Cycloheptatrienylidene[1,2]

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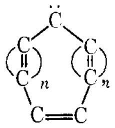
Abstract: Attempts have been made to generate cycloheptatrienylidene by thermal and photolytic decomposition of the sodium salt of tropone tosylhydrazone, by the reaction of ethyl N-nitroso-N-cycloheptatrienylcarbamate with base, by α-elimination from the dimethyl carbamate, and by decarboxylation of carboxycycloheptatrienyl fluoroborate. Of these four methods, only the first two gave results consistent with formation of the carbene and the first, thermal and photolytic decomposition of the tosylhydrazone salt was by far the superior. In the absence of acceptor and in the presence of nucleophilic alkenes, the primary reaction product was the formal dimer cycloheptatrienylidene. In the presence of dimethyl fumarate, fumaronitrile, and maleonitrile, the primary product was found to be the spirononatriene that would result from addition of cycloheptatrienylidene to the double bond. Reaction in the presence of a variety of other potential acceptors failed to give adducts. All three of the isolated spirononatrienes undergo rapid acid-induced ring opening to give heptafulvenes. They are also thermally unstable, rearranging at about 150° to give substituted indanes.

Incorporation of the vacant orbital of a singlet carbene into a cyclic conjugated ring of such a size that it becomes an integral part of an aromatic system (1, n = 0, 1, 2 . . .) will affect the properties of the carbene in at least three ways. First, the normal electrophilicity[5] of the carbene will be diminished as a result of delocalization of electrons into the vacant orbital. Second, by the same token, the potentially always available nucleophilicity (from the nonbonded pair) will be enhanced. Finally, the triplet state of the carbene will be destabilized relative to a nonaromatic system because one electron is forced to occupy a high-energy antibonding orbital. If this destabilization is pronounced enough the singlet state should become the ground state.[6]



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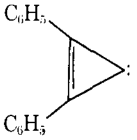
For some time now we have been interested in carbocyclic aromatic carbenes[7] and have reported the results of our investigation of the generation and properties of the substituted 2π-electron system, diphenylcyclopropenylidene 2.[8] Although most of the methods of generating this species have been unconventional (due to its unwillingness to yield to conventional approaches) the intermediate that has been generated indeed shows the anticipated low electrophilicity (no tendency to react with typical alkenes) and apparent nucleophilicity (reaction with electron-deficient double bonds). At the present time, experimental evidence for the multiplicity of the ground state is still unavailable although theory[6] leaves little doubt but that it is the singlet.



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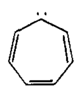

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At this time we would like to report the results of our attempts to generate the 6π-electron carbocyclic aromatic carbene—cycloheptatrienylidene 3.[3,9-11]

Generation of the Intermediate. Several approaches were taken in our attempts to generate cycloheptatrienylidene. These included photolytic and pyrolytic decomposition of the sodium salt of tropone tosylhydrazone (the Bamford–Stevens reaction[12]), reaction of the appropriate N-nitrosocarbamate with base, α elimination from N,N-dimethyl O-cycloheptatrienylcarbamate, and decarboxylation of carboxycycloheptatrienyl fluoroborate. Of these four methods only the first two gave results consistent with the carbene and the first, the decomposition of the tosylhydrazone salt, was by far the superior.

Decomposition of the Sodium Salt of Tropone Tosylhydrazone. The tosylhydrazone was synthesized either by treating tropone with tosylhydrazine or, better, by first converting tropone to the *gem*-dichloride followed by reaction with tosylhydrazine (>90%). The deep red tosylhydrazone was converted to its muddy brown sodium salt with sodium hydride in diglyme or tetra-

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(1) This research was supported by the U. S. Army Research Office (Durham) and the National Science Foundation to whom the authors are deeply grateful.

(2) Taken from the Ph.D. thesis of C. L. Ennis.[3]

(3) For a preliminary report of this work, see W. M. Jones and C. L. Ennis, *J. Am. Chem. Soc.*, **89**, 3069 (1967).

(4) Gulf Oil Fellow, 1966–1967.

(5) See (a) J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964, p 43; (b) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 164.

(6) For a far more sophisticated theoretical treatment of both the nucleophilicity and the ground-state multiplicity of this type of carbene, see R. Gleiter and R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 5457 (1968). The authors are indebted to Professor Hoffmann for making a preprint of his manuscript available prior to publication.

(7) Several heterocyclic aromatic carbenes have been studied. For lead references, see ref 3.

(8) W. M. Jones, M. E. Stowe, E. E. Wells, Jr., and E. W. Lester, *J. Am. Chem. Soc.*, **90**, 1849 (1968), and references cited therein.

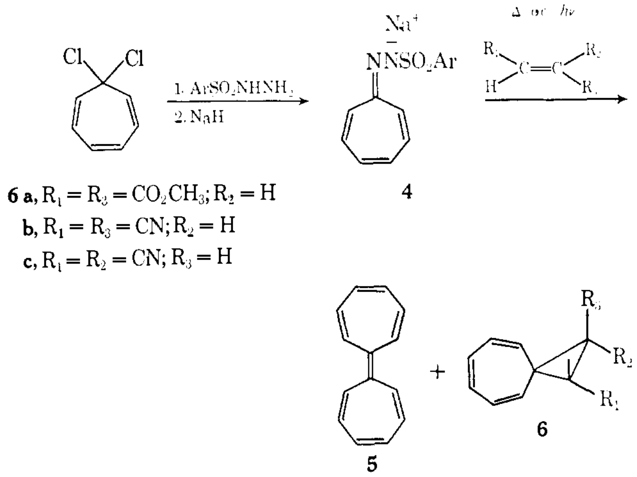
(9) For an independent report of the same system from thermal decomposition of **4**, see T. Mukai, T. Nakazawa, and K. Isobe, *Tetrahedron Lett.*, 565 (1968).

(10) For a report on the generation and properties of di- and triannelated cycloheptatrienylidenes, see I. Moritani and M. Nishino, *J. Am. Chem. Soc.*, **89**, 1257 (1967); I. Moritani, S. Murahashi, M. Nishino, Y. Yamamoto, K. Itoh, and N. Mataga, *ibid.*, **89**, 1259 (1967); I. Moritani, S. I. Murahashi, M. Nishino, K. Kimura, and H. Tsobomura, *Tetrahedron Lett.*, 373 (1966).

(11) For a report of a possible valence isomer of cycloheptatrienylidene, see T. Rose, C. MacKay, and R. Wolfgang, *J. Am. Chem. Soc.*, **89**, 1529 (1967).

