

108–116°, from the hexane extract. The latter was treated with diazomethane and the mixture of esters chromatographed on alumina. Petroleum ether elution gave 160 mg. (10%) of liquid methyl ester of the dihydro acid Xa, whose infrared spectrum was identical with that of an authentic specimen prepared by diazomethane esterification of a pure sample of Xa. Further petroleum ether elution yielded 20 mg. (1%) of methyl 1-methyl-3-naphthoate, m.p. 38–40° after crystallization from hexane.

(d) **Potassium *t*-Butoxide in *t*-Butanol.**—A potassium *t*-butoxide solution (0.2 g. of potassium in 30 ml. of *t*-butyl alcohol) of 1.50 g. of ketone was stirred at room temperature under nitrogen for 24 hr. The reaction mixture was diluted with water and extracted with ether. Drying and evaporation of the extract, alumina chromatography of the oily residue and elution with petroleum ether gave 0.86 g. of an inseparable oily mixture exhibiting 5.60 and 5.85 μ infrared peaks. Repeated alumina chromatography partly destroyed the 5.60 μ absorbing substance. The initial aqueous solution was acidified with 1 *N* hydrochloric acid and extracted with ether. Drying of the extract over magnesium sulfate and evaporation left 320 mg. (27%) of acid, m.p. 89–90°, which on crystallization from hexane afforded the dihydro-naphthoic acid Xa, m.p. 91–92.

Alkali Treatments of 1-Methyl-3,4-dihydro-3-naphthoic Acid (Xa) and Its Ester.—Refluxing of a sodium methoxide solution (10 mg. of sodium in 15 ml. of dry methanol) of 200 mg. of the acid Xa and the aforementioned work-up gave 192 mg. (96%) of starting material.

A sodium methoxide solution (10 mg. of sodium in 15 ml. of absolute methanol) of the methyl ester of Xa, prepared by diazomethane treatment of 250 mg. of acid Xa, was refluxed under nitrogen for 4 hr. The solution was diluted with water and extracted with ether. Drying of the extract over magnesium sulfate and evaporation led to 95 mg. of neutral oil whose ultraviolet spectrum revealed it to be a mixture of the methyl esters of Xa and IV. The basic aqueous solution was acidified with 1 *N* hydrochloric acid and extracted with ether. Similar work-up of this extract led to 112 mg. (45%) of 1-methyl-3-naphthoic acid, m.p. 195–198° after crystallizations from carbon tetrachloride-hexane and aqueous methanol.

1-Methyl-1,2,3,4-tetrahydro-3-naphthoic Acid (XV).—A solution of 400 mg. of ketone Ib¹² in 20 ml. of ethanol was hydrogenated exhaustively over 20 mg. of 5% palladium-charcoal at room temperature and atmospheric pressure.

Filtration of the catalyst, vacuum removal of the solvent, alumina chromatography of the oily residue and petroleum ether elution gave 230 mg. of liquid tetralone IIb, infrared spectrum (CCl₄), C=O 5.85(s) μ ; orange 2,4-dinitrophenylhydrazone, m.p. 177–178° after crystallization from ethanol-ethyl acetate. The ketone was used in the next experiment without further purification.

A potassium *t*-butoxide solution (60 mg. of potassium in 30 ml. of dry *t*-butyl alcohol) of 200 mg. of ketone IIb was stirred under nitrogen for 8 hr. The usual work-up yielded 94 mg. of an oily neutral mixture exhibiting 5.60 and 5.85 μ infrared peaks and an acidic fraction which on sublimation gave 67 mg. (37%) of an acid, m.p. 105–109°. Two crystallizations of the latter from hexane afforded acid XV, m.p. and m.m.p. 123–125° (*vide infra*).

A solution of 100 mg. of acid Xa in 20 ml. of ethanol was hydrogenated over 10 mg. of palladium-charcoal at room temperature and atmospheric pressure. Filtration of the catalyst and vacuum removal of the solvent yielded 94 mg. (94%) of solid. Crystallization of the product from hexane gave 1-methyl-1,2,3,4-tetrahydro-3-naphthoic acid (XV), m.p. 124–125; ultraviolet spectrum (95% ethanol), λ_{max} 266 m μ (ϵ 532), 273 m μ (ϵ 548) and λ_{min} 248 m μ (ϵ 242) and 270 m μ (ϵ 333).

Anal. Calcd. for C₁₂H₁₄O₂: C, 75.76; H, 7.42. Found: C, 75.94; H, 7.42.

Cyclobutanone XXI–XXII.—A potassium *t*-butoxide solution (4.1 g. of potassium in 200 ml. of *t*-butyl alcohol) of 19.5 g. of 2-methyl-2-dichloromethylcyclohexanone (XX), m.p. 33–35°,¹⁸ was stirred under nitrogen for 24 hr. The usual work-up led to 15.0 g. of neutral products exhibiting 5.60 and 5.85 μ infrared absorption bands. Three vacuum distillations gave 7.0 g. of pure cyclobutanone XXI–XXII, b.p. 45° (0.07 mm.); infrared spectrum (CCl₄), C=O 5.60 (s) μ .

Anal. Calcd. for C₈H₁₁OCl: C, 60.55; H, 6.99. Found: C, 61.00; H, 7.24.

The infrared spectra of all other distillation fractions showed them to contain mostly starting ketone XX and some more product XXI–XXII.

The cyclobutanone could be converted in 80% yield into its semicarbazone, m.p. 234–235° after crystallization from aqueous methanol.

Anal. Calcd. for C₈H₁₁ON₂Cl: C, 50.11; H, 6.54; Cl, 16.44. Found: C, 49.96; H, 6.93; Cl, 16.92.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER 20, N. Y.]

Syntheses of 4,12-Dimethyl[2.2]metacyclophane

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Two syntheses of 4,12-dimethyl[2.2]metacyclophane (IV) are described.

Undoubtedly, one of the most stimulating concepts introduced into aromatic chemistry is the generalization from simple molecular orbital theory known as the Hückel rule.⁵ This requirement that aromatic stability in conjugated, planar, monocyclic polyenes is associated with those molecules having $4n + 2\pi$ electrons has been amply confirmed by Doering,⁶ Dauben,⁷ Dewar⁸ and

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(2) Alfred P. Sloan Foundation Postdoctoral Fellow, 1956–1957.
(3) Alfred P. Sloan Foundation Postdoctoral Fellow, 1957–1958.
(4) To whom inquiries should be addressed: University of Oregon, Eugene, Ore.

(5) E. Hückel, *Z. Elektrochem.*, **43**, 752 (1937).
(6) W. von E. Doering and L. H. Knox, *THIS JOURNAL*, **76**, 3203 (1954). For a summary, see W. von E. Doering, "Theoretical Organic Chemistry (Kekulé Symposium)," Butterworth Scientific Publications, London, 1959, p. 35.

