Classical Carbonium Ions. Part III.[1a] The Preparation and Acetolysis of Some Alkyl 2,4-Dinitrophenyl Ethers

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A generally applicable method is described for converting alcohols, including a variety of tertiary alcohols, into their 2,4-dinitrophenyl ethers, and other methods are reviewed. The acetolysis of a number of these compounds is shown to proceed by a mechanism similar to that for secondary alkyl picrates; these two sets of derivatives thus allow comparison between the behaviour of tertiary and secondary cationic fragments.

In discussions of the mechanism of solvolysis reactions the leaving group is often treated as unimportant, yet much evidence indicates that in solvents where reaction occurs *via* ion-pairs, which are the majority, the nature of the associated anion affects the behaviour of the cationic fragment.[1] Frequently it is necessary to compare secondary with tertiary carbonium ions; such comparisons have usually involved simultaneous changes in solvent, leaving group, temperature, or two or three of these important parameters together. The use of 2,4,6-trinitrophenoxide as leaving group, and the convenient preparation of a wide range of the required alkyl picrates, were recently described;[1a] such derivatives are unobtainable, and would react inconveniently fast, for most tertiary alcohols. It was however an advantage of the nitrophenoxide type of leaving group that 2,4-dinitrophenoxides would be expected to be available for tertiary systems and to solvolyse at convenient rates, yet to show a chemical resemblance to picrate far closer than that of, say, bromide to toluene-*p*-sulphonate. We now report that these expectations are realised. As compared with the leaving groups so far studied for tertiary systems, 2,4-dinitrophenoxide has the considerable advantage over halide ions that 2,4-dinitrophenyl ethers may, in general, be prepared from alcohols with retention of stereochemical integrity. Relative to 4-nitro- or 3,5-dinitro-benzoate, there is the important advantage that only solvolytic reactions occur, and some added convenience in that they are more reactive. They share with the picrates of less reactive systems the ease with which reactions may be followed spectrophotometrically in dilute solutions,[1a] while the fact that both can be solvolysed in acetic acid in the same temperature range makes possible the first defensible comparisons of the behaviour of secondary and tertiary alkyl cations.

RESULTS AND DISCUSSION

Preparation of Tertiary 2,4-Dinitrophenolates.—The preparation of primary and secondary 2,4-dinitrophenol-

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[1] (*a*) Part II, M. L. Sinnott and M. C. Whiting, *J. Chem. Soc.* (*B*), 1971, 965; (*b*) S. G. Smith, *Tetrahedron Letters*, 1962, 979; (*c*) S. G. Smith and J. P. Petrovitch, *J. Org. Chem.*, 1965, **30**, 2882; (*d*) S. G. Smith and D. J. W. Goon, *J. Org. Chem.*, 1969, **34**, 3127; (*e*) H. M. R. Hoffmann, *J. Chem. Soc.*, 1965, 6748, 6753, 6762; (*f*) G. M. Fraser and H. M. R. Hoffmann, *J. Chem. Soc.* (*B*), 1967, 265, 425; (*g*) D. L. Griffith and B. Singerman, *Chem. Comm.*, 1968, 438.

ates presents no difficulty,[1a,2] but prior to this work few tertiary 2,4-dinitrophenolates had been reported and no solvolysis data had been published. Whalley[2i] reported t-butyl, t-pentyl, and diacetone alcohol 2,4-dinitrophenolates as oils obtained from the alcohols, 1-fluoro-2,4-dinitrobenzene, and triethylamine. Yakobson and Vorozhtsov[3] prepared t-butyl and dimethyltrifluoromethylcarbinyl 2,4-dinitrophenolates as crystalline solids in good yield, using caesium fluoride as catalyst. Mosely and Swain[4] prepared triphenylcarbinyl 2,4-dinitrophenolate in 90% yield by treating the silver salt of dinitrophenol with triphenylcarbinyl chloride in dioxan; solvolysis rates at 25° proved too fast to measure.

