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SYNTHESIS OF CONDENSED HETEROCYCLIC SYSTEMS FROM OCTACHLORONAPHTHALENE[1]

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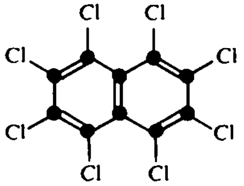
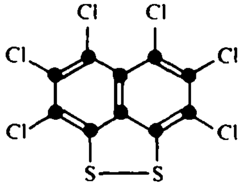
Abstract—The polycyclic compounds II, III and IV are readily prepared from I by displacement of chlorine. The possible mechanistic significance of these reactions, and spectral characteristics of the products, are noted.

ALTHOUGH octachloronaphthalene (I) has been known at least since 1876[2] and is an inexpensive product marketed as "Halowax 1051" (Koppers Company), little is known of its chemistry. Only one nucleophilic displacement reaction seems to have been reported, the formation of the tricyclic dithiole II from sodium disulfide.[3] This lacuna in the literature is rather curious, considering the amount of attention that has been given to hexachlorobenzene, while nucleophilic displacement reactions of octafluoronaphthalene were reported almost as soon as the compound had been obtained for the first time.[4]

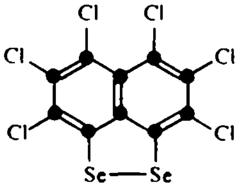
The interesting reaction discovered by Thelin[3] proceeds smoothly under mild conditions (refluxing alcohol); the structure of the product (II) is established by elemental analysis and mol. wt. determination. The inertness of I to other nucleophiles (OH^-, SH^-) even under more severe conditions suggests that II is perhaps formed by simultaneous bidentate attack of S_2^{-2} at two peri positions. In this way the reaction would be facilitated by favorable geometry as well as the activation of both chlorine atoms. (Much more severe conditions are, of course, required for the reaction of chlorobenzenes with metal sulfides or polysulfides.[5, 6])



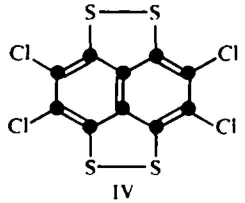
I



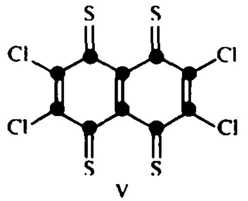
II



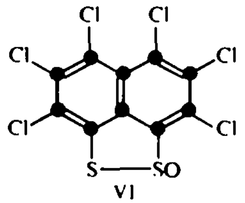
III



IV



V



VI

Interestingly enough, I shows a persistent tendency to pairwise replacement of the peri chlorine atoms. Thus the diselenole III is formed smoothly in high yield by fusion with selenium at 340°, and under similar conditions sulfur displaces all four peri chlorine atoms to give the bis-dithiole (IV). These reactions are conveniently performed in a test tube heated in a metal bath; a slow stream of nitrogen passed through the melt provides gentle agitation, excludes air, and carries off the sulfur or selenium chlorides formed in the reaction. The favored character of peri replacement is again shown by the inertness of hexachlorobenzene to selenium under these conditions.

The UV absorption spectra of II, III and IV are all similar in form,[1] with a broad maximum in the range 405–439 mμ (log ε 3·9–4·0; for details see experimental). Compared with the parent naphtho[1,8-cd]1,2-dithiole,[7] II shows an expected bathochromic shift, about 33 mμ. Resemblances such as that between II and III are usually observed when ring sulfur atoms are replaced by selenium. The not unexpected similarity of IV supports the bisdithiole structure as against the alternative formulation V: analogous quinonoid structures are, of course, not possible for II and III in the ground state.

In the mass spectrometer, II, III and IV each gives in addition to its molecular ion, a series of ions formed by progressive loss of chlorine atoms. Both singly charged and (at much lower intensity) the corresponding doubly charged ions are observed.

Oxidation of II with CrO_3 proceeds fairly smoothly to the oxide VI. Results are best when II is used in excess; it is readily recovered from the reaction mixture by virtue of its insolubility. Higher oxidation products are also obtainable, as well as corresponding derivatives of IV, but these are harder to purify and characterize.

EXPERIMENTAL

Melting points are corrected.

