Tetrahedron, 1960, Vol. 11, pp. 183 to 198. Pergamon Press Ltd. Printed in Northern Ireland

HEPTAFULVENE (METHYLENECYCLOHEPTATRIENE)[1]

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Abstract—Heptafulvene (Chart 2, I), a conjugated, non-benzenoid hydrocarbon of theoretical interest, has been synthesized by a Hofmann elimination on trimethyl 7-cycloheptatrienylmethyl ammonium iodide. Non-isolable, stable only in dilute solution, I is assigned the heptafulvene structure on the basis of catalytic hydrogenation to methylcycloheptane; indication of a methylene group from I. R. and ozonolysis to formaldehyde; association of elaborate visible and U. V. spectrum with a highly conjugated system; marked sensitivity to acid; and reaction with acetylene dicarboxylic ester to give (ultimately) an azulene derivative.

"NON-BENZENOID AROMATIC"[3] defines a class of conjugated, *cyclic* olefins which may be substituted *ad libitum*, and may have, in theory, a lower energy content (a greater π-electron delocalization energy) than their apposite *acyclic* analogues.[4] It is in such systems of coplanar conjugated double bonds that the efforts of theoreticians to simplify the otherwise prohibitively complicated quantum mechanical analysis of larger molecules have met with success.[6-9]

The interest of organic chemists stems from a traditional concern with the synthesis of new types of molecules and a natural desire to make available for experimental examination substances, the properties of which have, in part, already been anticipated by theoretical analysis. The promise of substantial π-electron delocalization energy in many of the hypothetical systems has been hopefully equated with a chemical stability beyond the ordinary[10] and has aroused a particular enthusiasm among organic chemists.

The theory of aromatic character changed from the empirical generalization of

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[1] This work is taken from a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of the Graduate School of Yale University, May, 1955. Preliminary announcements are to be found in Abstracts of Papers presented at the 126th Meeting of the American Chemical Society, New York, N.Y., 12 September 1954, p. 10–O and *Angew. Chem.* **67**, 429 (1955). See also *Theoretical Organic Chemistry* pp. 41–44. Butterworths, London (1959).

[2] We acknowledge gratefully the support of the Office of Ordnance Research, United States Army, in the form of contract DA-19-059-ORD-1562 with Yale University.

[3] W. Baker and J. W. F. McOmie in J. W. Cook, *Progress in Organic Chemistry* Vol. III, p. 44. Butterworths, London (1955).

[4] In extending the definition to include conjugated *acyclic* molecules, Dauben[5] jeopardizes the very bound on which its usefulness depends.

[5] H. J. Dauben, Abstracts of Papers presented at 126th Meeting of the American Chemical Society, New York, N.Y., 12 September 1954, p. 18–O.

[6] E. Hückel, *Grundzuge der Theorie ungesättigter und aromatischer Verbingungen.* Verlag Chemie, Berlin (1938).

[7] B. Pullman and A. Pullman, *Les Theories Electronique de la Chimie Organique.* Masson et Cie, Paris (1952).

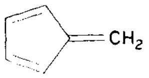
[8] C. A. Coulson, *Valence.* Oxford University Press, Oxford (1951).

[9] Y. K. Syrkin and M. E. Diatkina, *Structure of Molecules and the Chemical Bond.* Butterworths, London (1950).

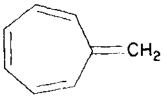
[10] The association of "π-electron delocalization energy" with such characteristics as "stability," "aromaticity" and "reaction by substitution" is based on analogy with traditional benzenoid aromatic chemistry and has no general theoretical justification. Stability depends on the difference in free energy between that of the starting molecules and that of the transition state for the hypothetical chemical change. Knowledge or predictions of the free energy of the starting system alone cannot define the necessary difference.

the "rule of six"[11] to the modern quantum mechanical description when E. Hückel[6] in 1931 developed the molecular orbital method of calculating the energies of π-electrons in planar systems of double bonds. The aromatic character of benzene was reflected in an "experimental" stabilization energy and a theoretically calculable π-electron delocalization energy. The remarkable properties of Thiele's[12] cyclopentadienide anion found satisfactory theoretical explanation. The existence of a positively charged, seven-membered cycle as a relatively stable carbonium ion was predicted and established several years later by the discovery of the water-soluble, stable tropylium ion.[13] Instead of one, three aromatic systems emerged: the pentagonal system with the anionic cyclopentadienide ion as its parent, the neutral benzene (or hexagonal) system and the heptagonal system headed by the cationic cycloheptatrienylium ion. References to members of the pentagonal family are to be found in a recent paper by Lloyd and Sneezum[14], while a reasonably detailed view of the heptagonal family can be obtained from articles by Pauson[15] and Doering and Krauch[16].

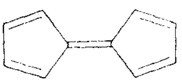
In the years following Hückel's pioneering work, the molecular orbital theory was elaborated and applied to many novel, unknown systems of conjugated double bonds. Among these, the simple mono- and dicyclic systems of five- and seven-membered rings fell quite naturally into a group of eight: fulvene and heptafulvene (I); fulvalene, sesquifulvalene and heptafulvalene; and pentalene, azulene and heptalene. At the start of this work, eight years ago, only two of the eight systems were known: the fulvene type which had long been recognized in its many derivatives[17] (although only recently free of substituents[18]) and the azulene type, long a center of



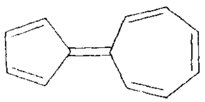
Fulvene



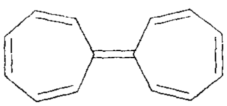
Heptafulvene (I)



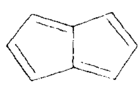
Fulvalene



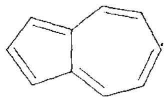
Sesquifulvalene



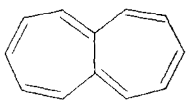
Heptafulvalene



Pentalene



Azulene



Heptalene

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[11] See W. Hückel, *Theoretische Grundlagen der organischen Chemie* (5th Ed.), Vol. I, pp. 507–524. Akademische Verlag, Leipzig (1944).

[12] J. Thiele, *Ber. Dtsch. Chem. Ges.* **33**, 666 (1900); *Liebigs Ann.* **319**, 226 (1901).

[13] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.* **76**, 3203 (1954).

[14] D. Lloyd and J. S. Sneezum, *Tetrahedron* **3**, 334 (1958).

[15] P. L. Pauson, *Chem. Rev.* **55**, 9 (1955).

[16] W. von E. Doering and H. Krauch, *Angew. Chem.* **68**, 661 (1956).

[17] J. H. Day, *Chem. Rev.* **53**, 167 (1953); E. D. Bergmann, *Progress in Organic Chemistry* Vol. III, p. 81. Butterworths, London (1955).

[18] J. Thiec and J. Wiemann, *Bull. Soc. Chim. Fr.* 177 (1956).

intense activity and interest.[19] In this and two papers to follow, the first syntheses of three more of the eight, **heptafulvene** (I), **heptafulvalene** and **fulvalene,** are described.

