

activity. Whether or not pre-equilibrium hydration of the amidine is involved, reaction by this mechanism should have a positive Hammett ρ -constant. Actually, the observed slope of a $\log k$ vs. σ plot varies from 0 to -3 . The curvature of the Hammett plot may be due to a change in the rate-limiting step of the reaction when the structure of the aryl group is changed. It cannot be due to hydrolysis by two competing mechanisms, since in this case the plot would be concave upward rather than downward.

The small inverse variation of hydrolysis rate with hydroxide ion concentration for amidines with elec-

tron-releasing substituents (Table I) may be due to rate-determining reaction of protonated amidine or protonated amidine hydrate with water, or to a rate-determining unimolecular reaction of either of these species. A more detailed pH profile for the reaction should show whether a reaction of this nature actually occurs, or whether the small rate changes observed are the result of salt effects.

Acknowledgment.—The competent assistance of Mr. Carl P. Ruiz, and a grant from Research Corporation which partially supported this work, are gratefully acknowledged.

[CONTRIBUTION FOR THE EVANS CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO]

Syntheses of the Three Isomeric Diethyl- and Dineopentyltetramethylbenzenes¹

BY MELVIN S. NEWMAN, JOHN R. LEBLANC,² HAROLD A. KARNES,² AND GEORGE AXELRAD¹

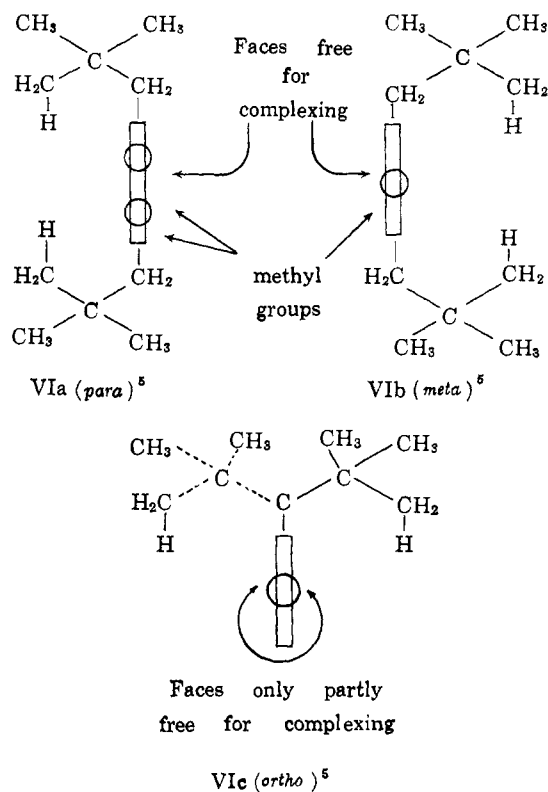
RECEIVED AUGUST 21, 1963

The syntheses of the three isomeric diethyl- and dineopentyltetramethylbenzenes has been accomplished. Differences in the tendencies of the *o*-isomers as compared to the *m*- and *p*-isomers to complex with tetracyanoethylene and 2,4,7-trinitrofluorenone have been observed and briefly discussed. New syntheses of compounds containing cyclopropyl rings have been noted in the lithium aluminum hydride, sodium in liquid ammonia, and Raney nickel reductions of bis-[2,2-bis-(iodomethyl)-propyl]-durene (VIIa) to yield bis-[1-methylcyclopropyl]-methyl]-durene (VIIIa).

Marked differences in the equilibrium constants for the interaction of hexamethylbenzene and hexaethylbenzene with iodine and iodine monochloride have been determined.³ The low values for hexaethylbenzene were explained in terms of steric effects.³ To understand these effects better we have prepared the three isomeric diethyltetramethylbenzenes and dineopentyltetramethylbenzenes so that equilibrium constant determinations could be made not only with iodine but also with other reagents which form complexes with aromatic systems.

