, and A. S. Kende, *J. Amer. Chem. Soc.*, **89**, 2778 (1967).

(531) T. Miwa, M. Kato, and T. Tamano, *Tetrahedron Lett.*, 1761 (1969).

(532) H. Tanida, T. Yano, and M. Ueyama, *Bull. Chem. Soc. Jap.*, **45**, 946 (1972).

(533) S. Ito, K. Sakan, and Y. Fujise, *Tetrahedron Lett.*, 775 (1969).

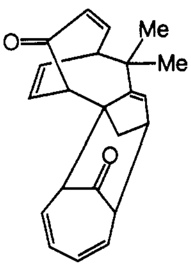
(534) D. M. Bratly and G. I. Fray, *J. Chem. Soc., Perkin Trans. 1*, 195 (1972).

(535) K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, **92**, 4145 (1970).

(536) (a) S. Ito, H. Takeshita, Y. Shoji, Y. Toyooka, and T. Nozoe, *Tetrahedron Lett.*, 3215 (1968); (b) T. Uyehara, N. Sako, and Y. Kitahara, *Chem. Ind. (London)*, 41 (1973).

(537) (a) K. N. Houk, L. J. Luskus, and N. S. Bhacca, *J. Amer. Chem. Soc.*, **92**, 6392 (1970); (b) N. S. Bhacca, L. J. Luskus, and K. N. Houk, *Chem. Commun.*, 109 (1971); K. N. Houk, L. J. Luskus, and N. S. Bhacca, *Tetrahedron Lett.*, 2297 (1972); (c) S. Ito, Y. Fujise, and M. Sato, *ibid.*, 691 (1969).

4 π-electrons and the partner 6 π-electrons is the cycloaddition of tropone with cycloheptatriene.[537c]

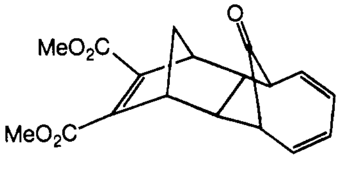


440

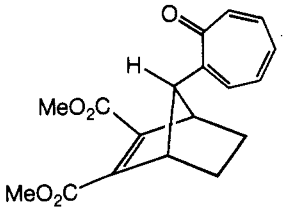
Competitive experiments for the reactions of benzyne with tropone or substituted tropones showed that substituents (Cl, OMe, OH) at C(2) in the tropone nucleus enhance the reactivity.[523]

Six π Electrons. The next thermal symmetry-allowed process is the [6 + 4] cycloaddition. Under the heading "Four 4 π Electrons" above, we have already encountered [6 + 4] cycloadditions as competitive processes. This was found for the reactions of tropone with 2,5-dimethyl-3,4-diphenylcyclopentadienone,[535] butadiene or isoprene,[526a] and 2-chlorotropone with cyclopentadiene.[533] Other examples are the reactions of tropone with cyclopentadiene[538a] or diphenylnitrileimine.[539]

Another case in which tropone uses 6 π electrons is that of the cycloaddition with dimethyl quadricyclenedicarboxylate to give **441**. This is so far the unique example of a $[_{\pi}6 + _{\sigma}2 + _{\sigma}2]$ thermal cycloaddition.[540a] A similar cycloaddition was observed with quadricyclene itself.[540b] In the case above, **442** was observed as a by-product, probably from a radical path.[540a]



441

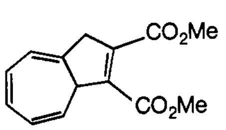


442

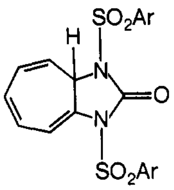
Another peculiar case of substitution, rather than cycloaddition, was observed with guaiazulene and maleic anhydride where 1-azulylsuccinic anhydride was obtained.[540c]

A kinetic investigation of the [6 + 4] cycloaddition of tropone with cyclopentadiene[538a] has shown that the reaction mechanism is similar to that of the classic Diels -Alder cycloaddition.[538b]

Eight π Electrons. [8 + 2] cycloadditions have been observed with heptafulvene and dimethyl acetylenedicarboxylate to give the azulene derivative **443**,[117] and with 8-cyanoheptafulvene and enamines to give similar azulene derivatives.[541] Moreover, *N*-arenesulfonyl troponeimines undergo [8 + 2] cycloaddition with arylsulfonyl isocyanates to give **444**.[542] Such a type of a cycloaddition has also been observed with tropones and dichloroketene,[543a] mesylsulfene,[543b] enamines,[479,529] or 2,5-dimethyl-3,4-diphenylcyclopentanone.[535]

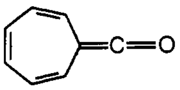


443

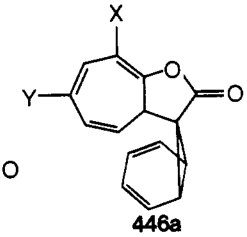


444

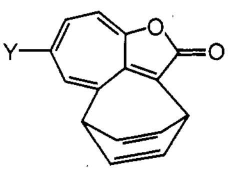
A special ketene is 8-oxoheptafulvene (**445**). This was synthesized by the general method for ketenes, *i.e.*, by the treatment of 7-chlorocarbonylcycloheptatriene with triethylamine[544] (an eliminative route resembling that used to obtain heptafulvene itself from **146**[117]). On the treatment of **445** with tropone or 2-methyl- or 2-chlorotropone, compounds of type **446a** (X = Y = H; X = Me, Y = H; or X = Cl, Y = H, respectively) were obtained *via* [8 + 2] cycloaddition.[544a] With 2-methoxytropone or 5-bromo-2-methoxytropone **446a**-type products (X = OMe, Y = H, or X = OMe, Y = Br, respectively) were isolated together with **446b**-type compounds (Y = H or Br, respectively) and heptafulvalenes.[544b] The first step in the route to the latter and **446b**-type compounds is thought to be a [2 + 2] cycloaddition between the cycloheptatrienone carbonyl group and the ketene.[544b] In contrast, with cyclopentadiene **445** undergoes the usual [2 + 2] cycloaddition of ketenes (at the exocyclic carbon–carbon double bond).[544]



