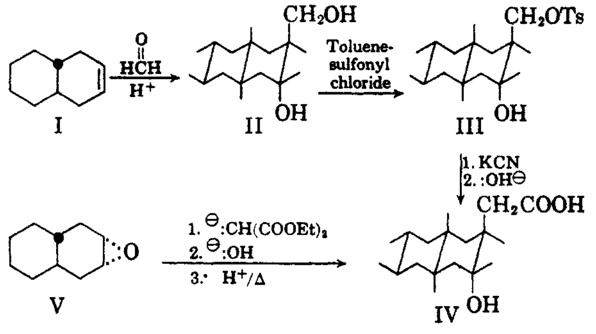
action was performed in dimethyl sulfoxide solution[8] and gave an uncrystallizable nitrile (4.43 μ). The nitrile was subjected to alkaline hydrolysis and yielded a hydroxy acid, IV.

The acid, IV, was identical in all properties with one prepared by Johnson and Bauer[9] through the opening of 2,3-epoxy-*trans*-decalin, V, with the anion of malonic ester, followed by hydrolysis and monodecarboxylation. This method could only give rise to a diaxial product, IV, hence the Prins product, II, must have the diaxial conformation.



EXPERIMENTAL

trans-2(a)-Hydroxymethyl-3(a)-hydroxy-trans-decalin, II. A mixture of 12 g. (0.4 mole) paraformaldehyde, 90 ml. glacial acetic acid, and 2 ml. sulfuric acid was heated to 85° while stirring. After solution was effected the temperature was lowered to 65° and 19 g. (0.14 mole) *trans*-Δ^2-octalin was allowed to drop into the stirred reaction mixture over a period of 0.5 hr. The mixture was then stirred at room temperature for 10 hr. and subsequently diluted with 150 ml. of water and extracted with three 150-ml. portions of ether. The combined ether extracts were then washed with 200 ml. water and with saturated sodium carbonate solution until the ethereal solution was neutral. The ethereal solution was then washed with 200 ml. of water and dried over anhydrous magnesium sulfate. The ether was removed and the residual oil was dissolved in a solution of 12 g. sodium hydroxide in 150 ml. ethanol and refluxed for 2 hr. The reaction mixture was diluted with 300 ml. water and extracted with three 200-ml. portions of ether. The solution was dried, the ether removed, and the residual oil crystallized on standing. Recrystallization from benzene yielded 8 g. (25%) of the product, m.p. 159–160°.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.93; H, 10.35.

trans-2(a)-Tosyloxymethyl-3(a)-hydroxy-trans-decalin, III. A solution of 20 ml. pyridine, 1 g. (0.006 mole) *p*-toluene sulfonyl chloride, and 1 g. (0.005 mole) *trans*-2(*a*)-hydroxymethyl-3(*a*)-hydroxy-*trans*-decalin was allowed to react at room temperature for 1 hr. The solution was then poured into an ice slurry of dilute hydrochloric acid. The resulting precipitate was filtered and recrystallized from Skellysolve B. White needles, m.p. 103.5–104° were obtained in a yield of 1.10 g. (55%).

Anal. Calcd. for $C_{18}H_{26}O_4S$: C, 62.93; H, 7.46; S, 9.88. Found: C, 63.40; H, 7.43; S, 9.47.

trans-2(a)-Cyanomethyl-3(a)-hydroxy-trans-decalin. A stirred mixture of 1.0 g. (0.003 mole) of the monotosylate, III, 1.2 g. (0.18 mole) potassium cyanide, and 20 ml. dimethylsulfoxide was heated at 210° for 5.5 hr. The reaction mixture was diluted with 150 ml. of water and extracted with three 100-ml. portions of ether. The ethereal extracts were then washed with two 75-ml. portions of water and dried over anhydrous magnesium sulfate. The ether was removed and the residual oil would not crystallize. Attempts to purify the oil by distillation failed. The infrared spectrum was in good agreement with the expected product and a sharp nitrile band at 4.43 μ was observed.

