XXXII.—*The Isomerism of the Oximes. Part XXXVII. Allyl*-p-*nitrobenzaldoximes,* O- *and* N-*Allylhydroxylamines, and Sulphime* S-*Ethers.*

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Claisen (*Z. angew. Chem.*, 1923, **36**, 478; *Annalen*, 1925, **442**, 210) has shown that unsaturated alkyl halides, acting upon sodium phenoxide, give *O*- or *C*-alkyl derivatives according as the reaction occurs in an ionising or a non-ionising solvent, and that saturated alkyl halides give only *O*-alkyl derivatives. Now, in the methylation

of aldoximes the formation of *O*- and *N*-methyl derivatives is probably due to an ionic and a non-ionic reaction respectively (Brady and Goldstein, J., 1926, 2403). It seemed likely, therefore, that the use of an unsaturated alkyl halide might give a greater proportion of *N*-ether. The allylation of aldoximes presented special difficulties: the compounds in many cases did not crystallise and there was a tendency for the formation of resinous polymerisation products; *p*-nitrobenzaldoxime, however, gave a crystalline O-*allyl* and N-*allyl* ether. The relative amounts of the two ethers obtained from the α-oxime did not seem to differ materially from those of the methyl ethers, but a quantitative determination was impracticable, since extensive resinification occurred when attempts were made to hydrolyse the mixture of ethers in order to estimate the *N*-allylhydroxylamine (compare Brady and Goldstein, *loc. cit.*).

O-*Allylhydroxylamine hydrochloride* has been obtained by the hydrolysis of O-*allylbenzhydroxamic acid*, and a solution of *N*-allylhydroxylamine hydrochloride from *N*-allylbenzaldoxime.

Cinnamyl and styryl halides, reacting with aldoximes, gave only resinous products.

The sulphime *S*-ethers, R·CH:N·SR′, of Zincke and Farr (*Annalen*, 1912, **391**, 60, 74) are analogous to the oxime *O*-ethers and an attempt has been made to obtain them in stereoisomeric forms but without success. Only one ether is obtained by the action of *o*-nitrophenylsulphamine, $NO_2 \cdot C_6H_4 \cdot S \cdot NH_2$, on benzaldehyde and on *m*-nitrobenzaldehyde and no isomeric change is brought about by the action of ultra-violet light (compare Brady and Klein, J., 1927, 893).

EXPERIMENTAL.

Allylation of α-p-*Nitrobenzaldoxime.*—Sodium (1·4 g.) was dissolved in alcohol (75 c.c.) and α-*p*-nitrobenzaldoxime (10 g.) added, followed by allyl iodide (10 g.). After being heated under reflux for 3 hours, the mixture was kept over-night; yellow crystals (5 g.) then separated. Recrystallised from dilute alcohol, they gave α-O-*allyl*-p-*nitrobenzaldoxime* in very pale yellow needles, m. p. 75° (Found: N, 13·7. $C_{10}H_{10}O_3N_2$ requires N, 13·6%). This compound is volatile in steam, gives no hydrochloride, and, like other *O*-ethers, is very difficult to hydrolyse.

The mother-liquor from the above preparation was diluted with water; the brown solid precipitated (5 g.), on repeated crystallisation, gave more of the *O*-allyl ether. Concentration of the aqueous mother-liquor, followed by extraction with chloroform, gave a substance (1 g.) which after two crystallisations from benzene and light petroleum was found to be *N*-allyl-*p*-nitrobenzaldoxime, identical with the compound obtained from the β-oxime.

Allylation of β-p-*Nitrobenzaldoxime.*—If the above method be employed with the β-oxime, resinification occurs.