(7) H. J. Dauben, Jr., and H. Ringold, *THIS JOURNAL*, **73**, 876 (1951), and related papers.

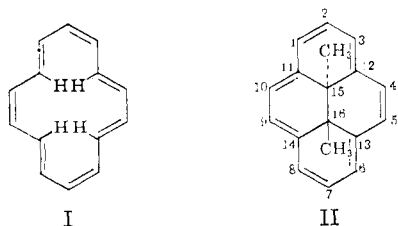
Breslow⁹ for small rings and observations by Sondheimer¹⁰ indicate it for large rings. However, testing the Hückel rule with rings of intermediate size presents both synthetic and theoretical difficulties. Molecular models indicate that in the case of compounds such as cyclotetradecaheptaene (I) the steric interference of the *internal* hydrogens would be sufficiently great to cause twisting and result in an appreciable deviation of the conjugate unsaturation from planarity. However, the presence of saturated atoms within a π -electron cloud should not in itself affect appreciably the delocalization energy.

(8) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2021, 2026 (1956), and related papers.

(9) (a) R. Breslow and C. Yuan, *THIS JOURNAL*, **80**, 5991 (1958); (b) R. Breslow and H. Höver, *ibid.*, **82**, 2644 (1960); see also, D. G. Farnum and M. Burr, *ibid.*, **82**, 2651 (1960).

(10) F. Sondheimer and R. Wolovsky, *Tetrahedron Letters*, **3**, (No. 3) (1959).

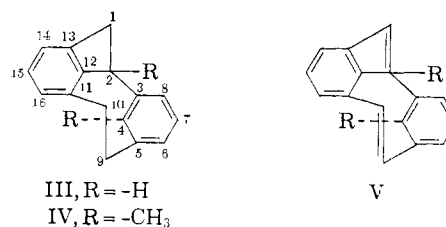
Thus, if in place of each pair of *internal* hydrogen atoms there is substituted a saturated carbon atom in an appropriate fashion, the peripheral conjugate polyene system can again become essentially planar. Although a number of compounds with internal saturated atoms and a near-planar peripheral conjugated system appear plausible, the work to be described was directed toward the synthesis of a particularly likely example, *trans*-15,16-dimethyl-15,16-dihydropyrene (II).



A simple and obvious route for the synthesis of II would be the methylation of the dianion derived from pyrene. This seemed particularly attractive since Neunhoeffer and Woggen¹¹ have claimed that treatment of pyrene with sodium followed by acidification yields 15,16-dihydropyrene. Our attempts to alkylate the sodium adduct of pyrene with methyl iodide led to complex mixtures of which the predominant product appeared to be 4-methyl-4,5-dihydropyrene. Its assignment of structure is based on spectral evidence as well as its dehydrogenation under mild conditions to 4-methylpyrene.¹² With a more reactive halide, allyl bromide, the reaction with the sodium adduct of pyrene appeared less complex but again the predominant product, as indicated from spectral data, was 4-allyl-4,5-dihydropyrene. In our hands, the simple acidification of the sodium adduct of pyrene gave a complex mixture and we could obtain no positive evidence for the presence of 15,16-dihydropyrene.

With the abandonment of the direct approach from pyrene, preliminary studies were made of several possible routes for the synthesis of II and of these the use of 4,12-dimethyl[2.2]metacyclophane has appeared to be most promising. Both from chemical studies^{13a} and from X-ray crystallographic data^{13b} it is known for certain that [2.2]-metacyclophane, which was first prepared by Pellegrin in 1899,¹⁴ is correctly represented by the three-dimensional projection III. From molecular models of III it can be seen that the two benzene rings are arranged in a stepwise fashion with carbon 12 being directly over carbon 4. Thus, the hydrogens at the 4- and 12-positions do not interfere with each other but instead project out over the face of the neighboring benzene ring. The effects of this unusual relationship are clearly evident in the n.m.r. spectrum of [2.2]metacyclophane.¹⁵ The ring current in the neighboring

benzene ring causes a chemical shift of about 3 τ units to higher field for the signal of the 4- and 12-protons at 60 Mc. It is apparent that replacing the hydrogens at the 4- and 12-positions by more bulky substituents such as methyl should have only a slight effect in increasing steric interactions. Also the close proximity of the 4- and 12-carbon atoms should make bond formation between them a very facile process. That this is true is evident from the easy conversion of [2.2]metacyclophane to pyrene both under catalytic dehydrogenation conditions^{13a} and during attempted bromination.¹⁶ As a logical deduction, then, it would be expected that an unsaturated (2.2)metacyclophane such as V would spontaneously reorient itself to give the more stable arrangement shown by II. Therefore, the objective of the present study has been to devise a satisfactory synthesis of V.



Previous syntheses of (2.2)metacyclophane have utilized the Wurtz reaction between *m*-xylyl dibromide and sodium.^{13a,14} Müller and Röscheisen improved the procedure by adding tetraphenylethylene to permit a homogeneous reaction.¹⁷ In our hands, the latter procedure has proved a reliable and convenient method, giving (2.2)metacyclophane in about 33% yield. The preparation of 2,6-di-(bromomethyl)-toluene (IX) was readily accomplished starting with 2-nitro-6-chlorotoluene and is outlined in Scheme 1. Treatment of IX with sodium under the conditions used previously with *m*-xylyl dibromide gave 4,12-dimethyl[2.2]metacyclophane (IV) in 4% yield. In addition, the dibenzyl derivative X was isolated in 1.8% yield. Since analytical data and molecular weight determinations do not distinguish satisfactorily between IV and X, additional evidence regarding their structures was needed. As will be described later, each of these hydrocarbons has been synthesized separately by an alternate method and there can be little doubt about the correctness of their structural assignments.¹⁵

The n.m.r. spectrum of IV is in good accord with its structure.¹⁵ Again, the signal due to the 4- and 12-methyl groups shows a strong chemical shift to high field due to the ring current in the neighboring benzene ring and is found at 9.44 τ units whereas the methyl resonances for toluene

(15) D. J. Wilson, V. Boekelheide and R. W. Griffin, Jr., *THIS JOURNAL*, **83**, in press (1961).

(16) V. Boekelheide, W. S. Lindsay and R. W. Griffin, Jr., unpublished results.

(17) E. Müller and G. Röscheisen, *Ber.*, **90**, 543 (1957).

