line **14**, m.p. 87–98°. Two recrystallizations from petroleum ether (b.p. 65–110°) gave **14** melting at 112.0–112.5° (lit.[13] m.p. 114–115°).

Metalation of α-Pinene (20).—To 0.183 mole of amylsodium–sodium chloride suspension in pentane was added 25.0 g. (0.183 mole) of α-pinene. The container was sealed under helium and was shaken occasionally during the reaction period. After 59 days the reaction mixture was carbonated with an excess of solid carbon dioxide. The product was hydrolyzed, filtered, and extracted three times with 150-ml. portions of ether. The aqueous layer was acidified (dilute H_2SO_4), extracted twice with 200-ml. portions of ether, saturated with sodium chloride, and extracted five times with 150-ml. portions of ether. The combined ether extracts were dried over calcium sulfate, filtered, and evaporated to yield 28.947 g. of yellow oil. From the crude acid there crystallized 2.392 g. of white, crystalline *endo*-2(10)-pinene-3-carboxylic acid (**22**), m.p. 90–95°, and a second crop (0.190 g.) of **22** melting at 81.5–89.0°. The acid was recrystallized three times from petroleum ether (b.p. 65–110°) to give 1.064 g. of **22** melting at 98.0–98.5° (further recrystallization did not raise the melting point), showing $\nu_{\max}^{\mathrm{KBr}}$ 1640 and 895 cm.$^{-1}$. The ultraviolet spectrum showed only end absorption.

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95; neut. equiv., 180. Found: C, 73.34; H, 8.71; neut. equiv., 182.

A third crop of **22** (3.056 g.), m.p. 73–83°, crystallized from the mother liquor and was identified as **22** by the infrared spectrum and the undepressed mixture melting point. The yield of **22**, based on unrecovered hydrocarbon, was 18.3%. The mother liquor was distilled to a temperature of 100° at 0.1 mm. to give 17.946 g. of liquid. The liquid was fractionated to give 1.345 g. of caproic acid, identified by the infrared spectrum, and 10.627 g. (34.5% yield, based on unrecovered hydrocarbon) of the known mertenyl carboxylic acid (**23**), b.p. 115° at 0.5 mm. (lit.[11] b.p. 95° at 0.05 mm.), and a nonvolatile residue. The acid **23** was identified by its n.m.r. spectrum and by pyrolysis. A 0.55-g. sample of **23** was mixed with 0.031 g. of anhydrous sodium carbonate and was pyrolyzed at 180° to give a mixture[11] of α- and β-pinenes which were identified by gas chromatography.

Paracyclophanes. III. Octamethyl[2.2]paracyclophane. A Highly Strained Cyclophane[1]

DANIEL T. LONGONE AND LYDIA H. SIMANYI

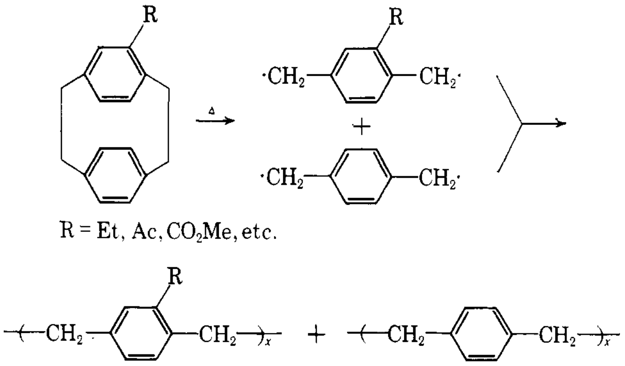
Department of Chemistry, University of Michigan, Ann Arbor, Michigan

Received June 26, 1964

The Hofmann-type pyrolysis of pentamethylbenzyltrimethylammonium hydroxide has been investigated as a route to octamethyl[2.2]paracyclophane (tetramethyl-*p*-xylylene dimer). This dimer, isolated in low yield, represents an extreme case of transannular eclipsing of alkyl groups. Such eclipsing leads to destabilization of the already strained [2.2]paracyclophane system. Other products formed in the pyrolysis reaction, in addition to high-melting polymer, are pentamethylbenzyl alcohol, the corresponding ether, and the tetramethyl-*o*-xylylene dimer, octamethyldibenzocyclooctadiene.