(12) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952); for more recent references, *cf.* W. Kirmse, B. G. von Bulow, and H. Schepp, *Ann.*, **691**, 41 (1966).

hydrofuran. Either pyrolysis in diglyme or photolysis (through a Pyrex filter) in tetrahydrofuran gave a nearly black crystalline product in 33 and 65% yield, respectively. This solid showed all of the properties reported[13] for the formal dimer of cycloheptatrienylidene-heptafulvalene **5**.[14] When the pyrolysis or photolysis was carried out in the presence of the electron-deficient acceptor olefin (4 molar excess) dimethyl fumarate, the corresponding spirononatriene **6a** (see below for structural proof) was formed in 38 and 50% yields, respectively. Heptafulvalene was formed in 9 and 10% yields, respectively. With the exception of fumaronitrile and maleinitrile, which gave the *trans*- and *cis*-dinitriles **6b** and **6c**,[15] no success was experienced in attempts to add the intermediate to other multiple bonds. Those investigated in which results pointed to formation of the intermediate without trapping (*i.e.*, formation of heptafulvalene in yields comparable to reactions without acceptor) include *cis*-2-butene, cyclohexene, N-piperidylcyclohexene, *trans*-1,2-dibromoethylene, methyl cinnamate, and β-chloromethyl acrylate. Other possible acceptors which were found to be unstable to the reaction conditions include maleic anhydride, methyl-β-acetyl acrylate, and the mixed methyl ester-dimethylamide of fumaric acid. Dimethyl acetylenedicarboxylate was also examined. In this case, no heptafulvalene was formed but no cycloheptatriene remained either.



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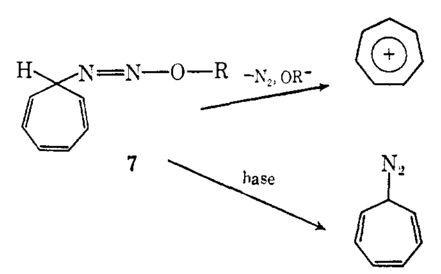
6a, $R_1 = R_3 = CO_2CH_3; R_2 = H$
b, $R_1 = R_3 = CN; R_2 = H$
c, $R_1 = R_2 = CN; R_3 = H$

5

6

Reaction of O-Ethyl N-Nitroso-N-cycloheptatrienylcarbamate with Base. A second standard method for generating diazoalkanes and, hence, potential carbenes is the reaction of the appropriate N-nitrosocarbamate with base.[16] This reaction, which proceeds through intermediates of type **7**,[16] would not *a priori* be expected to be very useful for generating diazocycloheptatriene **8** because of the possible competing collapse of the intermediate diazotate to give the very stable tropyl cation. However, despite this obvious limitation, treatment of the cycloheptatrienyl nitrosocarbamate with base in the absence of appropriate acceptors gave up to 13% of the dimeric heptafulvalene. In the presence of dimethyl fumarate, a low yield (*ca.* 4%) of the spirononatriene was formed.



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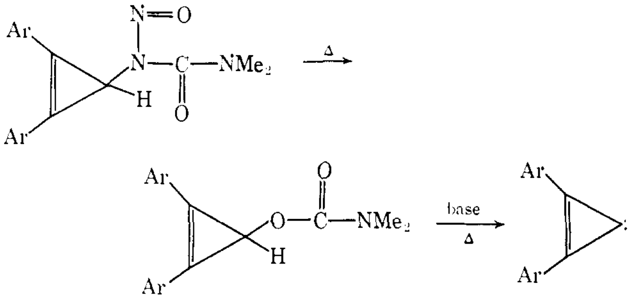
α **Eliminations.** Diphenylcyclopropenylidene has been most effectively produced by base-induced α elimination of N,N-dimethylcarbamic acid from the carbamate **9** which is normally generated *in situ* from the nitrosourea. In the cycloheptatrienyl case, the appropriate nitrosourea **10** was synthesized by the reaction sequence outlined in the scheme. However, attempts to convert this to the carbamate **11** were not successful. Even at temperatures as low as 10° the nitrosourea decomposed giving as the only identifiable product dimethylcycloheptatrienylamine **12**. Quite surprisingly, when a cold solution of the nitrosourea was treated with sodium methoxide in methanol, in addition to the amine there was formed 2% of heptafulvalene. In a similar reaction with dimethyl fumarate, 0.5% of the spirononatriene was formed. These results are surprising since the conversion of nitrosourea to diazoalkanes normally require at least one N-H.[16] However, since the yields of desired products were so low, this was simply chalked up as an interesting curiosity and examined no further.



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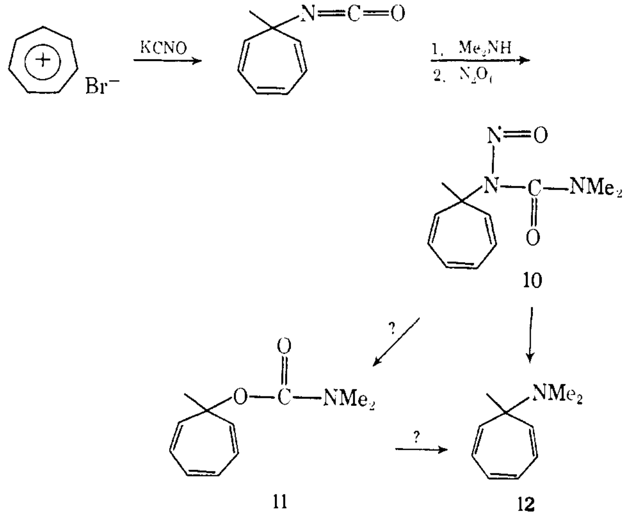

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[13] W. von E. Doering in "Theoretical Organic Chemistry. The Kekule Symposium," Academic Press, New York, N. Y., 1959, p 44.

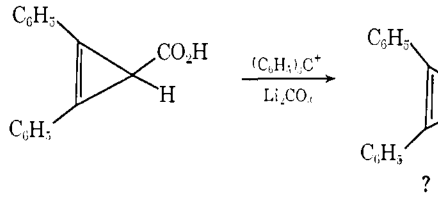
[14] Since heptafulvalene is unstable to both reaction conditions, these represent minimum yields.

[15] Reaction of the intermediate with the two dinitriles is completely stereospecific: unpublished results of B. N. Hanion, C. L. Ennis, and R. C. Joines.

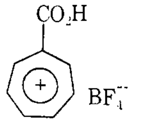
[16] *Cf.* H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, New York, N. Y., 1961, pp 21-23.

Low yields of diphenylcyclopropenylidene products were also obtained from base induced α elimination of RCO_2H from the corresponding acetate, benzoate, and p-nitrobenzoate. Cycloheptatrienyl acetate was synthesized[17] and treated with potassium t-butoxide in the presence of dimethyl fumarate. Two days reflux in heptane showed no evidence of cycloheptatrienylidene products.

Hydride Abstraction and Decarboxylation. Hydride abstraction–decarboxylation from diphenylcyclopropenecarboxylic acid using the triphenylmethyl cation as the abstracting agent and lithium carbonate to remove the proton was found to give a good yield of a product that may have arisen from reaction of the carbene with triphenylmethyl cation.[18]



Carboxycycloheptatrienyl fluoroborate **13**, which is



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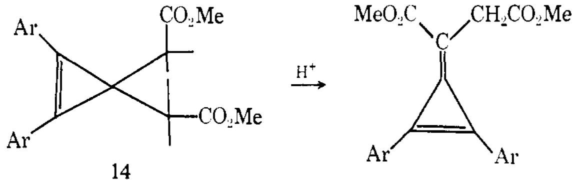
much easier to work with than the known carboxycycloheptatrienyl bromide,[19] was therefore synthesized and attempts were made to effect proton abstraction and decarboxylation. All attempts failed. However, it must be admitted that all reasonable approaches to this problem have not been exhausted and that further work on this is anticipated.