445



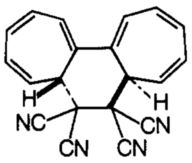
446a



446b

Another case of [8 + 2] cycloaddition is that between tropone and diphenylketene.[545]

Fourteen π Electrons. Heptafulvalene (**166**) was found to react with tetracyanoethylene to give the product (**447**) of a $[_{\pi}14_{a} + _{\pi}2_{s}]$ cycloaddition.[546]



447

G. Photoreactivity

With the exception of the photodecomposition of the sodium salt of tropone tosylhydrazone (**176**),[135] the pho-

(538) (a) S. Ito, K. Sakan, and Y. Fujise, *Tetrahedron Lett.*, 2873 (1970); (b) H. Tanida and H. R. Pfaendler, *Helv. Chim. Acta*, **55**, 3062 (1972).

(539) K. N. Houk and C. R. Watts, *Tetrahedron Lett.*, 4025 (1970).

(540) (a) H. Tanida, T. Tsushima, and Y. Term, *Tetrahedron Lett.*, 399 (1972); (b) H. Tanida and T. Tsushima, *ibid.*, 395 (1972); (c) S. Ito, H. Takeshita, and T. Makino, *Bull. Chem. Soc. Jap.*, **44**, 1982 (1971).

(541) M. Oda and Y. Kitahara, *Synthesis*, **3**, 367 (1971).

(542) R. Gompper, A. Studeneer, and W. Elser, *Tetrahedron Lett.*, 1019 (1968).

(543) (a) J. Ciabattoni and H. W. Anderson, *Tetrahedron Lett.*, 3377 (1967); (b) J. Ciabattoni and M. Cabell, *ibid.*, 2693 (1968).

(544) (a) N. Morita, Y. Kitahara, and T. Asao, *Tetrahedron Lett.*, 869 (1972); (b) T. Asao, N. Morita, C. Kabuto, and Y. Kitahara, *ibid.*, 4379 (1972); (c) T. Asao, N. Morita, and Y. Kitahara, *J. Amer. Chem. Soc.*, **94**, 3655 (1972).

(545) R. Gompper, A. Stenemeer, and W. Elser, *Tetrahedron Lett.*, 1019 (1968).

(546) W. von E. Doering, unpublished; quoted in ref 515.

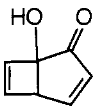
tovalence isomerization of some tropenylium and azulenium ions[547] and 2,3-homotropone (**245**),[190b] and a few photonucleophilic substitutions with azulenes,[426c,548] most examples of photoreactions concern cycloheptatrienones. With these, photodecompositions, -valence isomerizations, and -cycloadditions have been found. This work[549] as well as the photochemistry of natural troponoids[550] (in connection of which, recently the structure of γ-lumicolchicine has been confirmed[551]) have been reviewed. Therefore, mention will be made here only of recent developments in this area.

As regards photodecompositions, it has been shown that on the photolysis of tropone in the vapor phase benzene and CO are produced with 30% yield,[552] whereas the yield of these products for photolysis in solution was only 1%,[553] the major path being dimerization reactions (see below). Moreover, addition of an inert gas led to a decrease of the yield for the vapor-phase photolysis.[552] These observations have been rationalized in terms of a mechanism whereby electronically excited tropone changes isoenergetically into vibrationally excited tropone in the ground state which, *via* norcaradienone, expels CO to give benzene.[552] This is in accord with orbital symmetry analysis which predicts that this reaction should be thermally allowed,[514a] as it has been, in fact, verified in pyrolytic studies.[514]

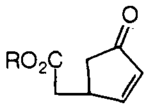
Except for the above example, thermal and photochemical reactions in this area give different products, as noticed in section V.E., because they usually occur *via* ground and electronically excited states, respectively.

Also the photolysis of 2-azidotropone seems to proceed through the same intermediate as the thermal reaction.[444] Here, however, it is the side chain which is involved.

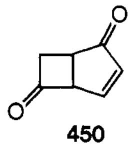
As regards valence isomerizations, it has been shown that tropolone on irradiation in a variety of solvents first gives the bicyclic compound **448**, which then undergoes further photochemical reactions to give **449a**, **449b**, or **450** in water, methanol, or hexane, respectively.[554] Thus, tropolone gives the type-B[549] cyclization. From product analysis only, this seems to be the main path also for photolysis of 5-phenyltropolone in neutral media.[549a] However, 5-phenyltropolone reacts by type-C cyclization[549] in acidic media[549a] in accord with the directive effect of the phenyl group at C(5) found for 2-methoxytropone.[555]



448



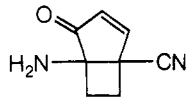
449a, R = H
b, R = Me



450

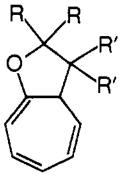
In contrast with most other substituted tropones, 2-aminotropone is photochemically very stable, like tropolonate anion.[297] This was attributed to the availability of a low-lying charge-transfer electronically excited state for these species.[297]