Heptafulvene (I) was first treated theoretically by Berthier and Pullman in 1949[20] by the molecular orbital (LCAO) and the valence bond methods. π-Electron delocalization energies of 1·994 β (β_{benzene} = 18 kcal/mole; S = 1) and 0·779 γ (γ_{benzene} = 34 kcal/mole; S = 0·25) were calculated by the former method and 0·57 α (α_{benzene} = 33 kcal/mole) by the latter. More refined calculations[21] based on Wheland and Mann[22], predicted a π-electron delocalization energy of 0·46 γ. The simple MO (LCAO) method predicts a dipole moment of 4·6 D[20] with the ring positive, while the refined method predicts 0·85 D in the same direction.[21] Calculations by the self-consistent field method of Roothaan leads to a small dipole moment (0·14 D) in the opposite direction,[23] while use of the Pariser–Parr method gives a value of 0·6 D, again in the direction of the ring positive. Calculations of the predicted light absorption have also been made.[21, 24]

The only published report on the attempted synthesis of heptafulvene is by Grundmann *et al.*[25] and describes failures to effect the synthesis by the elimination of water from α-, β- and γ-cycloheptatrienyl-carbinols and dimethylcarbinols. Our initial approach, equally abortive, involved the corresponding carbinols in the so-called "norcaradiene" series (Chart 1: B and E). All the contributors to the Buchner acid problem had, up to that time, agreed in assigning the "norcaradiene" structure to the parent acid and the 7-cycloheptatrienyl arrangement to other acids Buchner to the γ,[26] De Jong to the γ[27] and Grundmann and Ottmann to the α[28] Firmly convinced that the "norcaradiene" and "7-cycloheptatriene" carboxylic acid arrangements could not represent more than a single substance between them, we worked exclusively with the "norcaradiene" series, content to attribute failures to factors other than incorrect choice of starting material. Later, it was shown[29,30] that the α- and γ-acids were the 2- and 1-cycloheptatrienyl carboxylic acids, that the δ-acid did not exist[29] and that the so-called Buchner or "norcaradiene" carboxylic acid was most probably the 7-cycloheptatrienyl carboxylic acid.[29,31,32]

The reaction of ethyl "norcaradiene" carboxylate (Chart 1, A) with methylmagnesium iodide produced the crystalline dimethyl-7-cycloheptatrienylcarbinol (Chart 1, B) which rearranged exothermically to β,β-dimethylstyrene (Chart 1, C) on acid-catalyzed dehydration.[33]

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[19] F. Gordon, *Chem. Rev.* **50**, 127 (1952); K. Hafner, *Angew. Chem.* **70**, 419 (1958); see also the first two pages of D. H. Reid, *Tetrahedron* **3**, 337 (1958).

[20] G. Berthier and B. Pullman, *Trans. Faraday Soc.* **45**, 484 (1949).

[21] E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman and B. Pullman, *Bull. Soc. Chim. Fr.* **18**, 684 (1951).

[22] G. E. Wheland and D. E. Mann, *J. Chem. Phys.* **17**, 246 (1949).

[23] A. Julg, *J. Chim. Phys.* **52**, 50 (1955).

[24] A. Julg and B. Pullman, *J. Chim. Phys.* **52**, 481 (1955).

[25] Ch. Grundmann, G. Ottmann and G. Gollmer, *Liebigs Ann.* **582**, 178 (1953).

[26] E. Buchner, *Ber. Dtsch. Chem. Ges.* **31**, 2241 (1898).

[27] A. W. K. De Jong, *Rec. Trav. Chim.* **56**, 198 (1937).

[28] Ch. Grundmann and G. Ottmann, *Liebigs Ann.* **582**, 163 (1953).

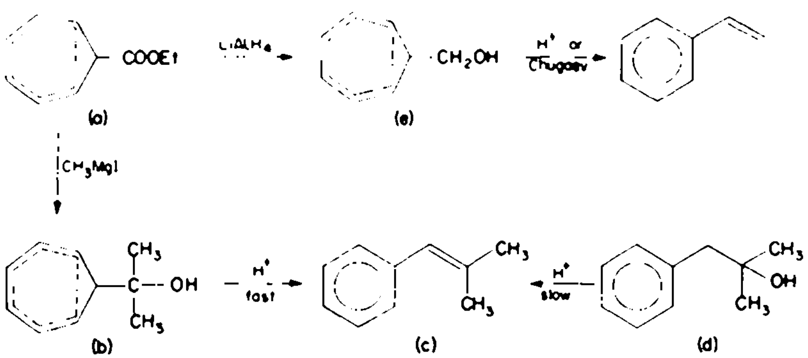
[29] W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, *J. Amer. Chem. Soc.* **78**, 5448 (1956).

[30] K. Alder, H. Jungen and K. Rust, *Liebigs Ann.* **602**, 94 (1956).

[31] In addition to having been largely responsible for the failure of Grundmann *et al.*[24], the incorrectness of the earlier structural assignments to the Buchner acids appears also to have sabotaged at least one attempted tropylium ion synthesis. Cf. footnote 8 in M. J. S. Dewar and R. Pettit, *J. Chem. Soc.* 2021 (1956).

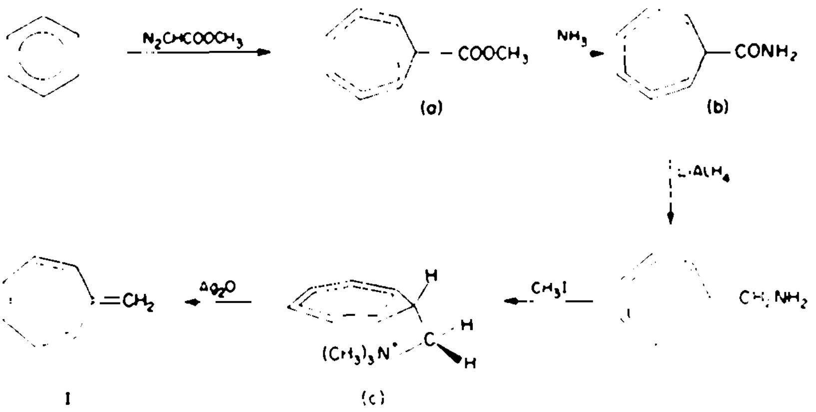
[32] See also M. V. Evans, Jr. and R. C. Lord, Abstracts of Papers presented at the 135th Meeting of the American Chemical Society, Boston, Massachusetts, 5 April 1959, p. 64R.

[33] C. R. Ganellin and R. Pettit, *J. Chem. Soc.* 576 (1958) have effected the same transformations independently.



The contrast between the remarkable exothermicity of this dehydration-rearrangement and the (qualitatively) thermoneutral dehydration of the isomeric dimethylbenzylcarbinol (Chart 1, D), both to the same product, is one of the few instances where the liberation of the resonance energy of benzene is easily palpable. Attempts to convert 7-cycloheptatrienyl-carbinol (Chart 1, E) to heptafulvene (I) were also unsuccessful: dehydration by acid-catalyzed elimination and by the Chugaev sequence (generally considered to be a non-acidic mode of dehydration) led to styrene.

Hoping that milder, but still strongly alkaline, conditions might permit retention of the cycloheptatriene system during the introduction of the fourth double bond, we turned to the Hofmann elimination (Chart 2). The starting material, 7-cycloheptatrienylcarboxamide (Chart 2, B: Buchner's "norcardienyl" carboxamide), is prepared more quickly, in better yield and in a higher state of purity from *methyl* 7-cycloheptatrienyl carboxylate (Chart 2, A) than from the ethyl ester. If the structure of the amide follows from its method of preparation and from its saponification to 7-cycloheptatrienyl carboxylic acid. The reduction of the amide with lithium aluminum hydride at room temperature gives a mixture of amines which can be converted to a mixture of the corresponding trimethyl ammonium iodides. It is



convenient to effect purification at this point, although a tedious fractional crystallization is required to separate the desired trimethyl 7-cycloheptatrienylmethyl ammonium iodide from a dihydro derivative. The formation of the dihydro derivative can be diminished substantially by carrying out the reduction at 0°. The ultraviolet spectrum of trimethyl 7-cycloheptatrienyl ammonium iodide (Chart 2, C) has (after compensation for absorption by iodide ion) a maximum at 255 mμ (log ε 3·53). On the basis of essential identity of this spectrum with that of the preceding 7-cycloheptatrienylmethylamine (λ_{max} 253; log ε 3·51) and the starting 7-cycloheptatrienylcarboxamide (λ_{max}258; log ε 3·47), it is concluded that no change in ring structure has occurred during the reduction and exhaustive methylation.

The Hofmann elimination of trimethylamine from C (Chart 2) must be effected in a special way because of the extreme instability of heptafulvene (I). An aqueous solution of the trimethylammonium hydroxide is prepared in the usual manner with excess of silver oxide and is concentrated *in vacuo* at 25° to a thick oil, whereupon decomposition sets in. A trap either empty or containing a solvent, is connected and cooled to -70°. The decomposition is then completed *in vacuo* in a water bath at 50° as rapidly as possible. In the absence of solvent, a red film condenses which can be saved by dissolving in cold solvent within a minute or so, but which otherwise changes quickly to a colorless polymer. In the presence of solvent, the vapors dissolve at once to give deep red solutions of heptafulvene with the formation of little or no polymer. It is noteworthy that the product has been purified once by distillation in the course of the preparation itself.