Structure and Chemistry of the Spirononatrienes. The structure of the dicarboalkoxy and dicyanospirononatrienes **6** rest firmly on their analyses, nmr, ir, and uv spectra (Experimental Section). Furthermore, from decoupling experiments of Mukai, Nakazawa, and Isobe,[9] it is clear that the carboalkoxy groups in **6a** are *trans*. In the case of the dinitriles **6b** and **6c**, stereochemical assignments also rest on their nmr spectra. Thus, the symmetry of the *trans* compound (**6b**) leads to equivalent 2,7-hydrogens on the cycloheptatriene ring and, as a result, they appear as a simple broadened doublet at τ 4.53. On the other hand, the 2,7-hydrogens on the cycloheptatrienyl ring of **6c** are not equivalent and therefore appear as a pair of doublets.

The chemistry of the adducts also supports the gross spirononatriene structure assignments. Thus, in a manner exactly analogous to the spiropentene **14** which opens to a triafulvene,[8] the spirononatrienes react with acid (although considerably more sluggishly than the spiropentenes) to give the ring-opened heptafulvenes **15**. Furthermore, as has been independently observed by Mukai, Nakazawa, and Isobe,[9] spirononatriene (**6a**) undergoes facile thermal rearrangement (half-life *ca.* 1.5 hr at 130°) to give the indane **16**. Although the mechanism of the thermal rearrangement has not been studied in detail, one observation has been made that must be consistent with any proposal. The rate of isomerization is, at least to a small degree, solvent dependent; at 150° in n-decane and triglyme, the half-lives were 20 and 8 min, respectively.[20]



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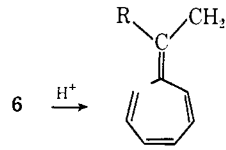

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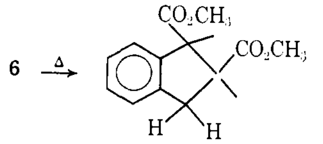

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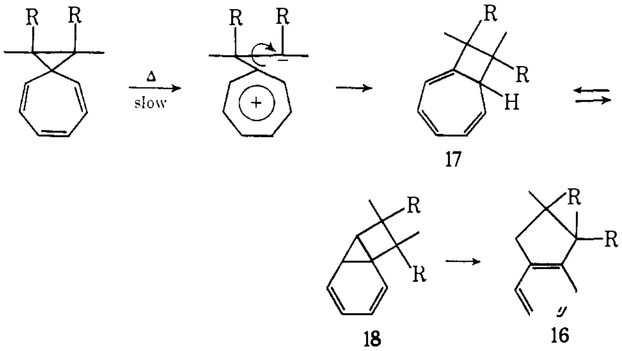
At least one mechanistic scheme[21] that meets these requirements is the following. Formation of the zwitterionic intermediate is attractive, not only because of the solvent effect and the probable loss of stereochemistry, but also because of the anticipated stability of the positive (tropylium) and negative (conjugated with CO_2R or CN) charges. Furthermore, formation of **17** from **6** is formally a "forbidden" 1,7-sigmatropic rearrangement,[22] a point that supports a two-step reaction. The conversion of **17** to the indane corresponds simply to a cycloheptatriene–toluene type of rearrangement, a reaction which, in this case, would be promoted by relief of ring strain and, possibly, a favorable equilibrium between **17** and **18**.[23]



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[17] C. M. Orlando, Jr., and K. Weiss, *J. Org. Chem.*, 27, 4715 (1962).

[18] S. D. McGregor and W. M. Jones, *J. Am. Chem. Soc.*, 90, 123 (1968).

[19] A. W. Johnson, A. Langemann, and M. Tisler, *J. Chem. Soc.*, 1622 (1955).

[20] Additionally, preliminary evidence indicates loss of stereochemical identity of the two substituent groups since the thermal decomposition of the *cis*- and *trans*-dicyanospirononatrienes (**6b** and **6c**) give product mixtures in which the obvious indane products appear to be identical. A shortage of the *cis* isomer and a call from the Air Force leave this conclusion tenuous at this time.

[21] Initially proposed by W. M. Jones and C. L. Ennis at the Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 3, 1967. This scheme as well as a possible alternative have been proposed by Mukai, Nakazawa, and Isobe.[9]

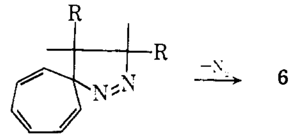
[22] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 2511 (1965).

[23] See J. A. Berson, D. H. Hartter, H. Klinger, and P. W. Grubb, *ibid.*, 90, 1669 (1968), and references cited therein.

Nature of the Intermediate. The intermediate (or intermediates) that leads (lead) to heptafulvalene (**5**) and the spirononatrienes (**6**) from both the thermal[9] and photolytic decompositions of the sodium salt of the tosylhydrazone are of vital interest. Three species must be considered: the sodium salt of the tosylhydrazone (**4**), diazocycloheptatriene (**8**), and the carbene (**3**).

Although mechanisms involving any combination of the three species can be written to explain formation of heptafulvalene, the sodium salt of the tosylhydrazone is probably not directly involved (other than as a precursor to other intermediates) since the dimer is also formed from the reaction of base with the nitrosocarbamate. Furthermore, precedence[24] and rational mechanistic considerations argue against the dimer resulting from a combination of two molecules of the diazoalkane. As a result, the carbene is implicated more or less by default. Whether the dimer arises from action of a carbene on a diazoalkane[24,25] or a combination of two carbenes[26] is an open question. There is particularly sound precedence for the former.[27]

The mechanism of the spirononatriene formation is also unclear. Direct reaction between the salt of the tosylhydrazone and the acceptor was excluded by a crude kinetics study in which it was found that the rate of nitrogen evolution was independent of the acceptor concentration. Unfortunately, the other two reasonable possibilities—pyrazoline (**19**) formation followed by nitrogen expulsion and carbene addition to the ester—promise to be uncommonly difficult to distinguish in this type of system for several reasons. First, although traces of a substance that may be diazocycloheptatriene have been observed,[29,29a] the chances of isolating pure diazocycloheptatriene are so slim that kinetic studies on the thermal reaction probably will not be possible. In addition, the dipolar properties[30] of diazocycloheptatriene and cycloheptatrienylidene would be expected to be much more similar (both should be reactive with electron-deficient carbon–carbon double bonds and unreactive with electron rich carbon–carbon double bonds) than in most diazoalkane–carbene pairs. Finally, the substituents on pyrazoline **19** are of such a nature that they would probably promote thermal decomposition to cyclopropane under the reaction conditions.[31,32]



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In other words, the commonly invoked arguments to distinguish between pyrazoline and carbene mechanism simply cannot be applied to this type of system. Possible arguments that may be brought to bear on this question include a kinetics study of the effect of varying conditions on the relative yields of dimer and spirononatriene, and the stereochemistry of the addition.[33] The former is under investigation and results of the latter[15] will be published elsewhere.

In summary, isolation of the dimer strongly suggests formation of the carbene under the reaction conditions. The absence of addition products in the presence of high concentration of electron-rich alkenes (without decreasing the yield of heptafulvalene) supports the conclusion that cycloheptatrienylidene is of low electrophilicity. The role of the carbene in the formation of spirononatriene is still an open question although some circumstantial evidence[32,33] points in that direction. Furthermore, the nucleophilicity of the carbene as well as its ground-state multiplicity are, at this time, unknown. Both are under intensive investigation.