Other work on similar photovalence isomerizations concerns 5-aminotropolone,[556a] 3,4-benzotropolone,[556b] 6-hydroxy-2,3-benzotropone,[556c] and tetra-*O*-methylpurpurogallin.[556d] It was also shown that 2-amino-5-cyanotropone undergoes photovalence isomerization to give **451**.[556c] These reactions have also been considered from the standpoint of static indexes of reactivity.[557]



451

Photodimerizations of troponoids have already been reviewed.[549b] Briefly, tropone in acetonitrile gave a mixture of [6 + 4], [6 + 2], and [4 + 2] dimers[558a] and, in aqueous sulfuric acid, also a little [6 + 6] dimer.[558b] Dimerization products were also observed for 2-chlorotropone.[558b] Recently, it has been found that tropone undergoes [8 + 2] photocycloaddition with simple olefins, like isobutene, tetramethylethylene, and 1,1-dichloroethylene, to give products of type **452**.[559] It is difficult to explain these results other than in terms of a nonconcerted, multistep process. Photolysis of tropone also gave cycloaddition products of the photochemically forbidden variety.[560]



452

It is also worth mentioning that cyclobutadieneiron tricarbonyl, which gave clean [6 + 2] photocycloaddition with both tropone ketal and other cycloheptatrienes,[561] gave only polymeric materials on irradiation in the presence of tropone.[561]

The photodimerization of tropone has been considered in detail from the point of view of the conservation of orbital symmetry.[562] However, more thorough discussions of the principles underlying pericylic and related photochemical transformations have recently appeared.[563]

Tropenylium ions are long known to undergo photochemical transformations.[547a] These have been reconsidered recently in several laboratories. The nature of the products which may be isolated after uv irradiation is strongly affected by the nature of the solvent.[547b] Irradiation of tropenylium fluoborate in 5% aqueous sulfuric acid gave **454** and a derived ether **455**, very likely through the

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(547) (a) H. J. Dauben, F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Amer. Chem. Soc.*, **79**, 4557 (1957); (b) E. E. van Tamelen, R. H. Greeley, and H. Schumacher, *ibid.*, **93**, 6151 (1971); (c) H. Hogeveen and C. J. Gaasbek, *Recl. Trav. Chim. Pays-Bas*, **89**, 1079 (1970); (d) R. F. Childs and V. Taguchi, *Chem. Commun.*, 695 (1970).

(548) J. A. J. Vink, C. M. Lock, J. Cornelisse, and E. Havinga, *J. Chem. Soc., Chem. Commun.*, 710 (1972).

(549) (a) L. B. Jones and V. K. Jones, *Fortschr. Chem. Forsch.*, **13** (2), 307 (1969); (b) K. F. Koch, *Advan. Alicyclic Chem.*, **1**, 257 (1966); D. J. Pasto in "Organic Photochemistry," O. L. Chapmann, Ed., Marcel Dekker, New York, N. Y., 1967, pp 155–196.

(550) K. Schaffner, *Fortschr. Chem. Org. Naturst.*, **22**, 72 (1964); W. C. Wildman and B. A. Pursey in "The Alkaloids," Vol. XI, R. H. F. Manske, Ed., Academic Press, New York, N. Y., 1968, pp 407–457.

(551) L. Canonica, D. Danieli, P. Manitto, and G. Russo, *Tetrahedron Lett.*, 607 (1969).

(552) T. Mukai, T. Sato, M. Takahashi, and H. Mikumi, *Bull. Chem. Soc. Jap.*, **41**, 2819 (1968).

(553) O. L. Chapmann, *Advan. Photochem.*, **1**, 326 (1963).

(554) A. C. Day and M. A. Ledlie, *Chem. Commun.*, 1265 (1970).

(555) T. Mukai and T. Miyashi, *Tetrahedron*, **23**, 1613 (1967).

(556) (a) S. Seto, H. Sugiyama, S. Takenaka, and H. Watanabe, *J. Chem. Soc. C*, 1625 (1969); (b) M. Yoshioka, I. Saito, M. Hoshino, and S. Ebine, *Chem. Commun.*, 782 (1970); (c) M. Yoshioka and M. Hoshino, *Tetrahedron Lett.*, 2413 (1971); (d) T. J. Murphy, *Diss. Abstr. B*, **28**, 3652 (1968); *Chem. Abstr.*, **69**, 35811 (1968); (e) T. Nozoe, T. Hiroi, T. Kobayashi, and H. Hayashi, *Tetrahedron Lett.*, 3501 (1970).

(557) G. Feler, *Theor. Chim. Acta*, **10**, 33 (1968).

(558) (a) A. S. Kende and J. E. Lancaster, *J. Amer. Chem. Soc.*, **89**, 5283 (1967); (b) T. Mukai, T. Tezuka, and Y. Akasaki, *ibid.*, **88**, 5025 (1966).

(559) T. S. Cantrell, *J. Amer. Chem. Soc.*, **93**, 2540 (1971).

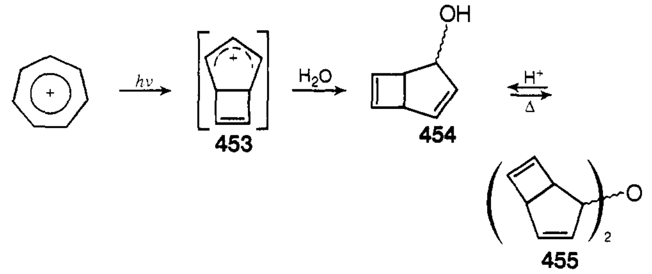
(560) K. N. Houk and D. J. Northington, *J. Amer. Chem. Soc.*, **93**, 6693 (1971).