Heptafulvene cannot be isolated; at least, trapping at - 170°, extracting with propane and concentrating *in vacuo* at −60° gives only colorless polymer. On concentration, a distillable, perhaps dimeric, material is produced first, but it rapidly polymerizes further. Even dilute solutions of I are not indefinitely stable. A 0·03 M solution in hexane from which trimethylamine has been removed by washing wih water shows appreciable decomposition within an hour at −60°, whereas a 0·003 M solution is essentially unchanged in this time. Appreciable stabilization is effected by trimethylamine or the use of ethers as solvent. Thus, a 0·02 M solution in tetrahydrofuran from which trimethylamine has not been removed retains half the original material after four days at room temperature.

The task of proving the structure of heptafulvene (I) and of gaining information about its chemical and physical properties has been made difficult and often frustrating by the instability of the substance and by the need at all times to work in dilute solution.

A striking feature of heptafulvene is its absorption spectrum in the ultraviolet and visible region, shown in Fig. 1. In this elaborate spectrum, two broad bands are discernible, one with its most intense absorption at 279 mμ (35,850 cm^{-1}; 4·44 eV) and the other with its maximum absorption at 427 mμ (23,450 cm^{-1}; 2·90 eV). The spectrum is surely indicative of a highly unsaturated, conjugated system.[34]

The extinction coefficients could be determined with only limited precision because of uncertainties in the determination of concentration. By assuming a quantitative yield in the best of several preparations, a minimum value for the extinction coefficient at 426 mμ (in tetrahydrofuran as solvent) of 300 was found. By hydrogenating a hexane solution, concentrating, chromatographing in pentane, concentrating, adding carbon tetrachloride and concentrating again, it was possible to determine the final amount of methylcycloheptane (35·5 per cent of theory). Based on the assumption

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[34] Cycloöctatetraene is far from planar and yet possesses an extensive absorption spectrum (Am. Pet. Inst. Res. Proj. 44, Ultraviolet Spectrul Data, Serial No. 180). Although this example serves as a general caution to concluding that absorbing conjugated systems are essentially planar, it does not weigh very heavily in the present case because of the much greater intensity and range of absorption of heptafulvene.

of quantitative reduction, an extinction coefficient of 490 is calculated. This is a maximum value because some methylcycloheptane must have been lost by codistillation during the isolation procedure. An intermediate and probably most reliable value of 370 is obtained on the basis of the quantitative determination of hydrogen absorption (in Diethyl Carbitol as solvent) obtained during measurements of the heat of hydrogenation.[35]

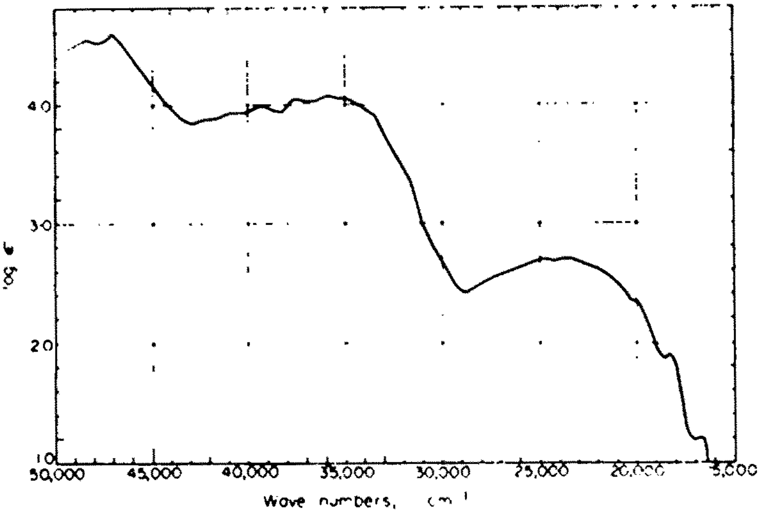

Fig. 1. Ultraviolet and visible absorption spectrum of heptafulvene (I) in n-hexane solution

The isolation of methylcycloheptane from the catalytic reduction may be taken as strong evidence that no rearrangement of carbon skeleton occurred during the Hofmann elimination. Barring sequences such as rearrangement to 1-cycloheptatrienylmethyl trimethyl ammonium ion and elimination to allyilidenemethylenecyclobutene, one might have expected styrene as the product of a completely concerted elimination from the valence tautomeric 7-norcaradienylmethyl trimethyl ammonium ion. In this connection, it is relevant that an anti-parallel configuration is available to the 7-cycloheptatrienylmethyl ammonium ion (Chart 2, C).

The presence of the methylene group in heptafulvene is indicated by the isolation of formaldehyde in low yield on ozonolysis. Confirmation is found in the infrared spectrum. Solutions of heptafulvene are concentrated quickly to ca. 1 per cent at which time they are deep-red and short-lived. Infrared spectra are taken as rapidly as possible and compared with the spectra of the same solutions measured two hours later, after the heptafulvene has completely disappeared. Among the bands listed in the experimental section, strong bands at 6·31 μ (1585 cm^{-1}) and at 11·75 μ (852 cm^{-1}) are attributable to the exocyclic methylene group. Sheppard and Simpson[36] find 1650 ± 11 cm^{-1} (medium) and 889 ± 3 cm^{-1} (strong) for the double-bond stretching and carbon-hydrogen out-of-plane wagging modes of aliphatic unsymmetrically disubstituted olefins. The shift to lower energies and stronger intensities is to be expected of the absorptions of the methylene group in heptafulvene. In this molecule,

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[35] R. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer and D. W. Wiley, *J. Amer. Chem. Soc.* **79**, 4127 (1957).

[36] N. Sheppard and D. M. Simpson, *Quart. Rev.* **6**, 1 (1952).

the anticipated dipole moment could lead to an intensification of the stretching mode and a weakening of the methylene-carbon bond.

A reaction simulant of a Diels–Alder occurs between heptafulvene and dimethyl acetylene dicarboxylate. Although less reactive dienophiles have no effect on heptafulvene, this one reacts in a period of days to give a colorless adduct (Chart 3, B). Air-oxidation affords the deep blue dimethyl azulene-1,2-dicarboxylic acid (Chart 3, C). Although this is not a known derivative, the spectrum is quite similar to that reported by Anderson and Tazuma for methyl azulene-1-carboxylate[37] (Fig. 2). The reaction can be rationalized as the 1,3 (or 1, 8) concerted addition to heptafulvene by analogy with the Diels-Alder reaction or as a two-step ionic process (Chart 3, A) like that favored by Boekelheide for the similar reaction of pyrrocoline with dimethyl acetylene dicarboxylate.[38] The formation of a derivative of azulene, containing as it does the original structural element of methylenecycloheptatriene, constitutes further support for the structural assignment.

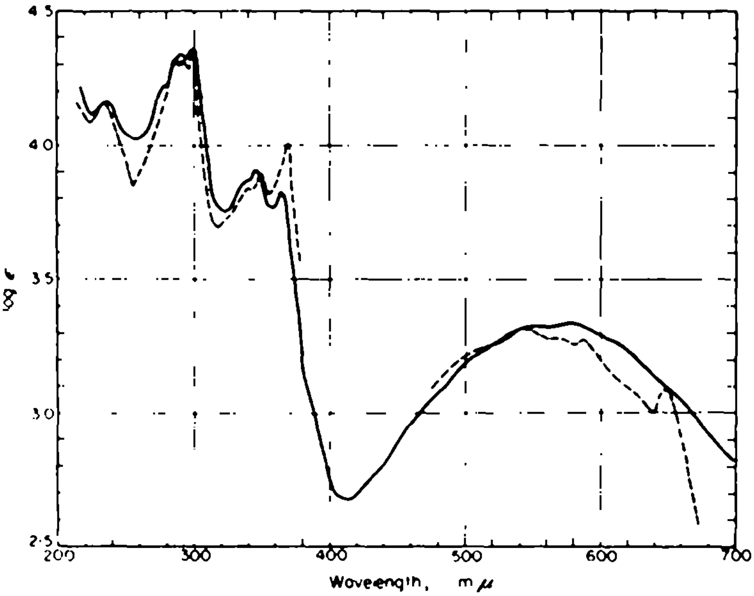

FIG. 2. Ultraviolet and visible spectra of 1-carbomethoxyazulene in cyclohexane (– – – –) and of 1, 2-dicarbomethoxyazulene (·— · ·) in isoöctane.

