

THE 1,1,2,3,4,5,6-HEPTAMETHYLBENZENONIUM ION

W. VON E. DOERING, M. SAUNDERS

Sterling Chemistry Laboratory, Yale University, New Haven, Conn.

H. G. BOYTON, H. W. EARHART, E. F. WADLEY, W. R. EDWARDS

Humble Oil and Refining Co., Baytown, Texas

and

G. LABER

Hickrill Chemical Research Foundation Inc., Katonah, N.Y.

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Abstract—The terminal product in the Friedel and Crafts methylation of benzene and its methyl homologues is 1,1,2,3,4,5,6-heptamethylbenzenonium ion (I), a new comparatively stable carbonium ion. The ion decomposes slowly in aqueous acid to methanol and hexamethylbenzene (III) and can be synthesized from these products by treatment with sulfuric acid. (I) is in rapidly reversible equilibrium with a proton and a neutral molecule, $C_{13}H_{10}$ to which the structure 4-methylene-1,1,2,3,5,6-hexamethylcyclohexadiene-2,5 (II) has been assigned.

THE catalyst in reactions of the Friedel and Crafts type often becomes inactive after a relatively short time. In the methylation of benzene and its methyl homologues with methyl chloride and aluminum chloride at 80° ,¹ deactivation sets in rapidly with the consumption of relatively large quantities of catalyst. In this paper the major cause of the loss of catalyst activity is uncovered.

To find out whether organic substances might be inactivating the catalyst, aliquots from the upper and lower phases of the reaction mixture were removed at intervals during the methylation. After being washed with water, these samples were examined by low-voltage mass-spectrographic analysis.² In the upper hydrocarbon layer, the expected increase in concentration of the higher methylated homologues through hexamethylbenzene was observed. In the dense, lower, liquid layer, which contained all the aluminum chloride, substances corresponding to mass 176 developed rapidly and reached a high concentration (ca. 40 per cent) by the time the catalyst was no longer active. In addition there was a high concentration (relative to the upper layer) of penta- and hexa-methylbenzene, consistent with the greater basicity of these hydrocarbons.³

The remarkable mass number 176 corresponds to $C_{13}H_{20}$ and is consistent with the hypothesis that one more carbon atom (CH_2) has been added to hexamethylbenzene (162). Whatever the detailed structure may be, it is immediately evident that the substance responsible for the 176 mass number must be more basic than hexamethylbenzene, since it is present only in the lower layer. By taking advantage of the fact that the new substance is indeed so basic as to be extractable from pentane

¹ C. Friedel and J. M. Crafts, *C. R. Acad. Sci., Paris* **84**, 1392 (1877); *Ann. Chim. Phys.* (6) **1**, 449 (1884); O. Jacobsen, *Ber. Dtsch. Chem. Ges.* **14**, 2624 (1881); L. I. Smith and F. J. Dobrovolsky, *J. Amer. Chem. Soc.* **48**, 1413 (1926).

² F. H. Field and S. H. Hastings, *Analyt. Chem.* **28**, 1248 (1956).

³ D. A. McCauley and A. P. Lien, *J. Amer. Chem. Soc.* **73**, 2013 (1951).

tetrachloride solution (Fig. 1) shows three peaks located at 70, 189 and 216 cycles per second (relative to benzene hydrogens). Their intensities have been determined by operating with a rapid-sweep⁵ technique and correspond to 2.0, 6.5 and 11.5 hydrogen atoms, respectively (after normalization to a total of 20). The 70 c/s peak corresponds in position to that indicated for vinyl hydrogen.⁶ In the infrared spectrum of (II) there is a strong band at 855 cm^{-1} suggestive of an asymmetrically

