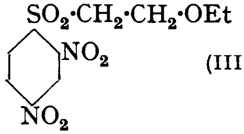
NOTES.

The Thermal Decomposition of Chloromercuric β-Ethoxyethanesulphonate. By JAMES D. LOUDON and NATHAN SHULMAN.

THIS investigation was undertaken in the hope of synthesising β-ethoxyethylmercurichloride (I, R = Et) and of providing thereby decisive evidence bearing on the disputed structure (I or II) of the products obtained by the interaction of ethylene and mercuric chloride in aqueous or alcoholic solution (for R = Et, cf. Schoeller, Schrauth, and Essers, *Ber.*, 1913, **46**, 2868; and general summary by Nesmajanow and Freidlina, *Ber.*, 1936, **69**, 2019). Unfortunately, the essential synthetic step, *viz.*,

(I.) $OR\cdot CH_2\cdot CH_2\cdot HgCl$

(II.) $(CH_2{:}CH_2),HgCl(OR)$


(III.)

$$OEt\cdot CH_2\cdot CH_2\cdot SO_2Na + HgCl_2 \longrightarrow OEt\cdot CH_2\cdot CH_2\cdot HgCl + NaCl + SO_2$$

(cf. Loudon, J., 1933, 823; 1935, 535) could not be realised, since *chloromercuric* β-*ethoxyethanesulphinate*, $OEt\cdot CH_2\cdot CH_2\cdot SO_2\cdot HgCl$, produced in the initial stage of the reaction, decomposed on heating to give ethylene—identified as *bis*-(2 : 5-*dichlorophenylthio*)*ethane* $[\cdot CH_2\cdot S\cdot C_6H_3Cl_2]_2$ —instead of the expected mercurial. Moreover, test experiments showed that Schoeller's compound (I or II, R = Et) was not an intermediary in the reaction, since under similar conditions it was recovered unchanged, and only yielded ethylene at considerably higher temperatures. The decomposition of the sulphinate appears, therefore, to be analogous to the formation of olefins, instead of Grignard compounds, from the action of magnesium on β-halogenoalkyl ethers (Boord *et al.*, *J. Amer. Chem. Soc.*, 1930, **52**, 651, *et seq.*; Tallman, *ibid.*, 1934, **56**, 126).

Sodium β-ethoxyethanesulphinate was prepared for these experiments by a procedure which is of advantage when the corresponding thiol is more readily available than the sulphonyl chloride or when reduction of the latter is unsatisfactory. β-Ethoxyethylthiol was converted into the 2 : 4-*dinitrophenylthio-ether* and thence by oxidation into the *sulphone* (III), from which, after scission with piperidine and treatment with alkali, the required sulphinate was obtained in good over-all yield.

2 : 4-*Dinitrophenyl β-ethoxyethyl sulphide.* An alcoholic solution (10·6 g. in 50 c.c.) of β-ethoxyethylthiol (Boord and Swallen, *loc. cit.*) was treated with an aqueous solution of sodium hydroxide (4 g. in 10 c.c.) and added slowly to 2 : 4-dinitrochlorobenzene (20 g.) dissolved in cold dioxan. Sodium chloride and some bis-2 : 4-dinitrophenyl disulphide separated, and after filtration, the filtrate deposited the required *product*, which crystallised from alcohol in yellow needles, m. p. 65—66° (Found : N, 10·1. $C_{10}H_{12}O_5N_2S$ requires N, 10·3%). The corresponding *sulphone* (III), m. p. 97°, was obtained by oxidising the sulphide with hydrogen peroxide in acetic acid (Found : N, 9·2. $C_{10}H_{12}O_7N_2S$ requires N, 9·2%).

Chloromercuric β-ethoxyethanesulphinate. The sulphone (III) was heated with piperidine (2 mols.) in benzene solution for 5 minutes. After cooling, the solution was shaken with water containing just less than 1 mol. of sodium hydroxide, and the aqueous extract was concentrated somewhat to ensure removal of piperidine. At this stage the presence of the sodium salt of the required acid was demonstrated by heating a portion of the aqueous solution with 2 : 4-dinitrochlorobenzene in alcohol, whereby the sulphone (III) was regenerated. The remainder of the sulphinate solution was treated hot with a solution of mercuric chloride in warm water, yielding the *product* as crystalline flakes, which were collected, washed, and dried in a vacuum desiccator (Found : Cl, 9·5; Hg, 53·4. $C_4H_9O_3ClSHg$ requires Cl, 9·5; Hg, 53·75%).