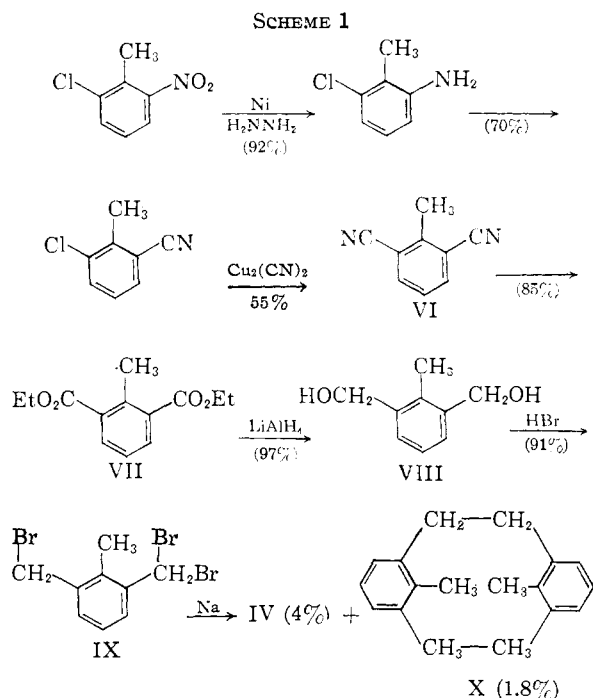
(11) O. Neunhoeffer and H. Woggen, *Angew. Chem.*, **386** (1954); see also, O. Neunhoeffer and H. Woggen, *Ann.*, **600**, 34 (1956).

(12) We are indebted to Professor M. S. Newman for an authentic sample of 4-methylpyrene for comparison.

(13) (a) W. Baker, J. F. W. McOmie and J. M. Norman, *J. Chem. Soc.*, 1114 (1951); (b) C. J. Brown, *ibid.*, 3278 (1953).

(14) M. Pellegrin, *Rec. trav. chim.*, **18**, 458 (1899).

(18) Although two spatial arrangements—with the benzene rings stepwise and *trans* or with the benzene rings over each other and *cis*—are possible, our assignment of the *trans* arrangement as in IV has been made by analogy with [2.2]metacyclophane¹⁴ and on the basis that the n.m.r. data are compatible only with IV. An X-ray crystallographic study of this compound is currently in progress.

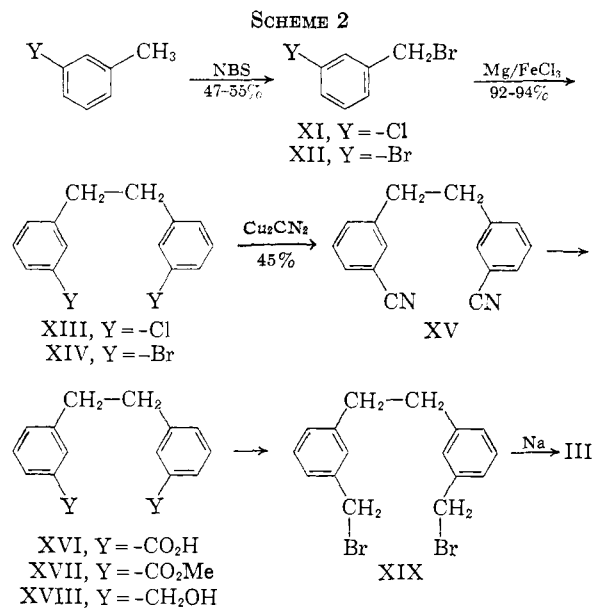


and the xylenes occur in the range of 7.6–7.8 τ . The n.m.r. spectrum thus provides strong support for the spatial representation given by IV and from this model it is perfectly understandable why bulkier groups than hydrogen can be placed at the 4- and 12-positions without undue steric interference.

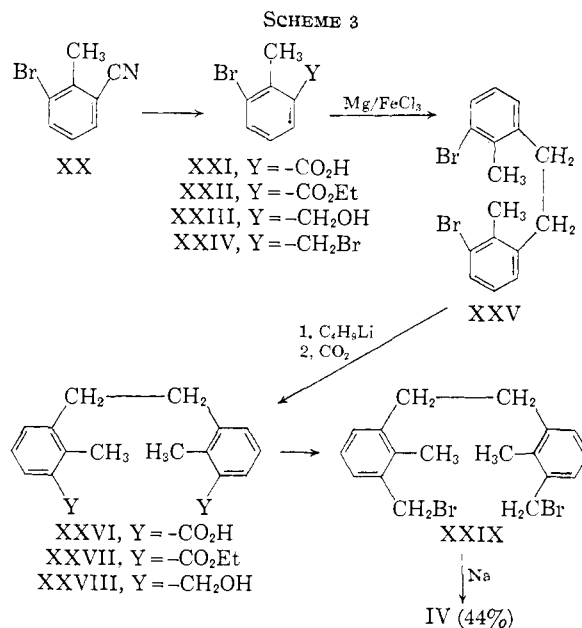
Although the method outlined above was successful, the final step involving the dimerization of IX proceeded in rather low yield. Since the dimerization must involve a two-stage process with its attendant possibilities for side reactions, it was decided to explore an approach utilizing a dibenzyl as an intermediate. In this case the final ring closure would require the formation of only one bond. The synthesis of [2.2]metacyclophane was studied first using this approach and the reaction scheme employed for its preparation is outlined in Scheme 2.

The final step in Scheme 2, the ring closure of XIX with sodium, proceeded in high yield (77%). Even though it had been expected that this step would be an improvement over the dimerization reaction with *m*-xylyl dibromide, it is surprising that the formation of a *meta*-bridged, ten-membered ring should occur so easily without the use of a high-dilution technique.

With this result we were encouraged to reinvestigate the synthesis of 4,12-dimethyl[2.2]metacyclophane (IV) using an approach involving ring closure of the appropriate dibenzyl and the reaction sequence used is outlined in Scheme 3. The starting material, 2-bromo-6-cyanotoluene (XX), was obtained in a straight-forward manner in two steps from the 2-chloro-6-aminotoluene used in Scheme 1. As given in Scheme 3, the successive steps in the synthesis are indicated by the numbered compounds and each of these reactions proceeded easily and in high yield. The final stage, the ring closure of XXIX, again occurred smoothly to give



4,12-dimethyl[2.2]metacyclophane (IV) in 44% yield. It is apparent that this method is quite a feasible one for preparing variously substituted (2.2)metacyclophanes when the appropriate dibenzyls can be provided in a reasonable fashion. The fact that the hydrocarbon IV from Scheme 3 was identical with that from Scheme 1 also provides good evidence for its assigned structure.



The availability of the intermediate diol XXVIII in Scheme 3 made it possible to carry out a convenient synthesis and proof of structure of the hydrocarbon X. When XXVIII was subjected to hydrogenation over a palladium-on-charcoal catalyst, it was converted to X in good yield, its identity being established by spectral comparison and a mixture melting point determination.

