

Carbon-alkylation of Simple Nitronate Anions

By ALAN R. KATRITZKY,* GEORGE DE VILLE, and RANJAN C. PATEL
(School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ)

Summary Aliphatic nitro-compounds are α -alkylated in good yields by 1-substituted-2,4,6-triphenylpyridinium cations.

THE importance of nitro-aliphatic compounds in the inter-conversion of organic functional groups is highlighted in a recent review,¹ which further states: 'apart from radical anion chain processes,² . . . there are only two cases of C-alkylation of a simple nitronate anion (both) intramolecular cyclisations.'³ Kornblum's radical chain reaction generally requires additional activation.⁴

We now report that simple nitronate anions react regio-specifically with 1-substituted-2,4,6-triphenylpyridinium cations to yield the corresponding mono α -C-alkylated nitro-compounds. The pyridinium cations are readily available (yield >80%) from 2,4,6-triphenylpyrylium tetrafluoroborate and the corresponding primary amine.⁵ 1-Benzyl-2,4,6-triphenylpyridinium tetrafluoroborate reacted with the sodium salt of nitromethane (performed from sodium ethoxide†) in ethanol at 80 °C to yield ω -nitroethylbenzene (74%). Similar results were obtained from the reactions of *p*-methylbenzyl-, *p*-chlorobenzyl-, and

m,*p*-dichlorobenzyl-2,4,6-triphenylpyridinium tetrafluoroborate with the sodium salt of nitromethane (yields 52–68%) and from the reactions of the foregoing four benzylpyridinium cations with the sodium salt of nitroethane (yields 54–57%). Additionally, the parent 1-benzylpyridinium tetrafluoroborate reacted with the sodium salt of 2-nitropropane to give 2-methyl-2-nitro-1-phenylpropane (47%); in dimethylsulphoxide the yield increased to 62%.

Alkylation of nitronate anions proceeded slowly in refluxing ethanol, and in refluxing pentanol mixtures formed, but more satisfactory results were found in dimethylsulphoxide. 1-n-Hexyl- and 1-n-butyl-2,4,6-triphenylpyridinium tetrafluoroborate reacted with the anions of nitroethane and 2-nitropropane to give the corresponding 2-nitro-n-octane and -hexane and 2-nitro-2-methyl-n-octane and -hexane (average 55%).

These reactions provide useful new syntheses of a variety of previously difficultly accessible simple mono-nitro-compounds; their mechanism (ionic or free radical) is still under investigation.‡

(Received, 12th April 1979; Com. 394.)

† We found it advantageous to use an excess of the nitro-compound with stoichiometric amounts of sodium ethoxide and pyridinium cation.

‡ *Added in proof:* Since this manuscript was submitted a report has become available of the C-alkylation of nitronate anions by irradiation with alkylmercury halides; G. A. Russell, J. Hershberger, and K. Owens, *J. Amer. Chem. Soc.*, 1979, **101**, 1312.

¹ D. Seebach, E. W. Colvin, F. Lehr, and T. Weller, *Chimia*, 1979, **33**, 1.

² N. Kornblum, *Angew. Chem. Internat. Edn.* 1975, **14**, 734.

³ S. J. Etheredge, *Tetrahedron Letters*, 1965, 4527; S. Gabriel, *Chem. Ber.*, 1903, **36**, 570.

⁴ N. Kornblum, S. D. Boyd, and N. Ono, *J. Amer. Chem. Soc.*, 1974, **96**, 2580.

⁵ For cognate work with these intermediates see *inter alia*: A. R. Katritzky, N. F. Eweiss, and P.-L. Nie, *J.C.S. Perkin I*, 1979, **433**; A. R. Katritzky, U. Gruntz, D. H. Kenny, M. C. Rezende, and H. Sheikh, *ibid.*, p. 430; A. R. Katritzky, U. Gruntz, N. Mongelli, and M. C. Rezende, *ibid.*, in the press.