In the preparation of the 7-cycloheptatrienylmethyl amine by the lithium aluminum hydride reduction of 7-cycloheptatrienylcarboxamide, a dihydro derivative was obtained as its crystalline trimethyl 7-cycloheptadienyl ammonium derivative. This material, showing no absorption in the ultraviolet above 210 mμ, was transformed by Hofmann elimination into an olefin with a maximum at 284 mμ and absorption in the infrared indicative of a methylene group. Although we have made no further

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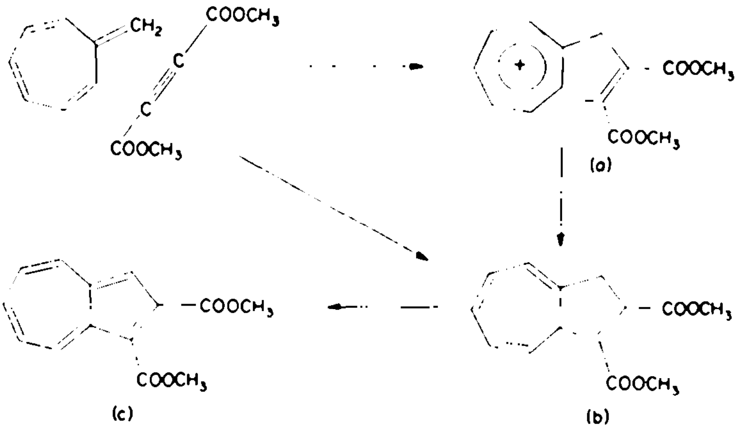
[37] A. G. Anderson, Jr. and J. J. Tazuma, *J. Amer. Chem. Soc.* 75, 4979 (1953).

[38a] V. Boekelheide, *16th National Organic Chemistry Symposium*, American Chemical Society, Seattle, Washington, 15 June 1959, p. 32; [b] A. Galbraith, T. Small and V. Boekelheide, *J. Org. Chem.* **24**, 582 (1959).

effort to prove the structure, it has since been shown by Matteson *et al.* that 3-methylenecyclohepta-1,4-diene, a product of the pyrolysis of 5-methylenebicyclo[2.2.1] heptene, and our product are almost certainly identical.[39]



Attempts to duplicate the synthesis of methylenecycloheptatriene in the 2-cycloheptatrienyl series failed completely. Lithium aluminum hydride reduction of the corresponding carboxamide gave a very unstable amine from which no crystalline quaternary ammonium salt could be obtained.

Recently, Matteson, Drysdale and Sharkey[39] have reported the formation of methylenecycloheptatriene in the pyrolysis of 5-methylenebicyclo[2.2.1]heptene. Produced to the extent of about 0·05 per cent of theory and identified through the highly characteristic absorption spectrum, methylenecycloheptatriene was obtained in higher yield (1 per cent) by the catalytic dehydrogenation (chromia-alumina at 490°) of a mixture of 3-methylene-cycloheptadiene-1,4- and 1,5. Even at quite high temperatures, methylenecycloheptatriene is more stable in the gas phase than in the condensed. In this regard, its behavior is reminiscent of that of *p*-xylylene.[40]

One of the most characteristic properties of methylenecycloheptatriene is sensitivity to acids. Unchanged by amines and potassium hydroxide, indeed protected by their presence, heptafulvene is polymerized very rapidly by dilute acid. Shaking a pentane solution with 0·001 N aqueous hydrochloric acid leads to the instantaneous disappearance of color and precipitation of a polymer. The methylene carbon atom of methylenecycloheptatriene could be a strong Lewis base if the expected tendency to form the stable tropylium ion system[13] were not opposed by too large an aromatic resonance energy in the intact conjugated system of four double bonds. The addition of a proton might thus be expected to lead rapidly to methyltropylium ion. Methylenecycloheptatriene, having behaved as a Lewis base in the very addition of a proton, could now react at its methylene carbon with methyltropylium ion in the first step of a polymerization. There is ample analogy for the Lewis acidic properties of the tropylium ion in its varied reactions with bases to form 7-substituted cycloheptatrienes.[13] This description is quite comparable to that accepted for the

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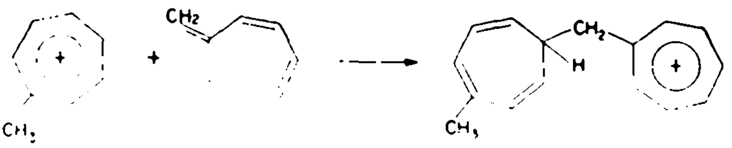
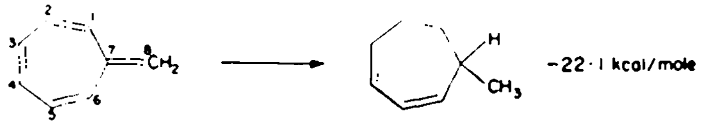
[39] D. S. Matteson, J. J. Drysdale and W. H. Sharkey, Abstracts of Papers presented at 136th Meeting of the American Chemical Society, Atlantic City, N.J., 13 September 1959, p. 30P; *J. Amer. Chem. Soc.* **82**, 2853 (1960).

[40] L. A. Errede and M. Szwarc, *Quart. Rev.* **12**, 301 (1958).





acid-catalyzed polymerization of isobutylene.[41] The marked difference in rate parallels the much easier formation of the tropylium cation.

When methylenecycloheptatriene is reacted at −70° by adding a solution in hexane rapidly to a large excess of hydrogen bromide in hexane, the polymerization is apparently avoided and a crystalline, yellow, water-soluble salt is formed instead. Although this bromide cannot be recrystallized and its structure has not been adequately determined, it is most probably methyltropylium bromide. Indeed, Dauben *et al.*[42] report that the bromide is hygroscopic and unstable and feel that the stability previously claimed by Dewar and Pettit[43] is doubtful.

Phenyllithium, like the weaker nucleophillic reagents, ammonia and hydroxide ion, does not add to heptafulvene. This behavior is in marked contrast to that of fulvene and its derivatives which do react with strong bases by addition. The calculated π-electron delocalization energies of fulvene and heptafulvene are quite close (0·50 and 0·57 α, 1·466 and 1·994 β, and 0·638 and 0·779 γ, respectively)[7] while those of the cyclopentadienide and cycloheptatrienide anions (2·48 and 2·12 β)[6] are also quite close. Disregarding questions of rate, activation energy and strain, the difference in exothermicity in the reaction with a base should be in the order of 0·89 β in favor of reaction with fulvene. Perhaps this difference represents adequate theoretical justification for the failure of heptafulvene to react. It is certainly relevant that no indication of acidity in the methylene hydrogen atoms of cycloheptatriene has been reported as yet.[44]

In respect to the carbonium ions, one has the opposite situation. Here the π-electron delocalization energies of the 5- and 7-membered cations are given as 1·14 and 3·00 β, respectively, leading to a difference of 1·33 β favoring addition of a proton to methylenecycloheptatriene. Either by this approach or by the more qualitative rule of six, the behavior towards acids and bases finds reasonable explanation.

Correlation of the theoretical and observed visible-ultraviolet absorption spectrum of heptafulvene is of interest. A self-consistent field type of calculation[23] predicts 420 mμ (2·95 eV) and 242 mμ (5·11 eV) as the position of the two transitions of lowest energies. Calculation according to the method of Pariser and Parr gives 450 mμ (2·75 eV) and 364 mμ (3·40 eV)[24] although a presumably identical type of calculation carried out by McEwen[45] gives 441 mμ (2·81 eV) and 289 mμ (4·28 eV)

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[41] G. M. Burnett, *Mechanism of Polymer Reactions* pp. 407 *et seq.* Interscience, London (1959).

[42] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Amer. Chem. Soc.* **79**, 4557 (1957).

[43] M. J. S. Dewar and R. Pettit, *J. Chem. Soc.* 2021 (1956).

