NOTES.

Some Ethers of 4-Chloro-2-nitro-3 : 5-dimethylphenol. By BRYNMOR JONES.

IN Part X of the series "The Halogenation of Phenolic Ethers and Anilides" (J., 1941, 267) velocity coefficients for the chlorination of some ethers of 4-chloro-2-nitro-3 : 5-dimethylphenol were recorded. It is now found that one of these is incorrectly reported. The value $k = 0{\cdot}0728$, given in the last column of Table II, is for the hexyl ether and not for the benzyl ether : no measurements were made with the latter.

The following properties of the ethers inadvertently omitted from Part X, are now placed on record.

4-Chloro-2-nitro-3 : 5-dimethylphenol, m. p. 90°, prepared from 4-chloro-3 : 5-dimethylphenol by nitration with concentrated nitric acid in glacial acetic acid and purified by steam distillation and crystallisation from ligroin (b. p. 90—120°), was converted by standard methods into the following ethers. Each of these ethers was purified by crystallisation from glacial acetic acid and from ethyl alcohol; from the latter solvent they all crystallised in pale yellow, slender prisms : *methyl* ether, m. p. 166° (Found : C, 50·3; H, 4·7. $C_9H_{10}O_3NCl$ requires C, 50·1; H, 4·7%); *ethyl* ether, m. p. 107° (Found : C, 52·6; H, 5·3. $C_{10}H_{12}O_3NCl$ requires C, 52·3; H, 5·3%); n-*propyl* ether, m. p. 68° (Found : C, 54·3; H, 5·8. $C_{11}H_{14}O_3NCl$ requires C, 54·2; H, 5·8%); n-*hexyl* ether, m. p. 41° (Found : C, 59·4; H, 7·2. $C_{14}H_{20}O_3NCl$ requires C, 58·8; H, 7·1%); p-*bromobenzyl* ether, m. p. 105° (Found : C, 47·8; H, 3·3. $C_{15}H_{13}O_3NClBr$ requires C, 48·6; H, 3·5%). The *benzyl* ether, m. p. 105° (Found : C, 61·7; H, 4·9. $C_{15}H_{14}O_3NCl$ requires C, 61·8; H, 4·8%), was obtained by the nitration of 4-*chloro*-3 : 5-*dimethylphenyl benzyl ether*, m. p. 57° (Found : C, 72·7; H, 6·0. $C_{15}H_{15}OCl$ requires C, 73·0; H, 6·1%), in glacial acetic acid, 2—3 mols. of fuming nitric acid being used.—THE UNIVERSITY, SHEFFIELD, 10. [*Received, April 29th*, 1943.]

The Polymerisation of Acetaldol. By L. N. OWEN.

IN connection with other work, it was necessary to determine the ease of polymerisation of aldol, and cryoscopic determinations in water and in dioxan showed that dimerisation of freshly distilled aldol is complete in a few hours, though, as the experimental figures show, the rate varies somewhat with different samples (see Table I). In these two solvents there was no alteration in the molecular weight of each sample over a period of several hours, from which it follows that further dimerisation is inhibited when the aldol is in solution. In one instance, when an aqueous solution of viscous aldol was kept for several weeks, there was a gradual fall in the molecular weight, in agreement with the observations of Späth, Lorenz, and Freund (*Ber.*, 1942, **75**, 1029), though the possible attainment of an equilibrium was not investigated.

In acetic acid, the observed molecular weight is independent of the age of the aldol and corresponds to a mixture of 20% monomer with 80% dimer, though in view of the abnormal values which are not uncommon in cryoscopic work these figures may not be a true indication of the existence of an equilibrium mixture. There can be no doubt, however, that this solvent, unlike water and dioxan, favours polymerisation, and this conclusion is supported by the observation that the addition of a small quantity of acetic acid to freshly distilled mobile aldol produces a rise in temperature, followed by an increase in viscosity which is more rapid than that observed during the normal polymerisation of aldol.

Experiments in benzene solution failed owing to the low solubility of paraldol in this solvent (approximately 0·2% at 10°). Nowak (*Monatsh.*, 1901, **22**, 1140) experienced the same difficulty, although Connolly (this vol., p. 42) has recorded figures for the molecular weight of paraldol determined by the cryoscopic method in benzene.

The addition to monomeric aldol of typical anti-oxidants failed to prevent polymerisation.

TABLE I.

Age of aldol (mins.)		3	5	15	20	45	60	120	240	1440	4320
% Dimer present (by weight) from M in	dioxan	—	46	42	76	106	—	—	106	106	103
	water	13	—	—	—	—	71	—	98	—	98
	acetic acid	—	80	—	—	—	79	79	81	80	82

Acetaldol was supplied by A. Boake, Roberts and Co., Ltd., in the form of a semi-solid polymer. By distillation under reduced pressure it was obtained as a mobile oil, b. p. 80°/16 mm. This gradually became viscous and after several hours crystallisation of the paraldol usually commenced.

Solubility of Crystalline Paraldol in Benzene.—The solid paraldol was separated from adhering oil, washed with ether, and dried in a vacuum. A small amount (50 mg.) dissolved readily in warm benzene (20 c.c.), but on cooling to 10° crystallisation began. After ½ hour at 10°, the feathery needles were collected and dried. Yield 12 mg., m. p. 88°. The solubility at 10° was therefore approximately 0·2%, and it was evident that for cryoscopic experiments in benzene the permissible concentration was so low that the results would be of little value.