Experimental Section

General. Melting points were taken in a Thomas–Hoover Unimelt apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Ultraviolet spectra were recorded on a Cary 14 or Cary 15 double-beam spectrophotometer using 1-cm silica cells. Infrared spectra were recorded with a Beckman Model IR10 spectrophotometer. In all cases where the KBr technique was not used, sodium chloride plates were substituted. Nuclear magnetic resonance spectra were determined on a Varian A-60A high-resolution spectrometer with a variable-temperature probe. Chemical shifts are reported in τ values from internal tetramethylsilane standard. Mass spectra were determined on a Hitachi Model RMU-6E mass spectrometer.

Analytical thin layer chromatography (tlc) was accomplished on 2 in. × 8 in. plates coated in these laboratories with 0.25-mm layers of E. Merck HF_{254} silica gel; components were visualized by their quenching of fluorescence under ultraviolet light. Gas–liquid partition chromatography (glpc) was conducted on a Wilkens Aerograph Model 600-B, or 600-D Hi-Fi instruments, with flame ionization detectors using nitrogen carrier gas; preparative scale work was accomplished on a Wilkens Aerograph dual column temperature programmer gas chromatograph, using helium carrier gas.

All photolyses were carried out with a Hanovia 450-W high-pressure mercury immersion lamp, and unless otherwise noted, a Pyrex vessel was used. Tetrahydrofuran for the photolysis reactions was dried by distillation from lithium aluminum hydride.

Materials. Sodium hydride was obtained from Alfa Inorganics, Inc. It was weighed as a dispersion, washed three times with pentane, and used as a powder for each reaction. All technical hydrocarbon solvents were distilled before use.

The cycloheptatriene used in the following reactions was generously donated by Shell Chemical Co. and contained 9% toluene.

7,7-Dichlorocycloheptatriene was prepared by the method of Kitihara and coworkers[35] with the following modifications. Thionyl chloride was used as both solvent and halogenating agent. Tropone[36] was added dropwise to an excess of thionyl chloride at 0° (reverse addition caused vigorous decomposition with no pro-

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(24) H. Reimlinger, *Chem. Ber.*, **97**, 339 (1964).

(25) H. Reimlinger, *Angew. Chem.*, **74**, 153 (1962).

(26) H. E. Zimmerman and D. Paskovich, *J. Am. Chem. Soc.*, **86**, 2149 (1964).

(27) The dimer could also arise from an initially formed azine.[28] Tropone azine is stable to the thermal reaction conditions.

(28) H. Staudinger and J. Goldstein, *Ber. Deut. Chem. Ges.*, **49**, 1923 (1916); H. E. Zimmerman and S. Sumasekhara, *J. Am. Chem. Soc.*, **82**, 5865 (1960).

(29) Unpublished results of A. B. Turner.

(29a) Note Added in Proof. Upon slow vacuum pyrolysis of **4**, a trace of a diazoalkane codeposits with **5** on a cold finger. This appears in such small quantity that identification has not been possible but it definitely does not show properties anticipated for diazocycloheptatriene.

(30) *Cf.* R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **2**, 633 (1963).

(31) *Cf.* W. M. Jones, D. G. Baarda, and P. O. Sanderfer, *J. Org. Chem.*, 32, 1367 (1967), and references cited therein.

(32) In at least two cases where a diazoalkane gives a highly labile 1-pyrazoline, the reaction was successfully diverted to the stable 2-pyrazoline tautomer by conducting the reaction in a base-washed flask in the presence of triethylamine (W. M. Jones, T. H. Glenn, and D. G. Baarda, *J. Org. Chem.*, **28**, 2887 (1963)). These conditions showed no effect on spirononatriene formation.

(33) Pyrazoline decomposition should be, at most, stereoselective,[31,34] whereas carbene addition should be stereospecific. Thus, the stereospecificity of the reaction[15] under photolytic conditions points to a carbene.

(34) *Cf.* T. V. Auken and K. L. Rinehart, *J. Am. Chem. Soc.*, **84**, 3736 (1962); W. M. Jones and W. T. Tai, *J. Org. Chem.*, 27, 1030 (1962), and references cited therein.

(35) Y. Kitihara, T. Asao, and M. Funamizu, Japanese Patent 11,628 (1964); *Chem. Abstr.*, 61, P16021e (1964).

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

duction of the desired product). At the end of the addition the solution was refluxed gently for 5 min on a steam bath. Removal of excess thionyl chloride on a rotary evaporator gave the dichloride as a yellow crystalline solid which was used without further purification.

2,4,6-Cycloheptatrienone *p*-Toluenesulfonylhydrazone Hydrochloride. A solution of 450 mg (2.42 mmol) of *p*-toluenesulfonylhydrazine in 5 ml of absolute ethanol was added rapidly with stirring to a solution of 304 mg (2.45 mmol) of 7,7-dichlorocycloheptatriene in 5 ml of absolute ethanol. The dark red solution was rapidly stirred at room temperature for 30 min. The yellow solid which formed was filtered, washed with ether, and dried *in vacuo* to give 600 mg (90%) of the desired salt. Three recrystallizations from methanol–ether gave an analytical sample, mp 170° dec with complete liquifaction and gas evolution at 210°.

Anal. Calcd for $C_{14}H_{15}N_2O_2SCl$: C, 54.10; H, 4.83; N, 9.03. Found: C, 54.37; H, 5.03; N, 9.26.

The spectral data were: ir (KBr, cm^{-1}) 3180, 2930, 2700 (broad), 1638, 1595, 1522, 1498, 1450, 1348, 1254, 1233, 1190, 1165, 1090, 1030, 905, 833, 812, 766, 710, 648, 583, 555, 546, 442, 375; uv (EtOH) 229 mμ (ε 13,200), 315 (15,700); nmr (D_2O) τ 2.56 (complex multiplet, 10 H, aromatic and cycloheptatriene proton), 7.73 (singlet, 3 H, methyl); mass spectrum (70 eV) 274, 156, 155, 139, 119 (base peak), 107, 91, 90, 89, 78, 77, 65, 53, 51, 50, 39, 38, and 36; metastable peaks, 46.5 and 60.5.

2,4,6-Cycloheptatrienone *p*-Toluenesulfonylhydrazone. To a vigorously stirred mixture of 50 ml of 10% aqueous $NaHCO_3$ solution and 25 ml of dichloromethane was added 1.00 g (3.22 mmol) of the hydrochloride salt. After 15 min, gas evolution had ceased and the two layers were separated. The aqueous layer was washed twice with 10-ml portions of dichloromethane. The organic fractions were combined, dried over magnesium sulfate, and concentrated on a rotary evaporator to give the *p*-toluenesulfonylhydrazone as a dark red solid. Recrystallization from benzene–pentane afforded 850 mg (96%) of the free hydrazone. The *p*-toluenesulfonhydrazone has two distinct crystalline forms: dark red plates, mp 142.5–143.5°, and light red needles, mp 144–145°. Both forms gave identical infrared spectra in Nujol mulls. Several recrystallizations from benzene–pentane gave an analytical sample.

Anal. Calcd for $C_{14}H_{14}N_2O_2S$: C, 61.30; H, 5.11; N, 10.22. Found: C, 61.50; H, 5.13; N, 10.06.

