This mixture was refluxed, with good stirring until solid polymer formed. Stirring and heating were continued until the polymer formed rather fine particles. The polymer was removed by filtration, washed with boiling water, and dried. The polymer was reprecipitated twice from ethanol with 20% aqueous sodium chloride solution. The product was then extracted with water in a Soxhlet extractor until the extract gave a negative test for chloride ion. The polymer was then dried at about 20 mm. vacuum and 60°.

Titration of the polymer with 0.1 *N* sodium hydroxide gave a neutral equivalent of 160.49. Found: C, 63.37 and 63.08; H, 4.82 and 4.69.

Anal. Calcd. for a neut. equiv. of 164.8: C, 63.15; H, 4.99.

These data agree with formula I. The infrared spectrum of the polymer was consistent with formula I.

Determination of the molecular weight of the polymer by light scattering on a Brice-Phoenix Instrument in either alcohol or acetone gave values of 6700 ± 15%.

Preparation of metal chelates. Zinc(II). A 0.015-mole sample (2.04 g.) of zinc(II) chloride was dissolved in 100 ml. of water, and 1 ml. of hydrochloric acid (concd.) was added to effect complete dissolution. A 0.02-mole sample of salicylic acid formaldehyde polymer (3.6 g.) was added to 18.5 ml. of 1 *N* sodium hydroxide and 100 ml. of ethanol. The resulting solution had an apparent *p*H of 5.5. The polymer solution was added dropwise to the zinc solution under rapid stirring with magnetic stirrer. Sodium hydroxide, 1 *N*, was added to maintain an apparent *p*H of 5.2. A white precipitate formed which was filtered through a Büchner funnel 24 hr. after precipitation was complete, washed with 100 ml. of water followed by 100 ml. of alcohol, air dried, then placed into a Soxhlet extractor and extracted with ethanol for 24 hr. The resulting product was placed into an Abderhalden apparatus and dried *in vacuo* for 24 hr. over phosphorus pentoxide at the temperature of refluxing ethanol and then analyzed for carbon, hydrogen, and zinc in a conventional manner. The results of these analyses are given in Table I.

The preparations of the other chelates were carried out in the same manner. The amounts used were:

Nickel(II): 0.015 mole of nickel(II) chloride, hexahydrate (3.57 g.) and 0.02 mole of polymer (3.6 g.).

Aluminum(III): 0.01 mole of aluminum(III) chloride, hexahydrate (2.4 g.) dissolved in 100 ml. of water, and 0.03 mole of polymer (5.4 g.) dissolved in 250 ml. of ethanol under addition of 10 ml. of 1 *N* sodium hydroxide. Apparent *p*H was 2.5.

Iron(III): 0.01 mole of iron(II) chloride hexahydrate (2.7 g.) and 0.03 mole of polymer (5.4 g.) dissolved in 250 ml. ethanol upon addition of 10 ml. of 1 *N* sodium hydroxide. Apparent *p*H was 1.3.

UO_2^{+2}: 0.015 mole of uranium(VI) nitrate hexahydrate (7.53 g.) and 0.02 mole of polymer.

Thermal stability of chelates. Samples of metal chelates prepared and dried as described before were heated from room temperature to constant weight at a rate of 5°/min. on a thermobalance (system of P. Chevenard) which measures and registers weight continually as the temperature of the material is raised.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE ISRAEL INSTITUTE FOR BIOLOGICAL RESEARCH]

Homologs of Diphenylmethane. I. Homologs with an Even Number of Rings

ARJEH B. GALUN, ASHER KALUSZYNER, AND ERNST D. BERGMANN

Received March 15, 1961

The condensation of chloral or 1-aryl-2,2,2-trichloroethanols with substituted benzenes to give 1,1-diaryl-2,2,2-trichloroethanes is described. The trichloroethanes were converted to the corresponding diphenylmethane derivatives by heating them with potassium hydroxide solution in boiling diethylene glycol.