The synthesis and properties of a wide variety of [*m.n*]paracyclophanes have been extensively investigated by Cram's group.[2] Ample evidence has been presented for the existence of transannular electronic and steric effects in the reactions and physical properties of these ring systems. Due to its synthetic accessibility,[3] and its rigid and unique geometry, [2.2]-paracyclophane (1) holds a central position in this series. A refined X-ray analysis of the structure, thermal expansion, and molecular vibrations of 1 at 93°K. and at room temperature has been described recently.[4] The maximum separation between benzene rings (*ortho* carbons) is 3.09 Å., while the *para* carbons are only 2.75 Å. apart (Fig. 1). Puckering of the rings is achieved by increasing the bond angles (θ) between the methylene bridges and the benzene rings from 90 to 111° and by folding the rings (through 14°) away from each other along the line of the *para* carbon atoms. At room temperature the bond length between the methylene carbon atoms is 1.63 Å., but this reduces to 1.56 Å. at 93°K.

This strained system should exhibit more or less facile thermolysis of the bridge methylene bonds, its susceptibility to such cleavage modified by the electronic and steric effects of appropriate substituents. A systematic study of the stability of [2.2]paracyclophane and its derivatives is lacking; however, fragmentary information is available in the literature. While hydrocarbon 1 appears stable up to its melting point (287°), it has been pyrolyzed to polymer at 550°[5] and affords[6] both 4,4'-dimethylbibenzyl and *p,p'*-dimethyl-*trans*-stilbene on prolonged heating to 400°. Vapor phase pyrolysis (550–600°) of a variety of aryl-substituted derivatives of 1 (ethyl, acetyl, carbomethoxy, dibromo, dichloro, and trichloro) yields[5] the monomeric *p*-xylylenes evidenced by the isolation of the corresponding homopolymers, the latter formed subsequent to a fractional condensation technique.



Increased nuclear substitution, especially by aromatic moieties, can lead to destabilization of the cyclophane ring system. Benzo[2.2]paracyclophane (2) and

---

[1] Research supported in part by the U. S. Army Research Office (Durham). For previous papers in this series, see (a) D. T. Longone and F.-P. Boettcher, *J. Am. Chem. Soc.*, **85**, 3436 (1963); (b) D. T. Longone and C. L. Warren, *ibid.*, **84**, 1507 (1962).

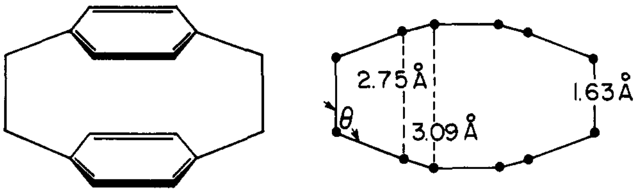
[2] D. J. Cram and L. A. Singer, *ibid.*, **85**, 1084 (1963), and previous papers in this series.

[3] H. E. Winberg and F. S. Fawcett, *Org. Syn.*, **42**, 83 (1962). A number of monosubstituted [2.2]paracyclophanes are known: L. A. Singer and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1080 (1963).

[4] K. Lonsdale, H. J. Milledge, and K. V. K. Rao, *Proc. Roy. Soc.* (London), **A255**, 82 (1960). For an earlier study, see C. J. Brown, *J. Chem. Soc.*, 3265 (1953).

[5] W. F. Gorham, German Patent 1,085,673 (1960); *Chem. Abstr.*, **55**, 22920 (1961).

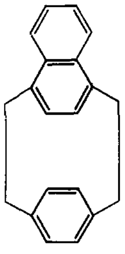
[6] J. R. Schaefgen, *J. Polymer Sci.*, **15**, 203 (1955).



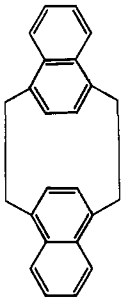
1

Fig. 1.—[2.2]Paracyclophane, with structural profile along plane through the *para* carbon atoms.

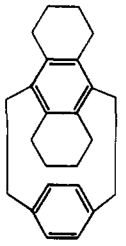
anti-dibenzo[2.2]paracyclophane (**3**), as well as their synthetic percursors, are quite stable under the conditions utilized for their isolation and characterization.[7] In contrast to the stability of its precursor **4**, the dibenzo[2.2]paracyclophane **5** decomposes on attempted purification.[7] The related tetrabenzo[2.2]paracyclophane (**6**) polymerizes rapidly in the solid state at 280° and in solution above 100°.[8] The observations cited above do not allow for a clear understanding of the factors which may destabilize the [2.2]paracyclophane system. For example, the reasons for the marked instability of **5** relative to **3** (and to a lesser extent to **6**) are not apparent.