(561) J. S. Ward and R. Pettit, *J. Amer. Chem. Soc.*, **93**, 262 (1971).

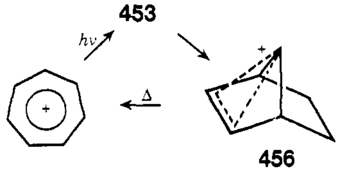
(562) L. Salem, *J. Amer. Chem. Soc.*, **90**, 553 (1968).

(563) R. C. Dougherty, *J. Amer. Chem. Soc.*, **93**, 7187 (1971); W. Th. A. M. van der Lugt and L. J. Oosterhoff, *ibid.*, **91**, 6042 (1969).

valence isomer (**453**) of tropenylium ion. In ethanol or ethanol-water mixtures, without added acid, neither **454** nor **455** was observed, while various ditropenyls or ethoxyditropenyls were obtained *via* ethoxycycloheptatriene.[547b] In contrast, phenyltropenylium ion was recovered unchanged after uv irradiation.[547b]



Using a very acid solvent like fluorosulfuric acid, and irradiating directly in a nmr tube placed in the probe at low temperature, tropenylium ion was observed to rearrange into 7-norbornadienyl ion (**456**),[547c,d] a reverse of the thermal rearrangement of **456** into tropenylium ion.[564] Here too, **453** is a likely intermediate along the photochemical route.[547c,d] Irradiation of tropone in fluorosulfuric acid (where hydroxytropenylium ion is formed) at low temperature in the nmr gave two observable products related to **453** and **456**.[547d] Clearly, tropenylium ion, as expected for its 6-π-electron aromatic structure, behaves very much like benzene which, on irradiation, gives Dewar benzene.[565]

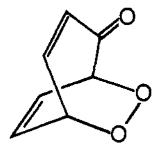


Uv irradiation of azulenium ion in 50% sulfuric acid gave 2,2-di(1′-azulenyl)propane and a related species by an unclear mechanism.[547a]

Also the uv irradiation of homotropenylium ion in fluorosulfuric acid in the nmr probe at low temperature has been carried out without assigning the structure to the product(s), however.[547c]

The photoreplacement of the nitro group from 1-nitroazulene by cyanide ion[426c] has been already mentioned in section V.A.1.a.iv. More recently azulene was found to give 1-cyanoazulene in 32% yield on the uv irradiation in *t*-BuOH-H_2O mixtures in the presence of potassium cyanide.[548] No other example of photosubstitution has been reported and further studies in this area would be welcomed.

Photooxygenations have been discovered. Endo peroxides have been obtained from the uv irradiation of tropone (sensitized with hematoporphyrin),[566] 2-methoxytropone,[567a] tetra-*O*-methylpurporogallin,[567b] and heptafulvene[566] in the presence of oxygen. The epidioxide **457**, which is fairly stable in aprotic solvents, obtained from the photooxydation of tropone,[566] underwent either isomerization to 5-hydroxytropolone on the treatment with triethylamine or selective dehydration to tropolone with thiourea.[566] Thermal cleavage of **457** (in refluxing xylene) gave 2,5-dihydroxybenzaldehyde.[566]



457

Upon uv irradiation in the presence of oxygen, phenyltropenylium ion, which proved to be stable under anaerobic conditions as stated above, underwent a change to biphenyl (in aqueous sulfuric acid) or (in acetonitrile) to 2- and 4-phenylbenzaldehyde together with *cis*- and *trans*-2,2′-diphenylstilbene which have been tentatively explained as originating from a norcaradiene species.[547b]

H. Reactions at a Side Atom or Chain

Tropones behave as nucleophilic reagents, through their carbonyl oxygen, toward several reagents. Besides protonation of the carbonyl oxygen, which has already been mentioned in the section V.G,[547d] typical electrophilic reagents, which are capable of O-alkylating tropones, are trialkyloxonium salts. This has been discussed in previous sections when dealing with the preparation of aminothiotropones (**129**),[98] dithiotropolone (**127**),[98] and 8,8-dicyanoheptafulvene (**153**).[122] Also **70b** can be O-ethylated with triethyloxonium fluoborate.[49]

Another typical electrophilic reagent which can acylate the tropone oxygen is acetyl fluoborate.[568] This has been encountered above for the preparation of heptafulvene (**147**) and sesquifulvalene.[119b]

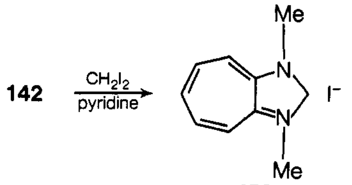
Some examples of [8 + 2] cycloaddition reactions of tropones, which are probably multistep processes initiated by nucleophilic attack of the tropone oxygen to either ketenes[543a] or sulfenes,[543b] followed by cyclization, have been encountered in section V.F.

Also the tropolone hydroxyl oxygen may behave as a nucleophilic atom toward a variety of reagents. Thus, it can be easily methylated with diazomethane[1] or benzhydrylated with diazodiphenylmethane[9] in ether, or alkylated with methyl alcohol under acidic conditions.[569]

Allylation of the tropolone oxygen as been achieved by the treatment of anhydrous sodium 3,5,7-trimethyltropolonate with allyl bromide in DMSO.[517a]

Acylation of the tropolone hydroxyl oxygen can be achieved with either alkyl or aryl acyl chlorides in the presence of pyridine.[569]

Aminotroponeimines (**128**) also undergo reaction with electrophiles at nitrogen. Thus, on the treatment of *N,N′*-dimethylaminotroponeimine (**142**) with methylene iodide in the presence of pyridine, the byciclic product **458** has been obtained.[114] Moreover, from aminotroponeimine itself (**459**) and trifluoroacetic anhydride the bicyclic compound **460** was obtained.[114]



458

Also the amino group of either 2-aminotropone and 4- or 5-aminotropolone possesses nucleophilic character to some extent. In fact, with ketenes addition to the nitro-

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(564) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Amer. Chem. Soc.*, **89**, 6350 (1967).