Higher homologs of diphenylmethane, containing alternating phenylene and methylene groups C_6H_5-$CH_2(C_6H_4CH_2)_nC_6H_5$ are practically unknown, and many simple derivatives of diphenylmethane, especially those containing different substituents in the two benzene rings, were hitherto prepared by complicated routes and in low yields.

We found that derivatives and higher homologs of diphenylmethane are easily prepared by condensing aromatic compounds with either chloral or 1-aryl-2,2,2-trichloroethanols (I, VIII),[1] followed by degradation of the trichloromethyl groups and decarboxylation of the carboxylic acids so obtained. The last two steps were carried out without isolation of the intermediate products (see chart).

These "D.D.T.-type" condensations gave in most cases good yields of pure materials. For optimal yields the conditions of the initial condensation reaction had to be slightly modified from compound to compound, but using about 700 ml. of concentrated sulfuric acid per mole of reactants reasonable yields may be expected. Some sulfonation is usually encountered; it is therefore advisable to avoid the use of oleum unless the aromatic components are at least slightly deactivated–(*e.g.*, in bromobenzene. The sulfonation products, if formed, are easily separated from the trichloroethanes by water extraction. The trichloroethanes were smoothly converted into the corresponding diphenylmethanes by potassium hydroxide in refluxing diethylene glycol (five hours at 185°). Shorter reaction times and lower temperatures effect only dehydrohalogenation, yielding 1,1-diaryl-2,2-dichloroethylenes. Analogously, the condensations of 2,2,2-trichloro-1-phenylethanol (I) with *m*-bromotoluene and of 1-(*p*-bromophenyl)-2,2,2-trichloroethanol (VIII) with chlorobenzene were studied; the products (IX and X) were converted into 4 - bromo - 2 - methyldiphenylmethane (XI) (see below) and 4-bromo-4′-chlorodiphenylmethane (XII), respectively. Also from 1,1-di(*p*-

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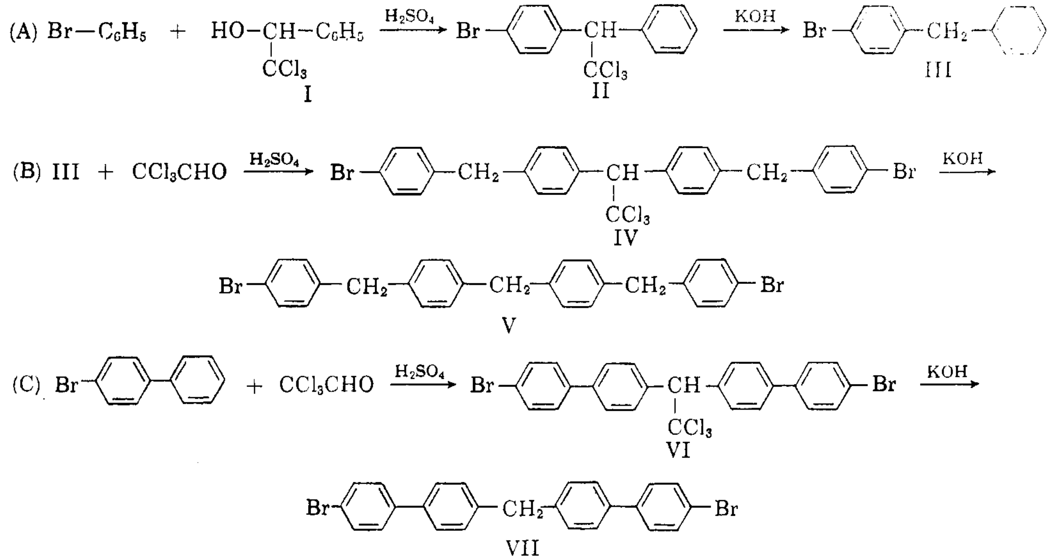
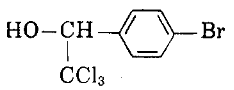
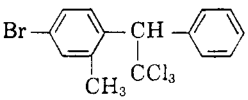
[1] F. D. Chattaway and R. J. K. Muir, *J. Chem. Soc.*, 701 (1934).



