Homologs of Diphenylmethane. II. Homologs with an Odd Number of Rings

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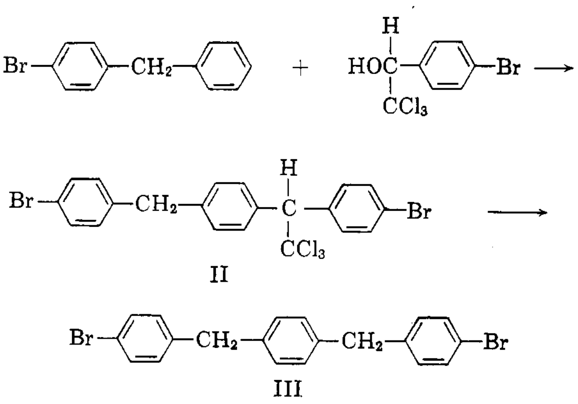
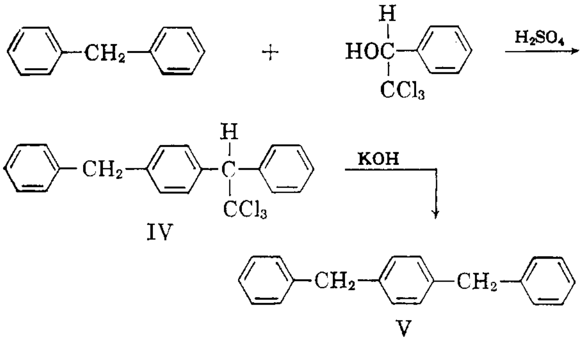
Diphenylmethane homologs of the general formula $p\text{-}XC_6H_4CH_2(C_6H_4CH_2)_nC_6H_4X\text{-}p$, ($n$ = 1 and 3) where X is hydrogen or halogen, have been prepared either from 1,1-diaryl-2,2,2-trichloroethanes, as described previously, or by reduction of suitably constituted diketones.

In a previous publication[1] we reported the preparation of several derivatives and homologs of diphenylmethane *via* 1,1-diphenyl-2,2,2-trichloroethanes. We tried to extend the method to systems containing an odd number of rings, but all attempts to condense 2,2,2-trichloro-1-phenylethanol with 4-bromodiphenylmethane in its free *para* position or diphenylmethane with 1-*p*-bromophenyl-2,2,2-trichloroethanol failed.

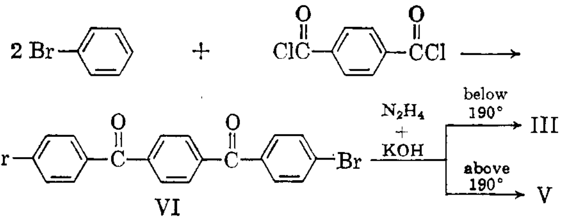
Equally negative results were obtained in experiments to synthesize the carbinol $BrC_6H_4CH_2C_6H_4CHOHCCl_3$ (I) from the monomagnesium derivative of *p,p'*-dibromodiphenylmethane and chloral or by condensation of trichloroacetonitrile or trichloroacetic anhydride with *p*-bromodiphenylmethane in the presence of aluminum chloride (and subsequent reduction). Eventually we succeeded in condensing 1-(*p*-bromophenyl)-2,2,2-trichloroethanol with *p*-bromodiphenylmethane to II; the product could be hydrolyzed and decarboxylated in one step to III:



Analogously, diphenylmethane was condensed with 2,2,2-trichloro-1-phenylethanol and the resulting compound (IV) hydrolyzed and decarboxylated with potassium hydroxide to *p*-dibenzylbenzene (V), which has been prepared before by different routes.[2]

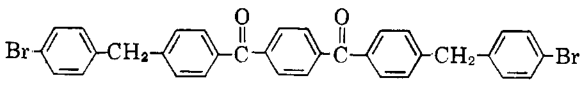


In order to prove the structure of compounds III and V, they were also prepared by the route indicated in the following chart:

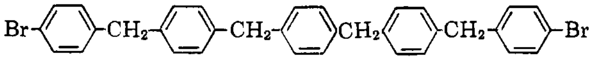


Ketone VI which is obtained in good yield, is difficult to reduce. Catalytic hydrogenation yielded a bromine-free compound, and Clemmensen reduction resulted in an unidentified product.[2a,3] Huang-Minlon reduction gave mixtures of III and V in which V predominates if higher temperatures or prolonged reaction times are employed.[4]

The analogous sequence based on terephthaloyl chloride and *p*-bromodiphenylmethane gave compound VII; in this case Huang-Minlon reduction (to VIII) did not present any undue difficulties.