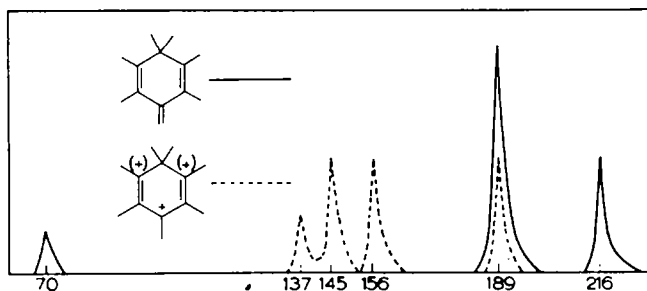


FIG. 1. Nuclear magnetic resonance in c/s from benzene.

disubstituted olefin ($\text{CH}_2 = \text{C}$). Finally, the presence of the methylene group is confirmed by the formation of formaldehyde in the ozonolysis of (II).

The other two peaks in the n.m.r. spectrum of (II) are accommodated by the remaining methyl groups. The position of the 216 c/s peak of relative intensity 6.5 is consistent with the presence of the geminate dimethyl group. Paraffinic methyl hydrogen absorbs at higher fields than vinyl methyl, although the exact position of such peaks is strongly dependent on the conditions of measurement.⁷ Confirmation of the geminate dimethyl group is to be found in the presence of two bands at 1359 and 1380 cm^{-1} in the infrared spectrum⁸ of (II). The remaining peak at 189 c/s and relative intensity 11.5 reflects the four vinyl methyl groups hypothesized in structure (II). It may be remarked that the singlet character of the 189 and 216 c/s peaks is incompatible with their origin in ethyl or isopropyl groups, which always appear as multiplets.⁹

The ultraviolet spectrum of (II) (Fig. 2) shows a maximum at $257\text{ m}\mu$ ($\log \epsilon 4.27$) indicative of a conjugated system containing at least two double bonds. The maximum lies at too low a wave length to be consistent with the fully conjugated system in structure (IIb). For such a system of three double bonds the calculated maximum absorption is at $318\text{ m}\mu$.¹⁰ For a cross-conjugated system of type (IIa) insufficient analogies are available to permit estimation of the position of maximum absorption. It might reasonably be expected to lie beyond $239\text{ m}\mu$, the value expected of the related conjugated diene. A further argument supporting (IIa) can be based on the singlet character of the 70 c/s peak. In structure (IIb) the two hydrogens of the exocyclic methylene group are quite differently situated and might be expected to suffer different degrees of chemical shift, with a resultant increase in the complexity of absorption in the vinyl hydrogen region.

⁵ Cf. R. B. Williams, *Ann. N. Y. Acad. Sci.* **70**, 890 (1958).

⁶ L. H. Meyer, A. Saika and H. S. Gutowsky, *J. Amer. Chem. Soc.* **75**, 4567 (1953).

⁷ A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.* **26**, 1651 (1957).

⁸ N. Sheppard and D. M. Simpson, *Quart. Rev. Chem. Soc.* **7**, 19 (1953).

⁹ R. E. Glick and A. Bothner-By, *J. Chem. Phys.* **25**, 362 (1956).

¹⁰ L. Dorfman, *Chem. Rev.* **53**, 47 (1953).

The available data is therefore consistent with the *cross-conjugated* structure, 4-methylene-1,1,2,3,5,6-hexamethylcyclohexadiene-2,5 (IIa). The molecule is accordingly the terminal completely methylated homologue in the semibenzene series studied by von Auwers and Ziegler.¹¹ The lack of ultraviolet spectral data in their work precludes comparison with the spectrum of (II). All the examples synthesized by von Auwers suffered rapid rearrangement to the related isomeric benzene on treatment with acid. Such an aromatizing rearrangement is structurally impossible in (II). As a consequence, (II) is much more stable in acid than any of its lower homologues.