Qualitative Tests on the Ease of Polymerisation of Aldol.—Freshly distilled aldol was treated in portions of 0·1 g. with about 1 mg. of each of the following substances : acetic acid, benzoic acid, quinol, pyrogallol, α-naphthol, β-naphthol, *p*-aminophenol. With acetic acid and benzoic acid there was a rise in temperature and marked increase in viscosity within 10 minutes. The other samples became viscous in about 1 hour, behaving in this respect in the same way as pure aldol.

Molecular-weight Determinations.—Hess and Frahm (*Ber.*, 1938, **71**, 2627), working with specially purified dioxan, found 4·83° for the cryoscopic constant. This figure was used for the present work.

The aldol was freshly distilled before each determination of molecular weight, a first fraction being rejected. A second fraction, of about 1 g., was then collected and kept at room temperature (18—21°) for the appropriate length of time. The amount required for the determination was then weighed out by difference from the receiver directly into the solvent in the cryoscopic apparatus. The figures given for the " age of aldol " refer to the time which elapsed between collection of the specimen and its addition to the solvent.

Data.—(a) *In dioxan.*

Age of aldol (mins.)	5	15	20	45	240	1440	4320
G. of aldol	0·185	0·083	0·129	0·197	0·134	0·231	0·161
G. of dioxan	11·0	11·1	11·0	11·0	11·1	11·0	11·0
$\Delta\theta$	0·71	0·325	0·40	0·46	0·31	0·54	0·39
M	114	111	142	188	188	188	181

(b) *In water.*

Age of aldol (mins.)	3	60	240	4320
G. of aldol	0·274	0·267	0·167	0·427
G. of water	10·6	10·6	10·5	10·6
$\Delta\theta$	0·51	0·34	0·17	0·43
M	94	136	172	173 *

* After 6 days at room temperature, this aqueous solution had $\Delta\theta = 0{\cdot}59°$, whence $M = 126$; and after 26 days, $\Delta\theta = 0{\cdot}69°$, $M = 109$.

(c) *In acetic acid.*

Age of aldol (mins.)	5	5	60	120	240	1440	4320
G. of aldol	0·119	0·122	0·150	0·147	0·103	0·118	0·255
G. of acetic acid	11·3	11·1	11·2	11·0	11·3	11·2	11·1
$\Delta\theta$	0·28	0·29	0·36	0·36	0·24	0·28	0·60
M	147 *	148 *	146	145	148	147	149

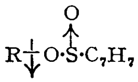
* In these two instances the freezing point of the solution did not attain a constant value until 20 minutes after the addition of the aldol, showing that polymerisation was taking place.

The author is indebted to Professor J. L. Simonsen, F.R.S., for his interest, and to Messrs. A. Boake, Roberts and Co., Ltd., for a grant and for permission to publish the results.—UNIVERSITY COLLEGE OF NORTH WALES, BANGOR. [*Received, June 9th*, 1943.]

Alkyl–Oxygen Fission in Sulphinic Esters.

By MICHAEL P. BALFE, JOSEPH KENYON, and ANDRÁS L. TARNOKY.

THE structural similarity between the carboxyl and the sulphinyl group suggests that in sulphinic esters alkyl–oxygen fission may be expected to occur analogously to its occurrence in some carboxylic esters (J., 1942, 556, 605; *Nature*, 1941, **148**, 196) :



$$\mathrm{R}\,\big\downarrow\,\mathrm{O{\cdot}}\overset{\displaystyle\mathrm{O}}{\overset{\uparrow}{\mathrm{S}}}\mathrm{{\cdot}C_7H_7}$$

Some recorded observations support this suggestion. The rearrangement of (—)-phenylmethylcarbinyl *dl-p*-toluene sulphinate to *dl-p*-tolyl-α-phenylethylsulphone (Arcus, Balfe, and Kenyon, J., 1938, 485) obviously involves alkyl–oxygen fission. (—)-Phenylmethylcarbinyl *dl-p*-toluenesulphinate on reaction with acetic acid gives the racemic acetate, and with ethyl alcohol gives the ethyl ether with extensive, though not complete, racemisation (Kenyon, Phillips, and Taylor, J., 1933, 173).

Ethyl (+)-β-*dl-p*-toluenesulphinoxy-β-phenylpropionate with formic acid gives a half racemised formate, and with ethyl alcohol a half racemised ethyl ether (Kenyon, Phillips, and Shutt, J., 1935, 1663). On the other hand, the acetate formed by interaction of (—)-β-octyl *dl-p*-toluenesulphinate and acetic acid shows no racemisation or change of configuration (Phillips, J., 1925, **127**, 2552) and (+)-β-butyl *dl-p*-toluenesulphinate (Kenyon, Phillips, and Pittman, J., 1935, 1072) reacts, without racemisation or change of configuration, with formic acid, yielding (+)-β-butyl alcohol, and with acetic acid, yielding a mixture of the alcohol and its acetate.

Thus, the racemising alkyl–oxygen fission reaction is promoted by the electron-release of an aromatic substituent in the alkyl group. The case of ethyl (+)-β-*dl-p*-toluenesulphinoxy-β-phenylpropionate is, however, somewhat complicated; in the two examples quoted above, the optically active portion of the ethyl ether is formed with inversion of configuration and that of the formate with retention of configuration; in addition (Kenyon, Phillips, and Shutt, *loc. cit.*), the sulphinate reacts with acetic acid with retention of configuration and absence of racemisation (acyl–oxygen fission).—BATTERSEA POLYTECHNIC, LONDON, S.W. 11. [*Received, May 17th*, 1943.]