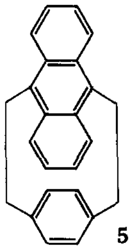
2



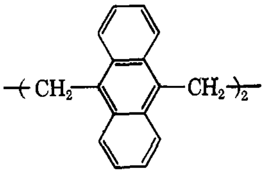
3



4



5

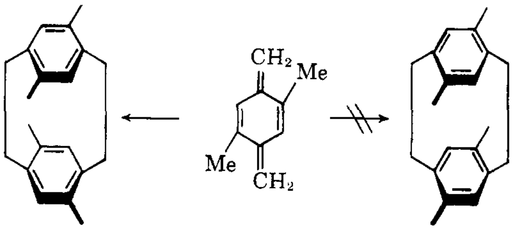


6

We are attempting to assess those factors which contribute to the destabilization of the already strained [2.2]paracyclophane system. Specifically, we are examining the effect of added ring strain brought about by the eclipsing of substituents on opposed aromatic rings. For reasons outlined below our initial work has been directed toward the synthesis of octamethyl[2.2]paracyclophane (**15**).

Results and Discussion

We have previously[1b] assigned structure **8** with noneclipsed methyl groups to the dimer of 2,5-dimethyl-*p*-xylylene (**7**). The alternative structure **9** was rejected on the basis of dimer stability and failure to observe spectral abnormalities associated with overcrowded alkyl groups. Examination of the crystallographic data for **1** indicates that eclipsed methyl groups on opposed aromatic rings could be accommodated with nuclei about 3.1 Å. apart. Such intramolecular methyl–methyl distances would be formally comparable to those which exist in the planar hexamethylbenzene (2.9 Å.)[9] and the nonplanar octamethylnaphthalene (α-methyl carbons 3.0 Å. apart).[10] In order to ensure transannular eclipsing of substituents, the dimerization of at least a trisubstituted *p*-xylylene is required. We chose to attempt the dimerization of tetramethyl-*p*-xylylene (**13** → **15**), both as a severe test for intramolecular crowding and to minimize the number of isomeric reaction products. For the generation of **13** the 1,6-Hofmann elimination[7,11] of the quaternary ammonium hydroxide **12** was examined.



8 7 9

The requisite pentamethylbenzyl bromide (**10**) was obtained both from the bromination of hexamethylbenzene and the bromomethylation of pentamethylbenzene. The yields in both cases were excellent (80–100%); however, the latter reaction proved to be more convenient in regard to product isolation. The quaternary ammonium bromide derived from **10** was converted to the corresponding hydroxide (**12**) in the usual manner. Pyrolysis of **12** in a toluene–water medium[11c] resulted in the smooth evolution of trimethylamine. The resulting reaction mixture afforded, in addition to insoluble high-melting polymer (polyxylylenes), a mixture of hydrocarbons, an ether, and substantial amounts of an alcohol. The latter two compounds were readily identified as pentamethylbenzyl alcohol (**16**) and the corresponding ether (**17**). These two products undoubtedly result from substitution by hydroxide and alcohol at benzyl carbon *via* both bimolecular and unimolecular pathways.[12] The analogous alcohol and ether are formed in the pyrolysis of *p*-methylbenzyltrimethylammonium hydroxide.[13] (See Scheme I.)

The hydrocarbon fraction (as much as 6% yield) contained no "spiro di-*o*-xylylene" structures[1a,11d] in that it decolorized negligible amounts of bromine. Subsequent examination indicated the presence of only two compounds which proved difficult to separate. One

---

(7) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Am. Chem. Soc.*, **85**, 1088 (1963).

(8) J. H. Golden, *J. Chem. Soc.*, 3741 (1961).

(9) L. O. Brockway and J. M. Robertson, *ibid.*, 1324 (1939).

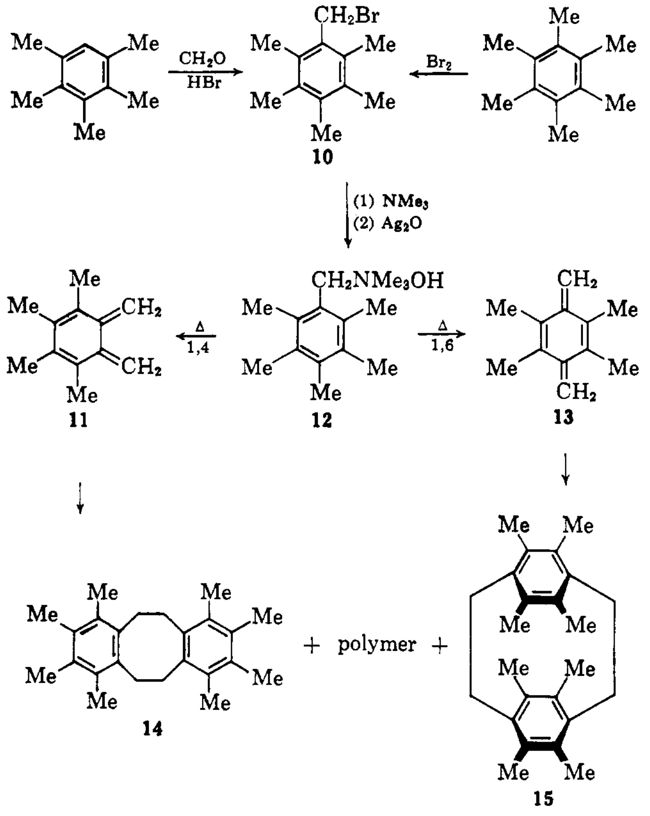
(10) D. M. Donaldson and J. M. Robertson, *ibid.*, 17 (1953).