The thinking behind the choice of these hydrocarbons for study is as follows. Examination of molecular models shows that in the *m*- and *p*-isomers the larger groups can readily exist in structures in which the bulky groups (methyl in case of the ethyl derivatives and *t*-butyl in case of the neopentyl derivatives) lie on the same side of the ring. However, in the *o*-isomers the tendency should be greater (particularly in the case of the neopentyl compound) to have these groups on opposite sides of the plane of the benzene ring. For this reason measurement of the equilibrium constants for several types of Lewis acid π -complexing reagents would be of interest as one might be able thus to define more accurately the geometrical requirements for complex formation. For example, in *o*-dineopentyltetramethylbenzene no π -complex would be likely to form if the π -complexing reagent needs to be fairly symmetrically oriented with regard to the six aromatic carbon atoms because one neopentyl group would be shielding each side of the benzene ring.⁴ However, if less symmetrical orientation is required by the π -complexing reagent, then complexing should still be possible if the Lewis acid in question were itself not too bulky. Similar effects, to a lesser degree, would be expected with the diethyl (or other alkyl) analog. The structures of the *p*-, *m*-, and *o*-dineopentyltetra-

methylbenzenes VIa, VIb, and VIc, respectively, are shown (not to scale) in the drawings. Only the features essential to the argument are shown.



When chloroform solutions containing the same molar concentrations of hydrocarbon and 2,4,7-trinitro-

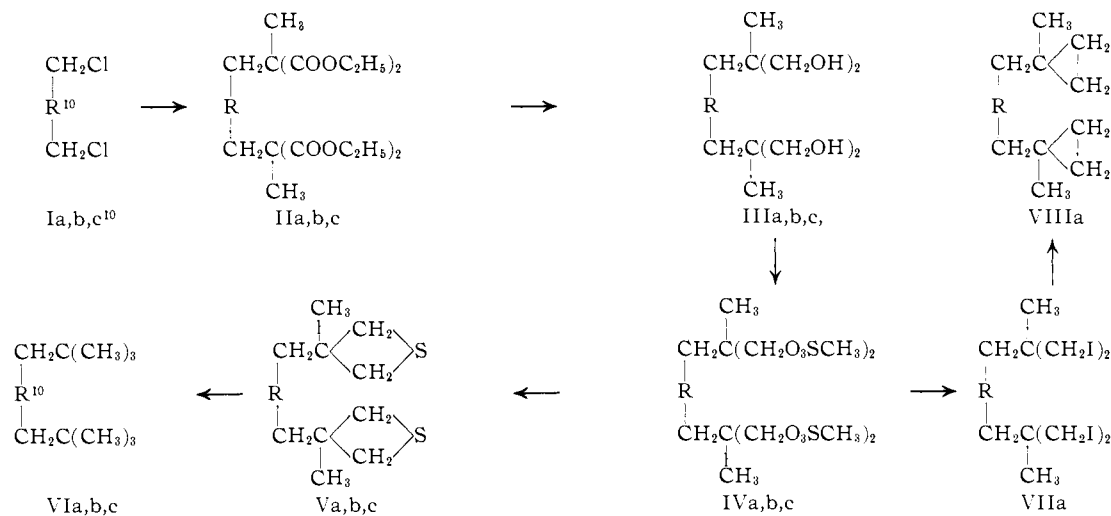
(5) The eye (in the *para* example) is looking at the benzene ring in its plane with the neopentyl groups shown on the same side. In the *meta* case the eye is looking at the compound in the same plane as the benzene ring but the ring is so situated that the methyl group between the two neopentyl groups is pointing directly at the eye. In the *ortho* case the two neopentyl groups are viewed from the plane of the benzene ring so that one is directly behind the other. For this reason the hydrogens in the methylene carbons are not shown. The circles represent methyl groups on the rings.

(1) This work was supported in part by research grants from The Petroleum Research Fund of the American Chemical Society (Type C grant) and the National Science Foundation.

(2) The work herein described formed part of the M.S. theses of J. R. LeBlanc (1960) and H. A. Karnes (1963) at O.S.U.

(3) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952).

(4) Actually a model can be made with both neopentyl groups on the same side, but such a conformation seems much less likely to exist.



fluorenone⁶ were examined with the eye, the relative extent of complex formation was: hexamethylbenzene > *p*-diethyltetramethylbenzene, *m*-diethyltetramethylbenzene > *o*-diethyltetramethylbenzene >> hexaethylbenzene. In the case of the dineopenyltetramethylbenzenes, the *p*- and *m*-isomers gave orange-red solutions of about the same intensity immediately. The behavior of the *o*-isomer was quite unexpected. When first prepared, the solution of the *o*-isomer and TNF was little different in color from a blank solution of TNF alone. However, on standing, the color gradually increased until it was comparable in intensity to that formed with the *p*- and *m*-isomers. We prefer to withhold any discussion of this phenomenon until we have done more experimental work.⁷

When tetracyanoethylene was used as the complexing agent, the *p*- and *m*-dineopenyl compounds gave immediate intense blue-violet solutions in chloroform, but the *o*-isomer solution had almost the same color as a blank. In the case of tetranitromethane, colors of about the same intensity were obtained with all three dineopenyltetramethylbenzenes. Thus a definite difference in the steric requirements of these two complexing agents is indicated. Studies in this area are being made.