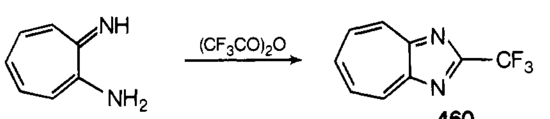
(565) E. E. van Tamelen, and S. P. Pappas, *J. Amer. Chem. Soc.*, **84**, 3789 (1962).

(566) M. Oda and Y. Kitahara, *Tetrahedron Lett.*, 3295 (1969).

(567) (a) E. J. Forbes and J. Griffiths, *J. Chem. Soc. C*, 572 (1968); (b) *ibid.*, 575 (1968).

(568) M. Neuenschwander, W. K. Schenk, and R. Kyburz, *Chimia*, **25**, 361 (1971).

(569) W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **73**, 828 (1951).



459 **460**

gen, rather than cycloaddition, was observed.[570a] Formally related to this is the formation of 2-*tert*-butylaminotropone *N*-oxyl radical on treatment of 2-*tert*-butylaminotropone with perbenzoic acid.[570b] Deuteration of the ring allowed the hyperfine coupling constants of protons in the tropone ring to be assigned.[570b]

Also the [8 + 2] cycloaddition of isocyanates to tropone imines (section V.F) are thought to be initiated by nucleophilic attack of the imino nitrogen at the isocyanate C═O carbon.[542,571]

Compound **192** was obtained from 8-cyanoheptafulvene and ethoxydiphenylcyclopropenium cation.[145] This is an example of nucleophilic behavior of the exo carbon of heptafulvenes. It must be recalled that, in contrast, the ring C(5) atom of tropolone behaves as the nucleophilic center toward the same cation[138] as discussed in section D above.

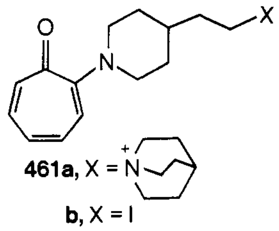
The oxidation of the methyl group of 2-methyl-4,5-benzotropone to a formyl group has been achieved in 50% yield with selenium dioxide.[572a] Also the behavior of the side chain of 4-acetyltropolone toward both oxidizing and reducing agents has been recently examined.[572b]

Oxidative degradation of chains or fused ring are long known,[1] and a typical example is the oxydation of the natural troponoid purpurogallin,[573] and of related natural troponoids,[574] to tropolone derivatives. A synthesis of 4-carboxytropolone involves oxidative degradation of the styryl double bond of 4-styryltropolone.[575]

Nucleophilic substitutions at side chains are also known. Thus, 2-bromomethyl-4,5-benzotropone undergoes replacement of bromine by OH, OMe, NHPh, pyridine,[576] and hexamethylenetetramine.[572a] The quaternary salt from the latter,[576] as well as 2-dibromomethyl-4,5-benzotropone,[572a] undergo hydrolysis to 2-formyl-4,5-benzotropone.

The acetate of tropolone undergoes ammonolysis to tropolone and acetamide.[577] Somewhat related to this case are the reactions of 2-methoxytropone with quinuclidine or with aryl mercaptides in hexamethylphosphoramide in benzene where, as stated in section V.1.b, clean demethylation by alkyl–oxygen bond breaking was observed.[450]

A detailed study of the chemical behavior of 2-quinuclidinium tropone (**340**) has shown that the reaction course depends very selectively on the reagent nature, other than, for certain reagents, on the nature of the solvent used. Whereas primary and secondary amines attack the seven-membered ring to give either replacement of the quinuclidinium moiety with rearrangement[470] or benzenoid contraction,[471] sulfur nucleophiles, like *p*-tolylmercaptide, replace, without rearrangement, the quinuclidinium group,[469] as summarized in sections V.1.f and V.3.a,c. Finally, other nucleophilic reagents attack the bicyclic skeleton. Thus, either a tertiary amine, like quinuclidine, in an aprotic solvent or iodide ion in ethanol attacks the saturated carbon atom adjacent to nitrogen to give compounds **461a** and **461b**, respectively.[293,436] The driving force for the facile opening of the bicyclic skeleton of **340** should arise from the possibility of delocalizing on the tropone skeleton the couple of electrons acquired by the nitrogen during the process.[436]



461a, X =
b, X = I

I. Miscellaneous Reactions

Of great synthetic importance are the reactions in which a nuclear hydroxyl group is replaced by halogen. With tropolone and thionyl chloride a good yield of 2-chlorotropone, together with some *o*-chlorobenzaldehyde, was obtained.[1] Of course, usymmetrically substituted tropolones give origin to two isomeric 2-chlorotropones.[1] However, with 3-bromo-6,7-benzotropolone 3,5-dichloro-6,7-benzotropolone was obtained.[578] This reaction occurs through an intermediate which has not been characterized but for which a structure related to **434** has been tentatively proposed.[578] With both 3- and 4-hydroxytropone, 3- and 4-chlorotropone, respectively, have been obtained with oxalyl chloride.[411] A previous statement[579] that these halotropones have been obtained with thionyl chloride was erroneously based.[411]