Recently Bowden, Cook, and Price[5] prepared t-butyl 2,4-dinitrophenolate (crystalline) from 1-fluoro-2,4-dinitrobenzene and sodium t-butoxide in t-butyl alcohol, and measured the rate of alkaline hydrolysis in aqueous dioxan.

Reaction of equimolar proportions of tertiary alcohol and 1-fluoro-2,4-dinitrobenzene with an excess of anhydrous caesium fluoride[3] gave good yields of ethers from less hindered, low-melting alcohols. Replacement of the methyl groups in t-butyl alcohol by ethyl groups lowered the yield of ether; the reaction failed with 3-ethylpentan-3-ol. The reaction was conveniently self-indicating, being effectively complete when the initial deep red solution had precipitated a yellow solid ($CsHF_2$).

It became clear that for a more general synthesis a more nucleophilic reagent than $[ROH \cdots F^-]$, the activated alcohol, was required. Since Pietra and del Cima[6] had obtained excellent yields in the reactions of t-butoxide with 1-fluoro-4-nitrobenzene, the reactions between metal alkoxides and 1-fluoro-2,4-dinitrobenzene seemed promising. Treatment of potassium alkoxide with 1-fluoro-2,4-dinitrobenzene in benzene or tetrahydrofuran gave a red colour which was interpreted as the Meisenheimer complex.[7] The red solution had turned brown within 10 min at room temperature for t-butoxide but took 8 h to change colour for the alkoxide from 3-ethylpentan-3-ol. The reaction was complete when the brown solution had deposited a yellow precipitate of potassium fluoride and potassium 2,4-dinitrophenolate. The reaction failed for alcohols which could readily eliminate, and with higher molecular weight alcohols there were solubility difficulties. As two molecules of a tertiary alcohol are needed to react with each atom of potassium, forming ROK,ROH, the yields were never more than 50%.

More generally, alcohols were completely converted into their alkoxides by adding ethereal phenyl-lithium to them in tetrahydrofuran solution; the alkoxides were then treated with 1-fluoro-2,4-dinitrobenzene at −78°. On warming, the Meisenheimer complex appeared at different times for different alcohols, slowing for more hindered alcohols and with increasing electron-donating inductive effect of the substituent for *para*-substituted 2-phenyl-2-propyl derivatives. Addition of water at this stage gave little if any ether; if, however, the solution of the Meisenheimer complex was added to light petroleum, lithium fluoride was precipitated, and decomposition then gave a fair yield of ether for a wide variety of tertiary alcohols. Phenyl 2,4-dinitrophenolate (formed from lithium phenoxide present in the lithium phenyl) and any unchanged 1-fluoro-2,4-dinitrobenzene were decomposed by dry piperidine to 2,4-dinitrophenylpiperidine in 10 min at room temperature; under these conditions the tertiary ethers were stable. The tertiary ether was separated from biphenyl, 2,4-dinitrophenylpiperidine, and unchanged alcohol by alumina chromatography. The method failed only with 2-(*p*-methylphenyl)propan-2-ol and 2-(*p*-nitrophenyl)propan-2-ol, in the former case undoubtedly because of extreme ease of heterolysis.

No ether was ever isolated when even a small excess of phenyl-lithium was used; the deep purple colour of 2,4-dinitrophenyl-lithium[8] was produced, leading to dark products of unknown composition.