trans-2(a)-Carboxymethyl-3(a)-hydroxy-trans-decalin, IV. The crude nitrile was dissolved in 20 ml. of a solution of 10% sodium hydroxide in diethylene glycol and heated at 170° for 3 hr. The reaction mixture was diluted with 100 ml. water and extracted with two 150-ml. portions of ether. The aqueous layer was made acidic with 5*N* HCl and extracted with three 100-ml. portions of ether. The ether solution was then washed with water and dried. The ether was removed and the residual oil was chromatographed on a silicic acid–chloroform column using chloroform as the eluant. The acid was removed from the column as a distinct yellow band with 50% ethanol in chloroform. The solvent was removed and the residue crystallized on standing. Recrystallization from ethyl acetate gave 0.3 g. (50% based on the tosyl compound) of white crystalline material, m.p. 115–116°. There was no depression of melting point on admixture of this acid with that prepared by Johnson and Bauer. The infrared spectra were superimposable.

Anal. Calcd. for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 68.26; H, 9.40.

Acknowledgment. We are grateful to Dr. W. S. Johnson and Dr. V. Bauer for a sample of *trans*-2-(*a*)-carboxymethyl-3(*a*)-hydroxy-*trans*-decalin.

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Some Reactions of 1,1,1-Trichloro-2-propanol[1]

O. R. Pierce, E. E. Frisch, and D. D. Smith[2]

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The dehydration of 1,1,1-trichloro-2-propanol has been studied by various researchers who have assigned to the product either the structure 3,3,3-trichloro-1-propene[3–5] or 1,1,2-trichloro-1-propene.[6] In this laboratory it was found that dehydration of the alcohol with phosphorus pentoxide did produce 1,1,2-trichloro-1-propene in confirmation of the work of Kirrmann.[6] Reaction of 1,1,1-trichloro-2-propanol with alumina at elevated temperatures or with zinc chloride in hydrochloric acid solution

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[1] Presented before the Organic Division, 132nd Meeting of the American Chemical Society, New York, September, 1957.

[2] Present address: Aerojet-General Corporation, Azusa, Calif.

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[4] M. S. Kharasch, E. H. Rossin, and E. K. Fields, *J. Am. Chem. Soc.,* **63,** 2558 (1941).

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gave 1,1-dichloroacetone in low yield resulting from dehydrochlorination rather than dehydration.

EXPERIMENTAL

Preparation of 1,1,1-trichloro-2-propanol. Methylmagnesium bromide (2*M* solution in ether) was added to a cold ethereal solution of chloral. The hydrolyzed mixture was dried and distilled, b.p. 69–71°/25 mm., m.p. (from ligroin) 46–48°. The average yield of several preparations was 75%. The structure of this material was confirmed by nuclear magnetic resonance spectroscopy.

A. *Reaction with alumina.* The alcohol was heated and swept by means of a stream of nitrogen into a one-inch diameter glass tube packed with 8 mesh alumina. The tube was heated over the length of its packing by a tube furnace, one foot in length. The temperature of the reacting surfaces was maintained between 200–250°. The exit end of the tube was connected to a Dry Ice-cooled trap. At the conclusion of the reaction, the product in the trap was washed with water, dried, and distilled. The product thus obtained had the properties: b.p. 115°, n_D^{25} 1.4440. It was shown by infrared analysis to contain a carbonyl group, and a qualitative test for chloride ion following sodium fusion was positive.

Anal. Calcd. for $C_4H_4Cl_2O$: Cl, 55.8; C, 28.3. Found: Cl, 55.8; C, 28.8.

The 2,4-dinitrophenylhydrazone was prepared; m.p. (from ethanol) 110–112°.

Anal. Calcd. for $C_9H_8Cl_2N_4O_4$: N, 18.2. Found: N, 17.9.

The semicarbazone was prepared, and found to behave as follows on heating: sintering at 163°, melting with decomposition between 173–175°.

Anal. Calcd. for $C_4H_7Cl_2N_3O$: Cl, 36.5. Found: Cl, 35.8.

