

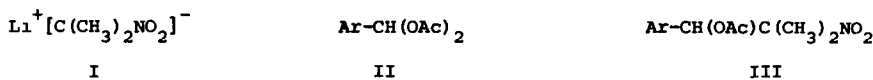
AN UNUSUAL REACTION OF BENZYLIDINE DIACETATES: AN IONIC CHAIN MECHANISM
FOR THE SUBSTITUTION OF AN ACETATE GROUP BY THE 2-NITRO-2-PROPANIDE ION.¹

Diana J. Girdler and Robert K. Norris.*

Department of Organic Chemistry, The University of Sydney, N.S.W. 2006, Australia

(Received in UK 2 December 1974; accepted for publication 6 January 1975)

Our interest in the $S_{RN}1$ radical anion-radical chain substitution reaction,² prompted an investigation of the reaction of the lithium salt of 2-nitropropane (I) with *p*-nitrobenzylidene diacetate (IIa) in dimethyl sulphoxide. The compound (IIIa),⁴



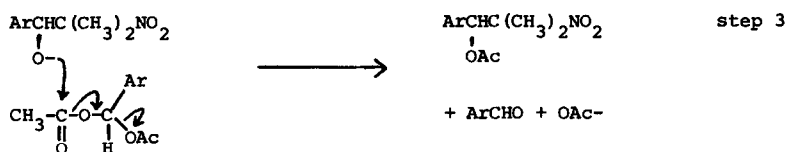
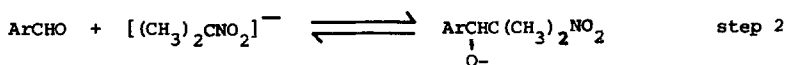
- a. Ar = *p*-NO₂C₆H₄
- b. Ar = *m*-NO₂C₆H₄
- c. Ar = C₆H₅
- d. Ar = *p*-NCC₆H₄
- e. Ar = *p*-BrC₆H₄
- f. Ar = *p*-CH₃OC₆H₄
- g. Ar = *m*-CH₃OC₆H₄

in which one of the acetate groups has been replaced by a (CH₃)₂(NO₂)- group, was obtained in high yield (80%) after 3 hours at room temperature. This reaction, involving the substitution of a relatively poor leaving group at an unreactive site,⁵ by a poor nucleophile acting in an anomalous fashion,⁶ was at first thought to be occurring by an $S_{RN}1$ process. However the reaction was not catalysed by light, nor was it inhibited by oxygen and/or *p*-dinitrobenzene. Both light catalysis and inhibition by electron scavengers are typical characteristics of the $S_{RN}1$ process.^{2,3,8,9} Further evidence against the operation of the radical chain $S_{RN}1$ process was the conversion of other benzylidene diacetates (IIb-e) into

the corresponding derivatives (IIIb-e) even in the absence of the nitro group (IIc-e).

The yields and reaction times for these conversions using (IIb-g) (1.0 mmol) and (I) (2.0 mmol) in DMSO (40 ml) at 25° were: IIIb,⁴ 63%, 3 hours; IIIc,⁴ 33%, 2 weeks; IIId,⁴ 95%, 2 hours; IIIe, 73%, 3 days; IIIf, nil, 2 weeks; IIIg, nil, 2 weeks. In the reaction of (IIf) and (IIg)⁴ the unchanged starting materials were recovered in good yield.

The following mechanism, which avoids the (unlikely) direct substitution pathway is proposed for the conversion (II) \longrightarrow (III).

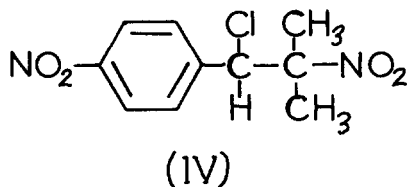


The initiation, step 1, may involve the nitroalkane anion attacking the acetyl carbonyl (analogous reaction to step 3). The Henry condensation [step 2], then occurs and the resulting alkoxide ion removes an acetyl group from the starting material regenerating the free aldehyde, which propagates the reaction by returning to step 2. The reaction then, is an ionic chain process. Confirmation of this mechanism was obtained in several experiments. Addition of 7 mole% of *p*-nitrobenzaldehyde to the reaction of (I) with (IIa) gave an 85% yield of (IIIa) in *ca.* thirty minutes - a sixfold increase in reaction rate. Addition of 100 mole% of the aldehyde gave an 85% yield of (IIIa) in less than five minutes. The following "crossed experiment" was also performed. The otherwise unreactive diacetate (IIf) (1.0 mmol), *p*-nitrobenzaldehyde (1.0 mmol) and the lithium salt (I) (2.0 mmol) in DMSO (20 ml) were allowed to react for 2.5 hours.

Work-up gave the derivative (IIIa, not IIIf) in 70% yield and *p*-methoxybenzaldehyde (50% yield; isolated as its 2,4-dinitrophenylhydrazone). Clearly the alkoxide formed by condensation of (I) with *p*-nitrobenzaldehyde removes an acetyl group from (IIf) generating the unreactive *p*-methoxybenzaldehyde and the derivative (IIIa). The failure of compounds (IIf,g) to give the corresponding derivatives (IIIf,g) even in the presence of equimolar amounts of the corresponding aldehydes is presumably due to the unfavourable position of the condensation equilibrium (step 2).

The monoacetates (III) produced in these reactions are readily cleaved by methanolic hydrogen chloride under reflux to give the corresponding alcohols, $\text{ArCH(OH)C(CH}_3)_2\text{NO}_2$, often more readily obtained in this way than by direct condensation of (I) with the appropriate aldehyde.

By way of contrast with the above ionic process, it is interesting to note that *p*-nitrobenzylidene dichloride readily reacts, via an $\text{S}_{\text{RN}}1$ process to give, *inter alia*, the substitution product (IV).⁴ This reaction exhibits the usual catalytic and inhibition effects associated with $\text{S}_{\text{RN}}1$ processes. A more detailed investigation of the reaction of *p*-nitrobenzylidene dichloride and of other *p*-nitrobenzylidene derivatives with the salt (I) is currently proceeding



Footnotes and References.

- 1) This investigation was supported by a grant from the Australian Research Grants Committee.
- 2) G.A. Russell and R.K. Norris, "Radical Ions" in S.P. McManus, "Organic Reactive Intermediates", Chapter 6, Academic Press, New York (1973); the term $S_{RN}1$, not used in the above review was suggested by J.F. Bunnett.³
- 3) J.K. Kim and J.F. Bunnett, *J. Amer. Chem. Soc.*, 92, 7463 (1970)
- 4) Satisfactory elementary analyses and spectral properties have been obtained for all new compounds.
- 5) *p*-Nitrobenzyl acetate undergoes substitution of the benzylic acetate group to only α .30% after 11 days in DMSO under the same reaction conditions. The products are the result of a very slow $S_{RN}1$ process.
- 6) The ambident anions of nitroalkanes inevitably undergo mainly *O*-alkylation reactions⁷ (except in the case of $S_{RN}1$ reactions⁴).
- 7) "Open Chain Nitrogen Compounds", P.A.S. Smith, Volume II, p. 413, W.A. Benjamin, New York (1966)
- 8) N. Kornblum, S.D. Boyd, and N. Ono, *J. Amer. Chem. Soc.*, 96, 2580 (1974) and references therein.
- 9) G.A. Russell, R.K. Norris, and E.J. Panek, *J. Amer. Chem. Soc.*, 93, 5839 (1971) and references therein.