[44] Cf. A. Streitwieser, *Tetrahedron Letters* No. 6, 23 (1960).

[45] Dr. Lenore McEwen, private communication.

as the expected positions. From the Fig. 1, three maxima centered at 426·5 mμ (23,450 cm^{-1}; 2·91 eV), 280 mμ (37,870 cm^{-1}; 4·43 eV) and 212 mμ (47,100 cm^{-1}; 5·84 eV) can be distinguished. Whether theory and experiment are in good agreement or not depends on criteria which have not been established. The fine structure shows frequency differences in the range of 1500 to 1700 cm^{-1} and is probably indicative of absorption to a vibrationally excited state. Distortion in the excited state presumably involves the bond between the rings and the methylene group.

Discussions of π-electron delocalization energy are complicated by questions of angular strain, compressional energy, non-bonded interactions, choice of model, variations in σ-bond strength and the reliability of the theoretical calculations themselves. Turner *et al.*[35] have already reported the only relevant thermodynamic datum. The heat of hydrogenation in solution is $-92{\cdot}6 \pm {\cdot}4$ kcal/mole. The reliability of the datum is discussed in that paper and due to the fleeting nature of heptafulvene itself, cannot be comparable to data relating to stable, isolable substances. It is pointed out there that the stabilization energy of heptafulvene is about 13·6 kcal/mole. In order to avoid as many doubtful corrections as possible, we would like here to call attention only to the apparent heat of hydrogenation of the exocyclic double bond—the one that completes the supposedly conjugated system in heptafulvene. This value is the difference between the heat of hydrogenation of heptafulvene ($-92{\cdot}6$ kcal/mole) and 7-methylcycloheptatriene (unknown, but not unreasonably taken to be equal to that of cycloheptatriene itself: $-70{\cdot}5 \pm {\cdot}4$ kcal/mole[46]). The heats of hydrogenation of methylene cycloheptane,[47a] methylene cyclohexane,[47a] methylene cyclopentane[46] and 2,4-dimethyl-1-pentane[47b] are $-26{\cdot}3$, $-27{\cdot}8$, $-26{\cdot}8$ and $-26{\cdot}7$ kcal/mole, respectively. The difference in heats of formation of unstrained, non-resonating methylcycloheptatriene and methylene cycloheptatriene calculated according to Franklin's group equivalent method[48] is $-26{\cdot}3$ kcal/mole. The stabilization energy arising from the closing of the conjugated system by the fourth double bond is at best 4·6 kcal/mole. This value may be increased a little by guesses of the extra strain in a double bond exocyclic to a planar cycloheptatriene ring.[49] However, it does not begin to compare with the discrepancy of 36·0 kcal found on completing the benzene ring by introducing the third double bond into 1,3-cyclohexadiene.

The small discrepancy of 4·6 kcal/mole could find an explanation outside of considerations of π-electron delocalization if the changes in carbon–carbon bond strength with hybridization recently proposed by Dewar and Schmeising[50] have suitable quantitative significance. The difference between the single bonds, C_1–C_7 and C_6–C_7 (sp^2–sp^2), in heptafulvene and the corresponding ones in 7-methylcycloheptatriene (sp^2–sp^3) amounts to 2 (10·5 − 6·0) or 9·0 kcal/mole. Another explanation appears if the cycloheptatriene discrepancy (7 kcal/mole) is magnified in methylenecycloheptatriene through a shortening of the C_1–C_6 distance.

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[46] R. B. Turner, W. R. Meador and R. E. Winkler, *J. Amer. Chem. Soc.* **79**, 4116 (1957).

[47a] R. B. Turner and R. H. Garner, *J. Amer. Chem. Soc.* **80**, 1424 (1958); [47b] R. B. Turner, D. E. Nettleton, Jr. and M. Perelman, *J. Amer. Chem. Soc.* **80**, 1430 (1958).

[48] J. L. Franklin, *Ind. Engin. Chem.* **41**, 1070 (1949).

[49] The question of coplanarity in tropilidene and heptafulvene is unresolved and, until it is (tropilidene and certain derivatives are being examined), there is not much point in trying to estimate the magnitude of the angular strain energies. Although we feel that the visible-ultraviolet spectrum is consistent with a planar structure for heptafulvene, the weight of evidence is not large. The geometry of the strain-free structure is quite far from that of the planar and leaves the double bonds at rather large angles to each other.

[50] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959).

Irrespective of valid arguments about the reality of resonance energy and π-electron delocalization energy, there is no striking discrepancy in the heat content of the exocyclic double bond in heptafulvene and ordinary unconjugated double bonds. In comparing chemical reactions of heptafulvene and isobutylene, little attention need be directed to differences in the heat content of the starting olefins. To a first approximation, it will suffice to consider effects of the different environments on the heat content of the hypothetical transition states. Such an argument has already been made in rationalizing the remarkable sensitivity of heptafulvene to acid.

By no traditional definition, can heptafulvene be said to be aromatic. Some of its properties, sensitivity to acids, resistance to bases, absorption of light and possibly the slightly low heat of hydrogenation, find qualitative explanation in theoretical terms. But the remarkable tendency to polymerize does not. It serves as a striking example of the danger in equating theoretically calculated π-electron delocalization energy with chemical stability.

EXPERIMENTAL[31]

Ethyl cycloheptatriene-7-carboxylate (ethyl "norcaradiene" carboxylate)

Solutions of 50 g ethyl diazoacetate in 5000 ml dry benzene are irradiated with pairs of General Electric RS sunlamps in Pyrex flasks cooled by streams of running water.[32] The evolution of nitrogen is complete and the solution has become colorless after 3–4 days. Four combined runs are worked by removing benzene by distillation, steam distilling the residue and extracting the distillate (ca. 7500 ml) with three 300-ml portions of ether. Distillation *in vacuo* gives 88 g (31 %) of ethyl cycloheptatriene-7-carboxylate, b.p. 85–86°/6 mm.

Dimethyl-7-cycloheptatrienylcarbinol (*Chart* 1, B)

In view of the close similarity between our preparation and that recently published by Ganellin and Pettit[33], details will not be given here beyond noting that two recrystallizations from pentane at 27° afforded material of m.p. 55·5–56·5° (reported[33] m.p. 59–60°; Found: C, 79·8; H, 9·3; O, 11·1. Calc. for $C_{10}H_{14}O$: C, 80·0; H, 9·4; O, 10·7%).

β,β-Dimethylstyrene (*Chart* 1, C)

(a) *From dimethyl-7-cycloheptatrienylcarbinol.* When 51 mg of carbinol, m.p. 56°, was crushed in a test-tube and treated with 1 ml 50% aqueous sulfuric acid at 10°, there was an immediate, intense evolution of heat. The oil which settled out was extracted with pentane and recovered by evaporative distillation. The infrared spectrum was identical with that of an authentic sample of *β,β*-dimethylstyrene.

(b) *From dimethylbenzylcarbinol* (*Chart* 1, D). A sample of the carbinol was prepared in the usual way from ethyl phenylacetate and methylmagnesium iodide. This carbinol was stable to 50% aqueous sulfuric acid at room temp and lost water only when heated to 100°, and then, slowly. The two samples of *β,β*-dimethylstyrene had identical infrared spectra.

7-Cycloheptatrienylcarbinol (*Chart* 1, E)

Methyl cycloheptatriene-7-carboxylate was prepared by irradiation of methyl diazoacetate in benzene in the same way and on the same scale as that described above for the ethyl ester. The yield of distilled product (b.p. 68–69·5°/5 mm; n_D^{25} 1·5102) was 32% of theory. By careful fractionation of the benzene, which had been crudely distilled from the irradiation reactions, an additional 6% could be recovered.

An ethereal (200 ml) solution of 22·5 g of this ester was added dropwise under nitrogen over a

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[31] Analyses by Schwarzkopf Microanalytical Laboratory, 56–19 37th Ave., Woodside 77, New York.

[32] This procedure was developed by Dr. L. H. Knox at the Hickrill Chemical Research Foundation, Katonah, N.Y., in May, 1949, and has proved itself in the ensuing years to be consistently convenient and reliable. It is similar to that published by G. O. Schenk and H. Ziegler, *Naturwissenschaften* **38**, 356 (1951); *Liebigs Ann.* **584**, 221 (1953); G. O. Schenk, *Z. Electrochem.* **55**, 505 (1951); *Angew. Chem.* **64**, 12 (1952).