The spectral data were: ir (KBr, cm^{-1}) 3240, 2038, 1603, 1567, 1471, 1393, 1304, 1310, 1228, 1187, 1170, 1092, 1042, 1003, 920, 864, 813, 743, 700, 660, 565, 547; uv (EtOH) 245 mμ (ε 7900) and 315 (13,100); nmr ($CDCl_3$) 1.84–2.70 (A_2B_2, 4 H, aromatic protons), 3.33–3.83 (complex pattern, 6 H, cycloheptatriene ring protons), 7.55 (singlet, 3 H, methyl protons); mass spectrum (70 eV) 274 (molecular ion), 180, 179, 156, 155, 139, 119 (base peak), 107, 91, 90, 89, 78, 77, 65, 63, 61, 50, and 39.

Photolysis of the Sodium Salt of 2,4,6-Cycloheptatrienone *p*-Toluenesulfonylhydrazone. Heptafulvalene. In a typical reaction 0.500 g (1.82 mmol) of the *p*-toluenesulfonylhydrazone was dissolved in 120 ml of dry tetrahydrofuran. The sodium salt was formed by addition of 50 mg (2.08 mmol) of sodium hydride powder to the dark red solution. When gas evolution had ceased (15 min), the photolysis vessel was swept with a stream of dry nitrogen for 10 min to remove hydrogen gas. Photolysis of the dark slurry was monitored by nitrogen evolution which stopped at 35 ml (85%) after 3 hr. The cold finger was coated with a light brown solid which ir showed to be sodium *p*-toluenesulfinate. The red solution was poured into 300 ml of water and extracted with three 50-ml portions of pentane. The pentane extracts were combined, dried over magnesium sulfate, and concentrated to a crude black solid. This solid was taken up in 10 ml of 5% ether in hexane and chromatographed on 20 g of basic alumina (Woelm, activity grade III) using 5% ether in hexane as eluent. The heptafulvalene was eluted rapidly as a sharp, dark red band. Uv determination of the yield as described below gave 107 mg (65%) of the dimer. Concentration of the solution gave a crude black crystalline solid which after several recrystallizations from methanol–water (pH 7–9) or sublimation gave permanganate-colored plates with mp 119–121° (lit.[37] mp 122°).

A satisfactory analysis was not obtained for this compound. The spectral data were: ir (KBr, cm^{-1}) 2900, 1540, 1440, 1265, 975, 935, 898, 888, 835, 805, 790, 781, and 712; uv (EtOH) 234 mμ (ε 24,000) and 362 (25,000) (lit.[37] λ_{max} 234 mμ (ε 22,000) and 362 (21,000); nmr ($CDCl_3$) 4.09 (structured singlet); mass spectrum (70 eV) 180 (molecular ion and base peak), 165, 152, 139, 115, 102, 90, 89, 76, and 63; metastable peaks, 130, 68.8 and 56.8.

Yields of heptafulvalene could be conveniently determined by chromatographing the crude reaction mixture on basic alumina (Woelm, activity grade III) using 5% ether and hexane as eluent. This allowed rapid elution of the dimer (which decomposes slowly on the column) while still giving excellent separation from other components. The fractions containing heptafulvalene were then combined and diluted to give a solution estimated to be about 10^{-5} *M*, and the exact concentration was then calculated from the uv absorption at 362 mμ. The extinction coefficient for this absorption was reported by Doering[37] as 21,000. The extinction coefficient calculated in these laboratories on freshly recrystallized and triply sublimed material were 26,000 and 25,000. Standing overnight, even under nitrogen led to partial decomposition as evidenced in one case, for example, by a decrease in the extinction coefficient to 21,400.

Photolysis of Sodium Salt of 2,4,6-Cycloheptatrienone *p*-Toluenesulfonylhydrazone in the Presence of Dimethyl Fumarate. 8,9-Dicarbomethoxyspiro[2.6]nona-2,4,6-triene. In a typical reaction 1.00 g (0.365 mmol) of the *p*-toluenesulfonylhydrazone was dissolved in 120 ml of dry tetrahydrofuran. The sodium salt was formed by addition of 100 mg (4.15 mmol) of sodium hydride powder to the dark red solution with vigorous stirring. When gas evolution had ceased (*ca.* 15 min), the photolysis vessel was swept with a stream of dry nitrogen to remove hydrogen gas. To this slurry was added 2.50 g (17.4 mmol) of dimethyl fumarate. After 4 hr of photolysis, nitrogen evolution had stopped (70 ml, 85%). The resulting light red solution was poured into 500 ml of water and extracted with three 200-ml portions of pentane. The pentane extracts were combined, dried over magnesium sulfate, and concentrated to a dark solid. This residue was taken up in 20 ml of 5% ether in hexane and chromatographed on 50 g of basic alumina (Woelm, activity grade III). Heptafulvalene came off rapidly with 5% ether in hexane and the yield, as determined by uv, was 38.7 mg (10%). Gradually increasing the ether concentration to 10% gave a mixture of dimethyl fumarate and the spirononatriene compound. Fractional crystallization gave 814 mg of recovered dimethyl fumarate and 421 mg (49.6%) of 2,4,6-cycloheptatrienone, mp 72–74°. Two recrystallizations from methanol–water (pH 7–9) gave an analytical sample with mp 76.5–77.5°.

Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 5.98. Found: C, 66.50; H, 5.93.

The spectral data were: ir (KBr, cm^{-1}) 3080, 3020, 3002, 2970, 1720, 1450, 1440, 1340, 1270, 1200, 1158, 1078, 1018, 895, 885, 872, 745, 705, 645, 590, 502, and 330; uv (EtOH) 262 mμ (ε 2800); nmr ($CDCl_3$) 3.20–3.83 (complex pattern, 4 H, 3, 4, 5, and 6 protons on cycloheptatriene ring), 4.55 (doublet, 2 H, 2 and 7 protons on cycloheptatriene ring), 6.31 (singlet, 6 H, ester methyls), and 7.69 (singlet, 2 H, cyclopropyl protons); mass spectrum (70 eV) 234 (molecular ion), 203, 175, 174, 116, 115 (base peak), 91, 90, and 89; metastable peaks, 131 and 76.

Photolysis of Sodium Salt of 2,4,6-Cycloheptatrienone *p*-Toluenesulfonylhydrazone in the Presence of Fumaronitrile. *trans*-8,9-Dicyanospiro[2.6]nona-2,4-triene. To a solution of 548 mg (2.0 mmol) of the *p*-toluenesulfonylhydrazone in 120 ml of dry tetrahydrofuran was added 62 mg (2.58 mmol) of sodium hydride powder. Vigorous gas evolution occurred and the sodium salt precipitated to form a dark brown slurry. When the reaction was complete (*ca.* 15 min), the reaction flask was flushed well with dry nitrogen to remove all nitrogen gas, and 780 mg (10.0 mmol) of fumaronitrile was added. After 2.5 hr of photolysis, nitrogen evolution had stopped at 42.5 ml (89%). The dark red solution was poured into 300 ml of water and extracted with three 100-ml portions of pentane. The pentane extracts were combined, dried over magnesium sulfate, and concentrated to a dark oily solid on a rotary evaporator. Tlc (33% ether in pentane) of the crude residue showed heptafulvalene as a dark spot and a second colorless spot. The second spot turned bright yellow after standing on the dry plate for 15 min, consistent with the behavior of the adduct of cycloheptatrienylidene and dimethyl fumarate. The nmr spectrum of the crude residue showed dimer, fumaronitrile, and a set of absorptions consistent with a spiro compound. The residue was taken up in 10% ether–hexane and chromatographed on 25 g of basic alumina (Woelm, activity grade III) using 10% ether in hexane as eluent. The dimer was eluted rapidly as a characteristic red band, and the yield was found to be 33 mg (18.5%). When the solvent polarity was increased to 20% ether in hexane, a white solid was obtained which was shown to be the dicyanospirononatriene, 97 mg (29%) with mp 110–114°.

