the calculated volume (260 ml.) of hydrogen was absorbed. Saponification of the product gave 4-phenyl-1-butanol (1.2 g.), b.p. 135–140° (14 mm.); further characterized as the phenylurethan, m.p. 50–52°. Previously reported[13] for 4-phenyl-1-butanol: b.p. 140° (14 mm.); phenylurethan, m.p. 51–52°.

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(13) J. von Braun, *Ber.*, **44**, 2871 (1912).

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# Preparation of Hexachloronorbornenes Containing Aromatic Substituents

BY E. F. JASON AND E. K. FIELDS

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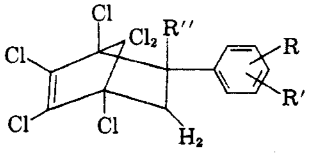
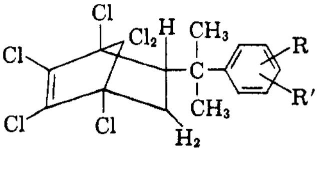
For studies in the 1,4,5,6,7,7-hexachloro-5-norbornene series, a variety of such hexachloronorbornenes containing aromatic rings with alkyl and hydroxyl groups were needed as intermediates. Norbornenes of this structure have not previously been reported. They were prepared in three different ways: (1) Diels-Alder condensation of hexachlorocyclopentadiene with substituted styrenes, (2) alkylation of 2-arylhexachloronorbornenes with alkyl halides and aluminum chloride, and (3) alkylation of ring-substituted aromatics with 2-isopropenylhexachloronorbornene,[1] the adduct of isoprene with hexachlorocyclopentadiene.

Ten new hexachloronorbornenes have been prepared and characterized. Four were made by the first two methods and have the structure:



Six were made by the third method and have the structure:



Physical constants and elemental analyses are listed in Table I. 2-Isopropenylhexachloronorbornene neither alkylated *p*-disubstituted benzenes nor polymerized with Lewis-acid catalysts.

## EXPERIMENTAL

Hexachlorocyclopentadiene was obtained from Hooker; isoprene, from Matheson; vinyltoluene (60% *meta* and 40% *para*) and *p*-isopropyl-α-methylstyrene, from Dow; styrene, isopropyl chloride, phenol, *o*-cresol, toluene, *o*-xylene, and *m*-xylene, from Eastman; ethanesulfonic acid, from Amoco. All chemicals were used without further purification.

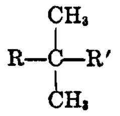
*Method 1. Preparation of 1,4,5,6,7,7-hexachloro-2-tolyl-5-norbornene.* To 40 ml. (0.25 mole) of hexachlorocylopentadiene at 145° was added 35 ml. (0.25 mole) of vinyltoluene in 2-ml. portions over 2 hr. After addition was complete, the reaction mixture was stirred an additional hour at 140 to 145°. Distillation of the resulting material through a 6-in. Vigreux column gave 92.5 g. of a mobile clear yellow oil, $n_D^{20}$ 1.5857.

*Method 2. Preparation of 1,4,5,6,7,7-hexachloro-2-isopropylphenyl-5-norbornene.* A mixture of 37.2 g. (0.1 mole) of 1,4,5,6,7,7-hexachloro-2-phenyl-5-norbornene, 100 ml. of carbon tetrachloride, and 2 g. of aluminum chloride was stirred at about 5°, while 22.4 g. (0.3 mole) of isopropyl chloride in 50 ml. of carbon tetrachloride was added dropwise over 45 min. The mixture was then allowed to warm to room temperature and was stirred for 16 hr. It was poured into ice water, the organic layer was separated, and the aqueous solution was extracted twice with carbon tetrachloride. The organic extracts were combined and dried over anhydrous sodium sulfate. Distillation of the resulting residue, after removal of solvent, gave 32.1 g. of the product as a viscous pale yellow oil, $n_D^{20}$ 1.5700. This oil, on standing at room temperature, slowly solidified.

*Method 3. Preparation of 2-phenyl-2-(1,4,5,6,7,7-hexachloro-5-norbornenyl)propane.* A mixture of 68 g. (0.20 mole) of isopropenylhexachloronorbornene,[1] 439.5 g. (5.62 moles) of benzene, and 3.6 g. of aluminum chloride was stirred and refluxed for 13 hr. The cooled reaction mixture was washed successively with water, dilute base, and water. The organic layer was separated, and the excess of benzene was removed by distillation. The residue was distilled to give 61.9 g. of the product as a pale yellow oil, $n_D^{20}$ 1.5839. This oil solidified on standing.[2]

## DISCUSSION

Although hexachlorocyclopentadiene reacts readily with a great variety of simple olefinic compounds to give hexachloronorbornenes in high yields,[3,4] Method 1 has the drawback that ring-substituted styrenes are not easily available. In Method 2, alkylation of the styrene adduct with a Friedel-Crafts catalyst again shows the amazing inertness of the chlorine atoms in hexachloronorbornene. Method 3 is the most versatile and could be used to prepare many new derivatives; the resulting quarternary connecting configuration *o*-cresol alkylated readily; *p*-cresol and *p*-xylene,



$$R-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-R'$$

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[1] Prepared by the procedure of S. H. Herzfeld *et al.*, *Chem. Abstr.*, **47**, 8775 (1953); U. S. Patent 2,606,910.

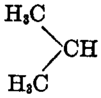
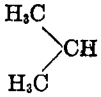
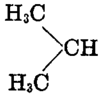
(2) Phenols were alkylated in *o*-dichlorobenzene solution at reflux for 11 hr. with ethanesulfonic acid as catalyst.

