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Abstract

Full Text

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NITRATION OF *p*-OXYDIPHENYLDIMETHYLMETHANE ACETATE IN THE PRESENCE OF UREA

Colbert and Denny (^{1}) showed that, in the nitration of ortho-oxydiphenyl benzenesulfonate, 2′- and 4′-mononitro derivatives are formed. The benzenesulfo group causes deactivation of all positions of the phenolic ring and is an ortho-para-directing substituent with respect to the other nucleus. The oxybenzoyl group possesses the same property (^{2}). In the case of nitration of the acetyl derivative of oxydiphenyl, such selectivity is not observed, and the nitro group enters both the phenolic and the benzene nucleus.

Chekhanskii (^{3}) showed that, in the nitration of symmetrical diphenylalkanes, an increase in activation of the benzene nuclei is observed as the length of the carbon chain in the terminal group connecting the benzene nuclei increases. In the case of *p*-oxydiphenyldimethylmethane, activation of both nuclei will be promoted both by the presence of the dimethylmethylene group and by the hydroxyl group.

Experimental Part

p-Oxydiphenyldimethylmethane

[structural formula: two phenyl rings joined through $C(CH_3)_2$, with OH on the para position of one ring]

The initial *p*-oxydiphenyldimethylmethane (a technical by-product of phenol-acetone production) was purified by recrystallization from a mixture of benzene and petroleum ether. The substance consists of white needle-like crystals with m.p. 72.5°. According to the literature data (^{4}), the product melts at 73–75°.

p-Oxydiphenyldimethylmethane acetate

200 g of *p*-oxydiphenyldimethylmethane were added, with stirring, to 100 g of KOH in 150 g of H_2O. For better dissolution of the phenol, 50 ml of ethyl alcohol were added to the resulting thick emulsion. Then 180 g of acetic anhydride were rapidly added to the solution. During this operation the mixture was cooled with pieces of ice. After standing for half an hour (with ice cooling), the solution separated. The solution was extracted with ether. After removal of the ether, there remained a colorless, viscous liquid distilling at 327° and atmospheric

pressure almost without decomposition. B.p. 180-182°/1.5 mm. Molecular weight found 250, calculated 254.

Found, %: C 80.35; 80.30; H 7.04; 7.12
$C_{17}H_{18}O_2$. Calculated, %: C 80.3; H 7.08

In the experiment described, the product was obtained in an amount of 190 g, which amounted to 80% of theory. The synthesized acetate had the following constants: d_4^{20} 1.085; n_D^{20} 1.5652; $\eta^{25}_{\text{efflux}}$ 138.1; η^{40} 42.4; η^{60} 14.5. The substance dissolved well in gasoline, benzene, *o*-xylene, and other solvents.

Nitration of the acetate

10 g of the synthesized acetate were added dropwise, with stirring, to 30 ml of 99% nitric acid, containing

containing 7 g of ammonium nitrate. The addition was carried out at 15-20°. The reaction proceeded with the evolution of nitrogen oxides. After being kept for 1 h at 40° and 1 h at 60°, the nitro mass was poured into water with pieces of ice. A yellow, fairly viscous mass was formed. Extraction with ether gave a small amount of a solid product which, after recrystallization from a mixture of ethyl alcohol and carbon tetrachloride, had m.p. 122°. A mixed sample with picric acid showed no depression of the melting point. The product dissolved in water with a yellow coloration and with KOH solution formed a yellow crystalline precipitate, which also indicates picric acid.

The formation of picric acid can be avoided if the addition of the acetate and especially the subsequent holding of the reaction mass are carried out at low temperature. In this case a yellow crystalline compound with m.p. 127° is formed in low yield. According to analytical data, this is a trinitro derivative of *p*-oxydiphenyldimethylmethane. Molecular weight found 356, calculated 347.

Found, %: C 52.88; 52.78; H 4.23; 4.11; N 12.17; 11.93

$$C_{15}H_{13}N_3O_7.$$

Calculated, %: C 51.9; H 3.75; N 12.1

In order to prevent the oxidizing action of conc. HNO_3, we carried out experiments on the nitration of the synthesized acetate in the presence of urea. Urea was added in small portions to cooled 99% HNO_3. To the resulting conc. HNO_3, free of nitrogen oxides, the acetate of *p*-oxydiphenyldimethylmethane was added. The data given in Table 1 show that the trinitro compound with m.p. 127-127.5°

Table 1

Experiment No.	Acetate, g	99% nitric acid, ml	Molar ratio acetate: acid	Ammonium nitrate, g	Urea, g	Addition temperature, °C	Holding I temperature, °C	Holding I duration, h	Holding II temperature, °C	Holding II duration, h	Holding III temperature, °C	Holding III duration, h	Product yield, g	Product melting point, °C	Product molecular weight
1	5	15	1:18	–	–	10	0–1	2	–	–	–	–	0.9	127	344
2	5	15	1:18	7	–	40	60	0.5	65–70	0.5	–	–	–	121	229
3	5	15	1:18	3.5	3.5	15–17	40	1	60	0.5	80	1	3.8	127.5	–
4*	5	15	1:18	3.5	1	10–15	40	1	60	1	80	0.5	–	122	229
5	5	15	1:18	3.5	1	10	40	1	60	2	–	–	2.9	127	–

* Experiment with addition of urea after the acetate to the nitric acid.

is formed in a markedly higher yield when urea is added. If, however, urea is added (experiment 4) after the phenol acetate has been added to nitric acid, only picric acid is formed. This indicates that oxidation processes of the phenol acetate develop predominantly in the initial stage of the nitration reaction.

To determine the positions of the nitro groups, the nitro compound obtained was subjected to oxidation with chromic acid. 0.42 g of the trinitro compound was dissolved in a small beaker in 10 ml of conc. H_2SO_4. To the solution, 3.2 g of potassium dichromate was added in small portions. The contents were stirred. The temperature rose to 60°, and the solution acquired a green color. The solution was then extracted with ether. After drying with calcium chloride and subsequent distillation of the ether, the ethereal extract gave a little (0.07 g) of a solid yellow substance soluble in KOH with a yellow

with coloration. M.p. 238-241°. For *p*-nitrobenzoic acid, m.p. 241°. The data obtained indicate the introduction of one of the three nitro groups into the nonphenolic ring of the molecule of *p*-oxydiphenyldimethylmethane.

$$C_6H_5{-}C(CH_3)_2{-}C_6H_4{-}OCOCH_3 \xrightarrow{HNO_3} NO_2{-}C_6H_4{-}C(CH_3)_2{-}C_6H_2(NO_2)_2{-}OH$$

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Note: Figure translations are in progress. See original paper for figures.