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(37) W. von E. Doering in "Theoretical Organic Chemistry. The Kekule Symposium," Academic Press, New York, N. Y., 1959.

Three recrystallizations from benzene–hexane gave an analytical sample with mp 121–123°.

Anal. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.55. Found: C, 78.82; H, 4.81; N, 16.70.

The spectral data were: ir (KBr, cm^{-1}) 3030, 2250, 1528, 1440, 1400, 1238, 1212, 1265, 1030, 970, 875, 830, 760, 705, 660, 625, 622, 485, and 450; uv (EtOH) 262 mμ (ϵ 2760); nmr ($CDCl_3$) 3.10–3.60 (complex pattern, 4 H, 3, 4, 5, and 6 protons of cycloheptatriene ring), 4.53 (doublet, 2 H, 2 and 7 protons of cycloheptatriene ring), and 8.01 (singlet, 2 H, cyclopropyl protons); mass spectrum (70 eV) 168 (molecular ion), 167, 141, 140, 128, 115, 90 (base peak), 89, 77, and 63; metastable peaks, 117.7 and 48.3.

Photolysis of the Sodium Salt of 2,4,6-Cycloheptatrienone *p*-Toluenesulfonylhydrazone in the Presence of Maleinitrile. *cis*-8,9-Dicyanospiro[2.6]nona-2,4,6-triene. This reaction was carried out as described above with one exception; maleinitrile was substituted for fumaronitrile. The yield of heptafulvalene was 17.6%. The spirononatriene was obtained in 30% yield (mp 116–118°) and was assigned the *cis* structure on the basis of the physical characteristics given below. An analytical sample was obtained after several recrystallizations from ether–pentane with mp 116–118.5°.

Anal. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.65. Found: C, 78.35; H, 4.77; N, 16.60.

The spectral data were: ir (KBr, cm^{-1}) 3020, 2245, 1532, 1444, 1399, 1378, 1353, 1315, 1274, 1208, 1169, 1058, 1009, 988, 940, 888, 811, 755, 702, 668, 619, 558, 516, 444, and 372; uv (EtOH) 262 mμ (ϵ 2720); nmr ($CDCl_3$) 3.10–3.35 (complex pattern, 2 H, 4 and 5 protons on cycloheptatriene ring), 3.40–3.80 (complex pattern, 2 H, 3 and 6 protons on cycloheptatriene ring), 4.25–4.55 (broad doublet, 1 H, 2 proton on cycloheptatriene ring), 4.55–4.85 (broad doublet, 1 H, 7 proton on cycloheptatriene ring), and 7.97 (singlet, 2 H, cyclopropyl protons); mass spectrum (70 eV) 168 (molecular ion), 167, 141, 140, 128, 115, 90 (base peak), 89, 77, and 63; metastable peaks, 117.7 and 48.3.

Thermal Decomposition of the Sodium Salt of 2,4,6-Cycloheptatrienone *p*-Toluenesulfonylhydrazone with and without Dimethyl Fumarate. Two 10-ml portions of dry diglyme (distilled from lithium aluminum hydride) were thermostated at 101.5° under nitrogen in a constant-temperature bath heated by refluxing dioxane. To one sample was added 288 mg (2.00 mmol) of dimethyl fumarate. Employing a solid addition tube, 368 mg (1.00 mmol) of the salt was added in each case. The rates of both reactions were followed by nitrogen evolution and were virtually identical, giving half-lives of *ca.* 11 min. Both solutions were evaporated to dryness *in vacuo* and worked up as usual. The yield of heptafulvalene in the reaction without dimethyl fumarate was 29.5 mg (33%). In the reaction with dimethyl fumarate, the yield of the spiro compound was found to be 90 mg (38%), while the heptafulvalene had dropped to 8.0 mg (9%).

Photolysis of the Sodium Salt of 2,4,6-Cycloheptatrienone *p*-Toluenesulfonylhydrazone in the Presence of Other Acceptors. In a typical reaction, 0.500 g (1.82 mmol) of the *p*-toluenesulfonylhydrazone, in 120 ml of dry tetrahydrofuran, was converted to the sodium salt with 53 mg (2.20 mmol) of sodium hydride powder. After gas evolution ceased, the reaction flask was flushed with nitrogen and a tenfold excess of the acceptor was added. The reaction was followed by nitrogen evolution and was normally complete within 3 hr. The crude reaction mixture was examined by tlc and nmr for evidence adducts. The yield of heptafulvalene was determined as in the previous reactions and varied from 30 to 70%. No evidence of an adduct was found in the reaction with *cis*-2-butene, cyclohexene, N-piperidylcyclohexene, *trans*-*p*-dinitrostilbene, 1,2-dibromoethylene, methyl *trans*-β-chloroacrylate, maleic anhydride, fumaramide, methyl cinnamate, dimethyl acetylenedicarboxylate, methyl-β-acetylacrylate, and the mixed methyl ester–dimethylamide of fumaric acid.

Photolysis of Heptafulvalene in the Presence of Dimethyl Fumarate. A solution of 17.3 mg (0.096 mmol) of heptafulvalene and 69 mg (0.48 mmol) of dimethyl fumarate in 50 ml of hexane was photolyzed with two Kenmore sunlamps through a Pyrex filter for 15 hr. At the end of this time, the colorless solution was concentrated and examined for products. Tlc, uv, and glpc of the reaction mixture showed that no spirononatriene had been formed. Dimethyl fumarate was the only identifiable compound.

Methyl N-Cycloheptatrienylcarbamate. To a solution of 13.3 g (0.10 mmol) of 2,4,6-cycloheptatrienyl-1-isocyanate[38] in 150 ml of dry benzene at 10° was added 5.4 g (0.10 mmol) of sodium methoxide in 30 ml of methanol. Reaction was vigorous and exothermic. An ir spectrum of the crude mixture showed no isocyanate peak and a new carbonyl at 1680 cm^{-1}. After filtration, the filtrate was concentrated on a rotary evaporator to a dark oil. After dissolving the oil in a small amount of dichloromethane, pentane was added slowly. The solid which formed was filtered and dried to give 7.3 g (44%) of the crude carbamate with mp 69–72°. No attempt was made to improve this yield. Three recrystallizations from hexane gave a pure sample with mp 78.5–80.5°.

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; O, 19.37. Found: C, 65.63; H, 6.73; O, 19.38.

