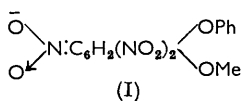


691. *Coloured Alkali Salts from sym.-Trinitrobenzene Derivatives.*
Part II. Phenoxy-compounds.*

By R. C. FARMER.

The action of alcohols on trinitrobenzene derivatives in presence of alkali was dealt with in Part I. Further experiments showed that this reaction was not confined to alcohols: other hydroxy-compounds (phenols, carboxylic acids, oximes) gave similar reactions. The phenoxy-compounds are dealt with in the present Part. They are analogous to the alkoxy-derivatives, but are very unstable, being readily dissociated to the free nitronic acids, which decompose immediately to the trinitro-compounds from which they were derived. The phenoxy-groups are also very readily displaced by methoxy-groups in presence of methoxide. It has not been found possible to reverse this displacement.

THE formation of intense red colours on addition of alcohols to trinitrobenzene derivatives in presence of alkali suggested the possibility of using this reaction for the detection of small quantities of alcohols. Qualitative tests showed, however, that other hydroxy-compounds gave similar reactions. Numerous phenols and carboxylic acids gave positive results. The hydroxy-group appears to be necessary; thus phenol reacts, but anisole does not. Alkali is also necessary to the reaction. Acids destroy the colour at once and regenerate the corresponding trinitro-compounds. Thus, the dimethoxy-quinonoid nitronate yields methoxy-trinitrobenzene; the diphenoxy-compound yields phenoxy-trinitrobenzene (2,4,6-trinitrodiphenyl ether). The phenoxy-quinonoid nitronates are very strongly hydrolysed in aqueous solution and are stable only in presence of a considerable excess of alkali. By analogy with the alkoxy-trinitrobenzene compounds, phenoxytrinitrobenzene would be expected to give the ion of a mixed methoxy-phenoxy-compound (I) with methoxide. The phenoxy-group was, however, at once split off and replaced by a methoxy-group. It is probable that the mixed methoxy-phenoxy-compound was formed momentarily; an analogous instance is given in the following paper, in which a methylnitramino-group is split off by methoxide, but in this case the reaction was relatively slow and it was possible to show that the compound initially formed contained a methoxy-group and a methylnitramino-group.

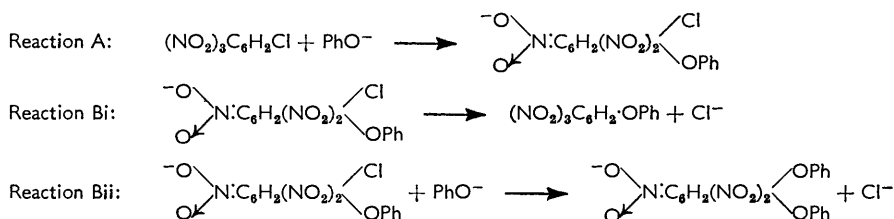


A solution of potassium phenoxide in methanol contains a small proportion of methoxide, and on account of the much greater reactivity of methoxide there is a marked tendency for the action of such a solution on picryl chloride to yield the methoxy- instead of the phenoxy-compound. This can be suppressed by the addition of phenol, and under these conditions trinitrodiphenyl ether can be obtained pure and in good yield.

The action of potassium phenoxide on picryl chloride in methanol is analogous to that of methoxide, forming a phenoxy-quinonoid compound which leads to trinitrodiphenyl

* Part I, preceding paper.

ether; but whereas in the latter case there are two distinct stages, the first almost instantaneous and the second very slow, the action of phenoxide is very rapid throughout. The stages in the formation of trinitrodiphenyl ether appear to be the following:



The diphenoxy-compound then dissociates to the free nitronic acid which decomposes to trinitrodiphenyl ether.

Reaction A is the normal reaction of a trinitrobenzene derivative (Part I). The formation of an unstable quinonoid compound is indicated by the evanescent red colour. The presence of the phenoxy-group is shown by the subsequent conversion into trinitrodiphenyl ether. It is supported by experiments in aqueous alkali in which the quinonoid nitronates are more stable.