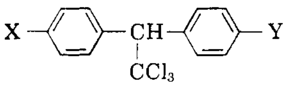
bromophenyl)-2,2,2-trichloroethane (XIII) and 2,2,2-trichloro-1,1-di(*p*-tolyl)ethane (XIV) the 4,4′-disubstituted diphenylmethanes were formed in almost quantitative yield by treatment with alkali in diethylene glycol.



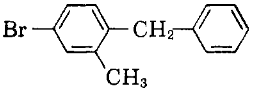
VIII



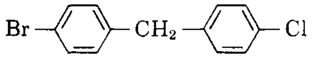
IX



X. X = Br, Y = Cl.
XIII. X = Br, Y = Br.
XIV. X = CH3, Y = CH3.



XI



XII

In order to prove the structures of IX and XI, IX was dehydrohalogenated and the product oxidized to 4-bromo-2-methylbenzophenone. This ketone has been obtained, for comparison, by an unambiguous route—*viz.*, by reaction of 4-bromo-2-methylbenzonitrile with phenylmagnesium bromide.

Spectra. The ultraviolet spectra of the new compounds are all practically identical, showing the longest absorption band at 275–279 mμ. This represents a bathochromic shift, compared with diphenylmethane (260 mμ),[2,3] undoubtedly due to the *para*-substitution by halogen.

The infrared spectra are included in Table I. In most cases a weak band appeared at 3400 cm.$^{-1}$; this is very much higher than the reported aromatic frequencies of diphenylmethane,[4] the methylene frequencies of which lie at 2912 and 2844 cm.$^{-1}$.

EXPERIMENTAL

Materials. For all condensations, one of the following three starting materials was used. Chloral (Method A): Commercial chloral was freshly distilled from sulfuric acid. 2,2,2-Trichloro-1-phenylethanol (Method B) was prepared by the method described.[5] 1-(*p*-Bromophenyl)-2,2,2-trichloroethanol (Method C) was synthesized from *p*-bromophenylmagnesium bromide and chloral,[6] *p*-bromobiphenyl according to Gomberg and Bachmann.[7] The diethylene glycol used was White Label 2,2′-oxydiethanol (Eastman Kodak Co.). For analyses and physical constants, see the Table.

1,1-Bis(4′-bromo-4-biphenylyl)-2,2,2-trichloroethane (VI). Method A. To a mixture of 32 g. of *p*-bromobiphenyl and 11.3 g. of chloral 85 ml. of sulfuric acid was added with stirring at 50°. After completion of the addition the mixture was stirred for 2 hr. at 70° and poured onto 700 g. of crushed ice. The aqueous layer was decanted and the residue triturated with ethanol. The material was recrystallized from acetone.

Di(4′-bromo-4-biphenylyl)methane (VII). The foregoing compound was hydrolyzed and decarboxylated in the following generally applicable manner: To 300 ml. of diethylene glycol a solution of 45 g. of potassium hydroxide in 25 ml. of water was added. The mixture was heated and water distilled until the temperature reached 185°. It was then allowed to cool to about 100°, and 59.6 g. of VI was added. The mixture was refluxed with stirring for 5 hr., poured onto 3 kg. of crushed ice, and left overnight. The aqueous layer was separated, extracted with ether, and the ether added to the main product. The residue of the ethereal solution was triturated with ethanol and recrystallized from acetone. Yield: 39.3 g. (82%).

When 2 g. of compound VI was refluxed for 30 min. with a slight excess of ethanolic potassium hydroxide solution, a 90% yield of *1,1-bis(4′-bromo-4-biphenylyl)-2,2-dichloroethylene*, m.p. 198° (from acetone), was obtained.

Anal. Calcd. for $C_{26}H_{16}Br_2Cl_2$: C, 55.8; H, 2.9. Found: C, 55.5; H, 2.8.