The syntheses of the three diethyltetramethylbenzenes (new compounds) were accomplished as follows. Durene was converted into 1,4-divinyldurene essentially as described⁸ and the latter was catalytically hydrogenated to 1,4-diethylidurene. The attempted Wolff-Kishner reduction of 1,4-diacetyldurene provided the diethyl compound in only 10% yield. By similar steps isodurene was converted into 1,3-divinyldurene and 1,3-diethyltetramethylbenzene. The *o*-isomer was prepared by rearranging acetyldurene to acetylprehnitene⁹ with aluminum chloride, reduction to ethylprehnitene, acetylation to acetylethylprehnitene, reduction to the corresponding alcohol, dehydration to vinyl ethylprehnitene, and finally reduction to *o*-1,2-diethyltetramethylbenzene. The yields in general were fairly good, although throughout emphasis was placed on purity of intermediates so that the final hydrocarbons would be pure.

The syntheses of the three dineopenyltetramethylbenzenes (new compounds) were carried out by the

route¹⁰ illustrated in the formulas I → VI. Several noteworthy observations were made during these syntheses.

Bis-chloromethylation of durene and isodurene using concentrated hydrochloric acid proceeded essentially as described.¹¹ However, when a similar procedure was used with prehnitene, only monochloromethylprehnitene was obtained. By cutting the hydrochloric acid concentration to 22% and raising the reaction temperature to 108°, bischloromethylprehnitene was obtained.

The tetraols III were converted to the corresponding tetramethyl derivatives IV in high yield (>90%) by treating cold solutions of III and methanesulfonyl chloride in chloroform with collidine. Yields by this route in general seemed superior to those obtained by adding methanesulfonyl chloride to solutions of the alcohols in collidine or pyridine.

In the conversion of the mesylates IV to the thietanes V high yields were obtained only when the water of hydration was removed from the sodium sulfide by distilling solutions of sodium sulfide hydrate in ethylene glycol until the boiling point of ethylene glycol was reached. This solution was then added to a solution of the tetramethanesulfonate in 2-ethoxyethanol (Ethyl Cellosolve) and the reaction carried out at 130–135°. In this way 50–67% yields of the bisthietanes V were obtained.¹² In two cases involving other bis-methanesulfonates (see Experimental part) yields of 65–69% of thietanes were obtained. Thus this modified procedure for preparation of thietanes appears to have more promise than previously used methods.¹³

Before using the route which involves reduction of a thietane to a neopentyl group as shown, V → VI, we converted the tetramethanesulfonate IVa of the *p*-isomer to the tetraiodide VIIa with the intention of reducing this to the neopentyl derivative VIa. However, when lithium aluminum hydride was used, the di-cyclopropyl derivative VIIIa was obtained in good yield.¹⁴ This result is of interest in connection with the mechanism of reduction of halides by lithium aluminum hydride as displacement of halogen by hy-

(11) M. J. Rhoad and P. J. Flory, *J. Am. Chem. Soc.*, **72**, 2216 (1950).

(12) The use of anhydrous potassium sulfide in absolute alcohol has been described by H. J. Backer and K. J. Keuning, *Rec. trav. chim.*, **52**, 502 (1933).

(13) Compare S. Searles, Jr., and E. F. Lutz, *J. Am. Chem. Soc.*, **80**, 3168 (1958); F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955).

(14) We thank Dr. P. Flanagan and M. Hamming of the Continental Oil Co., Ponca City, Okla., for n.m.r. and mass spectrographic data, respectively, on VIIa, and also on VIa,b,c. The mass spectra of VIa (86 m), VIb (87 m), and VIc (88 m) are on file at the A.P.I. Research Project 44, Chemical Thermodynamics Properties Center, Texas A. and M. College, College Station, Texas.

(6) M. Orchin and O. Woolfolk, *J. Am. Chem. Soc.*, **68**, 1727 (1946).

(7) Samples of the three dineopenyltetramethylbenzenes have been sent to Professor L. J. Andrews, University of California at Davis, for studies on halogen complexing.

(8) M. Lukin and B. B. Corson, *J. Org. Chem.*, **23**, 1007 (1958).

(9) G. Baddelly and A. G. Pendleton, *J. Chem. Soc.*, 807 (1952).