The spectral data were: ir (KBr, cm^{-1}) 3270, 3080, 2945, 1680, 1555, 1310, 1255, 1050, 700, and 440; uv (EtOH) 253 mμ (ϵ 4400); nmr ($CDCl_3$) 3.34 (complex pattern, 2 H, 3 and 6 protons on cycloheptatriene ring), 4.53 (complex pattern, 2 H, 2 and 7 protons on cycloheptatriene ring), 4.83 (broad peak, 1 H, nitrogen proton), 5.97 (quartet, 1 H, methyne proton), and 6.34 (singlet, 3 H, methyl protons); mass spectrum (70 eV) 165 (molecular ion), 150, 133, 106 (base peak), 91, 79, 77, 65, and 59.

Methyl N-Nitroso-N-cycloheptatrienylcarbamate. A stirred slurry of 250 mg (1.51 mmol) of methyl N-cycloheptatrienylcarbamate, 1.23 g (15.0 mmol) of anhydrous sodium acetate, and 0.5 g of anhydrous sodium sulfate in 15 ml of dry dichloromethane was cooled to −25°. An ether solution of dinitrogen tetroxide (0.48 *M*) (prepared by bubbling the gas into a tared volumetric flask of ether at −50° and noting the increase in weight) was added in 3-ml portions until the green color persisted for at least 10 min. Excess dinitrogen tetroxide and approximately half of the dichloromethane were removed *in vacuo* and 10 ml of anhydrous ether was added. The reaction mixture was then washed three times with ice-cold aqueous sodium bicarbonate solution saturated with salt and twice with ice-cold salt solution. The aqueous layers were combined and washed twice with dichloromethane. All organic fractions were combined, dried over sodium sulfate, and filtered through magnesium sulfate to remove the last traces of water. After removing the solvent *in vacuo*, the dark oil was taken up in 1:1 ether–pentane solution and passed through a short silica gel column which had been deactivated by packing in water-saturated ether. The yellow eluent was collected until it was colorless and concentrated under a stream of nitrogen. The yellow oil (237 mg, 80%) was reasonably pure by nmr. The oil was too unstable to purify for analysis.

The spectral data were: ir (KBr, cm^{-1}) 3020, 2960, 1755, 1510, 1440, 1360, 1310, 1200, 1150, 1070, 770, and 705; nmr (CCl_4) 3.38 (broad triplet, 2 H, 4 and 5 protons on cycloheptatriene ring), 3.75–4.10 (complex pattern, 2 H, 3 and 6 protons on cycloheptatriene ring), 4.70–5.10 (complex pattern, 2 H, 2 and 7 protons on cycloheptatriene ring), 5.20–5.50 (broad triplet, 1 H, methyne proton), and 5.89 (singlet, 3 H, methyl protons).

Decomposition of Methyl N-Nitroso-N-cycloheptatrienylcarbamate with Sodium Methoxide. To a stirred solution of 240 mg (1.23 mmol) of the nitrosocarbamate in 30 ml of anhydrous ether at room temperature were added 850 mg (15.7 mmol) of sodium methoxide and 2–3 drops of methanol. Quantitative nitrogen evolution occurred within 30 min. The solid was removed by vacuum filtration and the filtrate was concentrated to a dark oil on a rotary evaporator. This oil was taken up in 10 ml of 5% ether in hexane and chromatographed on 30 g of basic alumina (Woelm, activity grade III) using 5% ether in hexane as eluent. Heptafulvalene came off rapidly as a dark red band, and the yield, as determined by uv, was 8 mg (7%).

Decomposition of Methyl N-Nitroso-N-cycloheptatrienylcarbamate with Sodium Methoxide in the Presence of Dimethyl Fumarate. To a stirred solution of 237 mg (1.22 mmol) of the nitrosocarbamate in 30 ml of anhydrous ether were added 1.75 g (12.2 mmol) of dimethyl fumarate and 2–3 drops of methanol. After the olefin had completely dissolved, 600 mg (11.1 mmol) of sodium methoxide was added. Quantitative nitrogen evolution occurred within 1 hr and 15 min. The solid was filtered and discarded, and the filtrate was concentrated under a stream of dry nitrogen to 10 ml. The remaining solution was evaporated to dryness on a rotary evaporator and taken up in 10 ml of 5% ether in hexane. Careful chromatography of this solution on 30 g of basic alumina (Woelm, activity grade III) using 5% ether in hexane and gradually proceeding to 8% ether in hexane gave 7 mg (4%) of the spirononatriene which was pure by glpc.

N,N-Dimethyl-N′-cycloheptatrienylurea. To a solution of 2.5 g (19.0 mmol) of 2,4,6-cycloheptatrien-1-ylisocyanate in 20 ml of anhydrous ether at 0° was added 3 g (66 mmol) of dimethylamine.

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[38] W. von E. Doering and L. E. Helgen, *J. Chem. Soc.*, 482 (1961).

After stirring the solution for 10 min, the ether and excess dimethylamine were removed on a rotary evaporator to give 1.3 g (38%) of the urea as a crude solid with mp 110–115°. Three recrystallizations from benzene–hexane gave an analytical sample with mp 124–127°.

Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.93; O, 8.98. Found: C, 67.23; H, 7.94; O, 9.11.

The spectral data were: ir (KBr, cm^{-1}) 3320, 3010, 2930, 1625, 1525, 1380, 1302, 1235, 1198, 1127, 1069, 1058, 1010, 923, 864, 857, 772, 748, 730, 703, 625, 595, 461, 418, 393, and 262; μv (EtOH) 258 mμ (ε 4200); nmr ($CDCl_3$) 3.35 (complex pattern, 2 H, 4 and 5 protons on cycloheptatriene ring), 3.80 (complex pattern, 2 H, 2 and 7 protons on cycloheptatriene ring), 5.0 (broad doublet, 1 H, nitrogen proton), 5.83 (quartet, 1 H, methyne proton), and 7.18 (singlet, 6 H, methyl protons); mass spectrum (70 eV) 178 (molecular ion), 163, 133, 132, 106, 104, 91, 72 (base peak), 65, 46, 45, 44, and 15; metastable peaks, 149 and 99.5.

N,N-Dimethyl-N′-nitroso-N′-cycloheptatrienylurea. A mixture of 500 mg (2.81 mmol) of the urea, 2.30 g (28.1 mmol) of sodium acetate, and 0.5 g of sodium sulfate in 20 ml of dry dichloromethane was cooled to −25° with stirring. A solution of 0.29 *M* dinitrogen tetroxide in anhydrous ether was added in 3-ml portions until the green color persisted for at least 5 min. The excess dinitrogen tetroxide and *ca.* 10 ml of dichloromethane were removed *in vacuo* while maintaining the temperature between −25 and −30°. The nitrosourea decomposed rapidly above 0°, so the following steps were carried out as quickly as possible. The reaction mixture was added to 10 ml of cold anhydrous ether then washed twice with ice-cold 10% aqueous sodium bicarbonate solution and twice with ice-cold aqueous salt solution. The organic layer was quickly cooled to −20°, and sodium sulfate was added. After 15 min, the mixture was filtered to give an orange solution which was kept below −40° and used without further purification.