Yields of isolated 2,4-dinitrophenolates are given in Table 1 together with analytical and other data. In the absence of other chromophores, crystalline 2,4-dinitrophenolates are colourless when pure, but also slightly light-sensitive. U.v. maxima proved to be unexpectedly variable, presumably because the conformational equilibrium is affected by interactions between ramified alkyl residues, the nitro-group in position 2, and the hydrogen atom in position 6. Extinction coefficients were in the range $1{\cdot}10$—$1{\cdot}15 \times 10^4$ at 25° in iso-octane. In the same solvent 1-fluoro-2,4-dinitrobenzene showed a rising absorbance between 400 and 250 nm with no maximum and ε (280 nm) = 550. The ^1H n.m.r. spectra (CCl_4) of the ethers differ from that of 1-fluoro-2,4-dinitrobenzene in that the proton at position six appears as a doublet ($J_{5,6} = 9$ Hz) at τ 2·7 in the former, but as a triplet ($J_{5,6} = J_{6,1(F)} = 9$ Hz) at τ 2·5 in the latter; this allows the identification of unchanged reagent in crude products. Other absorption regions (H_3, doublet, $J_{3,5} = 3$ Hz, at τ 1·5; H_5, doublet of doublets, at τ 1·7) overlap those of the reagent. The i.r. spectra of the ethers and of the fluoride are extremely similar, but a band at 1608 cm^{-1} in the former corresponds to one at 1617 cm^{-1} in the latter, while in addition

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[3] G. G. Yakobson and N. N. Vorozhtsov, *Zhur. vsesoyuz khim. Obsch. im. D.I. Mendeleeva*, 1961, **6**, 360 (*Chem. Abs.*, 1961, **55**, 27,172).

[4] R. B. Mosely, Ph.D. Thesis, M.I.T., 1952.

[5] K. Bowden, R. S. Cook, and M. J. Price, *J. Chem. Soc.* (*B*), 1971, 1778.

[6] F. Pietra and F. del Cima, *Chem. Comm.*, 1968, 216.

[7] J. Meisenheimer, *Annalen*, 1902, **323**, 241.

[8] G. Köbrich and P. Buck, *Ber.*, 1970, **103**, 1420.

to a band at 3085 cm^{-1} present in both, the fluoride has a weaker band at 3100 cm^{-1}.

Treatment with piperidine at 100° regenerates alcohols from their 2,4-dinitrophenolates with retention of configuration.

Solvolysis of 2,4-*Dinitrophenolates*.—Rates of acetolysis for a range of 2,4-dinitrophenolates are given in Table 2. The solvolyses of 2,4-dinitrophenolates are easy to follow since the u.v. spectra of the ethers are radically different from that of 2,4-dinitrophenolate anion and even that of 2,4-dinitrophenol.

TABLE 1

2,4-Dinitrophenolates synthesised *

Parent alcohol	Synthesis methods and yields	M.p. (t/°C)	Found % C	Found % H	Molecular formula	Required % C	Required % H	$\lambda_{max.}$/nm (iso-octane)
2-Methylpropan-2-ol	76,[a] 27,[b] 16 [d] †	64—64·5 [e]	50·5	5·25	$C_{10}H_{12}N_2O_5$	50·0	5·05	280·0
2-Methylbutan-2-ol	27,[a] 55,[b] 30 [c]	32·5—33·5	51·6	3·35	$C_{11}H_{14}N_2O_5$	52·0	5·55	282·0
3-Ethylpentan-3-ol [9]	20,[b] 26 [c]	46—47	55·8	6·55	$C_{13}H_{18}N_2O_5$	55·3	6·45	289·0
2,3,3-Trimethylbutan-2-ol [10]	3,[a] 30 [b]	59·5—60·5	55·4	6·5	$C_{13}H_{18}N_2O_5$	55·3	6·45	284·5
1α-Methyl-4β-t-butylcyclohexan-1β-ol [11]	3,[a] 33 [b]	134·5—135·5	61·0	7·0	$C_{17}H_{24}N_2O_5$	60·9	6·9	287·5
1α-Methyl-4α-t-butylcyclohexan-1β-ol [11]	7,[a] 17 [b]	107—108·5	61·1	7·0	$C_{17}H_{24}N_2O_5$	60·9	6·9	283·0
Adamantan-1-ol	26 [b]	172—172·5	60·1	5·7	$C_{16}H_{18}N_2O_5$	60·4	5·5	282·5
2-Methyladamantan-2-ol [12]	50 [b]	135—136	61·6	5·8	$C_{17}H_{20}N_2O_5$	61·5	6·0	290·0
2-Phenylpropan-2-ol [13]	30 [b]	94·5—95·5	59·4	4·7	$C_{15}H_{14}N_2O_5$	59·6	4·65	283·5
2-(*p*-t-Butylphenyl)propan-2-ol [13]	3 [b]	87—88 (decomp.)	63·2	6·35	$C_{19}H_{22}N_2O_5$	63·5	6·45	—
2-(*p*-Chlorophenyl)propan-2-ol [14]	25 [b]	82·5—83·0	53·3	3·65	$C_{15}H_{13}N_2O_5Cl$	53·5	3·9	283·5
2-(*p*-Bromophenyl)propane-2-ol [14]	10 [b]	101—101·5	47·6	3·65	$C_{15}H_{13}N_2O_5Br$	47·3	3·45	283·5
2-(*p*-Iodophenyl)propan-2-ol [14]	11 [b]	107—107·5	41·8	3·0	$C_{15}H_{13}N_2O_5I$	42·1	3·05	284·0
Diphenylmethanol	70 [a]	148—149 [f]	65·1	3·9	$C_{19}H_{14}N_2O_5$	65·2	4·05	284·8

