

Radical Nature of the Reaction of 4-Nitrobenzal Chloride with Sodium Hydroxide

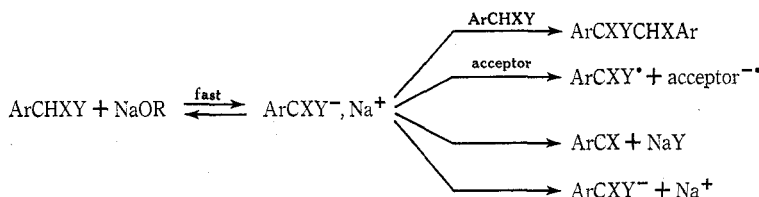
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Abstract

The reaction of 4-nitrobenzal chloride with sodium hydroxide in aqueous methanol gave products which can be accounted for as arising from the dimerization and cross-coupling of the radicals $4\text{-O}_2\text{NC}_6\text{H}_4\text{CCl}_2^\cdot$ and $4\text{-O}_2\text{NC}_6\text{H}_4\text{CHCl}^\cdot$.

The mechanism of the reaction of a number of arylalkyl halides with base has attracted considerable attention.¹⁻⁶ For these halides, depending on the reaction conditions, the following pathways have been postulated:



representing S_N2 , radical, carbene and rate-determining free carbanion formation pathways respectively.

We are particularly interested in arylalkyl halides carrying strongly electronegative substituents (e.g. NO_2) where there are conflicting views as to the exact nature of the reaction. For example, in a number reactions involving nitrobenzyl halides with sodium hydroxide some authors¹⁻³ favour S_N2 and radical mechanisms while others^{4,7} prefer the carbene pathway.

We have now examined the reaction of 4-nitrobenzal chloride with sodium hydroxide. In this system it was hoped that the chlorine substituent would promote carbene formation, since halogens are known to stabilize carbenes.⁸ The following products, characterized by their microanalytical and spectral data, were obtained

¹ Closs, G. L., and Goh, S. H., *J. chem. Soc. Perkin I*, 1972, 2103.

² Bethell, D., Cockerill, A. F., and Frankham, D. B., *J. chem. Soc. (B)*, 1967, 1287.

³ Shipp, K. G., and Kaplan, L. A., *J. org. Chem.*, 1966, **31**, 857.

⁴ Abdallah, A. A., Iskander, Y., and Riad, Y., *J. chem. Soc. (B)*, 1969, 1178.

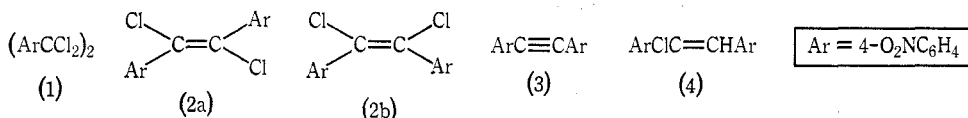
⁵ Closs, G. L., and Goh, S. H., *J. chem. Soc. Perkin II*, 1972, 1473.

⁶ Closs, G. L., and Coyle, J. J., *J. org. Chem.*, 1966, **31**, 2759.

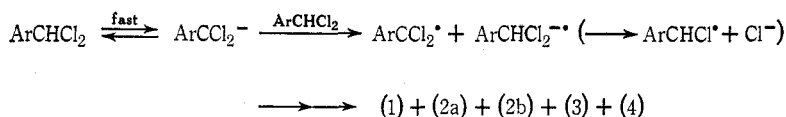
⁷ Rothberg, I., and Thornton, E. R., *J. Am. chem. Soc.*, 1964, **86**, 3296.

⁸ Kirmse, W., 'Carbene Chemistry' 2nd Edn, p. 133 (Academic Press: New York 1971).

from the reaction: (1) 34%, (2a) 18%, (2b) 12%, (3) 8% and (4) 10%. The yields of the products, estimated by n.m.r. spectroscopy of the chromatographed fractions, depended somewhat on the reaction conditions, as may be expected since the intermediate (4) can further react to yield (3) while (2b) can isomerize to the more stable (*E*) form (2a). The stereochemical assignment of the geometric isomers (2a) and (2b) follows from the n.m.r. spectra; the aromatic protons of (*Z*) isomers of stilbene derivatives are known to absorb at higher fields than the corresponding (*E*) isomers.^{1,9}



When the reaction was carried out in sodium deuterioxide to 60% completion the recovered 4-nitrobenzal chloride was found by n.m.r. and mass spectra to contain more than 90% deuterium; this indicates that carbanion formation is much faster than the subsequent reaction. This fact, coupled with the isolation of (1), provides evidence for the radical mechanism which may be written as



The products (3), (4), (2a) and (2b) can be expected to arise from the dimerization and cross-coupling of the radicals ArCHCl^\bullet and ArCCl_2^\bullet followed by elimination of HCl in the basic reaction medium.