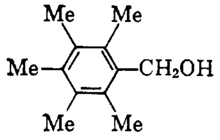
(11) (a) F. S. Fawcett, U. S. Patent 2,757,146 (1956); *Chem. Abstr.*, **50**, 14268 (1956); (b) H.-W. Bersch, *Angew. Chem.*, **69**, 237 (1957); (c) H. E. Winberg, F. S. Fawcett, W. E. Mochel, and C. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960); (d) the transient existence of xylylenes in the pyrolysis reactions of *o*- and *p*-methylbenzyltrimethylammonium hydroxides has been demonstrated by L. A. Errede, *ibid.*, **83**, 949 (1961).

(12) A. C. Cope and E. R. Trumbull in "Organic Reactions," Vol. XI, A. C. Cope, Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, Chapter 5.

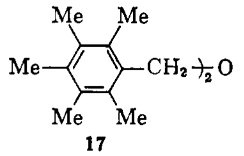
(13) See ref. 11d. The author suggests that the ether is formed from the reaction of alcohol with *p*-xylylene. This appears unlikely as *p*-xylylene is relatively unreactive toward nucleophiles and weak acids: L. A. Errede, J. M. Hoyt, and R. S. Gregorian, *J. Am. Chem. Soc.*, **82**, 5224 (1960). Also, in a case which cannot involve a xylylene, benzyl ether is a minor product in the decomposition of benzyltrimethylammonium hydroxide: E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 69 (1933).

Scheme I





16



17

component, which was not obtained in a pure state, has been assigned structure **14**, the dimer of *o*-xylylene **11**. The ultraviolet and proton magnetic resonance spectra are consistent with the proposed octamethyldibenzocyclooctadiene structure. Both high yields (20%)[11d] and no yields at all[11c,14] of *o*-xylylene dimer (dibenzocyclooctadiene) have been reported from the decomposition of *o*-methylbenzyltrimethylammonium hydroxide. We find, as in this case, that the pyrolysis of benzylammonium hydroxides containing both *o*- and *p*-methyl groups leads to hydrocarbon dimers derived from both 1,4- and 1,6-eliminations.[15]

The second hydrocarbon component was most readily isolated and purified by rapid fractional sublimation. It is a high-melting (316–318°), somewhat volatile material whose elemental and molecular weight analyses identify it as a tetramethylxylylene dimer.[16] This dimer is octamethyl[2.2]paracyclophane (**15**). The n.m.r. spectrum is in accord with the assigned structure: τ 6.86 singlet ($ArCH_2$) and 7.99 singlet ($ArCH_3$); integrated peak areas 1:3, respectively. In contrast, dimer **14** exhibits a τ 7.02 singlet ($ArCH_2$) and *two* singlets ($ArCH_3$) at 7.87 and 7.95; integrated peak areas 2:3:3, respectively.

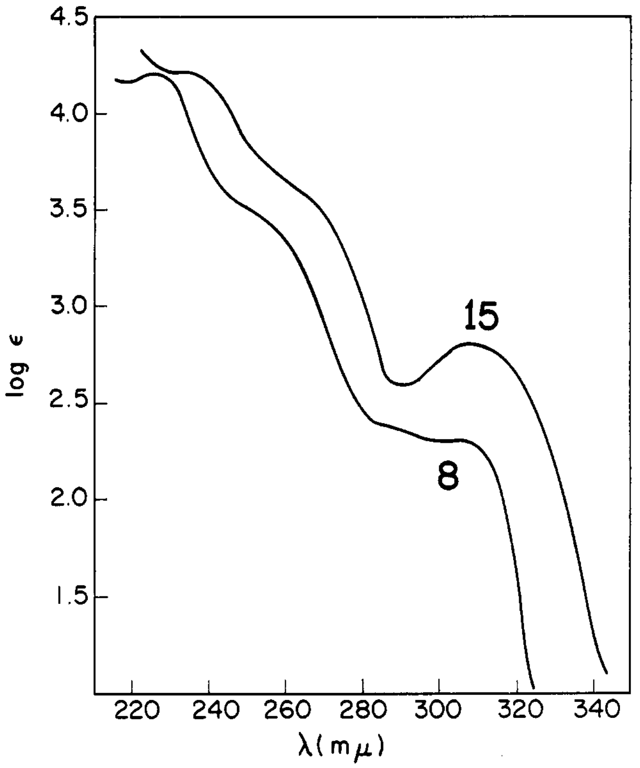


Fig. 2.—Ultraviolet absorption spectra (isooctane) of tetramethyl[2.2]paracyclophane (**8**) and octamethyl[2.2]paracyclophane (**15**).