VII



VIII

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(1) A. B. Galun, A. Kaluszyner, and E. D. Bergmann, *J. Org. Chem.*, in press.

(2) (a) F. Klages, E. Mergenthaler, and H. Haury, *Chem. Ber.*, **81**, 400 (1948). (b) E. Profft, G. Drechsler, and H. Oberender, *Chem. Abstr.*, **55**, 2564 (1961).

(3) *Cf.* E. L. Martin, *Org. Reactions*, **1**, 155 (1942).

(4) A similar observation has been reported by Ng. Ph. Buu-Hoï, Ng. H. Hoán, and Ng. D. Xuong, *Rec. trav. chim.*, **71**, 285 (1952).

Experimental

Attempted Condensation of Trichloroacetonitrile and *p*-Bromodiphenylmethane.—Gaseous hydrogen chloride was passed for 1 hr. at 50° and 2 hr. at 110° through a stirred mixture of 19.2 g. of trichloroacetonitrile,[5] 27.1 g. of *p*-bromodiphenylmethane[1] and 14.6 g. of aluminum chloride. The mixture was then poured into ice and treated with hydrochloric acid. The organic material was separated, dried, and recrystallized once from carbon tetrachloride and once from a benzene–petroleum ether mixture. Thus 14 g. of a compound subliming at 95° and melting (sealed tube) at 144° was obtained, which proved to be a polymer of trichloroacetonitrile.[6]

Anal. Calcd. for $(C_2NCl_3)_x$: C, 16.7; H, 0.0. Found: C, 16.9; H, 0.0.

From the combined mother liquors, practically all the *p*-bromodiphenylmethane was recovered unchanged.

1-(*p*-Bromophenyl)-1-[(*p*-(4-bromobenzyl)phenyl]-2,2,2-trichloroethane (II).—To a stirred mixture of 17.1 g. of 1-(*p*-bromophenyl)-2,2,2-trichloroethanol and 13.0 g. of *p*-bromodiphenylmethane, 21 ml. of concd. sulfuric acid was added at 10°. Stirring was continued at room temperature for 2 days and the mixture poured into ice-cold water. The organic material was separated, triturated with alcohol, and recrystallized from either alcohol or acetone. The product (14 g., 50%) melted at 123°.

Anal. Calcd. for $C_{21}H_{15}Br_2Cl_3$: C, 47.3; H, 2.8. Found: C, 47.0; H, 3.0.

α,α-Di(4-bromophenyl)-*p*-xylene (III).—Water was distilled from a mixture of 9 g. of potassium hydroxide, 60 ml. of diethylene glycol, and 4 ml. of water, until the boiling temperature reached 190°. Then 10.7 g. of the foregoing compound II was added and the mixture refluxed, with stirring, at 175–180° for 5 hr. The hot solution was poured onto ice and the organic product separated and triturated with alcohol. After recrystallization from alcohol or acetone, 7.7 g. (95%) of III, melting at 127°, was obtained. The product tends to yield supersaturated solutions.

Anal. Calcd. for $C_{20}H_{16}Br_2$: C, 57.7; H, 3.9. Found: C, 57.5; H, 3.7.

1-Phenyl-1-(*p*-benzylphenyl)-2,2,2-trichloroethane (IV). To a stirred mixture of 22.5 g. of 2,2,2-trichloro-1-phenylethanol and 16.8 g. of diphenylmethane, 70 ml. of concd. sulfuric acid was added at 10°. Stirring was continued for 4 hr. at 10° and the solution poured into an ice–water mixture. The organic material was separated and triturated with alcohol. Recrystallization from alcohol (or acetone) gave 15.1 g. (40%) of material melting at 117–118°. $\bar{\nu}_{max}^{KBr}$ 730 (monosubst. benzene), 785 (CCl_3), 830 (*p*-disubstituted benzene); no selective ultraviolet absorption.

Anal. Calcd. for $C_{21}H_{17}Cl_3$: C, 67.4; H, 4.6. Found: C, 67.4; H, 4.6.

In some runs oils were obtained, which required up to 3 weeks to crystallize; these oils can be used for the next step without further treatment.

1,4-Dibenzylbenzene (V).—One-step hydrolysis and decarboxylation of IV, carried out as described above for the preparation of III, gave an almost quantitative yield of 1,4-dibenzylbenzene. After recrystallization from acetone, the product melted at 84–85° (lit.,[2a,3] 85–86°).