Reaction B—in the action of methoxide on picryl chloride (Part I) it was found that about 40% of the picryl chloride acted as in reaction Bi and about 30% as in Bii, the rest being unchanged picryl chloride which entered into the reaction at a subsequent stage. In the action of phenoxide, the whole series of reactions occurred so rapidly that the proportions could not be determined. Reaction Bi leads directly to trinitrodiphenyl ether, whereas Bii is less direct and involves the presence of free picryl chloride in the later stage. Experiment showed that the formation of trinitrodiphenyl ether took place more readily when picryl chloride was present, but could nevertheless take place in absence of free picryl chloride. This appears to indicate that the two reactions occur simultaneously. The diphenoxy-quinonoid nitronate very readily yields the free nitronic acid, as shown by its hydrolysis in aqueous solution, and the free acid decomposes at once to trinitrodiphenyl ether. This immediate dissociation contrasts with the slow dissociation of the dimethoxy-compound (Part I), and accounts for the rapidity of the latter phase of the reaction.

EXPERIMENTAL

Test for Interaction of Hydroxy-compounds with Trinitrobenzene Derivatives.—A small quantity of the test substance was added to a saturated solution of trinitrotoluene in benzene and a drop of a saturated aqueous sodium hydroxide was added and well mixed. This formed a brownish sludge of the di- or tri-nitronate. Benzene was added to dilute the trinitrotoluene, and excess of water was added. The di- or tri-nitronate was converted into the quinonoid mononitronate, which gave a red solution. These conditions were necessary to inhibit the direct action of aqueous alkali on trinitrotoluene. Alcohols gave a strong reaction. Other hydroxy-compounds gave similar results, in particular numerous phenols and carboxylic acids. Mononitrophenols (*o*, *m*, *p*) reacted strongly, 2,4-dinitrophenol somewhat less strongly, and even trinitrophenol, functioning as a hydroxy-compound, gave a distinct reaction.

Action of Aqueous Phenoxide on Picryl Chloride.—A solution of picryl chloride in benzene (20%) was stirred vigorously with potassium phenoxide and alkali in aqueous solution. In dilute alkali no red colour was formed, but with 1.5–3.5*N*-alkali the solution became strongly red. On acidification the red colour disappeared at once and trinitrodiphenyl ether separated (m. p. and mixed m. p. 152–153°). Yields of 85–86% were obtained. The alkaline solutions were still red after 2 weeks at 0°, but trinitrodiphenyl ether separated out gradually. In alkali of lower concentration the red compounds were hydrolysed rapidly, with separation of trinitrodiphenyl ether. In concentrated alkali (16*N*) only an orange colour appeared (dinitronate), but on dilution to 2*N* the strongly coloured mononitronate was formed. On further dilution trinitrodiphenyl ether separated. The majority of organic solvents were unsuitable as solvents.

Liquid phenols were too acid and most other solvents gave unsatisfactory results, as it was

impossible to add sufficient alkali. Small yields of solids were obtained in some cases, but these did not give trinitrodiphenyl ether on acidification. Jackson and Earle,¹ using a mixture of ether and phenol, obtained a solid product, but no reactions were given and the presence of phenol appears to rule out this method.

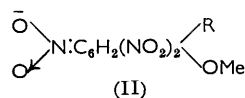
Action of Phenoxide on Picryl Chloride in Methanol.—On addition of a methanolic solution of potassium phenoxide to picryl chloride, it frequently happened that the dimethoxy-compound was formed instead of the phenoxy-derivative. An increase in the proportion of phenoxide up to 10 mol. gave no better result. It was necessary to suppress the methoxide ions to a minimum. The best results were obtained with about 1.05 mol. of phenoxide and 0.2 mol. of phenol per mol. of picryl chloride. The phenoxide solution was added slowly, as recommended by Willgerodt,² a transient red colour being formed with each drop. Chloride ions were formed rapidly and trinitrodiphenyl ether separated out (yield 86—88%; m. p. and mixed m. p. 153°). No dimethoxy-compound was present under these conditions, as shown by the rapid disappearance of the red colour (a methanolic solution of the red dimethoxy-compound retains its colour for weeks unchanged). Although the trinitrodiphenyl ether contained no dimethoxy-compound, it was frequently found that when the product was left in contact with the mother-liquor for a few hours, small red crystals of the potassium dimethoxy-compound were formed (about 1%) (Found: K, 11.2. Calc. for $C_6H_2O_8N_3K, CH_3 \cdot OH$: K, 11.3%). A similar formation of these red crystals occurred when potassium phenoxide was added to trinitrodiphenyl ether in methanol.