The further conversion of 4,12-dimethyl[2.2]metacyclophane to V would appear to be analogous to the conversion of [2.2]paracyclophane to the

corresponding diolefin, an elegant accomplishment reported recently by Dewhirst and Cram.¹⁹ However, despite much effort, we have been unable to duplicate this conversion in the (2.2)metacyclophane series. Treatment of 4,12-dimethyl[2.2]-metacyclophane (IV) under conditions designed to effect radical bromination led either to recovery of starting material or, under forcing conditions, to bromination in the benzene rings.¹⁷ Likewise, attempts to effect substitution at the methylene bridging atoms of IV with other reagents that involve intermediate radicals such as *t*-butyl hypochlorite,²⁰ lead tetraacetate and cumene hydroperoxide and cuprous chloride²¹ were without success. Also, oxidation of the methylene bridge was tried under various conditions including vanadium pentoxide-hydrogen peroxide,²² chromium trioxide and selenium dioxide but to no avail.

The dehydrogenation of [2.2]metacyclophane to pyrene was studied and the most favorable conditions found were applied to 4,12-dimethyl(2.2)-metacyclophane. This led to recovery of starting material and, when more forcing conditions were employed, pyrene was again formed.

After the present study was completed, a report by Baker, Buggle, McOmie and Watkins appeared describing 4,12-diaza(2.2)metacyclophane and work directed toward the over-all goal of the synthesis of 15,16-diaza-15,16-dihdropyrene.^{22a} Although their objective represents an extremely interesting compound, it should be pointed out that it would not constitute a test of the Hückel rule in intermediate-sized rings as would *trans*-15,16-dimethyl-15,16-dihdropyrene, since the *p*-electrons on nitrogen would undoubtedly become involved in the aromatic π -electron system.

Experimental²³

Methylation of the Sodium-Pyrene Adduct.—A mixture of 6.0 g. of pyrene in 150 ml. of 1,2-dimethoxyethane and 1.50 g. of sodium was boiled under reflux for 3 hr., cooled, and 4.2 g. of methyl iodide was added. The red color of the sodium-pyrene adduct was discharged and a precipitate of sodium bromide appeared. After removal of the precipitate and concentration of the filtrate, the residual oil was taken up in *n*-pentane and chromatographed over Woelm neutral alumina. From the later stages of the elution there was recovered 4.1 g. of pyrene. However, the first eluate contained 1.1 g. of a colorless oil, λ_{max} 215 (log ϵ , 4.46), 253 (4.44), 260 (4.55), 272 (4.50), 288 (3.82), 300 (3.82) and 340 μ (3.46). Although its spectrum is in reasonable agreement with that of a 4,5-dihdropyrene derivative, the analytical data indicated the oil to be a mixture containing more highly hydrogenated material (*Anal.* Calcd. for $\text{C}_{17}\text{H}_{14}$: C, 93.53; H, 6.47. Calcd. for $\text{C}_{17}\text{H}_{18}$: C, 91.84; H, 8.16. Found: C, 91.52; H, 8.01). Treatment of this oil with chloranil in boiling toluene converted it in high yield to a crystalline solid, m.p. 146–147°. The ultraviolet and infrared spectra of this solid, as well as its composition, indicated it to be a methylpyrene. Com-

parison with an authentic sample of 4-methylpyrene obtained from Professor Newman¹² both in their infrared spectra and by a mixture melting point determination showed them to be identical.

Allylation of the Sodium-Pyrene Adduct.—A mixture of 5.0 g. of pyrene and 1.25 g. of sodium in 150 ml. of 1,2-dimethoxyethane was boiled under reflux for 3 hr., cooled to -20° , and 10 g. of allyl bromide in 25 ml. of 1,2-dimethoxyethane was added slowly. The red color of the sodium-pyrene adduct was discharged and a precipitate of sodium bromide formed. The precipitate of sodium bromide was collected by filtration and the filtrate was concentrated leaving an oily residue. This was taken up in *n*-pentane and chromatographed on Woelm alumina. From the later fractions of eluate, 3.5 g. of pyrene was recovered, whereas the first eluate gave 0.80 g. of a colorless oil. The ultraviolet absorption spectrum of this oil agreed very closely with that of 4,5-dihdropyrene. When 600 mg. of the oil was subjected to hydrogenation over Adams catalyst using acetic acid as solvent at room temperature and atmospheric pressure, the hydrogen uptake corresponded to addition of one molecule of hydrogen. After removal of catalyst and solvent, the residual oil was distilled to give 500 mg. of a colorless oil, b.p. 140° at 10^{-3} mm., whose ultraviolet absorption spectrum was still in accord with that for a 4,5-dihdropyrene. It is therefore assigned the structure of 4-*n*-propyl-4,5-dihdropyrene.

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}$: C, 92.63; H, 7.37. Found: C, 92.25; H, 7.40.

2,6-Dicyanotoluene (VI).—The conversion of 2-chloro-6-nitrotoluene to 2-chloro-6-aminotoluene was carried out using Raney nickel and hydrazine according to the directions of Balcolm and Furst²⁴ and was accomplished in 92% yield. The further conversion of 2-chloro-6-aminotoluene to 2-chloro-6-cyanotoluene *via* the Sandmeyer reaction was done according to Weissberger, Bach and Strasser²⁵ and proceeded in 70% yield. Replacement of the chlorine atom with cyanide in the von Braun reaction was then carried out according to the procedure used by Newman for α -bromonaphthalene.²⁶ A mixture of 22.0 g. of 2-chloro-6-cyanotoluene, 18.0 g. of cuprous cyanide and 13 ml. of pyridine was heated at $230\text{--}240^\circ$ for 12 hr. in a nitrogen atmosphere. The warm mixture was then poured into 160 ml. of concd. ammonium hydroxide and 100 ml. of benzene was added. After the further addition of 100 ml. of ether with shaking, the solution was filtered and the benzene filtrate was washed successively with ammonium hydroxide, water, dilute acid and water. Concentration of the benzene extract gave a solid which, after recrystallization from ethanol, yielded 11.4 g. of flat needles, m.p. $134\text{--}135^\circ$.

Anal. Calcd. for $\text{C}_8\text{H}_6\text{N}_2$: C, 76.04; H, 4.25. Found: C, 76.15; H, 4.51.

Diethyl 2-Methylisophthalate (VII).—The hydrolysis of 2,6-dicyanotoluene (VI) was accomplished by boiling it with 20% aqueous potassium hydroxide for 5 hr. and gave after acidification 2-methylisophthalic acid in 87% yield as white crystals, m.p. $228\text{--}229^\circ$.²⁷ Esterification was effected by dissolving 28.5 g. of 2-methylisophthalic acid in 50 ml. of ethanol and 200 ml. of benzene, adding 10 ml. of sulfuric acid, and removing the water by azeotropic distillation. After 24 hr., the mixture was poured into water and the benzene layer was separated. The benzene extract was washed successively with aqueous sodium carbonate and water, and then dried. Concentration of the benzene solution followed by distillation of the residue gave 36.0 g. (96%) of a colorless oil, b.p. 143° at 1 mm.