Bromination of tropolone to 2-bromotropone was achieved with PBr_3,[580] whereas thionyl bromide led to 3,7-dibromotropolone.[581]

2-Fluorotropone was obtained from tropolone and sulfur tetrafluoride.[406,410,582]

Insertion of a methylene or substituted methylene into the tropone skeleton to give 2,4,6-cyclooctatrienone or 7-substituted 2,4,6-cyclooctatrienones has been obtained, in competition with cycloaddition reactions (described in section V.F),[519] on the treatment of tropone with diazomethane[519,520] or diazoethane[520] in ether. The ring-enlarged product is thought to arise from a pyrazolidine intermediate rather than from nucleophilic attack of the diazoalkane to the carbonyl carbon.[520] As evidence is cited the propensity of tropones to undergo nucleophilic attack in the α position to the carbonyl group.[520] There is more cogent evidence, however, that attack at the carbonyl carbon is not involved. This is the facility with which this reaction occurs in ether, whereas it is well known[583] that ketones require the presence of catalysts, like alcohols, to undergo ring enlargement with diazoalkanes *via* nucleophilic attack at the carbonyl carbon.[584] With diazopropane, bicyclo[4.2.0]octadienone was obtained, probably through cycloocta-2,2′-dimethyl-3,5,7-

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(570) (a) S. Seto, H. Sasaki, and K. Ogura, *Bull. Chem. Soc. Jap.*, **39**, 281 (1966); H. Toda, *Yakugaku Zasshi*, **87**, 1351 (1967); (b) T. Toda, E. Mori, and K. Murayama, *Bull. Chem. Soc. Jap.*, **45**, 1852 (1972).

(571) L. A. Paquette and N. Horton, *Tetrahedron Lett.*, 2289 (1968).

(572) (a) E. Lippmann and P. Apel, *Z. Chem.*, **10**, 434 (1970); (b) T. Nozoe, K. Takase, K. Shimuzu, and M. Yasunami, *Bull. Chem. Soc. Jap.*, **44**, 1951 (1971).

(573) Reference 1a, p 39; P. D. Collier, *J. Chem. Soc. C*, 2255 (1966).

(574) J. Slawinski, *Photochem. Photobiol.*, **13**, 489 (1971); *Chem. Abstr.*, **75**, 117734 (1971); P. D. Collier, *J. Chem. Soc. C*, 612 (1969).

(575) D. S. Tarbell, K. I. H. Williams, and E. J. Sehm, *J. Amer. Chem. Soc.*, **81**, 3443 (1959).

(576) E. Lippmann and P. Apel, *Z. Chem.*, **11**, 104 (1971).

(577) T. Sato, quoted in ref 1b, p 419.

(578) S. Ebine, *Bull. Chem. Soc. Jap.*, **35**, 117 (1962).

(579) Reference 1c, p 142.

(580) B. J. Abadir, J. W. Cook, J. D. Loudon, and D. K. V. Steel, *J. Chem. Soc.*, 2350 (1952).

(581) S. D. Saraf, *Can. J. Chem.*, **47**, 2803 (1969).

(582) V. A. Engelhardt, *J. Amer. Chem. Soc.*, **82**, 543 (1960).

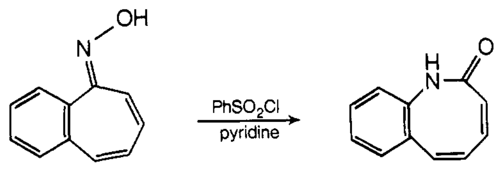
(583) C. D. Gutsche, *Org. React.*, **8**, 364 (1954).

(584) G. Fachinetti, F. Pietra, and A. Marsili, *Tetrahedron Lett.*, 393 (1971).

trien-1-one, and similar results were obtained also with either 2-methoxytropone or tropolone.[520]

Tropenylium ion reacts catalytically with diazomethane or diphenyldiazomethane to give ethylene or tetraphenylethylene, respectively.[585] This is in (at least formal) accord with the decomposition mode of 2-cycloheptatrienylethyl cations which give the above-type products.[586]

Another case of insertion is the Beckmann rearrangement of the oxime of 2,3-benzotropone (**462**) which gave only 1-benzazocin-2(1*H*)-one (**463**) as the isolated (68% yield) product.[587a] This route was also adapted to synthesize the isomeric 3-benzazocin-4(3*H*)-one.[587b] Ring expansion *via* the Beckmann rearrangement of the oxime of tribenzotropone has also been described.[587b]



462 **463**

Tropenylium salts in the presence of water undergo ring contraction to both benzaldehyde and other benzenoid compounds under the influence of either strong oxidants like H_2O_2 or CrO_3[588] or milder ones like Cu(II), Ag(I), or Fe(III).[589] Also halogens may cause such oxidative rearrangement so that aqueous solutions of tropenylium trihalides (and even of tropenylium halides, because of the air oxidation of the hydrogen halide to halogen) are unstable.[144] Therefore, these oxidative rearrangements are typical of 7-substituted cycloheptatrienes (here formed by hydroxyl addition to the tropenylium ion), whereas the tropenylium ion *per se* is stable.[144] A mechanism has been proposed in which the key step is the oxidation of the norcaradiene species formed from 7-hydroxycycloheptatriene.[589]

Very little is known about radical reactions. Besides the brief description of the generation of tropolone radicals by thermal decomposition of either diazonium salts or iodotropolones in the presence of copper,[590] we have already mentioned above other cases. These concern the oxidative cyclization of **335** into **336**[271] and the formation of **442** as a by-product in the cycloaddition of tropone with dimethyl quadricyclenedicarboxylate.[540a] Tropolone has been heated with benzoyl peroxide at 60–70°, and from the reaction mixture 3-hydroxytropolone and 3,5′-bitropolonyl have been isolated.[591] This[591] and previous results[590] seem to indicate that the C(3), C(5), and C(7) positions of tropolone are reactive toward radicals.[591]

It is also well known that cycloheptatrienones can be catalytically reduced to give cycloheptanones or cycloheptenones, according to the conditions.