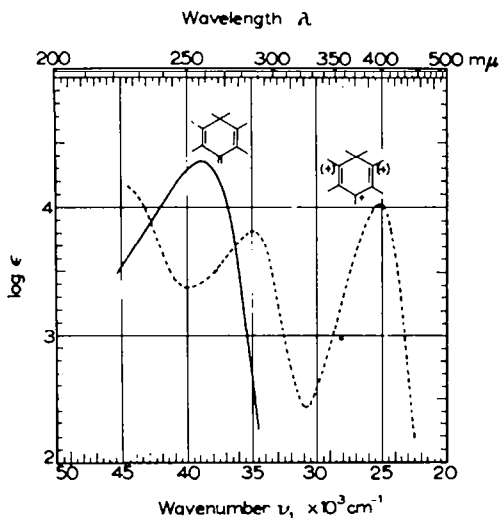


FIG. 2. Ultraviolet spectrum of (II).

The structure of the conjugate acid (I) of the semibenzene (II) is most clearly elucidated from the change in n.m.r. spectrum which occurs when (II) is converted to (I) in concentrated hydrochloric acid. The spectrum (Fig. 1) now consists of four peaks at 137, 145, 156 and 189 c/s with relative intensities corresponding to 3, 6, 6 and 6 hydrogen atoms, respectively, when normalized to a total of 21. The most significant change is the disappearance of the 70 c/s peak corresponding to the exocyclic methylene group and its replacement by the 137 peak of a methyl group. In structure (I) the 4-methyl group is unique, whereas the other types appear in pairs. The down-field shift suffered by the 4-methyl group is relatively large and is almost certainly caused by the positive charge in the ion. Consequent on the effect of this charge, the four vinyl methyl groups appearing at 189 c/s in (II) are split into two pairs in (I). The partial positive charge on carbon atoms 2 and 6 draws the two methyl groups at these positive positions down-field, leaving the 3- and 5-methyl groups less affected. The peak at 145 c/s in the n.m.r. spectrum of (I) is therefore assigned to the 2- and 6-methyl groups, while that at 156 c/s originates in the 3- and 5-methyl groups. Finally, the peak at 189 c/s must be ascribed to the geminate dimethyl group. Because of the unpredictable and probably large difference to be expected between carbon tetrachloride and concentrated hydrochloric acid as solvents, one cannot evaluate quantitatively the effect of the positive charge on the position

¹¹ K. von Auwers and K. Ziegler, *Liebigs Ann.* **425**, 217 (1921).

of the geminate dimethyl peak. However, it is noteworthy that the 4-methyl has been shifted more than the 2, 6-pair. A dispersion of charge by no-bonded structures of the type I α may be responsible.

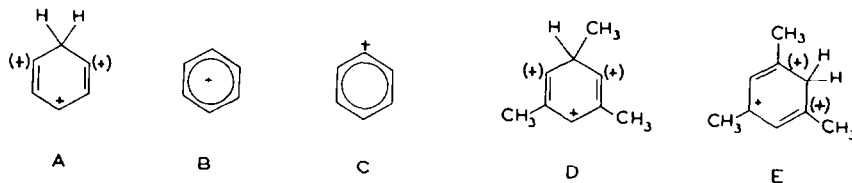
For the C₁₃H₂₁⁺ ion the structure 1,1,2,3,4,5,6-heptamethylbenzenonium* ion is accordingly preferred. The possibility that I have the structure of a Dewar " π -complex" (I α) cannot be rejected on the basis of present evidence. The hexagonally



symmetrical structure, (I β), considered in passing as a model for the " π -complex",¹⁷ requires an n.m.r. spectrum of two peaks of relative intensity ratio 3:18. The observed spectrum being completely inconsistent with this prediction, structure (I β) is rigorously excluded. This result is relevant to the general problem of benzene complexes of the C₆H₆·A⁺ type.¹⁸ In the near future it is hoped to present evidence to show that structures (I) and (I α) are quite close in energy. The isolation of the C₁₃H₂₁⁺ ion offers the first significant opportunity to distinguish between the two structures by X-ray crystallographic analysis. Such an investigation is already under way.