2 hr period to a stirred mixture of 7·4 g lithium aluminum hydride in 200 ml ether. After 12 hr, 30 ml water was added leaving a paste and a clear ether solution which was decanted. Three 60-ml portions ether which were used to triturate the paste were united with the main ether solution. Washing with water, drying over anhydrous magnesium sulfate and distilling through a 24 cm Vigreux column gave 14·4 g (78%) 7-cycloheptatrienylcarbinol: b.p. 83·5-85·5°/3·5 mm; n_D^{25} 1·5296 (Found: C, 78·4; H, 8·4. $C_8H_{10}O$ requires: C, 78·7; H, 8·3%).

Heating a small sample of this carbinol with 3 N aqueous sulfuric acid on the steam bath, followed by extraction with pentane and distillation, afforded styrene having an infrared spectrum identical with that of an authentic sample.

A solution of 9·15 g 7-cycloheptatrienylcarbinol in 60 ml toluene was added dropwise to a stirred suspension of 3·1 g sodamide in toluene (75 ml) at 80°. After being refluxed for 1·5 hr and then cooled to 50°, the mixture was treated with 25 ml carbon disulfide and refluxed over-night. The mixture was cooled again, treated with 15 ml methyl iodide and refluxed for 4 hr. The mixture was poured into 200 ml water and extracted with 200 ml ether. The thoroughly washed ether extract was dried and distilled, finally *in vacuo* to give 11·2 g (70%) very impure methyl xanthate, b.p. 81–86°/6 mm (Found: C, 46·3; H, 6·5; S, 42·1. $C_{10}H_{12}OS_2$ requires: C, 56·6; H, 5·7; S, 30·2%), which deposited yellow crystals of dimethyl trithiocarbonate (Found: C, 26·2; H, 4·4; S, 69·0. Calc. for $C_3H_6S_3$: C, 26·1; H, 4·4; S, 69·5%) on cooling at −70°. Pyrolysis by heating slowly to 360° in a metal bath led to the distillation of a mixture. Fractionation led to the isolation of 6 drops material, b.p. 46–48°/33 mm, having the same infrared spectrum as authentic styrene. Some dimethyl trithiocarbonate was recovered as well.

Methylenecycloheptatriene (*Chart* 2, I)

A mixture of 50·4 g methyl cycloheptatriene-7-carboxylate in 160 ml conc ammonium hydroxide was shaken vigorously at room temp for 8 hr and deposited faintly yellow crystals on cooling to 2°. These were filtered, washed with ice water and twice with small amounts of pentane and dried quickly *in vacuo in the dark*. Immediate recrystallization of the crude material (32·9 g) from 3500 ml absolute ether yielded 24·1 g colorless leaflets, m.p. 145–146°. From the mother liquor, an additional 6·0 g amide, m.p. 141·5–143·0°, was obtained (total yield: 30·1 g; 66% of theory). Sensitive to air, heat and light, the amide turns dark and melts at a lower temp unless stored at −20°. Further recrystallization serves only to lower the m.p. to 140–141°, the value reported in the literature[23,43] and obtained on purification of partially decomposed material.

Use of ethyl cycloheptatriene-7-carboxylate, as previously described,[43] requires a longer time (5–8 days) and yields impure product, m.p. 127–131°, whose m.p. can be raised no higher than 140–141° and then only by several recrystallizations, attended by such losses that in our hands the yield ranged from 8-25% of theory.

7-Cycloheptatrienylmethylamine

Cycloheptatriene-7-carboxamide (30·0 g) was added over an 8 hr period to stirred, ethereal (600 ml) lithium aluminum hydride (18·5 g) at 0° under prepurified nitrogen. After 35 hr with stirring at 0°, water (75 ml) was added, separating an ether layer which was decanted and an aqueous paste which was thrice triturated with 100 ml portions of ether. The combined ether solutions were washed once with water (200 ml) and twice with saturated aqueous sodium chloride (150 ml), dried over anhydrous magnesium sulfate and concentrated to a residue, distillation of which gave 18·8 g (70·4% of theory) of the amine, b.p. 58·0-58·5°/4·2 mm; n_D^{25} 1·5405; ultraviolet absorption spectrum in 95% ethanol: λ_{min} 224 mμ (log ε 2·92), λ_{max} 253 (log ε 3·51) (Found: C, 79·5; H, 9·3; N, 11·5. $C_8H_{11}N$ requires: C, 79·3; H, 9·2; N, 11·6%).

In the usual way from phenylisocyanate, N-(*7-cycloheptatrienylmethyl*)-N′-*phenylurea* was prepared, m.p. 98–99° after recrystallization from absolute ethanol; and from phenylisothiocyanate, N-(*7-cycloheptatrienylmethyl*)-N′-*phenylthiourea*, m.p. 110–111°, from 95% ethanol (Found: C, 70·5; H, 6·5; S, 12·8. $C_{15}H_{16}N_2S$ requires: C, 70·3; H, 6·3; S, 12·5%).

Trimethyl-7-cycloheptatrienylmethylammonium iodide (*Chart* 2, C)

A mixture of 7-cycloheptatrienylmethylamine (14·6 g), powdered potassium carbonate (40 g), methyl iodide (102 g) and absolute methanol (200 ml) was shaken occasionally over a 36 hr period.

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[43] E. Buchner, *Ber. Dtsch. Chem. Ges.* **29**, 106 (1896).

The solid residue, recovered by distillation, first on the steam bath, then *in vacuo*, was extracted in a Soxhlet apparatus with 300 ml chloroform for 14 hr. On being cooled, 26·9 g colorless needles, m.p. 188–190° (dec), crystallized. The concentrated mother liquor yielded an additional 5·6 g. Two recrystallizations of the combined material from absolute methanol gave 27·2 g (86% of theory) of quaternary ammonium salt as heavy needles; m.p. 194 ·195° (dec); ultraviolet spectrum compensated by an equimolar solution of potassium iodide both in 95% ethanol: λ_{max} 255 (log ϵ 3·53) (Found: C, 45·5; H, 6·2; I, 43·8; N, 4·7. $C_{11}H_{18}IN$ requires: C, 45·4; H, 6·2; I, 43·6; N, 4·8%).

Hofmann elimination. The apparatus centered about a 25 ml pear-shaped flask fitted through a ground 14/20 joint to a simple distillation head having an inlet capillary serving as a nitrogen inlet tube and an efficient vacuum boiling aid. The side arm passed into the inlet tube of the first of two simple traps, A and B, connected in series (side-arm test-tubes with concentric inlet tubes extending to within 2 cm of the bottom). The final outlet was a two-way stopcock allowing the introduction of nitrogen or the evacuation of the system.

In a typical run, 0·500 g (1·82 mmol) of the quaternary iodide was dissolved in 5 ml of distilled water (warming was necessary) and poured into a 15 ml centrifuge tube containing silver oxide, freshly prepared by treating 0·300 g (1·73 mmol) of silver nitrate in 3 ml of water with excess 2 N sodium hydroxide, centrifuging, separating by decantation and washing in similar fashion three times with distilled water. The resulting mixture was shaken and stirred for 5–10 min and centrifuged. The supernatant solution was decanted into the 25 ml pear-shaped flask along with two 2 ml washings of the precipitated silver iodide. The solution (10 15 ml) was now concentrated by distillation at 6 mm, the bulk of the water being collected in B, the second of the two traps, by cooling to −70°.

When the volume of the aqueous solution became so low that the viscosity increased noticeably, the more concentrated droplets on the side of the flask suddenly turned pale red. At this point, A, the first trap, was immersed in a dry-ice bath (it was convenient to have replaced B shortly before this time with a clean trap) and the pressure was lowered to 0·1 mm. The decomposition proceeded smoothly and could be accelerated by heating the pear-shaped flask to 35–40°. When no more liquid remained, nitrogen was admitted and about 25 ml of a suitable solvent was poured rapidly into trap A, attention being given to proper rinsing of the inside of the inlet tube. The red condensate, a mixture of water, trimethylamine and product, must be dissolved as soon as possible after it condenses and under no circumstances must it be allowed to warm to room temperature, for the red color of the product is then replaced by that of the colorless polymer. Among the solvents employed for the extraction were propane, butane, pentane, hexane, ether, tetrahydrofuran and carbon tetrachloride. In this way, dark red solutions of methylenecycloheptatriene (I) could be obtained.