Confirmatory evidence lies in its ultraviolet spectrum, with tetramethyl[2.2]paracyclophane (**8**)[1b] as a model (Fig. 2). The spectra of [2.2]paracyclophanes are characterized by loss of fine structure, bathochromic shifts, and decreased extinction coefficients relative to acyclic and larger cyclic models. These deviations have been associated with both benzene ring deformations and transannular effects.[17] In contrast to the spectrum of **15**, those of dimer **14** and hexamethylbenzene[18] display fine structure in the normal benzenoid region of 260–280 mμ. The spectrum of dimer **15** relative to that of dimer **8** exhibits, in addition to a small bathochromic shift (*ca.* 8 mμ), a significant increase in the extinction coefficients above 300 mμ. This difference is consistent with the suggestion that the longer wavelength bands in [2.2]paracyclophanes are associated with benzene ring deformations while the shorter wavelength bands are sensitive to transannular electronic effects.[7,17] Due to the rigidity of the [2.2]paracyclophane system, the severe overcrowding in **15** would be expected to alter primarily the benzene ring deformation rather than the transannular electronic interaction. A theoretical treatment of the ultraviolet spectra of overcrowded molecules is lacking; however, the spectroscopic results generally consist of bathochromic shifts, loss of vibrational structure, and, frequently, increased intensities.[19] The examination of other over-

---

(14) H. W. Bersch, K. H. Fischer, and A. v. Mletzko, *Arch. Pharm.*, **290**, 353 (1957).

(15) D. T. Longone, L. Simanyi, and J. Chow, unpublished results. The apparent contradictory results in the cited pyrolyses of *o*-methylbenzyltrimethylammonium hydroxide undoubtedly reflect differences in pyrolysis conditions.

(16) The linear "dihydrodimer," decamethylbibenzyl, is a known compound with m.p. 241–242°: W. J. Humphlett and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 3289 (1950).

(17) D. J. Cram, N. L. Allinger, and H. Steinberg, *ibid.*, **76**, 6132 (1954); D. J. Cram, R. H. Bauer, N. L. Allinger, R. A. Reeves, W. J. Wechter, and E. Heilbronner, *ibid.*, **81**, 5977 (1959); D. J. Cram and G. R. Knox, *ibid.*, **83**, 2204 (1961).

(18) G. H. Beaven and E. A. Johnson, *Spectrochim. Acta*, **14**, 67 (1959).

(19) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 448, 449.

crowded [2.2]paracyclophanes may establish the generality of a long wave-length hyperchromic effect in this ring system.

As was anticipated, dimer **15** is not very stable. Most isolation techniques result in significant losses. Pure material could be obtained only by rapid vacuum sublimation of crude samples. In solution, even at room temperature, and in the solid state the dimer slowly decomposes, evidenced by the formation of insoluble polymer and change in the melting point behavior. Stability is not perceptively improved through the use of an inert atmosphere. Decomposition presumably involves generation of a diradical *via* homolysis of a bridge bond and subsequent polymerization.

The instability of **15** indicates that it is formed in relatively good yield in the pyrolysis of **12**. Large losses must occur in the pyrolytic medium during the course of the reaction. The use of a low-pressure pyrolytic technique[11d] in which the *p*-xylylene **13** is removed from the reaction flask as it is generated would undoubtedly increase the yield of **15** substantially.

A study of the chemical reactivity of **15** as well as the attempted syntheses of other overcrowded [2.2]paracyclophanes is in progress.

Experimental[20]

Pentamethylbenzyl Bromide (10).—To a solution of 74.1 g. (0.500 mole) of pentamethylbenzene, 39.1 g. (1.30 moles) of paraformaldehyde, and 144 g. (1.40 moles) of sodium bromide in 280 ml. of glacial acetic acid at 80° was added dropwise and with stirring a mixture of 133 ml. of concentrated sulfuric acid and 130 ml. of glacial acetic acid. After total addition of the acid solution (4 hr.) the reaction mixture was stirred at *ca.* 90° for 1 hr., cooled, and then poured into 2 l. of ice–water. The solid product, tan in color, was removed by suction filtration and dried *in vacuo*. Distillation afforded 110 g. (91% yield) of product, b.p. 126–136° (0.3 mm.) and m.p. 79–81°. A portion was redistilled at 115–117° (0.2 mm.) to give an analytical sample with m.p. 84–85°.

Anal. Calcd. for $C_{12}H_{17}Br$: C, 59.76; H, 7.11. Found: C, 60.11; H, 7.17.