The ultraviolet spectrum of (I) (Fig. 2) [λ_{\max} 287 m μ (log ϵ 3.83), λ_{\max} 397 m μ (log ϵ 3.93)] extends into the visible, causing solutions of the ion to be yellow. These

* The system, C₆H₇⁺ (A), and its derivatives, have been named variously phenonium ion [D. J. Cram, *J. Amer. Chem. Soc.* **74**, 2129 (1952)], benzenium ion¹² and σ -complex.¹³ In naming the system it is desirable to provide for unequivocal numerical designations of substituents and to allow for the existence of the related cationic fragments, C₆H₆⁺ (B) [S. I. Weissman, E. de Boer and J. J. Conradi, *J. Chem. Phys.* **26**, 963 (1957)] and C₆H₅⁺ (C). "Phenonium" has been widely used in discussions of certain anchimerically assisted displacements and Wagner-Meerwein rearrangements and is perhaps best reserved for this purpose (see particularly footnote 6 in Muller *et al.*¹³). " σ -complex" is acceptable as a generic term, but is otherwise



useless. "Benzenium", although formally acceptable, is so obviously the appropriate designation for the molecule ion, C₆H₆⁺ (B) (e.g., anthracenium) that we consider it most unfortunate that Muller and co-workers should have diverted the word to the use of C₆H₇⁺. We would like to urge the adoption of "benzenonium" (naphthalenonium, pyrenonium, etc.). The suffix "onium" appropriately connotes the introduction of positive charge by the addition of a Lewis acid (H⁺, R⁺, Br⁺, etc.) and therefore finds analogy in ammonium, oxonium and the like. ("Benzonium" was considered and rejected because of the inappropriate implications of the term "benz".) The usual numbering systems are applicable without change and the designation of the position of a hydrogen can be accomplished by a system already well established [cf. *Chem. Abstr.* **39**, 5932 (1945)]. Thus the molecules D and E acquire the names I(1), 3,5- and I(2), 3,5-trimethylbenzenonium, respectively, in which the number in parenthesis designates the carbon atom which is quadrivalent by virtue of having at least one of its two extracyclic substituents be an hydrogen atom.

¹² N. Muller, L. W. Pickett and R. S. Mulliken, *J. Amer. Chem. Soc.* **76**, 4770 (1954).

¹³ H. C. Brown and J. D. Brady, *J. Amer. Chem. Soc.* **74**, 3570 (1952).

¹⁴ M. J. S. Dewar, *J. Chem. Soc.* 777 (1946).

¹⁵ M. J. S. Dewar, *Disc. Faraday Soc.* **2**, 50 (1947).

¹⁶ M. J. S. Dewar, *Bull. Soc. Chim. Fr.* [5], **18**, c71 (1951).

¹⁷ C. A. Coulson and M. J. S. Dewar, *Disc. Faraday Soc.* **2**, 54 (1947).

¹⁸ R. E. Rundle and J. D. Corbett, *J. Amer. Chem. Soc.* **79**, 757 (1957); see other pertinent references therein.

maxima are in felicitous agreement with those reported by Reid¹⁹ for the benzenonium ions obtained from alkyl-substituted benzenes in liquid hydrogen fluoride and boron trifluoride. 1,2,3,4,5,6-Hexamethylbenzenonium ion, for example, shows λ_{\max} 283 m μ ($\log \epsilon$ 4.31) and λ_{\max} 401 m μ ($\log \epsilon$ 4.42), while 1(2),3,5-trimethylbenzenonium ion (E) shows λ_{\max} 391 m μ ($\log \epsilon$ 4.43). It is gratifying to find these protium antecedents of (I) having closely similar spectra. Because of the ease with which they lose protons, their isolation in crystalline state has been accomplished only recently in the distinctive work of Oláh and Kuhn.²⁰

In Wheland's original quantum mechanical analysis of aromatic substitution²¹ and in Dewar's²² extension of this approach the benzenonium ion structure was used to represent the transition state. Since that time, the work of Melander on the mechanism of other aromatic substitutions,²³ that of McCauley and Lien²⁴ and H. C. Brown and Brady¹³ specifically in the Friedel-Crafts reaction and finally the above-mentioned isolation by Oláh²⁰ have made it clear that the benzenonium geometry in fact represents an intermediate. The discovery of (I) demonstrates even more convincingly that the benzenonium structure can be an energy minimum, if additional evidence were any longer necessary. The possibility nevertheless remains that cases may arise in which this geometry corresponds to a transition state rather than an intermediate. The present case is an especially favorable one in that three tertiary carbonium ion forms (Ia, b and c) contribute to the stabilization of the ion, whereas the unsubstituted benzenonium ion is represented by three higher-energy secondary forms.