J. Reactivity of Metal Complexes

Comparatively little is known about the reactivity of the metal complexes described in previous sections. With tropone metal π complexes the metal may alter substantially the reactivity with respect to the free ligand. Thus, troponeiron tricarbonyl (**285a**) shows an enhanced carbonyl reactivity toward ketonic reagents easily giving a phenylhydrazone and a 2,4-dinitrophenylhydrazone[220a] (for tropone see section V.A.1.c). In sharp contrast, troponechromium tricarbonyl (**285b**) does not show the type of reactivity of tropone toward either carbonyl reagent (section V.A.1.c) or hydrides or organomagnesium and organolithium compounds (section V.B). In fact, **285b** is destroyed by these reagents without either carbonyl condensation products or products of substitution or addition at C(2), which are typical of tropone, having been observed.[221] With the above carbanions one of the products was tricarbonylbenzechromium,[221] this ring-contraction reaction having no parallel in the chemistry of uncoordinated tropone. Because some **285b** was always recovered unchanged from the above reactions, it is considered that **285b** has a reduced reactivity, relative to tropone, toward nucleophilic reagents.[221] It has been tentatively proposed that the organic ligand in **285b** is more electron rich than tropone itself to account for such diminished reactivity.[221] Although in the crystal iron and chromium tricarbonyls show different type of bonding from the organic ligand, as shown by structures **395** and **397**, these reactivity problems are difficult to discuss owing to lack of knowledge of the actual nature of the reacting species in solution. Moreover, to overcomplicate the matter, it was found that triphenyltroponeiron tricarbonyls (**287, 288**), in contrast with the analogous complex of tropone (**285a**) and with tropone itself, was partly or totally destroyed, respectively, on standard treatment with 2,4-phenylhydrazine or hydroxylamine without either carbonyl condensation or C(2) substitution or addition products having been detected.[224]

The iron complexes **285a** and **287** or **288** undergo the expected catalytic reduction of the carbon–carbon double bonds.[220,224]

Another important point regards the reaction of troponeiron tricarbonyl (**285a**) with isopropylmagnesium bromide to give a carbinol by attack at the carbonyl group (Scheme XXI).[228] Such reactivity is typical of dibenzotropones[116,129] but not of tropone itself or of monocyclic tropones which are much more rapidly attacked at C(2) than at the carbonyl carbon[57] (section V.C).

Troponeiron (**285a**) and troponechromium (**285b**) tricarbonyl complexes show a strikingly different behavior also toward acids which has not been emphasized in the original paper.[592] Whereas the chromium complex, in parallel with the behavior of tropone, undergoes protonation at the organic ligand oxygen in aqueous mineral acid,[221] the iron complex undergoes protonation at C(2) in 98% sulfuric acid at 0°,[592] both species[221,592] having been isolated as the crystalline tetrafluoborates.

The chromium complex **285b** parallels the tropone behavior toward triethyloxonium fluoborate forming ethoxytropenyliumchromium tricarbonyl ion.[221]

As regards tropenylium ion metal complexes, the reactions of the chromium tricarbonyl complex with nucleophilic reagents have been studied in detail. Addition to the seven-membered ring, as for the free ligand, occurs with nucleophiles like methoxide, hydride, hydrosulfide, or certain carbanions like sodium *tert*-butylcyclopentadienide or sodium diethyl methylmalonate,[593] whereas with other carbanionic species like sodium cyclopentadienide or sodium diethyl malonate, ring contraction to benzenoid

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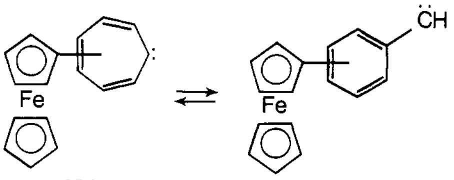
products was observed. For example, **285b** gave the corresponding benzenemetal tricarbonyl complex together with benzene under such conditions.[593] With phenyllithium, sodamide, sodium acetate, sodium hydrogen acetate, and often, though not always,[594] potassium cyanide products of reductive dimerization of the C_7H_7 unit were observed.[593]

The above addition reactions occur specifically from the opposite side from the metal ligand.[595] Moreover, with substituted complexes it was observed that the methoxy group directs entering of methoxide ion into the substituted position C(1) whereas sodium borohydride attacks mainly at C(3).[594] With the methoxycarbonyl group as a substituent, addition of methoxide, cyanide, or hydride occurs mainly at C(2) but, at least with cyanide, C(4) is also attacked.[594]

It was also found that the above methoxycarbonylchromium complex, in contact with either alumina or silica gel, undergoes ring contraction to benzenoid compounds.[594]

Addition of hydroxyl anion to the seven-membered ring of $[C_7H_7Fe(CO)_3]^+$ was observed on the mere dissolution of the crystalline tetrafluoborate in water.[232]