The infrared spectrum of the bromide is characterized by a very strong and sharp band at 1210 cm.$^{-1}$. This band may be characteristic of bromomethyl groups. We have examined a large number of aliphatic and aromatic bromomethyl compounds and find this band, usually the strongest in the spectrum, in the region 1205–1230 cm.$^{-1}$. We have noted a similar absorption (1150–1200 cm.$^{-1}$) in the case of iodomethyl compounds.[1a]

Bromide **10** was also obtained from the reaction of hexamethylbenzene (fivefold excess) in carbon tetrachloride with bromine, using essentially the procedure previously described.[21] In this case the benzyl bromide was not isolated; the reaction solids in ether solution were treated with anhydrous trimethylamine to afford crude quaternary ammonium bromide (86% based on bromine). The necessity of removing the large excess of hexamethylbenzene made this procedure less attractive.

Pentamethylbenzyltrimethylammonium Bromide.—A chilled solution of 3.6 g. (15 mmoles) of the benzyl bromide **10** in 50 ml. of ether was saturated with gaseous trimethylamine, depositing 4.0 g. (84% yield, as a monohydrate) of the quaternary ammonium bromide. Recrystallization from methanol–ether gave fine needles, m.p. 221–222°. The infrared spectrum (Nujol) reveals the presence of water of hydration (3500 cm.$^{-1}$).

Anal. Calcd. for $C_{15}H_{26}BrN \cdot H_2O$: C, 56.60; H, 8.87; N, 4.40. Found: C, 56.70; H, 8.89; N, 4.24.

The picrate, prepared in the usual manner, had m.p. 218.0–218.5°, after recrystallization from ethanol.

Anal. Calcd. for $C_{21}H_{28}N_4O_7$: C, 56.24; H, 6.29; N, 12.49. Found: C, 56.51; H, 6.34; N, 12.60.

Larger amounts of the quaternary ammonium bromide were conveniently prepared from bromomethylated pentamethylbenzene without prior purification of the benzyl bromide **10**. An ethereal solution of crude **10** (m.p. 71–74°), obtained from 48.8 g. (0.329 mole) of pentamethylbenzene and dried after precipitation from the reaction medium as described above, was washed with water and 0.5 *N* sodium hydroxide, dried over magnesium sulfate, and then saturated with gaseous trimethylamine. This treatment afforded 103.5 g. of the quaternary ammonium bromide, m.p. 211–220°. Recrystallization from ethanol–ether gave 89.3 g. with m.p. 219–221° and 6.2 g. with m.p. 217–219°; total yield was 91% based on pentamethylbenzene.

Pyrolysis of Pentamethylbenzyltrimethylammonium Hydroxide (12).—Pentamethylbenzyltrimethylammonium bromide was treated with freshly prepared silver oxide in the usual manner[12] to afford aqueous solutions of the hydroxide **12**. The limited solubility of the bromide in water (*ca.* 10 g./l. at room temperature) necessitated the use of large volumes of solvent. The resulting solutions of **12** were concentrated under reduced pressure and below 80°. In this manner, solutions containing 0.08 to 0.61 moles of **12** were prepared. While several eliminations were carried out under quite similar pyrolytic conditions, subsequent work-up and isolation of products involved variations in fractional recrystallizations and sublimations as well as column chromatographic separations. Once the desired dimer **15** had been tentatively identified and its thermal instability had been noted, it could be purified by sublimation from various crude samples, the latter derived from the gross separations indicated above. A synthesis of the optimum separation techniques evolved is outlined below as a general procedure.

An aqueous solution of **12** was added in portions (dropping funnel) to *ca.* 1.5 l. of hot toluene in a flask fitted with a Dean-Stark trap. During addition the mixture was stirred vigorously and the water was removed as rapidly as possible as the toluene–water azeotrope (84°). Evolution of trimethylamine was slow over this period but became quite vigorous once the water was removed and the temperature had risen to 110°. After *ca.* 2 hr., gas evolution diminished appreciably and became negligible after an additional 12 hr. at the reflux temperature. The reaction mixture was allowed to cool and the polymer (m.p. >360° dec.,[22] yield 20–60%), which had precipitated during the course of the reaction, was removed by suction filtration. A portion of the filtrate was tested for the presence of unsaturated species and found to decolorize negligible amounts of bromine. The filtrate was concentrated under diminished pressure and then chilled in ice to afford crystals of relatively pure alcohol **16**. The alcohol was removed and pentane was added to the filtrate to precipitate more alcohol along with smaller amounts of other reaction products. Separation of these solids and removal of solvent from the resulting filtrate provided a hydrocarbon-enriched, semisolid residue. Portions of this residue were dissolved in carbon tetrachloride and rapidly chromatographed (silica gel, pentane) to afford, in order, a hydrocarbon fraction containing dimers **14** and **15**, ether **17**, an unidentified carbonyl-containing (1755 cm.$^{-1}$) oil,[23] and alcohol **16**.