1-Phenyl-1-(p-bromophenyl)-2,2,2-trichloroethane (II). Method B. To a well agitated mixture of 113 g. of 2,2,2-trichloro-1-phenylethanol (I) and 100 g. of bromobenzene, 150 ml. of sulfuric acid was added dropwise, the temperature

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(2) P. Ramart-Lucas, *Bull. Soc. Chim. France*, **51**, 289 (1932); **1**, 719 (1934); **3**, 723 (1936).

(3) W. R. Orndorff, R. C. Gibbs, S. A. McNulty, and C. V. Shapiro, *J. Am. Chem. Soc.*, **49**, 1541 (1927); **50**, 831 (1928).

(4) A. Hidalgo, *Chem. Abstr.*, **48**, 8653 (1954).

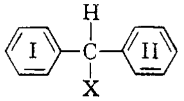
(5) E. D. Bergmann, D. Ginsburg, and D. Lavie, *J. Am. Chem. Soc.*, **72**, 5012 (1950).

(6) P. Hébert, *Bull. Soc. Chim. France*, [4], **27**, 45 (1920).

(7) M. Gomberg and W. E. Bachmann, *Org. Syntheses*, Coll. Vol. I, 113 (1943).

TABLE I

DERIVATIVES OF 1,1-DIPHENYL-2,2,2-TRICHLOROETHANE AND DIPHENYLMETHANE



Substituents in the Aromatic Rings		X = CCl_3								
						Carbon		Hydrogen		
I	II	No.	Method	Yield, %	M.P.°	Calcd.	Found	Calcd.	Found	Remarks
4-Br	4-Br	XIII	A		143					[a]
4-Br	—	II	B	90	96	46.1	46.2	2.8	2.8	[b]
4-BrC_6H_4	4-BrC_6H_4	VI	A	70	173	52.4	52.5	2.9	2.9	
4-CH_3	4-CH_3	XIV	A		89					[b]
4-Br	4-Cl	X	C	45	124	42.1	42.2	2.3	2.5	[c]
2-CH_3, 4-Br	—	IX	B	26	145	47.6	47.6	3.2	3.4	
4-(*p*-$BrC_6H_4CH_2$)	4-(*p*-$BrC_6H_4CH_2$)	IV	A	50	152	53.9	53.9	3.4	3.5	

[a] This compound has been described by O. Zeidler, *Ber.*, **7**, 1180 (1874), and by K. Brand and D. Kruecke-Amelung, *Ber.*, **72**, 1029 (1939), who reported melting points of 136–141° and 144°, respectively. [b] This compound has been obtained by a similar method by Chattaway and Muir,[1] who reported the same melting point. [c] G. H. Schneller and G. B. L. Smith, *J. Am. Chem. Soc.*, **70**, 4057 (1948), prepared the same compound by the condensation of (*p*-chlorophenyl)trichloroethanol with bromobenzene. [d] 4,4'-Dibromodiphenylmethane has been prepared by several routes—Beilstein's Handbuch der Organischen Chemie, Vol. V, p. 593, and Supplements. Direct bromination of diphenylmethane yields a mixture of isomers [N. E. Goldthwaite, *Am. Chem. J.*, **30**, 447 (1903)], which we were unable to separate. I. M. Hunsberger and E. D. Amstutz, *J. Am. Chem. Soc.*, **71**, 2635 (1949) obtained the 4,4'-dibromo compound as by-product in the preparation of 4,4'-dibromodiphenylacetic acid from the corresponding trichloroethane. [e] J. H. Speer and A. J. Hill[1] [*J. Org. Chem.*, **2**, 139 (1937)] ob-

rising to about 50°. The solution was heated for 3 hr. at 65°, poured onto crushed ice, and left overnight. The aqueous layer was separated and the solid product recrystallized from ethanol. Thus, 164.1 g. (90%) of II was obtained.

4-Bromodiphenylmethane (III). As described above, compound II was hydrolyzed and decarboxylated. The crude product was extracted with ether and insoluble material discarded. The ether was evaporated and the product purified by distillation. Yield, 90%. M_R, calcd., 63.08; M_R found, 63.25.