(10) R represents the appropriate tetramethylphenylene diradical: a, for the *p*-isomer, b for the *m*-, and c for the *o*-.

dride ion, postulated¹⁵ in certain cases, cannot be involved in this case.¹⁶ In the present case, the formation of an organometallic intermediate followed by cyclization involving intramolecular displacement of iodide ion offers an explanation.

In other experiments, the tetraiodide VIIa was reduced to the same di-cyclopropyl compound VIII with W-2 Raney nickel¹⁷ in alcohol and with sodium in liquid ammonia. These results obviously have a bearing on the mechanism of reduction of halides with these reagents, but as we have not studied these reactions in any detail we will not discuss them further.

The n.m.r. spectra of the *p*- and *m*-isomers VIa and VIb were in complete agreement with the proposed structures.¹⁴ However, in the *o*-isomer VIc a doublet at 7.12 τ appears. This phenomenon is under further study.

Experimental¹⁸

***p*-Diethyltetramethylbenzene.**—In a 1-l. flask equipped with stirrer, condenser, and thermometer were placed 500 ml. of carbon disulfide, 30 g. of durene,¹⁹ and 50 g. of acetyl chloride. The resulting solution was stirred at 5–10° and 158 g. of aluminum chloride was added in small portions during 1 hr. The resulting mixture was stirred 1.5 hr. at 10–15° and 22 hr. at reflux. After pouring on ice containing 400 ml. of concentrated hydrochloric acid, the reaction product, isolated in the usual way, was crystallized from 400 ml. of benzene to yield 26.8 g. of crude bisacetodurene. The filtrate upon concentration to 200 ml. and dilution with 150 ml. of petroleum ether, b.p. 60–70° (Skellysolve B), yielded an additional 22.4 g. of crude product. The combined crude product yielded upon two recrystallizations from benzene 44.4 g. (89%) of colorless bisacetodurene,⁸ m.p. 179–183°, sufficiently pure to use in the following step.

When the Friedel–Crafts condensation was allowed to proceed for only 2.5 hr. at room temperature and 1 hr. at reflux, the yield of pure product was only 26% (compare ref. 8).

Bis(α -hydroxyethyl)-durene was prepared by lithium aluminum hydride reduction and 15.0 g. of this was dehydrated over potassium acid sulfate to yield divinylidurene essentially as described.⁸ Catalytic hydrogenation of 12.8 g. of this crude diene in 200 ml. of methanol over Adams platinum catalyst under 20–40 p.s.i. of hydrogen was 80% complete after 1 hr. Crystallization of the product interfered at this stage. Ether was added, the catalyst filtered, solvent removed from filtrate, and the residue dissolved in ethyl acetate and reduced with fresh catalyst. Recrystallization of the resulting product from methanol eventually yielded 7.5 g. (59% from diol) of pure *p*-diethyltetramethylbenzene,²⁰ m.p. 101–102°.

Anal. Calcd. for C₁₄H₂₂: C, 88.3; H, 11.7. Found: C, 88.5; H, 11.6.

An attempt to carry out a Huang–Minlon–Wolff–Kishner reduction²¹ of diacetodurene afforded less pure diethyl compound in only 10% yield after 39 hr. at 195°.

***m*-Diethyltetramethylbenzene.**—Isodurene was prepared as described.²² To a solution of 28.0 g. of isodurene²³ and 37.5 g. of acetyl chloride in 400 ml. of carbon disulfide was added 180 g. of

aluminum chloride. After 2 hr. at 5–10°, 1 hr. at 10–35°, and 1 hr. at reflux there was obtained, after hydrolysis with ice and the usual work-up, 34.0 g. (75%) of twice recrystallized (benzene-petroleum ether, b.p. 60–70°, 1:4) diacetyl isodurene,²⁴ m.p. 121–122°. Reduction of 21.5 g. of this with lithium aluminum hydride in 600 ml. of ether in the usual way afforded 16.5 g. (75%) of pure bis-(α -hydroxyethyl)-isodurene, m.p. 155–156°, after recrystallization from chloroform.

Anal. Calcd. for C₁₄H₂₂O₂: C, 75.7; H, 10.0. Found: C, 76.1; H, 10.2.

Dehydration of 13.5 g. of the diol as for the *p*-isomer⁸ afforded 11.0 g. (97%) of divinylisodurene, b.p. 115–117° at 2–3 mm., *n*_D²⁰ 1.5516.

Anal. Calcd. for C₁₄H₁₈: C, 90.3; H, 9.7. Found: C, 90.0; H, 10.1.