Chemical and Physical Properties of Methylenecycloheptatriene

(a) *Stability.* The stability of the red solutions varied markedly with concentration, solvent and stray acidity. All attempts to concentrate solutions and isolate the product gave rise only to polymeric material. It should be mentioned that appreciable quantities of I codistilled unchanged in the attempted isolation experiments. The most determined effort involved preparing a solution in propane and removing the solvent *in vacuo* at −60°. However, just like pentane solutions evaporated at room temp on a watch glass, this procedure resulted in a tough polymeric film.

The *polymer* softened between 50–95° and became clear from 100 120°. It was partially soluble in chloroform and benzene, insoluble in methanol and paraffins, and turned yellow on standing in air. The polymer dissolves in 9 N sulfuric acid with an intense red color turning blue on diluting with water and colorless on the addition of aqueous alkali.

When a larger quantity of methylenecycloheptatriene was concentrated *in vacuo*, in addition to polymer, an oil, possibly *dimeric*, b.p. 80°/0·5 mm, could be distilled; λ_{max} 255, 263 mμ (log ϵ 3·68). The infrared spectrum taken in carbon tetrachloride and carbon disulfide contained the following absorption bands (in μ): 3·31 *s*trong; 3·39 s, 3·46 *m*edium, 3·51 m, 5·75 *w*eak, 5·85 *w*, 6·15 *m*, 6·20 *sh*oulder, 6·94 *s*, 7·25 *m*, 7·44 *m*, 7·53 *w*, 7·78 *w*, 8·10 *w*, 8·57 *m*, 9·20 *w*, 9·70 *w*, 9·90 *w*, 11·26 *s*, 11·78 *s*, 12·10 *m*, 12·42 *w*, 12·83 *m*, 13·05 *s*, 13·30 *s*, 13·38 *s*, 14·16 *v*ery *s*, 14·46 *s*, 14·64 *s*. The material darkened upon standing under nitrogen, and gave positive tests for unsaturation with potassium permanganate, bromine, and reacted vigorously with 9 N sulfuric acid.

Shaken with dilute aqueous acid (0·0001 N hydrochloric acid), solutions of I polymerized very fast. Consistently, solutions from which trimethylamine had been removed by washing with distilled water were far less stable than unwashed, protected solutions. For example, a washed hexane solution of I (0·3%) had decomposed (lost its color) appreciably in 30–40 min at −60°, whereas unwashed solutions and those of much lower concentration (0·03–0·003%) were considerably more stable. An ethanol or tetrahydrofuran solution (ca. 0·1%) still containing trimethylamine was only half-decomposed after 2–4 days. I appeared to be slightly soluble and stable in liquid ammonia (from which it could be extracted with absolute ether).

(b) *Hydrogenation to methylcycloheptane.* A sample of I from 0·500 g quaternary ammonium salt in a mixture of 10 ml pentane and 10 ml methanol (both layers were intensely red) was hydrogenated at 35 lb in a Parr apparatus over platinum oxide catalyst. Worked up by pouring into water, separating, drying and distilling the pentane through a 25 cm Vigreux column at a 10 to 1 reflux ratio, the reaction yielded a small residue which was distilled in an Emich tube to give 43 mg (23%) of methylcycloheptane: b.p. 136°; d_4^{24} 0·800; n_D^{24} 1·4392.

An authentic sample was prepared from cycloheptanone and methyl magnesium iodide by dehydration of the resulting 1-methylcycloheptanol with *p*-toluenesulfonic acid and hydrogenation of the resulting olefins: b.p. 136·1°; d_4^{24} 0·798; n_D^{24} 1·4390. The infrared spectra of the two samples, taken neat in a 0·1 mm cell, were superimposable from 2–15 μ but for two very weak shoulders (amounting to about 2% difference in % transmission) present in the authentic sample. The physical constants reported for methylcycloheptane are b.p. 135–136°, d_4^{18} 0·7981; n_D^{25} 1·4388.[54]

Quantitative hydrogenation was carried out in order to determine the extinction coefficient of the visible and ultraviolet spectrum. The first method depended on the quantitative isolation of methylcycloheptane. A solution of I from 0·500 g quaternary iodide in 20 ml hexane was washed thrice with 40 ml portions water, dried for 2 min. with anhydrous magnesium sulfate and made up to 20·0 ml. A 1·00 ml aliquot was removed, diluted to 10·00 ml and used to determine the absorption spectrum. The remaining 19 ml was hydrogenated at 50 lb in a Parr apparatus with platinum oxide for 28 hr. The resulting solution was concentrated carefully, passed through an 11 × 200 mm column of activated alumina, using 30 ml pentane. The eluate was concentrated, diluted with 5 ml carbon tetrachloride and concentrated further to 0·5 ml. This residue was diluted carefully to 1·00 ml. From the density of the infrared bands at 3·49, 6·82 and 7·24 μ (the spectrum corresponded well with that of authentic methylcycloheptane), the concentration of methylcycloheptane was calculated to be 0·58 M. On the assumption that this accurately represented the amount of methylenecycloheptatriene produced (corresponding to a yield of 38% of theory) the following extinction coefficients resulted: log ε 4·082, 2·681 and 2·689 at 279, 405 and 430 mμ, respectively. Any error resulting from loss of methylcycloheptane during the isolation procedure would lie in the direction of underestimating the concentration of I. Accordingly, these are *maximum* values for the extinction coefficients.

The second method, consequent on the experimental determination of the heat of hydrogenation at Rice University, Houston,[36] depended on the quantitative measurement of hydrogen absorption to within 1%. For this work, the procedure for preparing I was varied to improve the yield and minimize polymerization. The first trap A(*v.a.*) was changed to a 50-ml, ordinary side-arm distilling flask (with the side-arm set high and connected to the second trap B with standard taper joints) with a wider (10 mm) inlet tube (leading from the pear-shaped distilling flask) to within 1 cm of the bottom. By this means, it was possible for the vapors of I to pass directly into the solvent without first condensing on the walls. In these experiments, the solvent, Diethylcarbitol (the *bis* (β-ethoxyethyl) ether of ethylene glycol; b.p. 100°/37 mm) was introduced into trap A, as usual, at the first sign of decomposition and was maintained at −15° in a salt-ice bath. The whole apparatus was shaken gently by hand to facilitate rapid dilution of the product. Following one experiment, complete evaporation of the solvent left no residue, indicating the absence of polymerization. This change in procedure also improved the *relative* yield (determined from optical density) by a factor of 1·3.

In one of several experiments, 275 ml of solution prepared from 2·000 mmol of the quaternary ammonium iodide had an optical density of 0·174 (0·173 at 0·01 mm slit; 0·175 at 0·15 mm slit) at 429 mμ in a 1 cm cell after dilution by a factor of 12·5. On catalytic hydrogenation, 6·467 mmol hydrogen was absorbed, corresponding to 81% of the theoretical yield and an extinction coefficient of 370 (log ε 2·568) in Diethylcarbitol as solvent. To the extent that any part of the hydrogen absorbed should be associated with dimer or polymer, the concentration of I would in fact have been lower than that taken. The value calculated for the extinction coefficient is therefore a *minimum* one.

(c) *Absorption spectra.* The ultraviolet and visible spectrum of I is shown in Fig. 1.

The infrared spectrum was very difficult to obtain because of the instability of solutions more

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[54] G. Egloff, *Physical Constants of Hydrocarbons* Vol. II, p. 178. Reinhold (1940).

concentrated than 1%. A carbon tetrachloride solution of I was washed, dried, concentrated in a stream of nitrogen to about 1% and transferred at once to a 1 mm cell. A series of spectra were compared with that of the colorless solution remaining after 2 hr. A solution in paraffin oil was prepared by adding 0·5 ml to a pentane solution of I and concentrating. Combining the results of the two experiments gives a tentative, almost certainly incomplete spectrum: 3·25 μ *weak*, 3·32 *medium*, 5·16 *w*, 5·45 *w*, 6·31 *strong*, 6·48 *m*, 7·66 *w*, 8·60 *m*, 10·70 *w*, 10·86 *w*, 11·75 *s*, 12·05 *m*, 13·50 *very s*.