* Also synthesised in a non-crystalline form were the ethers from 3-methylpentan-3-ol [15] [$\lambda_{nax.}$ (iso-octane) 285·0 nm] 2-(*p*-fluorophenyl)propan-2-ol,[14] and 2-(*m*-bromophenyl)propan-2-ol.[14] † Dimorph, m.p. 55·7—55·9°, correct analysis.

[a] Caesium fluoride method. [b] Phenyl-lithium method. [c] Potassium method. [d] DABCO(1,4-diazabicyclo[2,2,2]octane) method.[1a] [e] Lit.,[3] 64·5°. [f] Lit.,[2j] 149—150°.

Acetolysis of the 2,4-dinitrophenolates obeys the classical criteria for an 'S_N1' or 'Lim' solvolysis, of a high enthalpy and near-zero entropy of activation, and insensitivity of the rate to added acetate ion. The b value for sodium acetate (up to 0·12 molar solution) obtained from the acetolysis of the t-butyl ether at 74° was 4 ± 1 l mol^{-1}. The activation parameters obtained from the Arrhenius equation ($\log k = A' + B'/T$) strictly apply to the mean temperature of the interval over which the rates were measured, but these values are within experimental error equal to those quoted at 100°. A three-parameter equation ($\log k = A + B/T + C \log T$) was fitted to the results from the acetolyses of 2-phenyl-2-propyl 2,4-dinitrophenolate.[16] $\Delta C_p^{\ddagger}$ Was found to be −31·5 ± 8·2 cal deg^{-1} (statistically significant at the 96% confidence limit), similar to values for the few reported solvolyses in non-aqueous solvents.[17] The three-parameter equation gave a lower standard deviation (0·0045 instead of 0·0069) for experimental values of log k than did the Arrhenius equation, only slightly larger than the estimated experimental error from the data of the individual runs. The activation parameters at the mean temperature of the interval over which rates were measured were within experimental error the same for either treatment. There is little doubt that the results for this substance justified this refined treatment; however, inspection indicated that those for the other (less reactive) ethers did not.

Diphenylmethyl 2-nitro-4-cyanophenolate was synthesised in the hope that replacement of a nitro-group by the less strongly charge-stabilising cyano-group would give a leaving group suitable for use with more reactive systems. The factor, of scarcely more than 2 in the rate ratio at 100°, does not indicate great usefulness for 2-nitro-4-cyanophenoxide as a leaving group, although the acetolysis is even easier to follow spectrophotometrically than that of a 2,4-dinitrophenolate.

EXPERIMENTAL

Solvents.—Tetrahydrofuran was dried by distillation from lithium aluminium hydride, diethyl ether by shaking vigorously overnight with freshly prepared sodium wire, toluene, benzene, dichloromethane, and light petroleum by distillation from calcium hydride.

Liquid alcohols were dried by distillation from calcium hydride, solid alcohols were dried in ether solution by calcium hydride, the solution being filtered and the ether removed under reduced pressure.