Catalytic hydrogenation of 11.0 g. of the diene in 100 ml. of methanol over platinum was complete in 1 hr. Distillation afforded 10.5 g. of *m*-diethyltetramethylbenzene as a liquid. Low temperature crystallization from methanol yielded 8.4 g. (75%) of pure hydrocarbon, m.p. 35.5–36.0°.

Anal. Calcd. for C₁₄H₂₂: C, 88.3; H, 11.7. Found: C, 88.6; H, 11.5.

***o*-Diethyltetramethylbenzene.**—Acetyldurene was isomerized to acetylprehnitene as described.⁸ On Huang–Minlon reduction²¹ (top temperature, 206°, 3 hr.) of 29.5 g. of ketone, the crude hydrocarbon produced was fractionated through a 2-ft. packed column (3/16 in. beads) to yield 19.5 g. (72%) of ethylprehnitene, b.p. 87.5–88.0° (4 mm.), *n*_D²⁰ 1.5228.

Anal. Calcd. for C₁₂H₁₈: C, 88.8; H, 11.2. Found: C, 88.7; H, 11.2.

To a slurry of 13.4 g. of aluminum chloride in 150 ml. of *o*-dichlorobenzene at 0–10° was added a solution of 7.0 g. of acetyl chloride in 30 ml. of *o*-dichlorobenzene during 45 min. After 1 hr. at 0–10°, 13.0 g. of ethylprehnitene in 30 ml. of *o*-dichlorobenzene was added during 1 hr. at 0–10°. A homogeneous brown solution resulted. After 1 hr. at 0–10° and 2 hr. at 10–25° the mixture was poured on ice and the product was isolated in the usual way. Distillation afforded 15.5 g. (95%) of solid acetyl-ethylprehnitene, b.p. 154–157° (9 mm.), which was good enough to process further. A small sample was purified by low temperature crystallization from methanol–water at –60° to yield pure acetyl-ethylprehnitene, m.p. 43.0–43.5°.

Anal. Calcd. for C₁₄H₂₀O: C, 82.4; H, 9.9. Found: C, 82.4; H, 9.7.

Reduction of 19.4 g. of the above ketone with lithium aluminum hydride in ether for 4.5 hr. at reflux, followed by the usual work-up, yielded 16.2 g. (83%) of recrystallized (from petroleum ether, b.p. 40–50°) α -hydroxyethyl-ethylprehnitene, m.p. 99–100°.

Anal. Calcd. for C₁₄H₂₂O: C, 81.5; H, 10.7. Found: C, 81.7; H, 10.6.

Dehydration of 8.0 g. of the above alcohol by heating with potassium acid sulfate as described above afforded 7.0 g. (96%) of vinyl-ethylprehnitene, b.p. 130.5–131.5° (9 mm.), *n*_D²⁰ 1.5402.

Anal. Calcd. for C₁₄H₂₀: C, 89.3; H, 10.7. Found: C, 89.0; H, 10.9.

Hydrogenation of 6.4 g. of the above olefin in 100 ml. of methanol over platinum at 20–30 p.s.i. of hydrogen was complete in 1 hr. at room temperature. Distillation followed by recrystallization from methanol yielded 5.1 g. (79%) of pure *o*-diethyltetramethylbenzene, m.p. 44.5–45.0°.

Anal. Calcd. for C₁₄H₂₂: C, 88.3; H, 11.7. Found: C, 88.5; H, 11.6.

Bischloromethyltetramethylbenzenes²⁵ (Ia, b, c).—The *m*-isomer Ib, prepared essentially as described,¹¹ melted at 115–116°. Since the reported¹¹ m.p. for Ib was 106–107°, our sample was analyzed.

Anal. Calcd. for C₁₂H₁₆Cl₂: Cl, 30.7. Found: Cl, 30.8.

When similar conditions for chloromethylation were applied to prehnitene, no bischloromethyl derivative was obtained. A better procedure is described below.

To a magnetically stirred mixture of 275 ml. of 22% hydrochloric acid, 20 g. of prehnitene,²⁶ and 90 ml. of *n*-decane heated to reflux was added 10 g. of paraformaldehyde in small portions during 10 min. This mixture was held at reflux for 6 hr. and at the end of the second and fourth hour 10-g. portions of paraformaldehyde were added. The cooled organic layer was filtered and the crude Ic obtained was washed with petroleum ether. The filtrate and washings were combined and the petroleum ether

(24) I. I. Smith and C. Guss, *J. Am. Chem. Soc.*, **59**, 805 (1937).

