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THE REACTION OF PHENYLNITROMETHANE WITH ACETIC ANHYDRIDE/SODIUM ACETATE

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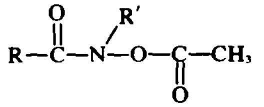
Abstract—Reaction of phenylnitromethane with acetic anhydride/sodium acetate at 80–85° produces N-benzoyl-N,O-diacetylhydroxylamine, which can be isolated in 30% yield. This compound was proposed previously as an intermediate in a similar reaction which had yielded only benzoic anhydride, triacetylhydroxylamine and acetanilide.

McKillop and Kobylecki[1] recently investigated the reaction of primary nitroalkanes with acetic anhydride/sodium acetate and proposed a complex mechanism for the reaction. Because the only isolable products from this reaction were benzoic anhydride triacetylhydroxylamine and acetanilide, the authors suggested[1] the possible occurrence of **1** or **2** as the intermediate(s). We have previously shown[2] that analogs of **2** were isolable in the acetic anhydride/sodium acetate oxidation of nitroethane and 1-nitropropane.



$$R-\overset{O}{\overset{\|}{C}}-N(R')-O-\underset{\underset{O}{\|}}{C}-CH_3$$

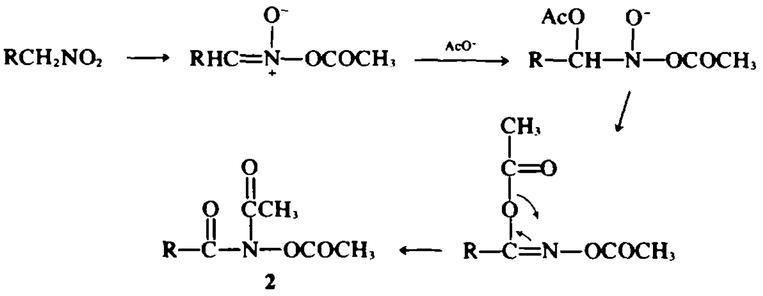
1: $R = C_6H_5$, $R' = H$
2: $R = C_6H_5$, $R' = COCH_3$
3: $R = CH_3CH_2CH_2$, $R' = COCH_3$
4: $R = C_6H_5CH_2$, $R' = COCH_3$

We here report that **2** is indeed isolable under reaction conditions similar to those employed[1] by McKillop and Kobylecki.

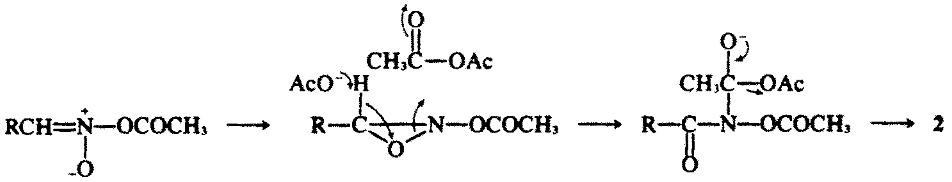
RESULTS AND DISCUSSION

Treatment of 1-nitrobutane, 1-nitro-2-phenylethane and phenylnitromethane with a slurry of acetic anhydride and anhydrous sodium acetate at 80–85° yielded, after work-up in the prescribed[2] manner, **3**, **4**, and **2** respectively. Thus, our earlier work has been extended to several additional primary nitroalkanes. As we observed previously,[2] if any of such compounds are heated at reflux (rather than 80–85°) in acetic anhydride/sodium acetate they are converted to triacetylhydroxyl-amine. There is thus little doubt but that **2** is indeed an intermediate in the more extensive oxidation observed by McKillop and Kobylecki.

In our original work,[2] which was apparently unknown to McKillop and Kobylecki, we suggested a 1,3-acyl migration step as a very likely one in the formation of the **2**–**4** compounds and would like to propose[3] the mechanism of Scheme 1 as an alternative pathway to that suggested[1] by McKillop and Kobylecki. The 1,3 O-to-N acyl migration is common in the Beckman rearrangement of O-acyl oximes[4] and similar systems.[5] The McKillop-Kobylecki mechanism (see 2→3 of their Scheme 5[1]) is somewhat confusing in that it appears to require both base and acid catalysis in the same step as well as the presence of a free $CH_3\overset{+}{C}=O$ species in acetic anhydride/sodium acetate. These anomalies may simply be due to a shorthand description of several consecutive steps as a



SCHEME 1



SCHEME 2

concerted process and we hence have modified the McKillop-Kobylecki mechanism into the rational alternative of Scheme 2.

It is to be noted that the two mechanisms predict different origins for oxygen of the $R\overset{\overset{O}{\|}}{C}-$ moiety. In Scheme 1, the source of the oxygen is the sodium acetate while in Scheme 2 the oxygen was originally on the nitro group.

Comparison of the experimental procedures for the isolation of **2** reveals no reason why we were able to isolate this compound while McKillop and Kobylecki could not since the reaction conditions and isolation procedures were quite comparable. In fact, our conditions were slightly more rigorous (Experimental) than those of McKillop and Kobylecki.

EXPERIMENTAL

The procedures for the oxidation of 1-nitrobutane, 1-nitro-2-phenylethane and phenylnitromethane were essentially identical to that previously reported.[2] For example, phenylnitromethane (1·0 g, 0·008 mole) was added to Ac_2O (5 g; 0·05 mole) and anhyd NaOAc (0·5 g) and the mixture was heated to 80–85° for 9 hr on a steam bath. (McKillop and Kobylecki reported heating at 60–80° for 4·5 hr). The product mixture was cooled, poured into 200 ml of water and the aqueous extracted 3 times with 100 ml portions of $CHCl_3$. The $CHCl_3$ soln was dried over $MgSO_4$, the solvent evaporated and the residue vacuum distilled to yield 0·5 g (30%) of **N-*benzoyl*-N,O-*diacetylhydroxylamine*** (**2**; b.p. 160° at 10 mm); NMR (CCl_4) 8·03τ(3H, CH_3COO), 7·57 (s, 3H, CH_3CON), 2·2–2·6 (m, 5H, aromatic protons); IR (neat) 1800 and 1715 cm^{-1} (Found: C, 60·01; H, 4·78; N, 6·20. Calcd for $C_{11}H_{11}NO_4$: C, 59·73; H, 4·98; N, 6·33%).

In a similar manner 1-nitrobutane was oxidized to yield 50% of **N-*n*-*butyryl*-N,O-*diacetylhydroxylamine*** (**3**; b.p. 85° at 2 mm); NMR ($CDCl_3$) 7·751τ(s, 3H), 7·70 (s, 3H), 7·40 (t, 2H), 8·30 (m, 2H), 9·03 (t, 3H); IR (neat) 1795 and 1715 cm^{-1} (Found: C, 50·96; H, 6·58; N, 6·88. Calcd for $C_8H_{12}NO_4$: C, 51·31; H, 7·00; N, 7·48%). Also 2-phenylnitroethane was oxidized to yield 33% of **N-*phenylacetyl*-N,O-*diacetylhydroxylamine*** (**4**); NMR (CCl_4) 7·92τ(s, 3H), 7·77 (s, 3H), 6·13 (s, 2H) and 2·81 (s, 5H); IR (neat) 1802 and 1720 cm^{-1} (Found: C, 61·32; H, 5·40; N, 6·16. Calcd for $C_{12}H_{13}NO_4$: C, 61·27; H, 5·57; N, 5·95%).

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