Anal. Calcd. for $C_{20}H_{18}$: C, 93.0; H, 7.0. Found: C, 92.9; H, 7.0.

***p*-Di(4-bromobenzoyl)benzene (VI).**—To a well stirred mixture of 20.3 g. of terephthaloyl chloride and 100 ml. of bromobenzene, 33 g. of powdered aluminum chloride was added over a period of 10 min. The mixture was stirred for 4 hr. at 120° and poured into ice and hydrochloric acid. The product was filtered and recrystallized from chloroform (at least 100 ml./g. is required). Thus, an 80% yield (35.6 g.) of material melting at 274–276° (sealed tube, sublimes at 260°) was obtained. $\bar{\nu}_{max}^{KBr}$ 840, 843 (*p*-disubstituted benzene); 1640 (carboxyl); $\lambda_{max}^{CHCl_3}$ 271 (2.72).

Anal. Calcd. for $C_{20}H_{12}Br_2O_2$: C, 54.1; H, 2.7. Found: C, 54.0; H, 2.7.

For preparative purposes VI is more conveniently recrystallized from dimethylformamide, although traces of this solvent adhere to it tenaciously.

α,α-Di(4-bromophenyl)-*p*-xylene (III).—Attempts to reduce the diketone (VI) catalytically or by the Clemmensen method met with failure. Therefore, the Huang-Minlon modification of the Wolff-Kishner reduction was used. A mixture of 4.4 g. of VI, 20 ml. of diethylene glycol, 2.6 g. of potassium hydroxide, and 2 ml. of 95% hydrazine hydrate was heated for 1 hr. at 130°. Water was then distilled until the boiling point reached 190°, and the mixture refluxed for 6 hr. and poured onto ice. The product was filtered, dissolved in hot ethanol, and left to crystallize which took about 2 weeks. Recrystallization from acetone gave a 20% yield of a product melting at 127° which proved identical (mixed melting point and infrared spectrum) with the compound III described above.

1,4-Dibenzylbenzene (V).—The reduction described in the preceding paragraph was repeated but the mixture was refluxed for 8 hr. at 200°. After recrystallization, a 40% yield of a product melting at 84–85° was obtained which proved identical (mixed melting point, infrared spectrum) with V, as obtained before.

1,4-Di[(*p*-bromobenzyl)benzoyl]benzene (VII).—A solution of 12.3 g. of *p*-bromodiphenylmethane, 40 ml. of nitrobenzene, and 5 g. of terephthaloyl chloride was cooled to −5° and 7.4 g. of powdered aluminum chloride added in portions and with stirring. The mixture was slowly heated to 80° and kept at this temperature for 1 hr. Dissolved hydrogen chloride was then removed under reduced pressure and the solution poured onto ice and subjected to steam distillation until all the nitrobenzene had been removed. The residue was extracted with chloroform, the solution decolorized with active charcoal and concentrated, and the residue recrystallized from toluene. Thus 7.7 g. (50%) of VII, melting at 175°, was obtained.

Anal. Calcd. for $C_{34}H_{24}Br_2O_2$: C, 65.4; H, 3.9. Found: C, 65.4; H, 4.2.

$\bar{\nu}_{max}^{KBr}$ 862 (*p*-disubstituted benzene); 1665 (carbonyl).

α,α'-Di[4-(*p*-bromobenzyl)phenyl]-*p*-xylene (VIII).—A mixture of 3.12 g. of VII, 10 ml. of diethylene glycol, 1 ml. of 95% hydrazine hydrate, and 1.4 g. of potassium hydroxide was heated on a water bath until all the hydroxide had dissolved. The mixture was then refluxed for 2 hr., water distilled until the boiling temperature had reached 190–200°, refluxed for another 5 hr. and poured onto ice. The precipitate was filtered and dried, giving a 60% yield of VIII. After two recrystallizations from a benzene–alcohol mixture and one from acetone (this step resulted in a marked loss of material) crystals melting at 165–166° were obtained.

Anal. Calcd. for $C_{34}H_{28}Br_2$: C, 68.5; H, 4.7. Found: C, 68.6; H, 5.1.

$\lambda_{max}^{CHCl_3}$ 272 (4.67); 344 (2.50).

Acknowledgment.—The authors are indebted to Rachel Zelnicker and Bracha Gershon for technical assistance.

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(5) W. Steinkopf, *Ber.*, **41**, 2540 (1908).

(6) The reported melting point for the trimer of trichloroacetonitrile is 96°; Beilstein, Vol. 26, p. 37.