1,1-Bis[p-(4-bromobenzyl)-phenyl]-2,2,2-trichloroethane (IV). Method A. To an ice-cooled, stirred mixture of 20 g. of 4-bromodiphenylmethane (III) and 5.5 g. of chloral 25 ml. of sulfuric acid was added. The mixture was stirred for 2 hr. at room temperature and for 2 hr. at 50° and poured onto crushed ice. The aqueous layer was separated and the solid product recrystallized from an acetone-alcohol mixture.

Bis[p-(4-bromobenzyl)phenyl]methane (V). Compound IV was hydrolyzed and decarboxylated, as indicated above. The product was recrystallized from acetone. Yield, 80%.

1,1-Bis[p-(4-bromobenzyl)phenyl]-2,2-dichloroethylene, m.p. 102° (from alcohol), was obtained in 90% yield by heating IV for 3 hr. at 150° in an alkaline diethylene glycol solution.

Anal. Calcd. for $C_{28}H_{20}Br_2Cl_2$: C, 57.3; H, 3.4. Found: C, 57.0; H, 3.5.

1-(4-Bromo-2-methylphenyl)-1-phenyl-2,2,2-trichloroethane (IX). Method B. A mixture of 22.5 g. of 2,2,2-trichloro-1-phenylethanol (I) and 17.1 g. of *m*-bromotoluene was cooled to −5° and a mixture of 30 ml. of 20% oleum and 57 ml. of conc. sulfuric acid slowly added with stirring. The stirring was continued for 2 hr. at 5° and 2 hr. at room temperature, and the product poured onto crushed ice and left overnight. The oily layer was washed several times with warm water and triturated with ethanol, until it crystallized. Two recrystallizations of the crude mixture of isomers (28 g.) from ethanol gave 12 g. of pure IX, m.p. 145°. From the ethanolic mother liquors, no other product was isolated in pure state.

1-(4-Bromo-2-methylphenyl)-1-phenyl-2,2-dichloroethylene. A solution of 1.6 g. of IX, 0.8 g. of potassium hydroxide, and 40 ml. of ethanol was refluxed for 10 hr., half the alcohol distilled, and the remainder poured into 60 ml. of water. The product was recrystallized from aqueous acetone, yielding 1 g. of 1-(4-bromo-2-methylphenyl)-1-phenyl-2,2-dichloroethylene, m.p. 51°.

Anal. Calcd. for $C_{15}H_{11}BrCl_2$: C, 52.7; H, 3.2. Found: C, 52.6; H, 3.4.

4-Bromo-2-methylbenzophenone. (a) The foregoing compound (1.0 g.) was oxidized by treatment with a mixture of 30 ml. of acetic acid and 5 g. of chromic acid for 5 hr. at 50°. The resulting solution was diluted with 100 ml. of water and extracted several times with ether. The ether extract was washed with an aqueous solution of sodium carbonate, dried over sodium sulfate, and concentrated, and the residue dissolved in ethanol and converted directly into the 2,4-dinitrophenylhydrazone, m.p. 238°.

Anal. Calcd. for $C_{20}H_{15}BrN_4O_4$: C, 52.8; H, 3.3. Found: C, 52.8; H, 3.4.

(b) *2-Methyl-4-nitrobenzonitrile.* A dispersion of 75.1 g. of commercial 2-amino-5-nitrotoluene in 126 ml. of concd. hydrochloric acid and 126 ml. of water was diazotized at 0–5° with a solution of 37.2 g. of sodium nitrite in 60 ml. of water and the filtered solution added to a hot solution of cuprous cyanide and 60 g. of potassium cyanide in 150 ml. of water. The cuprous cyanide had been prepared from 149 g. of copper sulfate in 480 ml. of water, 41.8 g. of sodium bisulfite in 120 ml. of water, and 41.8 g. of potassium cyanide in 120 ml. of water, filtered, and washed with hot water. The mixture was heated at 100° for 0.5 hr. and left to cool, and the supernatant liquid decanted. The residue was recrystallized

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(8) R. Schmitt, Ger. Patent **869,205** (1953) [*Chem. Abstr.*, 52, 16 02 (1958)].