The hydrocarbon fraction appeared (infrared and n.m.r. spectra) to contain only paracyclophane **15** and dimer **14**, the former predominating. The combined yield of dimers was about 5% based on quaternary ammonium bromide. Separations of **14** and **15** by column chromatography (silica gel, pentane) were generally successful in that the last fractions off the column contained **15** free from **14**; however, this treatment as well as subsequent recrystallizations of **15** at or above room temperature resulted in noticeable losses of product through the formation of insoluble polymer. A satisfactory final purification of **15** was accomplished with a minimum of loss by rapid sublimation (140–190° and 0.1 mm.) of chromatographic fractions. The sublimate

---

[20] All melting points are uncorrected. The infrared spectra were obtained with a Perkin-Elmer Infracord or a Perkin-Elmer spectrophotometer, Model 21; the ultraviolet spectra with a Cary spectrophotometer, Model 11; the n.m.r. spectra with a Varian A-60 instrument. We are indebted to Mr. B. E. Wenzel and Mr. F. Parker for much of the spectral work. Analyses were by Spang Microanalytical Laboratory, Ann Arbor, Mich. and Schwarzkopf Microanalytical Laboratory, New York, N. Y.

[21] J. R. Sampey, F. C. Fawcett, and B. A. Morehead, *J. Am. Chem. Soc.*, **62**, 1839 (1940). These workers did not carry out a preparative reaction. Pentamethylbenzyl bromide was not characterized nor even isolated from the bromination medium.

[22] Poly(tetramethyl-*p*-xylylene) obtained from the coupling reactions of *p*-di(halomethyl)durenes softens above 400°: J. H. Golden, *J. Chem. Soc.*, 1604 (1961). The lower melting point exhibited by our polymer may be due to the incorporation of tetramethyl-*o*-xylylene units into the polymer chains.

[23] A similar oil is produced in the pyrolysis of *o*-methylbenzyltrimethylammonium hydroxide (ref. 11d).

was recrystallized from carbon tetrachloride–acetone (1:5) at −78° to afford sharp-melting product which was immediately utilized for physical and analytical characterization.

Octamethyl[2.2]paracyclophane (15).—After sublimation and recrystallization as described above, this dimer had m.p. 316–318°. Its infrared spectrum exhibits bands (KBr, cm.$^{-1}$) at 2985 s, 2925 s, 2880 s, 1560 m, 1480 s, 1430 s, 1385 s, 1250 m, 1192 m, 1170 m, 1057 m, 1003 m, 983 m, and 726 s; ultraviolet (isooctane, see Fig. 2), λ_{max} 233 (log ϵ 4.21), 257 sh (3.69), and 307.5 mμ (2.84).

Anal. Calcd. for $C_{24}H_{32}$: C, 89.94; H, 10.06; mol. wt., 320. Found: C, 89.80; H, 10.00; osmometric mol. wt., 323.

After storage at 0° for periods of weeks to months, the melting point of the dimer was gradually lowered and broadened.

Octamethyldibenzocyclooctadiene (14).—All samples of this material contained varying amounts of **15** as a contaminant (spectra); no strong efforts were made to obtain pure material. Our best sample had m.p. 184–186°. The structural assignment of this product is based on its n.m.r. (see text) and ultraviolet spectra. The latter exhibits fine structure in the normal benzenoid region with λ_{max} (isooctane) 255 sh, 259 sh, 263, 267, 272, 276, and 281 mμ. While the spectral data define equally well the "monomeric" hydrocarbon, tetramethylbenzocyclobutene, both the high melting point of the product and the temperature of the reaction medium[11b] in which it is formed argue against this assignment.

Dimer **14** is most readily characterized in the infrared region by bands (Nujol, cm.$^{-1}$) at 1280 m, 1240 m, and 775 s.

Pentamethylbenzyl Alcohol (16).—This alcohol, along with polymer, represents the major product of the elimination reaction. It was isolated by precipitation from the reaction filtrate in yields as high as 20%; spectral examination of unresolved reaction mixtures indicated its formation in total yields of about 30–65%. After recrystallization from benzene–isooctane (1:4) it had m.p. 160.0–160.5° (lit.[24] m.p. 160.5°).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.77; H, 10.21.

The infrared spectrum of **16** exhibits strong bands (Nujol, cm.$^{-1}$) at 3320 and 1000 (CH_2OH), 1215, 1075, 1025 sh, 965 sh, and 805. The n.m.r. spectrum (carbon tetrachloride, 65°) has singlets at τ 5.31 (CH_2), 7.69 and 7.79 (CH_3), and 9.12 (OH).