We can discuss here an interesting benzenoid contraction of the tropenylium ion system. Thus ferrocenyltropenylium fluoborate reacted very rapidly with diisopropylethylamine in methylene chloride to give, besides diisopropylethylammonium fluoborate, which was obtained in quantitative yield, phenylferrocene (32%), *p*- (30%) and *o*-ferrocenylbenzaldehyde (22%), and a ferrocenyltropone (12%) as major products.[596] It must be noticed that the bulky amine abstracts a proton rather than adding to the tropenylium moiety (which has been tentatively suggested, section V.C, also in other similar cases[500a]). The carbenes **464a** and **464b** are possible intermediates of this complex process.[596] This sharply contrasts with the reported[500a] failure to generate cycloheptatrienylidene from tropenylium salts and hindered tertiary amines. However, carbene–carbene rearrangements have been unequivocally proved only for the conversion of phenylcarbene into cycloheptatrienylidene in the gas phase at high temperatures (250–600°).[597]

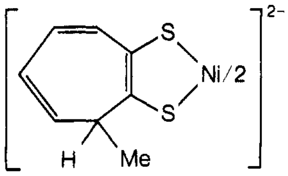


464a **464b**

As regards heptafulvene complexes, it has been briefly reported that **292** undergoes dimerization in boiling benzene and forms a 1:1 adduct with dimethyl acetylenedicarboxylate.[226] Moreover, **292** is protonated by strong acids.[226] It is interesting that protonation occurs on the ring.[228] In contrast, with the uncoordinated system protonation occurs at the exocyclic carbon to give tropenylium salts.[228] Iron tricarbonyl and chromium tricarbonyl heptafulvene π complexes differ in their reactivity toward electrophilic reagents.[228b] For example, the first are protonated at ring carbons whereas the latter are protonated at the exocyclic carbon.[228b] This seem rationalizable on the basis of diene and triene coordination in the iron and chromium complexes, respectively.[228b]

Very little is known about the reactivity of the chelate complexes. It has already been mentioned in section V.A.1.c. that the behavior of tropolone or 4-methyltropolone cupric chelates toward alkyl- or aryllithium reagents parallels that of the free ligands, 2-alkyl- or 2-aryltropones being the reaction products.[459]

Bis(dithiotropolonato)nickel(II) (**409**) has been found to add methyllithium at C(3) to give **465**, which has been isolated as the tetramethylammonium salt.[598] It has been proposed[598] that **465** is the result of direct nucleophilic addition of the carbanionic species to C(3) of the chelate complex, viewing the latter in terms of its minor contributing canonical form **410b**.[397]



465

It has been also reported that tropolone–Cu(II) chelate complex reacts with bromine in chloroform to give several products including 5-bromotropolone,[511b,599] whereas iodine, cyanogen bromide, acyl chlorides, or ketenes were ineffective.[599]

Clearly, the study of the reactivity of the metal complexes dealt with in this review is just at the beginning stage.

VI. Addendum

The organization of this addendum follows the general lines of the main text.

Selective functionalization of cycloheptatrienones at the α or α′ position can now be obtained.[600] This important synthetic problem in this area has been largely solved, and a set of rules for obtaining functionalization at either the α or the α′ position, at will, has been made available.[600]

The syntheses of 8,8′-biheptafulvenyl[601] and of 1,2-diazaazulene[602] have been described.

According to a recent report, the dibenzoazatropone **232** does not possess a quinoidal structure.[603] It is suggested that the ethoxyl group occupies the position of the carbonyl of **232**.[603] Moreover, the preparation of the first benzoazatropolones has been claimed.[603]

The stable heptafulvalene trianion has been prepared.[604]

New natural benzotropolones have been isolated from black tea.[605]

After the molecular structure of tropone had been solved by nmr spectrometry in a nematic solvent,[282] further structural studies of tropone have appeared.[606]

It has been established that stipitalide, isolated from *Penicillium stipitatum*, is 6-hydroxy-4-hydroxymethyltropolone-5-carboxylic acid δ-lactone.[607]

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The crystal structures of π-cycloheptatrienyliumcarbonylmolybdenum(0) tetrafluoborate,[608a] of the monohydrate of nickel tropolonate,[608b] and of tin tropolonate[608c] have been reported.

The competition of substitution and benzenoid rearrangement with α-functionalized cycloheptatrienones has been studied in great detail.[609] New ring contraction modes have been discovered, and a set of predictive rules for the competition between substitution and ring contraction and for the competition among the various contraction modes has been presented.[609]

Further studies of the kinetics of nucleophilic addition to tropenylium ion have been reported.[610]

Reasons for the relative sluggishness of C–C sigmatropic shifts with homotropenylium ion have been advanced.[611]

New studies of carbene–carbene rearrangement connected with species **177** have been reported.[612]

It has been suggested that tropenylium perchlorate should be added to the 1% w/w of water before storage to avoid its detonation.[613]

Further studies of thermal cycloadditions have been reported. High temperatures are required for the [4 + 2] cycloaddition of tropone (the dienophile) with 3,3-dimethyl-1-thio-1-phenylphosphole.[614a] Methyl groups at the 6 position of fulvene retard the rate of the [6 + 4] cycloaddition with tropone or chlorotropones.[614b] This has been attributed to a steric effect of the methyl groups.[614b] Perturbational MO calculations have been carried out on cycloaddition reactions of heptafulvenes.[614c]

The photochemical rearrangements of **457**-type compounds have been reported.[615]

The Wittig reaction on **191**-type compounds has given the first 2-troponylethylene derivatives.[616]

That tropolone acetate undergoes degenerate rearrangement of the acetate under very mild conditions has been discovered by ^{13}C nmr spectroscopy.[617]

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