TABLE I (*Continued*)

				X = H				
	B.P. or	Carbon		Hydrogen		Ultraviolet,[g]	Infrared,[h]	
No.	M.P./Mm.	Calcd.	Found	Calcd.	Found	mμ	cm.$^{-1}$	Remarks
—	64					229, 263, 270, 278	3400, 2941, 810[g]	[d]
III	163/13	63.2	63.2	4.5	4.5	262, 270, 278	3080, 2941, 847, 794, 746	n^{24}D 1.6028; d^{24} 1.342[e]
VII	225	62.8	62.7	3.8	3.8		3400, 2941, 833, 800	
—	150/10							
XII	58	53.5	55.6	3.6	3.7	227, 256, 262, 270 278	3400, 2941, 815, 785	[f]
XI	170/13	64.4	64.1	5.0	5.2	255, 262, 270, 279	3080, 2941, 833, 730	n^{21}D 1.6022; d^{21} 1.321
V	115	64.1	64.1	4.4	4.3	232, 268, 275	3400, 3000, 2950, 800	

tained the same compound by the reduction of 4-bromobenzophenone with hydriodic acid and red phosphorus in a sealed tube in 92% yield. [f] Di-*p*-tolylmethane has been obtained in a variety of ways (Beilstein's Handbuch der Organischen Chemie," Vol. V, 615, and Supplements) but its synthesis was relatively involved. The product from the Friedel-Crafts reaction between toluene and either chloroform or methyl chloride contained much dimethylanthracene which was not easily removed. The best method seems to have been the reduction of the corresponding benzophenone with hydriodic acid and acid and phosphorus [E. Ador and A. A. Rilliet, *Ber.* **12**, 2298 (1879)]. [g] As the compounds are only very slightly soluble, the extinction values are not very accurate and are not given here. [h] Monosubstituted benzenes are reported to absorb at 737–747 cm.$^{-1}$, *p*-disubstituted at 810–833 cm.$^{-1}$, 1,2,4-trisubstituted at 805–825 cm.$^{-1}$.

once from acetic acid and once from water, yielding 70% of 2-methyl-4-nitrobenzonitrile, m.p. 99° (lit.[8] 100°).

Anal. Calcd. for $C_8H_6N_2O_2$: C, 59.3; H, 3.7. Found: C, 59.2; H, 3.8.

4-Amino-2-methylbenzonitrile. As we were unable, in accordance with the observation of Mayer,[9] to reduce the nitro compound in ethanol with palladium on charcoal at atmospheric pressure, the following method was adopted: To a solution of 8 g. of the nitrile in 120 ml. of acetic acid and 30 ml. of water 20 g. of iron powder was added at 90–95° during 1.5 hr. The mixture was kept for another hour at the same temperature and 30 ml. of water was added. After two additional hours of heating the mixture was diluted with much water and extracted with ether. The ether was washed first with a solution of sodium bicarbonate, then with water, and dried. The addition of petroleum ether (b.p. 40–60°) precipitated 4-amino-2-methylbenzonitrile which melted after recrystallization from an ether–petroleum ether mixture at 76–77°. Yield, 80%.

Anal. Calcd. for $C_8H_8N_2$: C, 72.7; H, 6.1. Found: C, 72.5; H, 6.24.

4-Bromo-2-methylbenzonitrile. The foregoing compound (6.6 g.) was dissolved in 50 ml. of water and 5.3 ml. of concentrated sulfuric acid and diazotized at 0–5° with a solution of 3.3 g. of sodium nitrite in 6 ml. of water, and the resulting solution was added to a hot solution of cuprous bromide prepared from 3.15 g. of copper sulfate, 1 g. of copper turnings, 7.7 g. of sodium bromide, 1.5 g. of sulfuric acid, and 150 ml. of water by refluxing for 4 hr. The mixture was extracted with ether, the solution dried, and concentrated, and the residue recrystallized from aqueous ethanol, giving a 75% yield of 4-bromo-2-methylbenzonitrile, m.p. 62–63°.