Pentamethylbenzyl Ether (17).—This compound is a minor product (*ca.* 2–4% yield) of the reaction and had, after recrystallization from benzene–isooctane (1:4), m.p. 178–179° (lit.[25] m.p. 168°).

Anal. Calcd. for $C_{24}H_{34}O$: C, 85.15; H, 10.12. Found: C, 84.78; H, 10.06.

The infrared spectrum of **17** has bands (Nujol, cm.$^{-1}$) at 1355, 1085, 1040, and 1000 (all strong), 1580, 1510, 1235, 800, 725, and 715 (all medium). Its n.m.r. spectrum (carbon tetrachloride, 65°) has singlets at τ 5.39 (CH_2), and 7.72 and 7.79 (CH_3).

---

[24] O. Jacobsen, *Ber.*, **22**, 1215 (1889).

[25] R. Willstätter and H. Kubli, *ibid.*, **42**, 4151 (1909).

Condensations at the Methyl Group of Ethyl Acetoacetate by Means of Potassium Amide or Sodium Hydride[1]

JAMES F. WOLFE, THOMAS M. HARRIS, AND CHARLES R. HAUSER

Chemistry Department, Duke University, Durham, North Carolina

Received May 15, 1964

Certain condensations at the methyl group rather than at the more acidic methylene group of ethyl acetoacetate were effected through its dicarbanion, which was prepared by means of potassium amide in liquid ammonia. The dicarbanion was condensed with benzophenone to form the δ-hydroxy-β-keto ester which could be dehydrated to give the γ,δ-unsaturated β-keto ester. The dicarbanion also underwent alkylation and benzoylation at the γ-position, but the yields were low and alkylation failed with certain halides. Terminal aroylation of ethyl acetoacetate with ethyl benzoate was achieved by means of sodium hydride, but the corresponding β-diketone acid, instead of the β-diketone ester, was obtained.

Earlier papers have described condensations at the methyl group of such diketones as benzoylacetone and acetylacetone through their dicarbanions I, which were prepared by means of 2 mol. equiv. of potassium amide in liquid ammonia. For example, I was alkylated with benzyl chloride,[2] aroylated with methyl benzoate,[2] and condensed with benzophenone (aldol type)[3] to form terminal derivatives II, in which A is the appropriate group.

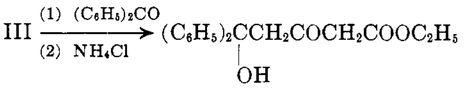
$$\underset{\text{I}}{RCO\bar{C}HCO\bar{C}H_2} \qquad \underset{\text{II}}{RCOCH_2COCH_2\text{-}A}$$

A recent paper has described similar terminal alkylations of the dicarbanions of acetoacetaldehyde and α-benzylacetoacetaldehyde.[4]

The present investigation has extended this novel mode of condensation to ethyl acetoacetate, which was converted to its dicarbanion III by treatment with 2 equiv. of potassium amide (eq. 1).

$$CH_3COCH_2COOC_2H_5 \xrightarrow[\text{liq. }NH_3]{2KNH_2} \underset{\text{III}}{\bar{C}H_2CO\bar{C}HCOOC_2H_5} \qquad (1)$$

Terminal aldol condensation of III was effected with benzophenone to form δ-hydroxy-β-keto ester IV in 50% yield (eq. 2). This reaction furnishes a good



$$\text{III} \xrightarrow[\text{(2) }NH_4Cl]{\text{(1) }(C_6H_5)_2CO} \underset{\substack{| \\ OH}}{(C_6H_5)_2C}CH_2COCH_2COOC_2H_5 \qquad (2)$$

IV

method for the synthesis of IV, which appears to be a new compound. Structure IV was supported by analysis and by absorption spectra. The spectra indicated that IV existed largely in the keto form. The infrared spectrum showed bands at 2.9, 5.75, and 5.85 μ for the hydroxyl,[5] ester,[6] and ketone[7] groups, respectively. The n.m.r. spectrum showed absorption for ten aromatic protons centered at 7.27 p.p.m., along with a triplet and a quartet centered at 1.20 and 4.10 p.p.m., respectively, characteristic of the methyl and methyl-

---

[1] Supported by the National Science Foundation.

[2] C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

[3] R. J. Light and C. R. Hauser, *J. Org. Chem.*, **26**, 1716 (1961).

[4] T. M. Harris, S. Boatman, and C. R. Hauser, *J. Am. Chem. Soc.*, **85**, 3273 (1963).

[5] See L. J. Bellamy, "Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 96.

[6] See ref. 5, p. 179.

[7] See ref. 5, p. 134.