Tetrahedron Letters No. 11, pp 973 - 974.

0040-4039/79/0308-0973$02.00/0

THE $S_{RN}1'$ REACTION.[1]

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Our interest in the effect of α-substitution on the course of the $S_{RN}1$ reaction in *p*-nitrobenzylic substrates,[2] prompted us to examine the reactions of the *p*-nitrophenylallyl chloride (1).[3] The reaction of this chloride with lithium 2-nitropropan-2-ide (2) gave 70 and 50% yields of the compound (3; $X=CMe_2NO_2$)[3] after 24 h ($Me_2SO;N_2;50°$) with and without sunlamp irradiation respectively. In the presence of oxygen, none of (3; $X=CMe_2NO_2$), which is stable to oxygen, was formed and instead a low yield (26%) of the ketone (4)[3,4] was isolated. On the basis of the above catalytic and inhibition effects[2,5] and further evidence presented below, we believe that the transformation (1) → (3) represents the first report of a radical anion, radical chain substitution reaction with allylic rearrangement, *i.e.* an $S_{RN}1'$ reaction, the steps of which are given in Scheme 1 ($X=Y=CMe_2NO_2$).

$$\underset{(1)}{\mathrm{ArCH{=}CHCH(Cl)Bu^t}} + \mathrm{Y^-} \longrightarrow (1)^{-\cdot} + \mathrm{Y^\cdot} \qquad \text{(i)}$$

$$(1)^{-\cdot} \longrightarrow \mathrm{Cl^-} + [\mathrm{Ar\overline{C}H\overline{-}\overline{C}H\overline{-}\overline{C}HBu^t}]^\cdot \qquad \text{(ii)}$$

$$[\mathrm{Ar\overline{C}H\overline{-}\overline{C}H\overline{-}\overline{C}HBu^t}]^\cdot + \mathrm{X^-} \longrightarrow [\mathrm{ArCH(X)CH{=}CHBu^t}]^{-\cdot} \ [\equiv(3)^{-\cdot}] \qquad \text{(iii)}$$

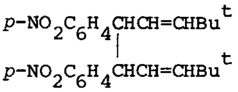
$$(3)^{-\cdot} + (1) \longrightarrow \underset{(3)}{\mathrm{ArCH(X)CH{=}CHBu^t}} + (1)^{-\cdot} \qquad \text{(iv)}$$

Scheme 1 ($Ar = p\text{-}NO_2C_6H_4$)

Other anions gave the $S_{RN}1'$ product (3). The anion of diethyl methylmalonate gave 80 and 44% yields of the ester (3; $X=CMe(CO_2Et)_2$)[3] after 2 h ($Me_2SO;50°$) under nitrogen and oxygen respectively, and sodium *p*-toluenesulfinate (5 equivalents) gave low yields (c. 25%) of the sulfone (3; $X=TolSO_2$)[3] after 2 weeks ($Me_2SO;50°;N_2$). The reaction time was reduced to 2 days (the yield was still low however) when the latter reaction was performed in the presence of the salt (2) (0.5 equivalents). Entrainment by this salt (Scheme 1; $Y=CMe_2NO_2, X=TolSO_2$) is a well established characteristic of the $S_{RN}1$ reaction.[5]

Further observations which support the mechanism shown in Scheme 1 are the lack of formation of the analogous product (3,Ar=Ph) from the chloride without a *p*-nitro group (1,Ar=Ph), and the isolation, in 85% yield of the *meso* and racemic forms of the dimer (5)[3] when the chloride (1) is treated with lithium nitroethanide (Me_2SO;50°;N_2;6h). The yield of (5) decreases to 11% under oxygen.

The effect of replacement of the t-butyl group in (1) by other alkyl groups is under further study, but it appears that steric hindrance by the t-butyl group hinders simple S_N2 processes in this system, and causes the resulting $S_{RN}1$ reaction to proceed with allylic rearrangement.



$$\begin{array}{l} p\text{-}NO_2C_6H_4\overset{}{C}HCH{=}CHBu^t \\ \qquad\quad\;\; | \\ p\text{-}NO_2C_6H_4CHCH{=}CHBu^t \end{array}$$

(5)

FOOTNOTES AND REFERENCES

1. This study was supported by Grant No. C73/15098 from the Australian Research Grants Committee.

2. R.K. Norris and D. Randles, *Aust. J. Chem.*, **29**, 2621 (1976); D.J. Freeman, and R.K. Norris, *Aust. J. Chem.*, **29**, 2631 (1976); D.J. Freeman, R.K. Norris and S.K. Woolfenden, *Aust. J. Chem.*, **31**, in press.

3. All new compounds had the expected analytical and spectroscopic properties. All alkenes were (*E*)-isomers; the allylically rearranged compounds (3) had a single absorption band in the u.v. near 270 whereas the conjugated compound (1) gave peaks at 220 and 300 nm.

4. This ketone, $p\text{-}NO_2C_6H_4CH(CMe_2NO_2)CH_2COBu^t$, was shown to arise from Michael addition of the salt (2) to the initially formed ketone, $p\text{-}NO_2C_6H_4CH{=}CHCOBu^t$, which arises from an S_N2 attack of the anion (2) on the chloride (1), and which otherwise decomposes under the reaction conditions.

5. N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975).

(Received in UK 21 December 1978)