Anal. Calcd. for C_8H_6BrN: C, 49.0; H, 3.1. Found: C, 48.7; H, 2.9.[10]

4-Bromo-2-methylbenzophenone. A solution of 1 g. of 4-bromo-2-methylbenzonitrile in 4 ml. of ether was added to a Grignard solution, prepared from 1.1 g. of bromobenzene and 1.2 g. of magnesium in 3 ml. of ether. The mixture was refluxed for 10 hr., and the ketimine which separated, filtered, and hydrolyzed by refluxing it for 3 hr. with 10% hydrochloric acid. After neutralization, the solution was extracted with ether, dried, and concentrated. The oily residue was directly converted into the 2,4-dinitrophenylhydrazone, which proved identical (mixed m.p.) with the compound obtained by oxidation of 1-(4-bromo-2-methylphenyl)-1-phenyl-2,2-dichloroethylene.

4-Bromo-2-methyldiphenylmethane (XI). IX (8.5 g.) was hydrolyzed and decarboxylated by heating for 5 hr. at 180° with a solution of 8.5 g. of potassium hydroxide in 50 ml. of diethylene glycol. The mixture was poured onto ice, extracted with ether, the ether removed, and the product distilled; yield, 84%. M_R, calcd., 67.70; M_R, found, 67.82.

1-(p-Bromophenyl)-1-(p-chlorophenyl)-2,2,2-trichloroethane (X). Method C. To a mixture of 15.2 g. of 1-(*p*-bromophenyl)-2,2,2-trichloroethanol (VIII) and 7.0 g. of chlorobenzene 30 ml. of sulfuric acid was added with stirring. The solution was stirred for 2 hr. at 70° and poured onto crushed ice. The organic product was triturated with ethanol and recrystallized from the same solvent.

4-Bromo-4'-chlorodiphenylmethane (XII). Hydrolysis and decarboxylation of the trichloroethane derivative (X)

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(9) M. Mayer, *J. prakt. Chem.*, [2], **92**, 137 (1915).

(10) The literature on the bromo-2-methylbenzonitriles is confused. H. A. Claus and Kunath [*J. prakt. Chem.*, [2], **39**, 489 (1889)] described their preparation, but were later proved to have assumed wrong structures [by, *e.g.*, W. Borsche and A. Herbert, *Ann.*, **546**, 277 (1941)]. Y. Asahina and M. Furukawa [*J. Pharm. Soc. Japan*, No. **429**, 967 (1917)] prepared 5-bromo-2-methylbenzonitrile, which was erroneously reported [*Chem. Abstr.*, **12**, 473 (1918)] as 4-bromo-2-methylbenzonitrile.

yielded 88% of the diphenylmethane derivative (XII), which was recrystallized from ethanol.

4,4'-Dibromodiphenylmethane and di-p-tolylmethane. Method A. These two known compounds were obtained in 95% yield from the corresponding trichloroethanes (XII) and (XIV) (see Table I).

Acknowledgment. The excellent technical assistance rendered by Rachel Zelnicker, Bathia Cohen, and Braha Gershon is gratefully acknowledged.

NESS-ZIONA, ISRAEL

[CONTRIBUTION NO. 475 FROM THE NATIONAL CHEMICAL LABORATORY, POONA, INDIA]

Terpenoids. XXVII. Base-Catalyzed Reactions with *N*-Lithioethylenediamine

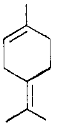
B. S. TYAGI, B. B. GHATGE, AND S. C. BHATTACHARYYA

Received October 9, 1961

The application of *N*-lithioethylenediamine previously examined by Reggel, Friedman, and Wender has been extended and its reactions towards several mono- and sesquiterpenoids with or without oxygen functions studied. Some of these underwent facile dehydrogenation, some were isomerized to conjugated products and the rest remained unchanged.