(25) We thank Dr. W. G. DePierri of the Humble Oil and Refining Co. for a gift of about 60% pure Ia, which on three crystallizations from toluene afforded Ia of 97 + % purity, m.p. 195.0–196.4°.

(26) We thank Dr. M. C. Hoff, Amoco Chemicals Corp., for a sample of prehnitene.

(15) L. W. Trevoy and W. G. Brown, *J. Am. Chem. Soc.*, **71**, 1675 (1949). See also L. J. Dolby and D. R. Rosencrantz, *J. Org. Chem.*, **28**, 1888 (1963), for a discussion of the lithium aluminum hydride reduction of tosylates.

(16) A similar formation of a cyclopropane ring has been observed here by Miss N. Gill on reduction of 1,8-diiodo-2,6-diiodomethyl-2,6-dimethyl-4-octyne.

(17) R. Mazingo, "Organic Syntheses," Coll. Vol. 111, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 181.

(18) All melting points are uncorrected. The term "worked up in the usual manner" means that a solution of the reaction products in an ether-benzene solution (approx. 1:1) was washed with dilute acid and/or alkali as the situation indicated and with saturated sodium chloride solution. The resulting solution was then filtered through a cone filter containing a layer of anhydrous magnesium sulfate. The solvent was distilled and the residue treated as indicated. All microanalyses were by the Galbraith Microanalytical Laboratory, Knoxville, Tenn.

(19) We wish to thank the Humble Oil Co. and The Shell Oil Co. for generous samples of durene.

(20) We are indebted to Messrs. D. R. Beasecker and W. D. Ross of the Monsanto Chemical Co., Dayton, Ohio, for determination of purity by v.p.c. analysis. They reported that all of the isomeric diethyltetramethylbenzene samples we supplied were "essentially free of any impurity."

(21) Huang–Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(22) L. I. Smith, "Organic Syntheses," Coll. Vol. 11, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 360.

(23) We thank the Humble Oil and Refining Co. and the Enjay Chemical Co. for generous samples of isodurene.

removed under vacuum. The decane solution was then treated as above with 275 ml. of 22% hydrochloric acid and 30 g. of paraformaldehyde. After refluxing for 11 hr., the mixture was processed as above to yield a further amount of crude Ic. The organic matter was then processed a third time with 275 ml. of 22% hydrochloric acid and 25 g. of paraformaldehyde for 23 hr. After the third hour, 10 g. of aldehyde was added and after 6 hr., 10 g. of aldehyde and 50 ml. of concentrated hydrochloric acid were added. The total crude Ic was vacuum distilled to yield 24.1 g. (70%) of Ic, b.p. 160–163° (4 mm.), m.p. 127–128°. This material was used in following steps. A pure sample, obtained with little loss after two recrystallizations from petroleum ether, b.p. 90–100°, melted at 138.4–139.0°. This was probably a polymorphic form.

Anal. Calcd. for $C_{12}H_{16}Cl_2$: C, 62.3; H, 7.0; Cl, 30.7. Found: C, 62.4; H, 7.0; Cl, 30.8.

Bis-(2,2-dicarboethoxypropyl)-tetramethylbenzenes (IIa,b,c).—To a solution of 65.0 g. of pure diethyl methylmalonate in 170 ml. of dry N-methylpyrrolidone²⁷ at 50° was added in portions 16.3 g. of a 53% sodium hydride suspension in mineral oil (Metal Hydrides Inc.), the temperature being held at 65–80°. The temperature was then raised slowly to 170° during 2 hr.²⁸ After cooling to 90° a solution of 33.0 g. of bischloromethylurene in 500 ml. of hot benzene was added. The mixture was held at reflux for 15 hr. during which 300 ml. of benzene was allowed to distill. After the usual work-up, the solvent was distilled and the residue was dissolved in 200 ml. of hot alcohol. The crystals which separated on cooling were washed with low boiling petroleum ether and recrystallized from 200 ml. of ethanol to yield 56.0 g. (78%) of IIa, m.p. 95.0–97.8°, sufficiently pure for further use. In other runs, the product melted at 87–88° and recrystallization failed to raise the m.p. Undoubtedly an impurity was present. Since this material gave as good results as did higher melting IIa, it was suitable for further use. The procedure described below for IIb,c would probably work also, but was not attempted.