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{O}_4$: C, 66.08; H, 6.83. Found: C, 66.02; H, 6.93.

2,6-Di-(hydroxymethyl)-toluene (VIII).—To a solution of 11.0 g. of lithium aluminum hydride in 200 ml. of ether there was added dropwise with stirring a solution of 29.0 g. of diethyl 2-methylisophthalate in 100 ml. of ether and the mixture was boiled under reflux for 3 hr. After decomposition of the excess lithium aluminum hydride with

(19) K. C. Dewhirst and D. J. Cram, *THIS JOURNAL*, **80**, 3115 (1958).

(20) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 386; see also, C. Walling, Abstracts of XVI National Symposium on Organic Chemistry, Seattle, Wash., 1959.

(21) M. S. Kharash and A. Fono, *J. Org. Chem.*, **23**, 324 (1958).

(22) W. Treibs, G. Franke, G. Leichsenring and H. Röder, *Ber.*, **86**, 616 (1953).

(22a) W. Baker, K. M. Buggle, J. F. W. McOmie and D. A. M. Watkins, *J. Chem. Soc.*, 3594 (1958).

(23) All melting points are corrected. Analyses by Micro-Tech Laboratories, Skokie, Ill., and Miss A. Smith.

(24) D. Balcolm and A. Furst, *THIS JOURNAL*, **75**, 4334 (1953).

(25) A. Weissberger, H. Bach and E. Strasser, *J. Chem. Soc.*, 68 (1935).

(26) M. S. Newman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 631.

(27) C. Graebe and Fr. Bossel, *Ann.*, **290**, 206 (1896), report the m.p. as $228\text{--}230^\circ$.

ethyl acetate, dilute sulfuric acid was added and the ether layer separated. Concentration of the ether extract left a solid residue which, after recrystallization from water, gave 18.3 g. (97%) of white needles, m.p. 123–124°.

Anal. Calcd. for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.88; H, 7.91.

2,6-Di-(bromomethyl)-toluene (IX).—A solution of 16.2 g. of 2,6-di-(hydroxymethyl)-toluene (VIII) in 100 ml. of 48% hydrobromic acid was heated at 50° for 0.5 hr. When the solution was cooled, the oil which had separated solidified. After the solid had been collected by filtration, it was taken up in *n*-hexane and chromatographed over Woelm alumina. The solid obtained from the eluate was recrystallized from *n*-hexane to give 26.9 g. (91%) of white crystals, m.p. 94–95°.

Anal. Calcd. for $C_9H_{10}Br_2$: C, 38.87; H, 3.60. Found: C, 39.07; H, 3.65.

4,12-Dimethyl(2.2)metacyclophane (IV).—To a stirred suspension of 4.0 g. of sodium in 150 ml. of boiling dioxane there was added dropwise over a period of 5 hr. a solution of 13.0 g. of 2,6-di-(bromomethyl)-toluene in 50 ml. of dioxane. After the addition was complete, the mixture was boiled under reflux for an additional 12 hr. Then the solution was decanted from the excess sodium and concentrated. Steam distillation of the residue gave 426 mg. (7.2%) of steam-volatile hydrocarbon. This was taken up in *n*-pentane and chromatographed over Woelm alumina. From the first eluate there was isolated 220 mg. (4%) of white crystals, m.p. 204–205°, whose composition and molecular weight are in agreement with that required for 4,12-dimethyl-(2.2)metacyclophane.

Anal. Calcd. for $C_{13}H_{20}$: C, 91.47; H, 8.53; mol. wt., 236. Found: C, 91.27; H, 8.60; mol. wt. (Signer, benzene), 236.

From the later eluates there was isolated 100 mg. (1.8%) of white crystals, m.p. 108–108.5°, whose composition and molecular weight are in agreement with that required for 2,2',3,3'-tetramethylbibenzyl (X).

Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30; mol. wt., 238. Found: C, 90.57; H, 9.61; mol. wt., 238. Found: C, 90.57; H, 9.61; mol. wt. (Signer, benzene), 235.

3,3'-Dichlorobibenzyl (XIII).—Treatment of *m*-chlorotoluene with *N*-bromosuccinimide gave *m*-chlorobenzyl bromide (XI) in 55% yield as an oil, b.p. 110–112° at 12 mm., m.p. 15°. A solution of 17.6 g. of *m*-chlorobenzyl bromide in 50 ml. of ether was warmed with 1.07 g. of magnesium turnings until ebullition occurred. Anhydrous ferric chloride (100 mg.) was added with rapid stirring causing the onset of a vigorous reaction. When the reaction had subsided somewhat, heating was begun and the mixture was boiled under reflux for 1 hr. It was then cooled and acidified with dilute sulfuric acid. After the ether extract had been separated, washed with water, and dried, it was concentrated to give 10.2 g. (94%) of a solid, m.p. 44–46°. By repeated recrystallization from ether at low temperatures, a sample of 3,3'-dichlorobibenzyl was obtained as white crystals, m.p. 50–51°.

Anal. Calcd. for $C_{14}H_{12}Cl_2$: C, 66.83; H, 5.02. Found: C, 66.95; H, 4.82.

3,3'-Dibromobibenzyl (XIV).—The preparation of *m*-bromobenzyl bromide (XII) from the reaction of *m*-bromotoluene with *N*-bromosuccinimide in the presence of benzoyl peroxide proceeded in 47% yield giving a colorless solid, m.p. 39–41°. The conversion of *m*-bromobenzyl bromide to 3,3'-dibromobibenzyl (XIV) was carried out as described above for the preparation of 3,3'-dichlorobibenzyl and proceeded in 92% yield giving white crystals, m.p. 65–66°, after recrystallization from ether.

Anal. Calcd. for $C_{14}H_{12}Br_2$: C, 49.44; H, 3.56; Br, 47.00. Found: C, 49.69; H, 3.95; Br, 46.94.

3,3'-Dicyanobibenzyl (XV).—The conversion of both 3,3'-dichlorobibenzyl and 3,3'-dibromobibenzyl to 3,3'-dicyanobibenzyl (XV) was investigated following the procedure described by Newman for α -bromonaphthalene.²⁶ With the dichloro derivative the yield of XV was only about 7%. However, the dibromo derivative XIV was con-

verted to XV in 45% yield giving white crystals, m.p. 163.5–164.0°, after recrystallization from benzene.

Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21. Found: C, 83.00; H, 5.39.

3,3'-Dicarboxybibenzyl (XVI).—A mixture of 9.2 g. of 3,3'-dicyanobibenzyl (XV), 80 ml. of concd. sulfuric acid and 60 ml. of water was boiled under reflux for 10 min. During the period of heating the acid separated as a white solid. The mixture was then cooled, poured onto ice and diluted with water. After the precipitate had been collected, it was redissolved in aqueous sodium bicarbonate solution and reprecipitated by the slow addition of dilute acid. The resulting solid was recrystallized from a benzene-acetone mixture to give 7.65 g. (72%) of white crystals, m.p. 264–265°.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22. Found: C, 71.02; H, 5.22.

3,3'-Dicarbomethoxybibenzyl (XVII).—A mixture of 7.5 g. of 3,3'-dicarboxybibenzyl (XVI), 200 ml. of methanol and 10 ml. of concd. sulfuric acid was boiled under reflux for 26 hr. After the mixture had cooled, solid barium carbonate was gradually added to neutralize the acid and the solution was taken up in ether and filtered. Concentration of the ether solution yielded a solid which, after recrystallization from methanol, gave 8.1 g. (98%) of white plates, m.p. 81.5–82.5°.

Anal. Calcd. for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08. Found: C, 72.58; H, 6.20.

3,3'-Di-(hydroxymethyl)-bibenzyl (XVIII).—A solution of 7.8 g. of 3,3'-dicarbomethoxybibenzyl (XVII) in 150 ml. of dry ether was added slowly with stirring to a solution of 1.5 g. of lithium aluminum hydride in 100 ml. of ether. After the addition was complete, the mixture was boiled under reflux for 15 min. and then the excess lithium aluminum hydride was decomposed by addition first of ethyl acetate and then dilute sulfuric acid. After the ether layer had been separated, it was washed with aqueous sodium bicarbonate, water, and dried. Concentration gave a colorless oil which, on cooling, afforded 6.3 g. (99%) of white crystals, m.p. 50–57°. These were sufficiently pure for use in the next step, but a sample for analysis prepared by recrystallization from an ether-methanol mixture melted at 58.0–58.5°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.35; H, 7.36.

3,3'-Di-(bromomethyl)-bibenzyl (XIX).—A mixture of 5.0 g. of 3,3'-di-(hydroxymethyl)-bibenzyl (XVIII) and 40 ml. of 48% hydrobromic acid was boiled under reflux for 2 hr. When the solution was cooled the oily layer crystallized and the resulting brown solid (7.2 g.) was collected by filtration. Recrystallization from *n*-hexane gave 6.16 g. (81%) of white crystals, m.p. 82–83°. Chromatography of these crystals over Woelm alumina using *n*-hexane for elution gave 5.80 g. (76%) of white needles, m.p. 87–88°.

Anal. Calcd. for $C_{16}H_{16}Br_2$: C, 52.20; H, 4.38. Found: C, 52.28; H, 4.50.

Cyclization of XIX to (2.2)Metacyclophane (III).—Sodium wire (2.3 g.) was pressed directly into a flask containing a solution of 300 mg. of tetraphenylethylene in 100 ml. of tetrahydrofuran with an atmosphere of nitrogen being maintained in the flask. As soon as the deep red color of the sodium adduct had developed, the solution was cooled with a Dry Ice-acetone-bath and a solution of 5.0 g. of 3,3'-di-(bromomethyl)-bibenzyl in 10 ml. of tetrahydrofuran was added at such a rate that the red color of the solution was never completely discharged. When the addition was complete (ca. 4 hr.), methanol was added to discharge the red color and the resulting mixture was filtered through glass wool to remove suspended sodium wire and sodium bromide. The precipitate was washed with ether and the combined ether washings and filtrate were washed with water, dried, and concentrated to give 2.92 g. of a crystalline solid, m.p. 127–130°, softening at 120°. The solid was then subjected to steam distillation to separate the desired hydrocarbon from any non-volatile polymeric material. The crystalline deposit in the steam distillate was collected by ether extraction and, after concentration, there was obtained 2.17 g. (77%) of white crystals, m.p. 132.5–133.0°.³⁰

(28) S. S. Jenkins, *THIS JOURNAL*, **55**, 2896 (1933).

(29) F. G. Mann and F. H. C. Stewart, *J. Chem. Soc.*, 2819 (1954).

(30) Reference 13 gives as the m.p. 132–133°.

When *m*-xylyl dibromide was treated in a similar fashion, (2,2)metacyclophane was obtained in yields ranging from 30–33%. However, when the dimerization of 2,6-di-(bromomethyl)-toluene was carried out using these conditions, the yield of 4,12-dimethyl(2,2)metacyclophane was no better than when sodium alone was used as described earlier.

3-Bromo-2-methylbenzoic Acid (XXI).—The conversion of 2-chloro-6-aminotoluene to 2-cyano-6-aminotoluene was accomplished in 72% yield following the von Braun procedure²⁶ and gave white plates, m.p. 95–96°, from a benzene-hexane mixture.³¹ The replacement of the amino group by bromine following the Sandmeyer procedure occurred in 88% yield giving 2-bromo-6-cyanotoluene (XX) as white needles, m.p. 44–45°. A mixture of 45.0 g. of XX was then hydrolyzed by treating it with a boiling aqueous 20% potassium hydroxide solution for 26 hr. In the early stages of the hydrolysis, the corresponding amide (m.p. 166–167°) separated, but this redissolved with evolution of ammonia on further heating. After filtration the basic solution was acidified and the precipitate collected. Recrystallization of the solid from aqueous ethanol gave 42.0 g. (85%) of white crystals, m.p. 151–152°.

Anal. Calcd. for C₈H₇O₂Br: C, 44.68; H, 3.26. Found: C, 44.70; H, 3.34.

Ethyl 3-Bromo-2-methylbenzoate (XXII).—A mixture of 42.0 g. of 3-bromo-2-methylbenzoic acid (XXI), 45 ml. of ethanol and 2 ml. of concd. sulfuric acid in 150 ml. of benzene was subjected to azeotropic distillation until no further water separated. After the benzene solution had been washed with aqueous sodium bicarbonate and water, it was concentrated and the residual oil distilled to give 37.4 g. (79%) of a colorless liquid, b.p. 112–113° at 1 mm.

Anal. Calcd. for C₁₀H₁₁O₂Br: C, 49.41; H, 4.56. Found: C, 49.34; H, 4.78.