The dry salt slowly decomposed at room temperature with formation of mercurous salts, and yielded sulphur dioxide on being heated. The formation of ethylene, when a suspension of the substance was refluxed in water or in an aqueous medium buffered to p_H 7, was shown by passing the evolved gases through a cold alcoholic solution of bromine, followed by addition of sodium hydroxide in slight excess, and by formation of the bis-thioether (cf. below). No organic mercury derivative could be detected at any stage of the experiments. A very rapid evolution of ethylene occurred when the salt or Schoeller's compound was heated under reflux in ethylene glycol.

Bis-(2 : 5-*dichlorophenylthio*)*ethane.* An aqueous-alcoholic solution containing ethylene dibromide (1 mol.), 2 : 5-dichlorophenylthiol (2 mols.), and sodium hydroxide (2 mols.) was gently warmed for 5 minutes. On cooling, the *product* separated; it crystallised from acetic acid in colourless plates, m. p. 125°. The samples obtained from the decomposition experiments had the same m. p. and mixed m. p. (after being washed with alcohol to remove contaminating bis-2 : 5-dichlorophenyl disulphide) (Found : C, 44·1; H, 2·5. $C_{14}H_{10}Cl_4S_2$ requires C, 43·75; H, 2·6%).

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Decompositions of Certain Diazo-perbromides derived from Azobenzene. By P. P. HOPF and R. J. W. LE FÈVRE.

IN the decomposition of the diazo-perbromides from 4-amino- and 2 : 4-diamino-azobenzenes we have found that, under certain conditions, simultaneous replacement of N_2Br_3 by Br and bromination in other parts of the molecule can occur. A useful method is thus available for the small-scale preparation of a number of bromo-azo-compounds which are inconvenient to obtain by the ordinary Sandmeyer reaction because of the inaccessibility of the necessary polyamines.

(1) Aminoazobenzene hydrochloride (23·5 g.) was suspended in water (500 c.c.) containing sulphuric acid (35 g.), a solution of sodium nitrite (15 g.) added, and the mixture kept for 24 hours at room temperature. To the filtered red solution, bromine (25 c.c.) in hydrobromic acid (*d* 1·7; 100 c.c.) was added slowly with stirring. The first-formed emulsion slowly solidified to purple crystals (yield, 80%) of azobenzene-4-diazo-perbromide, m. p. *ca.* 62° (decomp.).

This perbromide (14 g.) was refluxed in acetic acid (250 c.c.) for about 20 minutes, nitrogen and bromine being evolved. On cooling, 4 : 4′-dibromoazobenzene crystallised; it was recrystallised from acetic acid and washed with alcohol; yield 9 g., m. p. 205° (Werigo, *Annalen*, 1873, **165**, 199).

When absolute alcohol was used in place of acetic acid, no bromine evolution occurred and 4-bromoazobenzene (3 g.) separated on cooling, m. p. 89° after recrystallisation.

The identities of the last two preparations were established by mixed m. p. determinations with authentic specimens.

The perbromide (1 g.) was heated at about 60°; when the evolution of bromine was complete, the residue was found to be almost entirely 4-bromoazobenzene, requiring only one crystallisation from aqueous alcohol.

(2) 2 : 4-Diaminoazobenzene (2 g.), dissolved in water (150 c.c.) and sulphuric acid (7 g.), was cooled and diazotised with solid sodium nitrite (1·5 g.). The red solution gradually deposited crystals; these were collected after 24 hours, dissolved in water (600 c.c.), and treated with bromine (5 c.c.) in hydrobromic acid (*d* 1·7; 20 c.c.). After 2 hours the rust-red precipitate (yield, 90%) of the diperbromide was collected, m. p. about 109° (decomp.).

This substance (2 g.), when refluxed in acetic acid, gave no bromine but was partly transformed into an insoluble material (0·8 g.), m. p. above 290°. From the filtrate, by dilution, a red powder, m. p. 145—146° after several recrystallisations from alcohol, was obtained; this was apparently 2 : 4 : 4′-tribromoazobenzene (Valori, *Atti R. Accad. Lincei*, 1913, **22**, 131). The decomposition, when performed in alcohol, again produced the insoluble substance, but from the filtrate 2 : 4-dibromoazobenzene, m. p. 95—96°, was obtained in small yield (cf. Valori *loc. cit.*). Thermal decomposition without a solvent seemed to give the same unidentified substance as that formed in the two previous experiments (Found : C, 49·7; H, 3·2; N, 15·6; Br, 28·1%).—THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, LONDON, W.C.1. [*Received, May 9th,* 1939.]