It is not necessary to assume the formation of a carbene in this reaction even though chlorine substitution should facilitate its formation,⁸ in fact it would be difficult to explain the formation products other than (2a) and (2b). Attempts to trap a possible carbene by olefins using the phase-transfer catalyst technique were unsuccessful.^{10,11} It is not known whether the carbanion pair $\text{ArCXY}^-, \text{Na}^+$ or the free carbanion ArCXY^- or both are involved in the rate-determining step.² Kinetic studies should resolve this problem but titrimetric methods (chloride or hydroxide ion determination) are rendered difficult in this system due to the number of products formed.

Experimental

The 60-MHz proton magnetic resonance spectra were obtained with a Hitachi Perkin-Elmer R20B instrument using tetramethylsilane as internal standard. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne. Melting points are uncorrected.

Reaction of 4-Nitrobenzal Chloride with Sodium Hydroxide

4-Nitrobenzal chloride (1.2 g, 5 mmol) was dissolved in 50 ml of ethanol under nitrogen and 1M sodium hydroxide (50 mmol) in 50 ml of 80% aqueous ethanol was added. The reaction mixture was kept stirred under nitrogen at about 20°C for 75 min, after which the reaction mixture was acidified with cooling by adding concentrated hydrochloric acid. After addition of an equal volume of water

⁹ Güsten, H., and Salzwedel, M., *Tetrahedron*, 1967, **23**, 187.

¹⁰ Makosza, M., and Wawrzyniewicz, M., *Tetrahedron Lett.*, 1969, 4659.

¹¹ Goh, S. H., *J. chem. Educ.*, 1973, in press.

the yellow products were filtered and dried (0.70 g). Extraction of the filtrate with benzene yielded a further crop of solids (0.05 g). To estimate the yield of each of the products, 0.5 g of the crude product was chromatographed through 200 g of silica gel and eluted with methylene chloride-benzene solvent mixture. The order of elution of the products was (2b), (2a), (1), (4) and (3) respectively, with the last three compounds only partly separated. The chromatographed fractions were concentrated; the appropriate fractions were combined, pumped dry and weighed, and their n.m.r. spectra taken. Each of the isolated compounds had characteristic aromatic proton absorptions and their yields could thus be obtained from the n.m.r. integrations.

The following compounds were isolated by repeated column chromatography (alumina and silica gel) and recrystallizations.

1,2-Di(p-nitrophenyl)tetrachloroethane (1) was obtained from toluene as almost colourless prisms, m.p. 260–262° (Found: C, 40.9; H, 2.0; Cl, 34.4; N, 6.9. $C_{14}H_8Cl_4N_2O_4$ requires C, 41.0; H, 2.0; Cl, 34.6; N, 6.8%). δ (CH_2ClCH_2Cl , 60°) 7.71 (d, 4H) and 0.86 (d, 4H).

(*Z*)- α,α' -Dichloro-4,4'-dinitrostilbene (2b) crystallized from benzene-hexane as yellow plates, m.p. 153–154° (Found: C, 49.8; H, 2.5; Cl, 20.9; N, 8.0. $C_{14}H_8Cl_2N_2O_4$ requires C, 49.6; H, 2.4; Cl, 20.9; N, 8.3%). δ ($CDCl_3$) 7.37 (d, 4H) and 8.08 (d, 4H). This compound in solution slowly isomerized to the (*E*) isomer.

(*E*)- α,α' -Dichloro-4,4'-dinitrostilbene (2a) crystallized from benzene as straw rods, m.p. 213–214° (Found: C, 49.6; H, 2.4; Cl, 20.8; N, 8.2%). δ ($CDCl_3$) 7.77 (d, 4H) and 8.31 (d, 4H).

4,4'-Dinitrotolan (3) crystallized from chloroform as straw prisms, m.p. 208–209° (lit.¹² 210°). δ ($CDCl_3$) 7.65 (d, 4H) and 8.23 (d, 4H).

α -Chloro-4,4'-dinitrostilbene (4) was isolated in small quantities and recrystallized from methylene chloride-methanol to give bright yellow plates, m.p. 157–159°. δ ($CDCl_3$) 7.25 (s, 1H), 7.85 (br d, 4H) and 8.28 (d, 4H). The mass spectrum gave the molecular ion $C_{14}H_9N_2O_4Cl^+$ m/e 304 and 306 showing the presence of one chlorine atom. The compound reacted with sodium hydroxide to yield the tolan (3).

Acknowledgments

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¹² Ruggli, P., and Lang, F., *Helv. chim. Acta*, 1938, **21**, 38.