2-Bromo-6-hydroxymethyltoluene (XXIII).—A solution of 47.4 g. of ethyl 3-bromo-2-methylbenzoate (XXII) in 100 ml. of ether was added dropwise with stirring to a solution of 5.0 g. of lithium aluminum hydride in 150 ml. of ether and the resulting mixture was boiled under reflux for 2 hr. The excess lithium aluminum hydride was decomposed with ethyl acetate and a saturated aqueous solution of sodium sulfate was added to effect precipitation of the metallic hydroxides in a granular form. After removal of the precipitate, the ether solution was concentrated to give 35.6 g. (91%) of white plates, m.p. 101–102°. A sample, after further recrystallization from benzene, melted at 103–104°.

Anal. Calcd. for C₈H₉OBr: C, 47.78; H, 4.51. Found: C, 47.74; H, 4.59.

2-Bromo-6-bromomethyltoluene (XXIV).—A solution of 43.0 g. of 2-bromo-6-hydroxymethyltoluene (XXIII) in 250 ml. of 48% hydrobromic acid was boiled under reflux for 2.5 hr. When the solution was cooled, the oily layer solidified to a brown solid and it was collected by filtration. The brown solid was then taken up in *n*-hexane and chromatographed over Woelm neutral alumina. Concentration of the *n*-hexane eluate gave a colorless oil which, on cooling, solidified to give 50.4 g. (89%) of a white, crystalline solid, m.p. 31–32°.

Anal. Calcd. for C₈H₈Br₂: C, 36.40; H, 3.05. Found: C, 36.32; H, 2.98.

3,3'-Dibromo-2,2'-dimethylbibenzyl (XXV).—A solution of 21.0 g. of 2-bromo-6-bromomethyltoluene (XXIV) in 80 ml. of ether was boiled under reflux in the presence of 1.1 g. of magnesium turnings until there was evidence of reaction. Then, 150 mg. of anhydrous ferric chloride was added with vigorous stirring and cooling of the reaction mixture. When the reaction had subsided, the resulting mixture was boiled under reflux for 1 hr. The ether solution was then poured onto a mixture of ice and dilute sulfuric acid, and the ether layer was separated, washed with water, and concentrated. The resulting solid was recrystallized from *n*-hexane to give 8.8 g. (61%) of white crystals, m.p. 132–133°.

Anal. Calcd. for C₁₆H₁₆Br₂: C, 52.20; H, 4.38. Found: C, 52.08; H, 4.45.

3,3'-Dicarboxy-2,2'-dimethylbibenzyl (XXVI).—To an ethereal solution of *n*-butyllithium (prepared from 12.5 g. of *n*-butyl bromide and 1.6 g. of lithium in 200 ml. of ether) there was added a solution of 7.0 g. of 3,3'-dibromo-2,2'-dimethylbibenzyl (XXV) in 200 ml. of ether and the mixture was stirred at room temperature for 3 hr. An excess of solid carbon dioxide was then added and the whole was poured into water. The aqueous layer was separated and acidified. The resulting heavy precipitate was collected and recrystallized from glacial acetic acid to give 5.3 g. (94%) of white needles, m.p. 264–265°.

Anal. Calcd. for C₁₈H₁₆O₄: C, 72.46; H, 6.08. Found: C, 72.14; H, 6.00.

3,3'-Dicarboethoxy-2,2'-dimethylbibenzyl (XXVII).—A mixture of 12.2 g. of 3,3'-dicarboxy-2,2'-dimethylbibenzyl (XXVI), 150 ml. of ethanol and 10 ml. of concd. sulfuric acid was boiled under reflux for 24 hr. Part of the ethanol was removed by distillation and the residue was poured into water causing the separation of a white solid. This was collected and recrystallized from ethanol to give 12.5 g. (86%) of white crystals, m.p. 77.5–78.0°.

Anal. Calcd. for C₂₂H₂₆O₄: C, 74.55; H, 7.39. Found: C, 74.57; H, 7.63.

3,3'-Di-(hydroxymethyl)-2,2'-dimethylbibenzyl (XXVIII).—To a solution of 2.5 g. of lithium aluminum hydride in 100 ml. of ether there was added with stirring a solution of 12.0 g. of 3,3'-dicarboethoxy-2,2'-dimethylbibenzyl (XXVII) in 200 ml. of ether and the resulting mixture was boiled under reflux for 1.5 hr. After decomposition of the excess lithium aluminum hydride with ethyl acetate followed by dilute sulfuric acid, a solid separated from the ether layer. This was collected, warmed with dilute alkali, and then recrystallized from ethanol to give 8.2 g. (90%) of white crystals, m.p. 158–160°.

Anal. Calcd. for C₁₈H₂₂O₂: C, 79.96; H, 8.20. Found: C, 80.01; H, 8.15.

3,3'-Di-(bromomethyl)-2,2'-dimethylbibenzyl (XXIX).—A solution of 7.0 g. of 3,3'-di-(hydroxymethyl)-2,2'-dimethylbibenzyl (XXVIII) in 150 ml. of 48% hydrobromic acid was boiled under reflux for 36 hr. After the solution had cooled, the resulting solid was collected and recrystallized from a benzene-hexane mixture to give 7.9 g. (77%) of white needles, m.p. 142–143°.

Anal. Calcd. for C₁₈H₂₀Br₂: C, 54.56; H, 5.08. Found: C, 54.42; H, 5.22.

Cyclization of XXIX to IV was carried out as described previously for the cyclization of 3,3'-di-(bromomethyl)-bibenzyl (XIX). From 7.5 g. of 3,3'-di-(bromomethyl)-2,2'-dimethylbibenzyl (XXIX) there was obtained 1.95 g. (44%) of white crystals, m.p. 205°, after recrystallization from hexane of the steam-volatile hydrocarbon. A comparison of these crystals with the sample of 4,12-dimethyl(2,2)metacyclophane described earlier both in their infrared spectra and by a mixture melting point determination showed them to be identical.

2,2',3,3'-Tetramethylbibenzyl (X).—A solution of 240 mg. of 3,3'-di-(hydroxymethyl)-2,2'-dimethylbibenzyl in 50 ml. of glacial acetic acid was subjected to hydrogenation over 50 mg. of a 10% palladium-on-charcoal catalyst at room temperature and atmospheric pressure. When the absorption corresponding to two molecules of hydrogen was complete, the catalyst and solvent were removed and the resulting solid was taken up in *n*-pentane and chromatographed over alumina to give 170 mg. of white crystals, m.p. 110–111°. A comparison of these crystals with the by-product hydrocarbon obtained in the dimerization of 2,6-di-(bromomethyl)-toluene (IX) both in their infrared spectra and by a mixture melting point determination showed them to be identical.