EXPERIMENTAL

Preparation of crude 1,1,2,3,4,5,6-heptamethylbenzenonium aluminum tetrachloride

(I). The exhaustive methylation was carried out in a 5 l. three-necked flask equipped with stirrer, thermometer and gas inlet and outlet lines. To 1200 g of mixed trimethylbenzenes at 37° and 1093 g of powdered anhydrous aluminum chloride, methyl chloride was passed in below the liquid surface with vigorous agitation. The contents were heated quickly to 80° and methyl chloride was passed in at a rate of 650 g/hr for 8 hr, when the production of hydrogen chloride ceased. The dark-red liquid product was poured from the flask into a closed storage vessel where it crystallized below 80°.

When the crushed crude salt was treated with toluene at room temperature, two liquid layers formed: an upper layer having a purple fluorescence, which was decanted and discarded; and a very dark lower layer, from which dark crystals were precipitated on diluting with pentane. The solvent was decanted and the crystals were dried *in vacuo*. When the crystals were dissolved in dry ethyl acetate at 40°, a dark green solution was obtained, from which some insoluble material was removed by centrifuging and pipetting, an operation carried out twice. On cooling in ice and scratching, cooling further to -60° and finally filtering by centrifuging at -60°, greenish needles were obtained. A second crystallization gave bright-yellow needles, which were washed first with 1:1 ethyl acetate-pentane and then with pentane, with

¹⁹ C. Reid, *J. Amer. Chem. Soc.* **76**, 3264 (1954).

²⁰ G. Oláh and S. Kuhn, *Nature, Lond.* **178**, 1344 (1956).

²¹ G. Wheland, *J. Amer. Chem. Soc.* **64**, 900 (1942).

²² M. J. S. Dewar, *J. Chem. Soc.* 463 (1949).

²³ L. Melander, *Arkiv Kemi* **2**, 211 (1950).

²⁴ D. A. McCauley and A. P. Lien, *J. Amer. Chem. Soc.* **74**, 6246 (1952); *Ibid.* **75**, 2411 (1953); *Ibid.* **76**, 2354 (1954).

filtering each time by centrifuging. The material was dried *in vacuo* and stored at -60° excluding moisture (Found: C, 45.2; H, 6.1, Al, 7.9; Cl, 41.0. $C_{13}H_{21}AlCl_4$ requires C, 45.1; H, 6.1; Al, 7.8; Cl, 41.0 per cent)

4-Methylene-1,1,2,3,5,6-hexamethylcyclohexadiene-2,5 (II). A 43.3 g portion of the crushed crude salt of (I) was extracted in a Soxhlet apparatus with pentane for 2 hr. Concentration of the pentane solution afforded 3.71 g (8.5 per cent) of crude hexamethylbenzene (III). Sublimation at 12 mm and 60° followed by two recrystallizations from ethanol gave pure (III), m.p. $165.5-166.5^{\circ}$, which showed no depression on admixture with an authentic sample (obtained from Distillation Products), m.p. 166° .

The unextracted material was hydrolyzed with 300 ml of ice-cold water and extracted with two 200 ml portions of pentane. The combined pentane solutions were extracted with 30 ml portions of concentrated hydrochloric acid. The combined acid solutions were poured into 800 ml of ice-cold water, neutralized with sodium bicarbonate and extracted with pentane. The dried (anhydrous sodium sulfate) pentane solution was concentrated to 11.05 g (50 per cent) of a dark-yellow oil, which crystallized with ease. The infrared spectrum of this material is identical in all but the smallest detail with the spectrum of pure (II), m.p. $46.5-47.5^{\circ}$, obtained by three recrystallizations from methanol. Colorless material is most easily obtained by preceding the crystallization with one vacuum sublimation (Found: C, 88.0; H, 11.7. $C_{13}H_{20}$ requires C, 88.6; H, 11.4 per cent). The compound is so sensitive to air that special care is needed to obtain an analysis in which the carbon value is not 2-3 per cent low.