The yield of 1,1-dichloroacetone was poor, only 18 g. (0.14 mole, 28%) being obtained from 79 g. of the alcohol.

B. *Reaction with zinc chloride-hydrochloric acid.* A solution of zinc chloride (136 g., 1 mole) in concentrated hydrochloric acid (100 ml.) was prepared and a few grams of the alcohol was added. The mixture was heated to reflux and the remainder of the alcohol (82 g., 0.5 mole) was added slowly. After 5 hr. the mixture was distilled with steam. The organic layer was separated, dried, and distilled to yield 13.5 g. (21% yield) of 1,1-dichloroacetone, b.p. 115°, n_D^{25} 1.4440. The infrared spectrum of this material was superimposable on that obtained from the material from A above; a mixture of semicarbazone derivative with that from A melted without depression.

C. *Reaction with phosphorus pentoxide.* An intimate mixture of the alcohol (92 g., 0.56 mole) with excess phosphorus pentoxide was heated until no more distillation occurred. The resulting distillate was redistilled from phosphorus pentoxide then fractionally distilled. Three fractions were obtained: Fraction A (17 g.), b.p. 105–112°; Fraction B (13 g.), b.p. 112–115°; and Fraction C (34 g.), b.p. 115–116°, n_D^{25} 1.4790.

Fraction C was identified as 1,1,2-trichloro-1-propene by its physical properties and by comparison of its infrared spectrum with that from an authentic sample of 1,1,2-trichloro-1-propene.[6]

Fractions A and B were shown to contain, respectively, 69% and 80% 1,1,2-trichloro-1-propene by infrared analysis. The remainder of the material appeared to be a mixture of an acid chloride and anhydride.

The yield of 1,1,2-trichloro-1-propene was 69% based on the pure material in all fractions and 41% based on Fraction C alone.

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Cyclic Analogs of DDT-like Compounds

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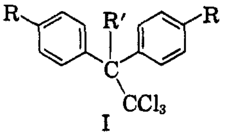
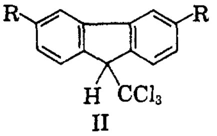
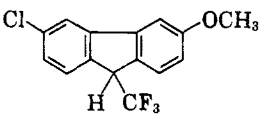
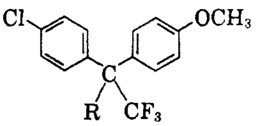
In view of the current theories on the correlation between geometrical structure and biological activity of the insecticides of the DDT group,[1] it seemed of interest to compare the insecticidal properties of 1,1-diaryl-2,2,2-trichloroethanes (I) and of the corresponding fluorenes (II). Unlike I, compounds of type II have a completely rigid molecular structure.


I


II


III


IV

Attempts to prepare 9-trichloromethylfluorene (II, R = H) by chlorination of 9-methylfluorene, by addition of hydrogen chloride to 9-dichloromethylenefluorene or by reaction between 9-fluorenyl sodium and carbon tetrachloride, failed.[2] Another route we explored and which is analogous to the well known conversion of benzilic acid into 9-fluorene-carboxylic acid under the influence of aluminum chloride, is the reaction of the recently[3] described diphenyltrichloromethylcarbinol (I, R = H; R′ = OH) with aluminum chloride. While in benzene mainly tarry material was formed, the reaction in carbon disulfide as solvent gave, in addition to much polymeric material, a compound of m.p. 164–166°, which was identified as $\alpha,\alpha,\alpha',\alpha'$-tetrachlorobibenzyl. Analogous rearrangements are known.[4]

Eventually, 3 - chloro - 6 - methoxy - 9 - trifluoromethylfluorene (III) and 1-(*p*-chlorophenyl)-1-(*p*-methoxyphenyl)-2,2,2-trifluoroethane (IV, X = H) were used for the comparative experiments. The choice of (III) and (IV, R = H) seemed reasonable since replacement of the *para*-chlorine atoms in DDT by methoxyl groups does not destroy the insecticidal activity.[5]

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