(3) E. A. Prill, *J. Am. Chem. Soc.*, **69**, 62 (1947); E. K. Fields, *J. Am. Chem. Soc.* **76**, 2709 (1954); C. W. Roberts, *Chem. & Ind.* (*London*), 110 (1958).

(4) H. E. Ungnade and E. T. McBee, *Chem. Revs.*, **58**, 249 (1958).

TABLE I

1,4,5,6,7,7-HEXACHLORONORBORNENES

| Preparation | R and Position | | R′ and Position | | Yield, Mole % | B.P. | | M.P. | Calcd. | | | Found | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | C | H | Cl | C | H | Cl |
| 1 | $CH_3$ | — | H | — | 95 | 180–185 | 0.8 | — | 43.1 | 2.6 | — | 42.6 | 2.6 | — |
| 1[a] |  $(H_3C)_2CH$ | 4′ | H | — | 40 | 171–175[b] | 0.3 | — | — | — | 49.2 | — | — | 49.0 |
| 2 |  $(H_3C)_2CH$ | 4′ | H | – | 77 | 165–170[c] | 0.2 | — | — | — | 50.7 | — | — | 50.8 |
| 2 |  $(H_3C)_2CH$ | — | $CH_3$ | — | 88 | 175–180 | 0.3 | — | 47.2 | 3.7 | — | 47.1 | 3.7 | — |
| 3 | H | — | H | — | 74 | 153–156 | 0.2 | 43–45 | 45.8 | 3.4 | — | 45.8 | 3.7 | — |
| 3 | $CH_3$ | — | H | — | 76 | 173–175 | 0.1 | — | 47.2 | 3.7 | 49.0 | 47.4 | 3.9 | 48.5 |
| 3 | $CH_3$ | 3′ | $CH_3$ | 4′ | 74 | 185–188 | 0.5 | 98–100 | 48.4 | 4.0 | 47.6 | 48.0 | 3.9 | 47.3 |
| 3 | $CH_3$ | 3′ | $CH_3$ | 5′ | 80 | — | — | 154–155 | 48.4 | 4.0 | 47.6 | 48.0 | 4.2 | 47.4 |
| 3 | OH | — | H | — | 69 | 210–212[d] | 0.5 | — | 44.3 | 3.2 | — | 44.0 | 3.2 | — |
| 3 | OH | 3′ | $CH_3$ | 4′ | 35 | 198–203 | 0.4 | 70–72 | 45.5 | 3.6 | 47.4 | 46.1 | 3.8 | 46.5 |

[a] In this example, R″ is $CH_3$; in all other cases, R″ is H. [b] Mol. wt.: calcd.: 432; found: 415 ± 12. [c] Mol. wt.: calcd.: 418; found: 413 ± 12. [d] Mol. wt.: calcd.: 434; found: 444 ± 13.

is stable to many chemical reactions, especially oxidation. However, its size limits alkylation with isopropenylhexachloronorbornene to the preparation of *m*- and *p*-substituted aromatics. Phenol and where the alkylating group would be forced to enter ortho to a ring substituent, did not alkylate at all.

Failure of isopropenylhexachloronorbornene to alkylate *p*-disubstituted benzenes indicates that the structures assigned to the products from *o*- and *m*-xylene and *o*-cresol in Table I are correct. The structures are confirmed by infrared absorption data. The major product from isopropenylhexachloronorbornene and *o*-xylene shows characteristic absorption for 1,2,4-trisubstituted benzenes in the 5–6 μ region. The corresponding compound from *m*-xylene shows typical absorption for a 1,3,5-trisubstituted benzene in the 5.5–6 μ region. Monosubstituted benzenes give mixtures of isomers.

Isopropenylhexachloronorbornene, although similar in structure to isobutylene, would not polymerize with the strong Lewis acids, boron trifluoride, or aluminum chloride. With isobutylene and boron trifluoride, it gave low-molecular-weight products. Its inability to enter into cationic polymerizations is undoubtedly due to its bulk.

Hexachloronorbornenes are useful as pesticides, vulcanizing agents, and lubricant additives.[4,5] The methods described make possible the ready synthesis of many new hexachloronorbornenes.

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(5) E. K. Fields, *J. Am. Chem. Soc.*, **78**, 5821 (1956).

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## Compounds Derived from Sodium β-Formyl-β-keto-α-nitropropionate[1]

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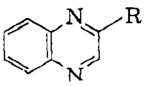
The formation of aldoximes by the pyrolysis of nitronic esters (conveniently obtained from the treatment of primary aliphatic nitro compounds with diazomethane) was reported by Arndt and Rose.[2] As part of our study of compounds derived from sodium β-formyl-β-keto-α-nitropropionate (I),[3] two nitro compounds readily obtained from compound I were subjected to this reaction.

Treatment of 2-nitromethylquinoxaline (IIa) with diazomethane gave the nitronic ester (IIb), which was not isolated, but on sublimation at 120–140° gave the previously reported[4] quinoxaline-2-aldoxime (IIc).



IIa. R = $CH_2NO_2$
IIb. R = $CH{=}NO_2CH_3$
IIc. R = $CH{=}NOH$

The same series of reactions applied to nitropyruvaldehyde phenylosazone (III) gave 1-phenyl-4-benzeneazopyrazole (VI) in place of the expected

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(1) Supported by research grant CY-2240 from the National Cancer Institute of the National Institutes of Health, U. S. Public Health Service.

(2) F. Arndt and J. D. Rose, *J. Chem. Soc.*, 1 (1935).

(3) P. E. Fanta, R. A. Stein, and R. M. W. Rickett, *J. Am. Chem. Soc.*, **80**, 4577 (1958) is the previous paper in this series.