Influence of Free Picryl Chloride in Solution during Reaction.—(1) Picryl chloride present in solution throughout the reaction; yield of trinitrodiphenyl ether, 84%. (2) Practically no free picryl chloride in solution during the mixing; yield, 61%. (3) Reagents mixed instantaneously; yield, 75%.

Action of Methanolic Potash on 2,4,6-Trinitrodiphenyl Ether and Derivatives.—On addition of methanolic potash to trinitrodiphenyl ether a deep red solution was obtained, but none of the expected methoxy-phenoxy-quinonoid nitronate was found. The phenoxy-group was at once split off and replaced by a methoxy-group, forming the dimethoxy-compound, which separated in the characteristic red crystals of its methanol solvate (yield, 91%) (Found: K, 11.15%). Acidification gave 96% of methyl picrate, m. p. 67°. The phenol resulting from the splitting off of the phenoxy-group was found in the filtrate from the red crystals.

Ethanolic potash reacted similarly, giving crystals of the diethoxyquinonoid nitronate (Found: K, 11.6. $C_{10}H_{12}O_8N_3K$ requires K, 11.5%). Acidification gave 96% of ethyl picrate, m. p. 78°, and the filtrate from the red crystals contained phenol.

The splitting off of the phenoxy-group takes place only in presence of alkali; boiling methanol or ethanol had no action on trinitrodiphenyl ether. The following trinitrodiphenyl ether derivatives were examined. In each case the primary product (II) was converted at once into (II; R = OMe), which separated as the potassium salt and was identified by crystal form, analysis, and conversion into trinitroanisole (m. p. 67.5°). The filtrate gave on acidification the substituted phenol corresponding to the group R.



3-Methyl-2',4',6'-trinitrodiphenyl ether was prepared from picryl chloride and potassium *m*-tolyloxide in methanol (yield, 84%), m. p. 149.5° (Found: C, 49.0; H, 2.8; N, 13.4. $C_{13}H_9O_7N_3$ requires C, 48.9; H, 2.8; N, 13.2%). It reacted as above; the nitronic potassium salt separated out and the filtrate contained *m*-cresol.

2,4,6,2'-Tetranitrodiphenyl ether. The nitrophenoxy-group was replaced by a methoxy-group. The solid product was the potassium dimethoxyquinonoid nitronate; the filtrate contained *o*-nitrophenol, m. p. 44°.

2,4,6,3'-Tetranitrodiphenyl ether. The solid product was as above and the filtrate contained *m*-nitrophenol, m. p. 96°.

2,4,6,4'-Tetranitrodiphenyl ether. The solid product was again the above potassium salt, and the filtrate contained *p*-nitrophenol, m. p. 114°.

2,4,6-Tribromo-2',4',6'-trinitrodiphenyl ether was prepared from picryl chloride and potassium tribromophenoxide in ethanol; it formed pale yellow, thick hexagonal laminæ, m. p. 179° (Found: C, 26.6; H, 1.0; N, 7.94. $C_{12}H_4O_7N_3Br_3$ requires C, 26.6; H, 0.7; N, 7.75%), and yielded the nitronic potassium salt and tribromophenol, m. p. 95°.

¹ Jackson and Earle, *Amer. Chem. J.*, 1903, **29**, 89.

² Willgerodt, *Ber.*, 1879, **12**, 1278.

Phenylazophenyl picrate was prepared from potassium phenylazophenoxide and picryl chloride in acetone-alcohol; it had m. p. 186° (Found: C, 52·7; H, 2·4; N, 17·3. $C_{18}H_{11}O_7N_5$ requires C, 52·8; H, 2·7; N, 17·1%), and yielded the nitronic potassium salt and phenylazophenol, m. p. 153°.

2,4,6,2',4',6'-Hexanitrodiphenyl Sulphide.—This contains two trinitrophenyl groups, but only one of these formed a nitronic compound. As in the above compounds, methanolic potash gave the dimethoxy-quinonoid nitronate (0·98 mol.) and the remainder of the molecule, $\cdot S \cdot C_6H_2(NO_2)_3$, was split off. It showed considerable decomposition. Thiopicric acid could not be identified.

All attempts to replace methoxy- or ethoxy-groups by phenoxy-groups in the quinonoid nitronates gave negative results.

KING'S COLLEGE, STRAND, LONDON, W.C.2.

[Received, April 24th, 1959.]