The spectral data were: nmr ($CDCl_3$) (−20°) 2.94–3.30 (poorly resolved triplet, 2 H, 4 and 5 protons on cycloheptatriene ring), 3.44–3.84 (complex pattern, 2 H, 3 and 6 protons on cycloheptatriene ring), 4.36–4.76 (complex pattern, 2 H, 2 and 7 protons) on cycloheptatriene ring), 5.29 (triplet, 1 H, methyne proton), and 6.71 and 6.80 (singlets, 6 H, methyl groups). Upon warming to 10°, the cycloheptatriene ring pattern broadened and lost all resolutions. The methyl peaks disappeared, and two new singlets appeared at τ 6.96 and 7.61.

Carboxycycloheptatrienylium Fluoroborate. A solution of 0.500 g (3.68 mmol) of 2,4,6-cycloheptatrienecarboxylic acid in 10 ml of dichloromethane was added dropwise over a 30-min period to a stirred solution of 1.50 g (4.55 mmol) of trityl fluoroborate.[39] The dark mixture was then refluxed for 1.5 hr under nitrogen. The mixture was filtered to give a light brown solid which, after drying *in vacuo*, weighed 665 mg (82%). The crude carboxytropylium fluoroborate charred at 150°, and melted with gas evolution at 165°. After several recrystallizations from nitromethane–benzene, an analytical sample was obtained which charred at 153° and melted with gas evolution at 165°.

Anal. Calcd for $C_8H_7O_2BF_4$: C, 43.25; H, 3.16. Found: C, 43.25; H, 2.99.

The spectral data were: ir (KBr, cm^{-1}) 3010, 2760, 2563, 2420, 1722, 1472, 1439, 1384, 1214, 1070, 850, 792, 734, 686, 534, 522, and 488; uv (EtOH) 272 mμ (ε 5700); nmr (CH_3NO_2) −0.1 (broad singlet, 1 H, carboxylic acid proton), 0.0–0.4 (complex pattern, 2 H, 2 and 7 protons on cycloheptatriene ring), and 0.5 (broad singlet, 4 H, 3, 4, 5, and 6 protons on cycloheptatriene ring).

Isomerization of 8,9-Dicarbomethoxyspiro[2.6]nona-2,4,6-triene to 8-Carbomethoxy-8-carbomethoxymethylmetholenecyclohepta-2,4,6-triene on Acid Alumina. A solution of 42 mg (0.18 mmol) of the spirononatriene in 5 ml of anhydrous ether was placed on a dry column of 5 g of acid alumina (Woelm, activity grade I). Upon contact, the column immediately turned bright yellow. The yellow band was eluted with acetone and concentrated to a dark yellow oil on a rotary evaporator. This oil was then taken up in pentane and cooled in Dry Ice to give a fluffy yellow solid. Recrystallization from pentane gave 38 mg (91%) of the heptafulvene as yellow needles with mp 48–50°. Two further recrystallizations gave an analytical sample with mp 49.5–51°.

Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.48; H, 5.88.

The spectral data were: ir (KBr, cm^{-1}) 3020, 2960, 2910, 1750, 1705, 1642, 1570, 1442, 1355, 1278, 1203, 1184, 1118, 1030, 822, 783, 744, 660, and 545; uv (EtOH) 245 mμ (ε 10,000) and 340 (13,000); nmr ($CDCl_3$) 2.57 (poorly resolved doublet, 2 H, 2 and 7 protons on cycloheptatriene ring), 3.40–3.85 (multiplet, 4 H, 3, 4, 5, and 6 protons on cycloheptatriene ring), 6.29 and 6.34 (singlets, 6 H, ester methyls), and 6.65 (singlet, 2 H, methylene protons); mass spectrum (70 eV) 234 (molecular ion), 203, 175 (base peak), 115, 91, 89, and 59; metastable peaks, 131 and 76.

Isomerization of 8,9-Dicyanospiro[2.6]nona-2,4,6-trienes to 8-Cyano-8-cyanomethylenecyclohepta-2,4,6-triene on Acid Alumina. Either the *cis*- or the *trans*-dicyanospiro compound was isomerized in the following way. A solution of 20 mg (0.12 mmol) of the spiro compound in 2 ml of anhydrous ether was added to a dry column of 5 g of acid alumina (Woelm, activity grade I). An additional 2 ml of anhydrous ether was added to wash the solution onto the column. The bright orange band which rapidly developed was then eluted with acetone to give a red solution. This solution was concentrated to 1 ml under a stream of dry nitrogen, and pentane was added to the cloud point. After cooling in the refrigerator for 1 hr, the red crystals of the heptafulvene were filtered and dried to give 15 mg (75%) with mp 97–99°. Recrystallization from benzene–hexane gave red plates with mp 99.5–100.5°.

Anal. Calcd for $C_{11}H_8N_2$: C, 78.55; H, 4.79; N, 16.55. Found: C, 78.43; H, 4.72; N, 16.51.

The spectral data were: ir (KBr, cm^{-1}) 2255, 2195, 1640, 1548, 1520, 1474, 1408, 1272, 1160, 912, 862, 821, 760, 715, 580, 523, and 500; uv (EtOH) 247 mμ (ε 9500) and 345 (17,000); nmr ($CDCl_3$) 2.83–3.30 (unresolved multiplet, 2 H, 2 and 7 protons on cycloheptatriene ring), 3.50 (broad singlet, 4 H, 3, 4, 5, and 6 protons on cycloheptatriene ring), and 6.72 (singlet, 2 H, methylene protons); mass spectrum (70 eV) 168 (molecular ion), 167, 141, 140, 128, 115, 90 (base peak), 89, 77, and 63; metastable peaks, 117.7, 92.5, 80.0, and 48.3.

Thermal Rearrangement of 8,9-Dicarbomethoxyspiro[2.6]nona-2,4,6-triene to 1,2-Dicarbomethoxyindane. A solution of 100 mg (0.43 mmol) of the spirononatriene in 1 ml of ether was injected into the preparative glpc on a $^3/_8$ in. × 5 ft 20% SE 30 on 60/80 Gas Chrom Z column at 150° and 50 psi in 0.1-ml portions. The two peaks which were eluted were collected at room temperature, The largest peak (retention time *ca.* 8 min) gave white crystals, mp 68–70°. Recrystallization from benzene–hexane gave 30 mg (30%) of *trans*-1,2-dicarbomethoxyindane with mp 70–72°. This sample was identical with a sample synthesized by the method of Cook and Stephenson.[40]

Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.51; H, 5.99.

The minor peak (retention time *ca.* 5 min) also gave a white solid, 2 mg, with mp 65–69°. Glpc showed this to be a 50:50 mixture of the two peaks. The infrared and uv spectra of the mixture are very similar to those of the *trans*-indane. As a result, the minor peak is tentatively assigned the structure of *cis*-1,2-dicarbomethoxyindane. The minor component has not yet been isolated in the pure form.

Thermal Rearrangement of 8,9-Dicarbomethoxyspiro[2.6]nona-2,4,6-triene to 1,2-Dicarbomethoxyindane in *n*-Decane and Triglyme. Two solutions were made consisting of 32.7 mg (0.14 mmol) of the spirononatriene in 0.5 ml of *n*-decane and 33.3 mg (0.14 mmol) in 0.5 ml of triglyme. The solutions were placed in nmr tubes and suspended in an oil bath at 150°. The reaction was followed by removing the tubes at 5-min intervals and examining their nmr spectra. The approximate half-lives as determined by the appearance of the aromatic protons of the indane were 20 and 8 min for the *n*-decane solution and the triglyme solution, respectively.

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