(d) *Ozonolysis*. A solution of 1·40 mmol ozone in methylene chloride at 70° was added to 1·38 mmol of I in 200 ml methylene chloride. As the last bit of ozone was added, the solution turned from red to yellow. Zinc powder and water were added. The methylene chloride was distilled at 40° directly into an aqueous solution of dimethyldihydroresorcinol (dimedon) buffered at pH 4. After 48 hr of occasional shaking, concentration gave a small amount of dark material which was recrystallized twice from methanol–water yielding 22 mg (6%) of the dimedon derivative of formaldehyde, m.p. 186–187°; m.p. 185–186·5° in admixture with an authentic sample. No tropone could be isolated.

(e) *Dimethyl azulene*-1,2-*dicarboxylate* (*Chart* 3, C). After 3 days at 4°, a solution of 3·43 mmol of I and 2·50 mmol dimethyl acetylene dicarboxylate in 100 ml tetrahydrofuran was concentrated on the steam bath. Benzene was added and the distillation was continued until the b.p. reached 80° and the volume was 25 ml. After the addition of 200 mg of palladium-on-charcoal (10%), a slow stream of air was passed through for 10 hr.

The mixture was filtered by passing through a short alumina column using ether as eluting solvent. The concentrated solution was chromatographed on a 13 × 50 mm alumina column with 200 ml of ether as the eluting solvent. A dark purple band separated from a dark brown, strongly adsorbed impurity. Concentration of the blue solution gave 194 mg of dark blue oil, which was chromatographed again. Middle fractions with closely similar infrared spectra were chromatographed a third time. The ultraviolet spectrum of this material is shown in Fig. 2. (Found: C, 70·3; H, 5·4; O, 24·0. $C_{14}H_{12}O_4$ requires: C, 68·9; H, 5·0; O, 26·3%.)

3-*Methylenecyclohepta*-1,4-*diene*

When the lithium aluminum hydride reduction of cycloheptatriene-7-carboxamide (*vide supra*) is carried out at room temp, exhaustive methylation of the resulting amine leads to a mixture of quaternary ammonium salts, m.p. 153–172°. Tedious fractional crystallization (aided by the appearance of two different crystalline forms –needle-like prisms and square prisms—at the fifth level which could be separated manually and used as seed) afforded trimethyl 7-cycloheptatrienylmethyl ammonium iodide, m.p. 190–191·5° (dec) and m.p. 192–193° (dec) in admixture with the sample above, and a new, light-sensitive quaternary ammonium iodide, m.p. 177–178°, apparently a trimethyl *cycloheptadienylmethyl* ammonium iodide: no maximal absorption; only end absorption: λ 204 mμ (log ε 3·42) (Found: C, 45·0; H, 7·0; I, 43·1. $C_{11}H_{20}IN$ requires: C, 45·1; H, 6·9; I, 43·3).

Subjected to the Hofmann elimination by the procedure above, but at 70–80°, this quaternary ammonium salt (0·300 g) gave a colorless liquid which was evaporatively distilled at 760 mm and 80°: λ_{max} 284, λ_{min} 236; infrared spectrum in μ: 3·24 *medium*, 3·31 *strong*, 3·42 *s*, 3·51 *m*, 5·60 *m*, 5·75 *m*, 5·82 *weak*, 6·24 *m*, 6·35 *m*, 6·90 *m*, 6·98 *s*, 7·08 *m*, 7·25 *w*, 7·58 *w*, 7·65 *w*, 8·05 *m*, 8·29 *m*, 8·59 *m*, 9·85 *w*, 10·03 *w*, 10·60 *m*, 11·21 *very s*, 11·37 *s*, 11·77 *m*, 12·30 *m*, 12·70 *vs*, 13·15 *m*, 13·68 *vs*, 13·92 *m*, 15·05 *m*.

2-*Cycloheptatrienylcarboxylic acid*

A mixture of 35·6 g crude methyl 7-cycloheptatrienylcarboxylate and 250 ml 2 N sodium hydroxide was refluxed for 1½ hr. The homogeneous red solution was cooled, extracted twice with ether, and acidified with 2 N sulfuric acid. The acidic mixture was extracted 4 times with 60-ml portions ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate and distilled on a water bath to dryness. The brown residue was sublimed to give 28·7 g of a mixture of phenylacetic acid and 2-cycloheptatrienylcarboxylic acid. Four recrystallizations of the mixture from *n*-hexane gave 12·3 g pure acid, m.p. 70–71°, and from the mother liquors, an additional 4·2 g was obtained, making the overall yield 51% of theory.

2-*Cycloheptatrienylcarboxamide*

A mixture of 12·6 g of the above acid and 24 g thionyl chloride was cautiously warmed on a steam bath with swirling, and refluxed for 1 hr. The excess thionyl chloride was removed *in vacuo*, and the residue dissolved in 500 ml absolute ether. The solution was then rapidly stirred in an anhydrous ammonia atmosphere; after 1 hr, the entrance tube for the ammonia was lowered into the mixture, and the ether solution was saturated with ammonia. The precipitated ammonium chloride was filtered and washed 3 times with warm fresh ether. The combined ether filtrates were concentrated on a water bath. Sublimation of the tan residue at 90° and 0·1 mm gave 10·8 g (86% of theory) of 2-cycloheptatrienylcarboxamide as colorless crystals, m.p. 129·5–130·5°.

Attempted preparation of 2-cycloheptatrienylmethyl amine

To a stirred mixture of 6·2 g lithium aluminum hydride and 200 ml ether, at −40° under an atmosphere of dry prepurified nitrogen, 10·5 g of the powdered amide was added over a period of 6 hr. The yellow mixture was stirred for an additional 20 hr at − 40 to −30°, and then allowed to warm to 0°. To the stirred mixture, 35 ml water was added dropwise keeping the temp of the reaction mixture at 0°. The dark brown ether solution was decanted from the pasty inorganic salts, which were then triturated twice with 100-ml portions of fresh ether. The combined ether solutions were dried at 0° over anhydrous magnesium sulfate for 3 hr, and then distilled under 300 mm pressure at 15°. All attempts to distill the resulting brown residue in a short path still yielded polymeric resin. Repetition of the reduction and immediate treatment of the crude ethereal solution with methyl iodide, potassium carbonate, and absolute methyl alcohol at room temp gave only a polymeric resin, from which no crystalline quaternary ammonium iodide could be obtained.

The reaction of methylenecycloheptatriene to acids

Bromine, iodine and boron trifluoride immediately polymerize heptafulvene. The same is true of aqueous hydrogen chloride and hydrogen bromide, although polymerization is slower with aqueous acetic acid or phenol. It was not possible to prepare a picrate; even at −120° only polymer and trimethylammonium picrate resulted from the reaction of ethanolic picric acid with a freshly prepared solution of heptafulvene.

The addition of a solution of heptafulvene in hexane to a solution of hydrogen bromide in hexane at −80° gave a crystalline, yellow precipitate. This material became gummy at −20° and was completely soluble in water.

The reaction of methylenecycloheptatriene to sodium

Reacting a piece of scraped sodium under a solution of methylenecycloheptatriene in tetrahydrofuran at room temperature produced a deep blue-black solution from which only intractable polymeric material could be isolated.

A solution of methylenecycloheptatriene in 20 ml of absolute ether from 0·500 g trimethyl 7-cycloheptatrienylmethyl ammonium iodide was dried over potassium hydroxide pellets at 0° for 30 min and pumped into a solution of sodium in 150 ml liquid ammonia at −60°. After 15 min stirring, the black solution was decolorized by adding methanol dropwise, diluted with additional ether, warmed to evaporate ammonia, washed twice with water, dried over magnesium sulfate, and distilled. The ether distillate had λ_{max} 252 mμ, whereas the residue yielded a couple of drops of material with λ_{max} 232 mμ and an inflection at 250 mμ.