In a recent communication in this journal Reggel has described the use of *N*-lithioethylenediamine for the isomerization of olefins and dehydrogenation of cyclic dienes to aromatic systems.[1] A possible mechanism of the reaction has also been described. This base-catalyzed, low-temperature reaction in homogeneous medium proceeds in high yield. In this respect, it differs from the high temperature conventional dehydrogenation procedures using sulfur, selenium, or palladized charcoal. Because of its possible usefulness in the study of terpenoids in which the dehydrogenation techinque is widely used for the elucidation of the carbon skeleton, it was felt that the scope and limitations of this reaction should be further elaborated by examining a number of compounds. The low temperature required in this dehydrogenation procedure is particularly useful in eliminating the possibility of group migration inherent in high temperature dehydrogenation carried out with sulfur or selenium. We have therefore examined several terpenoids and allied products and some of the results are presented in this communication.

Terpenoids giving p-cymene. Reggel has shown that limonene and phellandrene are converted quantitatively to *p*-cymene (VI).[1] We also found that under the same conditions terpinolene (I),[2a] perillyl alcohol (II),[2b] and carveol (IV)[2c] give *p*-cymene in high yield. The conversion of perillyl alcohol and carveol to *p*-cymene is of particular significance as Reggel has used this reagent only in the case of hydrocarbons. Formation of *p*-cymene from carveol presumably proceeded through the conjugated alcohol (V) followed by dehydration. In case of perillyl alcohol, because of the absence of an α-hydrogen, the allylic double bond must have migrated to form (III) to facilitate dehydration, followed by rearrangement to give *p*-cymene.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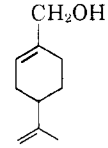

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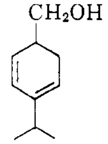

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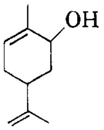

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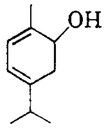

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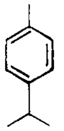
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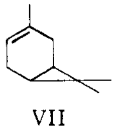
Compounds containing cyclopropane and cyclobutane rings. Because of the presence of cyclopropane and cyclobutane rings in many terpenoids, the behavior of these rings towards the reagent was examined. Δ^3-Carene (VII)[2d] gave a quantitative yield of cymenes, which, from comparative infrared analyses, was found to be a mixture of *p*-cymene (VI) and *m*-cymene (VIII)[3] in nearly equal proportions, the cyclopropane ring having been opened in two ways in conformity with the reactivity of Δ^3-carene toward other reagents.[4] The caged cyclopropane ring systems present in α-santalene (IX)[2e] and dihydro-α-santalene (X) were, however, stable toward this reagent. The tricyclic alcohol maaliol (XI),[5] containing a cyclopropane ring as in the case of Δ^3-carene, was also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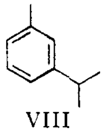
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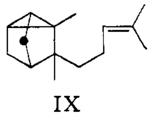
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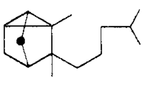
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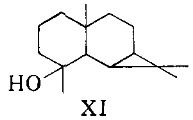

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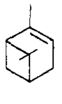
XII

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(1) L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, **23**, 1136 (1958).

(2) E. Guenther, "The Essential Oils," Vol. II, D. Van Nostrand Company, Inc., New York, 1952, (a) p. 31, (b) p. 185, (c) p. 204, (d) p. 50, (e) p. 114, (f) p. 59, (g) p. 398, (h) p. 405, (i) p. 415, (j) p. 504, (k) p. 270, (l) p. 181, and (m) p. 381.

(3) American Petroleum Research Institute Project 44, Serial Nos. 1586 and 1587.

(4) P. P. Pillay and J. L. Simonsen, *J. Chem. Soc.*, 359 (1928).

(5) R. B. Bates, G. Büchi, T. Mastsura, and R. R. Shaffer, *J. Am. Chem. Soc.*, **82**, 2327 (1960).