For the synthesis of the *m*-isomer IIb from Ib, 130 g. of diethyl methylmalonate was added to a solution at room temperature made by treating 12.0 g. of sodium with 100 ml. of absolute alcohol. After heating to reflux for 1 hr., 30.0 g. of Ib in 250 ml. of ethanol and 100 ml. of toluene was added dropwise. After refluxing for 3 hr., during which time 350 ml. of solvent was distilled, the cooled mixture was added to water. The usual work-up yielded a residue which was heated under vacuum until most of the excess methylmalonate was recovered. The yellow residue was dissolved in 200 ml. of low boiling petroleum ether. The colorless solid which separated was recrystallized from 65–100° petroleum ether to yield 53.0 g. (81%) of IIb, m.p. 77.4–83.0°, in two crops of material good enough for the next step. In other similar runs the yield was 66–71%.

In the case of the *o*-isomer IIc, the reaction was carried out essentially as for IIb, except that the time of reflux of the entire reaction mixture was 12 hr. The crude reaction product, after removal of excess methylmalonate, was crystallized from methanol to yield IIc, m.p. 63.0–63.8°, in 91% yield. At first only liquid IIc was obtained, but after 6 months seed crystals were obtained. In early work the crude IIc was distilled, b.p. 225–250° (1 mm.).

Anal. Calcd. for $C_{28}H_{42}O_8$: C, 66.4; H, 8.4. Found: C, 66.4; H, 8.3 (IIa); C, 66.5; H, 8.3 (IIb); C, 66.6; H, 8.3 (IIc).

Bis-[(2,2-bis-hydroxymethyl)-propyl]-durenes (IIIa,b,c).—In a typical reaction, 55.0 g. of IIa in 450 ml. of dry ether was added to a stirred suspension of 24 g. of lithium aluminum hydride in 400 ml. of tetrahydrofuran. After refluxing for 20 hr. the reaction mixture was cooled to 0–5° and treated carefully with 96 g. of water and 750 ml. of Methyl Cellosolve (ethylene glycol mono-methyl ether). This mixture was distilled to remove low boiling solvents and filtered hot through a filter aid (Hypo-flo Super Cel). The filter aid was washed with additional hot Methyl Cellosolve (500 ml.) and on cooling, 32 g. of crude III in two crops was obtained. Recrystallization from dimethylformamide (200 ml.) yielded 27.0 g. (74%) of IIIa, m.p. 207–210°.

For the reduction of IIb and IIc, only tetrahydrofuran was used as solvent. After reduction was complete (about 20 hr. for each) dilute sulfuric acid was added for decomposing excess lithium aluminum hydride. The hot solution was filtered to remove insoluble salts and the filtrates cooled and treated with saturated sodium carbonate solution and then saturated sodium chloride solution. The THF solutions were concentrated, and on cooling IIb and IIc crystallized. After recrystallization of IIIb from acetone-methanol (6:1) colorless IIIb, m.p. 129–131°, was

(27) We thank Dr. B. Lord and Mr. P. B. Dalton, Antara Chemicals, General Aniline and Film Corp., for a generous supply of *n*-methylpyrrolidone.

(28) The temperature went as high as 170° at the end by accident. At this temperature the reaction mixture turned black. The yield in this run was higher than others in which the temperature did not rise above 100°, but we did not check it to see if the high temperature was necessary.

obtained in 73% yield. Similarly IIIc, m.p. 196–199°, was obtained in 81% yield after recrystallization from THF-benzene (5:4).

Anal. Calcd. for $C_{20}H_{34}O_4$: C, 71.0; H, 10.1. Found: C, 70.9; H, 10.1 (IIIa); C, 71.0; H, 10.1 (IIIb); C, 71.3; H, 9.7 (IIIc).

Bis-[(2,2-bis-methanesulfonylmethyl)-propyl]-benzenes (IVa,b,c).—To a suspension of 23.5 g. of IIIa in 600 ml. of chloroform at –10° was added 71 g. of methanesulfonyl chloride. To this suspension was added dropwise 75.6 g. of collidine keeping the temperature below 5°. The heterogeneous mixture was stirred for 4 hr. at 5–15° and at room temperature for 15 hr. On reaching room temperature the mixture turned yellow and then black. The yellow precipitate was collected by filtration and washed with chloroform, ethanol, water, and ethanol. The solid was recrystallized from 200 ml. of boiling dimethylformamide (charcoal, Darco G-60) to yield 42.6 g. (94%) of IVa, m.p. 204–207° dec. In other runs in which the temperature maintained when the collidine was added was higher and when the reaction time below 15° was less than 4 hr., the yields ranged from 77–84%.