Sodium (0·7 g.) was dissolved in alcohol (20 c.c.), β-*p*-nitrobenzaldoxime (1·2 g.) added, the solution cooled to room temperature, and allyl iodide (0·7 c.c.) poured in; after 3 days a yellow crystalline material had separated and the whole was poured into water. The precipitate, after several crystallisations from benzene and light petroleum, gave N-*allyl*-p-*nitrobenzaldoxime* in pale yellow prisms, m. p. 112° (Found: N, 13·8. $C_{10}H_{10}O_3N_2$ requires N, 13·6%). With dry hydrogen chloride in dry chloroform, this ether gave a slightly gummy, very hygroscopic precipitate of N-*allyl*-p-*nitrobenzaldoxime hydrochloride*, m. p. 61—64° (Found: Cl, 14·1. $C_{10}H_{10}O_3N_2$,HCl requires Cl, 15·0%). The material was prepared for analysis by rapid pressure on porous tile, and the melting-point determination and the analysis were carried out at once.

O-*Allylhydroxylamine Hydrochloride.*—Benzhydroxamic acid (5 g.) in alcohol (16 c.c.) was treated with sodium hydroxide (1·5 g. in the minimum quantity of water) and allyl bromide (4 c.c.) in alcohol (10 c.c.), and the mixture heated under reflux for 30 minutes. The alcohol was removed on the water-bath, water (20 c.c.) added, and the oil extracted with chloroform. After removal of the solvent, cooling, and scratching, the residual oil solidified (5 g.), and crystallisation from benzene and light petroleum gave O-*allylbenzhydroxamic acid* in colourless needles, m. p. 58° (Found: N, 8·0. $C_{10}H_{11}O_2N$ requires N, 7·9%). This compound (4 g.) was heated under reflux with alcohol (10 c.c.) and concentrated hydrochloric acid (4 c.c.) for 45 minutes; the product was diluted with water and extracted several times with chloroform. Evaporation of the aqueous solution on the water-bath left a deliquescent crystalline mass, which, after being pressed on porous tile and dried in a desiccator, consisted of colourless leaflets of O-*allylhydroxylamine hydrochloride*, m. p. 172° (decomp.) (Found: Cl, 33·6; N, 13·4. C_3H_7ON,HCl requires Cl, 32·5; N, 12·8%). It had no reducing action on Fehling's solution and on treatment with *p*-nitrobenzaldehyde in alcohol gave α-*O*-allyl-*p*-nitrobenzaldoxime.

N-*Allylhydroxylamine Hydrochloride.*—β-Benzaldoxime (10 g.), suspended in alcohol (20 c.c.), was treated with sodium ethoxide (2 g. of sodium in 50 c.c. of alcohol), and allyl bromide (3 c.c.) added. After 12 hours, the alcohol was removed on the water-bath, water added, the oil extracted with chloroform, and the solvent removed. The crude *N*-ether could not be induced to crystallise, so it was heated under reflux with alcohol (20 c.c.) for 15 minutes, the odour of benzaldehyde soon being perceptible. The solution was evaporated on the water-bath, the aldehyde being carried off in the water

vapour. The semi-solid residue yielded nothing crystalline; in aqueous solution, however, it immediately reduced Fehling's solution in the cold, and on treatment with an alcoholic solution of *p*-nitrobenzaldehyde and aqueous sodium carbonate gave *N*-allyl-*p*-nitrobenzaldoxime.

Sulphime S-*Ethers*.—*o*-Nitrophenylsulphamine (1·4 g.; prepared by the method of Zincke and Farr, *loc. cit.*) in alcohol (25 c.c.) was heated under reflux for 10 minutes with *m*-nitrobenzaldehyde (1·3 g.). The solid which separated on cooling (2 g.), on crystallisation from benzene, gave m-*nitrobenzylidene*-o-*nitrophenylsulphamine* in lemon-yellow needles, m. p. 192° (Found : N, 13·9. $C_{13}H_9O_4N_3S$ requires N, 13·9%). Examination of the mother-liquors from the preparation and from the crystallisation gave no indication of the presence of an isomeride : a similar result was obtained in the case of benzylidene-*o*-nitrophenylsulphamine (m. p. 161°) prepared by Zincke and Farr's method.

Both benzylidene- and *m*-nitrobenzylidene-*o*-nitrophenylsulphamine were exposed in benzene solution for 48 hours in silica tubes to the light of a quartz-mercury lamp, but were recovered unchanged on removal of the solvent.

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