TABLE I

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

Preparation	R and Position		R′ and Position		Yield, Mole %	B.P.		M.P.	Calcd. C	Calcd. H	Calcd. Cl	Found C	Found H	Found 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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Compounds Derived from Sodium β-Formyl-β-keto-α-nitropropionate[1]

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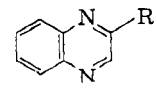
The formation of aldoximes by the pyrolysis of nitronic esters (conveniently obtained from the treatment of primary aliphatic nitro compounds with diazomethane) was reported by Arndt and Rose.[2] As part of our study of compounds derived from sodium β-formyl-β-keto-α-nitropropionate (I),[3] two nitro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

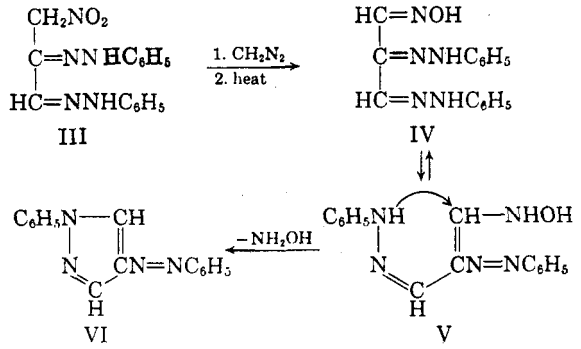
The same series of reactions applied to nitropyruvaldehyde phenylosazone (III) gave 1-phenyl-4-benzeneazopyrazole (VI) in place of the expected

(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.

oxime (IV). Formation of VI may be rationalized as occurring *via* cyclization of the hydroxylamine compound V (a tautomer of IV), with elimination of a molecule of hydroxylamine. This reaction is exactly analogous to the reported formation of VI by the acid-catalyzed elimination of phenylhydrazine from mesoxaldehyde trisphenylhydrazone.[5]



EXPERIMENTAL

Quinoxaline-2-aldoxime. 2-Nitromethylquinoxaline[3] was added in portions to an ether solution containing a threefold excess of diazomethane and a little ethanol. After several hours the solution was filtered and the excess diazomethane and solvent were removed from the filtrate by distillation. The residue was sublimed at 120–140°/0.5 mm., giving a pale yellow solid, m.p. 189–199°. Recrystallization of the crude material from chloroform gave quinoxaline-2-aldoxime, white solid, m.p. 202° (lit.,[4] m.p. 197–198°).

1-Phenyl-4-benzeneazopyrazole. Nitropyruvaldehyde phenylosazone[3] (2.96 g., 9 mmoles) was added in portions to 50 ml. of an ether solution containing 22 mmoles of diazomethane. Ethanol (75 ml.) was added until the osazone was almost completely dissolved. The reaction mixture was stirred for 1.5 hr., filtered, and the filtrate was distilled first at atmospheric pressure and then at reduced pressure to remove solvent. The residue was sublimed at 120–130°/0.1 mm. for 18 hr., giving a yellow-orange sublimate. Recrystallization of the crude material from ethanol gave 0.31 g. of yellow needles, m.p. 124.6–126.2°, $\lambda_{max}^{ethanol}$ 332 mμ (broad), log ε 4.18 (lit.,[5] m.p. 124–125°, $\lambda_{max}^{ethanol}$ 335 mμ (broad), log ε 4.4).

Anal. Calcd. for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87; N, 22.57. Found: C, 72.21; H, 5.09; N, 22.56.

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(4) Von W. Borsche and W. Doeller [*Ann.*, **537**, 39 (1939)] prepared IIc by treatment of the corresponding aldehyde with hydroxylamine.

(5) C. F. Huebner and K. P. Link, *J. Am. Chem. Soc.*, **72**, 4812 (1950).

Partial Side Chain Degradation in Alkali Fusion[1]

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Among the side reactions that can occur in the alkali fusion of alkylbenzenesulfonic acids, replacement of the sulfo group by hydrogen[3] oxidation of side chains,[4] and decarboxylation[5] are well known. Usually, alkyl groups—if attacked at all—are oxidized completely to carboxyl groups.[6] We have observed the conversion of an ethyl group into a methyl group in the alkali fusion of 4-ethyl-3,5-disulfobenzoic acid (I). This compound was prepared by the sulfonation of *p*-ethylbenzoic acid using a modification of the method of Asahina and Asano,[7] and characterized through its *p*-toluidine salt, it sulfonyl chloride, and its sulfonamide. The presence of the two sulfonic acid groups in the benzene ring was confirmed by sealed-tube oxidation with fuming nitric acid to 3,5-disulfoterephthalic acid.

Fusion of the barium salt of I with potassium hydroxide at 260–290° gave a mixture from which hydroxyterephthalic acid, 4-ethyl-3-hydroxybenzoic acid, *m*-hydroxybenzoic acid, and 3-hydroxy-4-methylbenzoic acid (II) were isolated together with several small, unidentified fractions. No 4-ethyl-3,5-dihydroxybenzoic acid was found. Compound II was obtained from a chromatographic separation of the mixture resulting from the alkali fusion, using moist silicic acid as the fixed phase and eluting with butanol-hexane mixtures. It was identified by its neutralization equivalent, carbon-hydrogen analysis, and by a mixed melting point determination.

The formation of II could be accounted for by assuming that the oxidation of the ethyl group occurred in steps, leading first to 2-hydroxyhomoterephthalic acid, which on side chain decarboxylation could yield II, which could then be oxidized further to hydroxyterephthalic acid. This is in agreement with the observation that 2,6-dimethoxyhomoterephthalic acid gives on decarboxylation 3,5-dimethoxy-4-methylbenzoic acid as one of the principal products.[8]

EXPERIMENTAL

4-Ethyl-3,5-disulfobenzoic acid (I). A mixture of 45 g. (0.3 mole) of twice recrystallized *p*-ethylbenzoic acid (m.p. 111–113°) and 180 g. of 65% oleum was refluxed for 8 hr. at

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