The ultraviolet spectrum was measured in a Beckman DU spectrometer in *iso*-octane solution: λ_{\max} 257 $m\mu$ ($\log \epsilon$ 4.27).

(II) is quite unstable in air, being converted in a few hours at room temperature to a brown oil showing a carbonyl and an hydroxyl group in its infrared spectrum. It reacts immediately with bromine and somewhat more slowly with potassium permanganate, and is completely insoluble in water, but dissolves easily in hydrochloric acid more concentrated than 4 N or aqueous acids of comparable strength to give solutions of (I). The ultraviolet spectrum of (II) in concentrated hydrochloric acid [(I) chloride] shows λ_{\max} 287 $m\mu$ ($\log \epsilon$ 3.83) and λ_{\max} 397 $m\mu$ ($\log \epsilon$ 3.93). (II) is precipitated from aqueous acid solutions of (I) chloride simply on dilution with water. Turbidity is noticed at concentrations below 3 N.

Ozonolysis of (II). After ozone had been passed into a solution of 2.5 g of (II) in 75 ml of ethyl acetate at -78° for $1\frac{1}{2}$ hr, the absorption became very slow, so the reaction was stopped and the solution was concentrated to 15 ml. An aliquot portion of 1.5 ml was shaken with 35 ml of N hydrochloric acid and 0.75 g of zinc dust for 15 min. To the hot filtered solution 5 ml of hot saturated dimedone and enough sodium acetate to bring the pH to 3 were added. A fine crystalline precipitate of the *formaldehyde derivative of dimedone*, (72 mg) m.p. $188-190^{\circ}$, was obtained.

Conversion of (I) to hexamethylbenzene (III). After 24 hr at room temperature the crystalline material which had precipitated from a solution of 298 mg of (II) in 15 ml of concentrated hydrochloric acid was extracted with pentane. Washing the pentane layer with aqueous sodium bicarbonate and concentrating gave a brown residue, from which 8 mg of colourless crystals sublimed at 12 mm and 50° . After two recrystallizations from ethanol, hexamethylbenzene, m.p. 166° , was obtained. Over a 3-week period a total of 166 mg of (III) was isolated.

A similar solution of (II) in hydrochloric acid developed a new peak in the n.m.r. spectrum on standing. This band was located at the same position as that shown by a solution of methanol in concentrated hydrochloric acid.

Synthesis of heptamethylbenzenonium ion (I) from hexamethylbenzene (III). A total of 218 mg of hexamethylbenzene (III) was added in small portions over a period of 1 hr to a solution of 20 ml of methanol in 100 ml of concentrated sulfuric acid at 95°. After 2 hr, the reaction mixture was cooled, poured on to 750 g of ice, neutralized first with sodium carbonate and finally with sodium bicarbonate and then extracted with 25 ml of pentane. The pentane layer was then extracted with three 3.5 ml portions of concentrated hydrochloric acid; the aqueous extract was neutralized with sodium bicarbonate and extracted with pentane: from the pentane layer, 17 mg of a brown oil was obtained. One crystallization from methanol furnished 5.5 mg of (II), m.p. 45–46°. The infrared spectrum was superimposable on that of the previously obtained (II).

Nuclear magnetic resonance spectra. All n.m.r. spectra were determined with the Varian Associates model 4300 V high-resolution spectrometer with super-stabilizer at 40.01 mc, with use of a spinning sample. Peak positions were measured relative to a benzene capillary by using the sideband superposition technique. Relative numbers of hydrogens were determined by a modified fast-passage technique.