In the cases of IVb and IVc the methanesulfonyl derivatives are soluble in chloroform and the work-up consisted of proper washings. Concentration of the chloroform solutions and dilution with ether caused separation of IVb and IVc as oils which slowly crystallized. Crystallization from acetone-methanol (3:1) yielded IVb, m.p. 139–142°, in 93% yield. Crystallization from acetone-ethanol (5:4) yielded IVc, m.p. 133–134°, in 95% yield.

Anal. Calcd. for $C_{24}H_{42}O_{12}S_4$: C, 44.3; H, 6.5; S, 19.7. Found: C, 44.7; H, 6.5; S, 19.9 (IVa); C, 44.3; H, 6.2; S, 19.6 (IV); C, 44.8; H, 6.4; S, 19.8 (IVc).

Bis-[(3-methyl)-3-thietanyl]-methyl-tetramethylbenzenes (Va,b,c).—To 150 ml. of ethylene glycol at 160° was added with stirring 19 g. of recrystallized (from alcohol) sodium sulfide nonahydrate in portions. The resulting solution was distilled until the boiling point of ethylene glycol was reached (to remove the water of hydration) and then cooled to 100°. A solution of 10.0 g. of IVa in 250 ml. of distilled Ethyl Cellosolve (ethylene glycol monoethyl ether) was treated dropwise with stirring with the above solution of sodium sulfide and the resulting mixture was held at reflux for 1 hr. On cooling, crude Va crystallized. After washing with water and methanol, the solid was taken into 200 ml. of methylene chloride and treated with Darco G-60. By a combination of crystallization from ethanol-chloroform (8:1) and chromatography over Woelm basic alumina there was obtained 3.4 g. (67%) of Va, m.p. 165–168°.

To a stirred solution at reflux under nitrogen of 120 g. of IVb in 2.3 l. of pure Ethyl Cellosolve in a 5-l. flask was added a freshly prepared solution of 75 g. of dehydrated sodium sulfide in 1.8 l. of ethylene glycol (prepared as described above). This mixture was refluxed for 2 hr. and then 1400 ml. of solvent distilled. After cooling to 5° the mixture was filtered through Celite (a filter aid). The sticky solid thus obtained was washed with 300 ml. of cold ethanol and the remaining solid was extracted into hot benzene (800 ml.). The original filtrate and washings were extracted with petroleum ether. These extracts and the benzene extract were combined and concentrated to dryness. The residue was taken up in benzene and passed through a column (3 × 36 in.) over Woelm basic alumina. On concentration of the benzene there was obtained 26.9 g. (44%) of Vb, m.p. 103.5–106.5°. Additional less pure Vb was obtained from the mother liquor. Further work was carried out on purified Vb.

The *o*-isomer IVc was processed essentially as the *m*-isomer. On cooling the concentrated reaction mixture as above, the solid which separated was nicely crystalline and Celite was omitted. A benzene solution of this solid was filtered and the benzene was removed from the filtrate. The residue was chromatographed over Woelm basic alumina in chloroform-benzene (1:3). On crystallization from benzene-alcohol, Vc, m.p. 164–166°, was obtained in 51% yield.

In each case, V-ac, more less-pure material could be isolated but in further steps, this Vb gave less-pure final VI, although less pure Va and Vc gave pure VI and Vlc.

Anal. Calcd. for $C_{26}H_{36}S_2$: C, 71.8; H, 9.0; S, 19.2. Found: C, 71.7; H, 9.2; S, 19.0 (Va); C, 71.9; H, 8.9; S, 19.0 (Vb); C, 71.8; H, 9.2; S, 19.0 (Vc).

Dineopentyltetramethylbenzenes (VIa,b,c).—A solution of 2.7 g. of Va in 400 ml. of ethanol and about 45 g. of W-2 Raney nickel¹⁷ was stirred at room temperature for 5 hr. and at reflux for 15 hr. Filtration and concentration yielded 3.0 g. of crude product which by crystallization from alcohol and sublimation at 90° and 1 mm. yielded 2.75 g. (72%) of VIa, m.p. 110.2–111.6°.

In a similar way except that the reaction with nickel was at 60° for 6 hr. and 10 hr. at 70°, VIb, m.p. 77.2–77.8°, was obtained in 71% yield, and Vlc, m.p. 96.0–97.5°, in 76% yield. All were reported pure.¹⁴

Anal. Calcd. for $C_{20}H_{34}$: C, 87.5; H, 12.5. Found: C, 87.6; H, 12.4 (VIa); C, 87.2; H, 12.7 (VIb); C, 87.6; H, 12.4 (Vlc).