3,4,5,6,7,8-*Hexachloronaphthol*[1,8-cd]-1,2-*dithiole* (II)'. A solution of Na_2S_2 was prepared by dissolving first 63 g (0·26 mole) of $Na_2S \cdot 9H_2O$ and then 8·4 g (0·26 g atom) of sulfur in 300 ml of refluxing EtOH. The warm solution was added over 2 hr to a stirred refluxing suspension of 80 g (0·198 mole) of octachloronaphthalene in 2 l of EtOH. Stirring and refluxing were continued for 3 hr. The mixture was chilled, filtered and the product washed with water and dried (yield, 65 g). Crystallization from dioxan (50 ml/g) gave 44 g (56%) of orange product, m.p. 283-5°. (Calc. for $C_{10}Cl_6S_2$: C, 30·2: Cl, 53·6; S, 16·2. Found: C, 30·3: Cl, 53·5: S, 16·5%). At a concentration of 15 mg/l in pyridine, this showed a peak at 405 mμ (log ε 4·00).

3,4,5,6,7,8-*Hexachloronaphtho*[1,8-cd]-1,2-*diselenole* (III). A mixture of 20·2 g (0·050 mole) of octachloronaphthalene and 10·0 g (0·127 g atom) of Se was fused for 7 hr in a metal bath at 335-340°, a gentle stream of N_2 being passed through the melt. After cooling, the product was ground and freed of small amounts of starting material by Soxhlet extraction with petroleum ether for approx 36 hr. The insoluble residue (22·1 g) was crystallized from boiling dimethylacetamide (20 ml/g) to give 17·7 g (72%) of tan needles, m.p. 318-320°. It gave yellow to tan crystals from pyridine, toluene, or 1,2-dichloroethane. (Calc. for $C_{10}Cl_6Se_2$: C, 24·4; Cl, 43·3; Se, 32·2. Found: C, 24·3: Cl, 43·1; Se, 32·4%). At a concentration of 20 mg/l in pyridine, this showed a peak at 415 mμ (log ε 3·93) and a shoulder at 370 mμ (log ε 3·58).

3,4,7,8-*Tetrachloronaphtho*[1,8-cd:4,5-c′d′]*bis*[1,2]*dithiole* (IV). A mixture of 12·0 g (0·0297 mole) of octachloronaphthalene and 30 g (0·94 g atom) of sulfur was fused for 15 min in a metal bath at 310–320°, a gentle stream of N_2 being passed through the melt. Evolution of sulfur chlorides was vigorous at the start, subsiding in 5-8 min. After cooling, the product was ground, freed of sulfur by digestion with CS_2, and crystallized from 350 ml of *o*-dichlorobenzene, yielding 8·8 g (73%) of yellow IV, m.p. 347-9° d. Pyridine gave golden yellow crystals of unchanged m.p. (Calc. for $C_{10}Cl_4S_4$: C, 30·8: Cl, 36·4: S, 32·8. Found: C, 30·9: Cl, 36·1: S, 33·1%). Under these conditions, II is converted to IV. At a concentration of 15 ml/l in pyridine, IV showed peaks at 430 mμ (log ε 4·08) and 405 mμ (log ε 3·95).

3,4,5,6,7,8-*Hexachloronaphtho*[1,8-cd]-1,2-*dithiole*-1-*oxide* (VI). During a 30 min period, 1·70 g (0·017 mole) of CrO_3 was added to a stirred refluxing suspension of 9·6 g (0·024 mole) of II in 350 ml AcOH. After stirring and refluxing 30 min longer, filtration of the hot mixture gave recovery of 4·5 g (47%) of unchanged starting material. The solid that separated from the AcOH on cooling was filtered, dried, and recrystallized from 100 ml of BuOAc (decolorizing charcoal) to give the greenish yellow VI, m.p. 229–231° (yield, 2·00 g) (38%, based on starting material consumed). Crystallization from AcOH raised the m.p. to 238–240°. (Calc. for $C_{10}Cl_6OS_2$: C, 29·1: Cl, 51·6: S, 15·5. Found: C, 29·5: Cl, 51·2: S, 15·4%). At a concentration of 20 mg/l in pyridine, this showed a peak at 385 mμ (log ε 3·53).

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