Attempted Dehydrogenation of 4,12-Dimethyl(2,2)metacyclophane.—A series of dehydrogenation experiments was first carried out with (2,2)metacyclophane itself. The mildest conditions for effecting the dehydrogenation of (2,2)metacyclophane to pyrene in good yield appeared to be the use of a 30% palladium-on-charcoal catalyst in boiling triethylene glycol (280–290°) for 18 hr. which gave pyrene in 61% yield. When 100 mg. of 4,12-dimethyl(2,2)metacyclophane and 100 mg. of a 30% palladium-on-charcoal catalyst in 2 ml. of triethylene glycol was boiled under reflux in a nitrogen atmosphere for 4 days, workup of the

(31) E. Noetting (*Ber.*, **37**, 1015 (1904)) gives 95.5°.

reaction mixture by chromatography over Woelm alumina using pentane for elution led to recovery of 66 mg. of 4,12-dimethyl(2,2)metacyclophane and 1.0 mg. of pyrene.

Attempts to Effect Substitution on the Bridged Methylenes of IV.—The various experiments using *N*-bromosuccinimide, *t*-butyl hypochlorite, lead tetraacetate, cumene hydroper-

oxide and cuprous chloride, vanadium pentoxide and hydrogen peroxide, chromium trioxide and selenium dioxide are not described in detail since invariably the outcome was one of recovery of starting material or the formation of complex, tarry mixtures from which no useful products could be isolated.

[CONTRIBUTION NO. 176 FROM THE CENTRAL RESEARCH LABORATORIES, MINNESOTA MINING AND MANUFACTURING CO., ST. PAUL, MINN.]

The Chemistry of Xylylenes. VIII. The Formation of Spiro-di-*o*-xylylene and Related Compounds¹

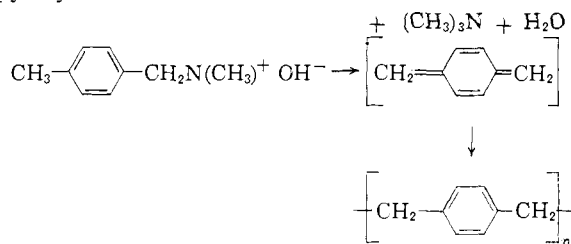
BY L. A. ERREDE

RECEIVED AUGUST 26, 1960

The Hofmann degradation of *o*-methylbenzyltrimethylammonium hydroxides at low pressure in a modified flow system is a convenient method for generating *o*-xylylene. *o*-Xylyl alcohol and bis-di-*o*-xylyl ether are formed as side products. Spiro-(5,5)-2,3-benz-6-methyleneundeca-7,9-diene (spiro-di-*o*-xylylene) is obtained in good yield when *o*-xylylene is warmed from -78° to room temperature. Cyclo-di-*o*-xylylene is also obtained in appreciable amount, but the ratio of the spiro to cyclic compounds is about 3 to 1. The spiro compound polymerizes at room temperature to high molecular weight poly-(*o*-xylylene). Spiro-di-*o*-xylylene reacts with I_2 or Br_2 to give the corresponding 2,2'-bis-(halomethyl)-bibenzyl, and it can be hydrogenated using Raney nickel catalyst to afford spiro-(5,5)-2,3-benz-6-methylundecane. It is suggested that the mechanism for addition of free radicals to spiro-di-*o*-xylylene involves attack at the *exo*-methylene group followed by aromatization to afford an *o*-substituted benzyl radical. This intermediate continues to react to give a variety of di-*o*-xylylene derivatives, depending upon the choice of experimental conditions.

Introduction

Fawcett, *et al.*,² have reported that poly-*p*-xylylenes and cyclo-di-*p*-xylylene were formed when *p*-methylbenzyltrimethylammonium hydroxide was decomposed in aqueous solution. They speculated that these products were formed from *p*-xylylene which is an extremely reactive molecule.³ Other workers have also demonstrated^{4,5} or postulated^{6,7} the transient existence of xylylenes in related pyrolysis reactions.



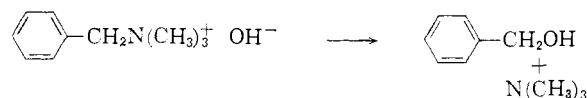
p-Xylylene, produced by fast flow pyrolysis of *p*-xylylene in gas phase, can be isolated in solution by instantaneous condensation of the pyrolyzate in a cold solvent. Hence, it appeared probable to us that degradation of the appropriate quaternary hydroxide might be a convenient method for isolating a variety of xylylenes, if the procedure could be modified to enable removal of the transient intermediates from the reaction flask as fast as

they are formed. Accordingly a flow technique was developed in our laboratory. It was only partially successful with *p*-xylylene, but it worked exceptionally well for *o*-xylylene.

Results and Discussion

It was verified that poly-(*p*-xylylene) and cyclo-di-*p*-xylylene are formed in high yield and high conversion² when *p*-methylbenzyltrimethylammonium hydroxide is decomposed in aqueous solution, and that *p*-xylylene in very small amount is volatilized when the decomposition is carried out at low pressure. It was found, however, that the proportion of monomer collected in the cold trap was increased markedly if the aqueous quaternary hydroxide was metered into an evacuated system where rapid concentration occurred by evaporation followed by flash thermal degradation as described in the Experimental section. In this way the monomer collected in the cold trap represented about 20% of the hydroxide decomposed; the rest polymerized in the decomposition flask before it could be removed by flash distillation.

Closer examination of the reaction products obtained *via* decomposition of *p*-methylbenzyltrimethylammonium hydroxide indicated that appreciable amounts of *p*-methylbenzyl alcohol and bis-(*p*-methylbenzyl) ether were produced as well as poly-(*p*-xylylene) and cyclo-di-*p*-xylylene. The alcohol possibly was formed *via* an alternative route for decomposition of the quaternary base since it was reported by Groves and Greenaway⁸ that decomposition of benzyltrimethylammonium hydroxide affords trimethylamine and benzyl alcohol as the major products. Bis-(*p*-methylbenzyl) ether



(1) Presented before the Organic Chemistry Division of the American Chemical Society at its 138th Meeting, September, 1960, held in New York.

(2) (a) F. S. Fawcett, U. S. Patent 2,757,146; (b) British Patent 807,196; (c) H. E. Winberg, F. S. Fawcett, W. E. Mochel and C. W. Theobald, *J. Am. Chem. Soc.*, **82**, 1428 (1960).

(3) (a) L. A. Errede and J. M. Hoyt, *ibid.*, **82**, 436 (1960); (b) L. A. Errede and B. F. Landrum, *ibid.*, **79**, 4952 (1957).

(4) M. Szwarc, *J. Polymer Sci.*, **6**, 319 (1951).

(5) M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959).

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(7) J. Rosenberg, Ph.D. Thesis under the supervision of W. J. Bailey submitted to the Graduate Council of Wayne University, 1951.

(8) C. E. Groves and A. J. Greenaway, *J. Chem. Soc.*, **57**, 778 (1890).