Dry acetic acid was obtained by distillation of commercial glacial acetic acid from freshly made tetra-acetyl diborate. In our hands the published method [18] was hazardously

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[12] P. von R. Schleyer and R. D. Nicholas, *J. Amer. Chem. Soc.*, 1961, **83**, 182.

[13] H. C. Brown, Y. Okamato, and G. Ham, *J. Amer. Chem. Soc.*, 1957, **79**, 1897.

[14] H. C. Brown, Y. Okamato, and G. Ham, *J. Amer. Chem. Soc.*, 1957, **79**, 1906.

[15] F. Hovorka, H. P. Lankelma, and A. E. Axelrod, *J. Amer. Chem. Soc.*, 1940, **62**, 187.

[16] G. Kohnstam, personal communication.

[17] G. Kohnstam, *Adv. Phys. Org. Chem.*, 1967, **5**, 121.

[18] W. C. Eichelburger and V. K. La Mer, *J. Amer. Chem. Soc.*, 1933, **55**, 3633.

violent, and the following procedure was preferred. Small amounts of powdered boric acid were added to 250 g of acetic anhydride at 70° with vigorous stirring; the temperature was slowly raised until initiation of the reaction was seen by the solution suddenly turning white with a sharp temperature increase. The solution was quickly cooled in ice–water and boric acid was added at a rate sufficient to keep the temperature steady in the range 80—100°, and until a total of 50 g of boric acid had been added. The solution was then stirred to consume unreacted boric acid. When the solution had cooled to 50° it was filtered through dry glass wool into a flask which was corked and placed in an ice-bath for 15 min, after which time tetra-acetyl diborate had crystallised. The very hygroscopic product was rapidly filtered at a water pump, washed three times with 20-ml portions of glacial acetic acid, and transferred immediately to the distillation flask. A litre of commercial grade glacial acetic acid was added and the mixture was refluxed for 1½ h. Rapid distillation through a lagged Dufton column yielded acetic acid, b.p. 118°/760 nm (950 ml) containing less than 0·02% (w/w) water, estimated by the Karl Fischer method, and less than 0·1% acetic anhydride, estimated from its extinction coefficient at 275 nm, before frothing prevented further distillation.

TABLE 2

Kinetic data on the acetolysis of 2,4-dinitrophenolates †

Parent alcohol	t/°C	k/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1} (kcal mol^{-1}) at 100°	$\Delta S^{\ddagger}$/kJ mol^{-1} (cal K^{-1} mol^{-1}) at 100°
2-Methylpropan-2-ol	72·35 ± 0·05	(1·32 ± 0·01) × 10^{-5}	115·1 ± 1·3	−5·9 ± 3·8
	76·50 ± 0·05	(2·23 ± 0·02) × 10^{-5}	(27·5 ± 0·3)	(−1·4 ± 0·9)
	99·8 ± 0·2	(2·80 ± 0·10) × 10^{-4} [a]		
	100·0	(2·86 ± 0·06) × 10^{-4} [b]		
2-Methylbutan-2-ol	72·40 ± 0·05	(3·30 ± 0·02) × 10^{-5}	113·9 ± 0·4	−2·5 ± 0·8
	78·30 ± 0·05	(6·63 ± 0·05) × 10^{-5}	(27·2 ± 0·1)	(−0·6 ± 0·2)
	99·2 ± 0·2	(6·19 ± 0·07) × 10^{-4} [a]		
	100·0	(6·75 ± 0·08) × 10^{-4} [b]		
2,3,3-Trimethylbutan-2-ol	68·10 ± 0·05	(2·93 ± 0·01) × 10^{-5}	118·9 ± 1·3	15·9 ± 3·3
	72·50 ± 0·05	(4·87 ± 0·02) × 10^{-5}	(28·4 ± 0·3)	(3·8 ± 0·8)
	77·60 ± 0·05	(9·95 ± 0·06) × 10^{-5}		
	88·3 ± 0·2	(3·32 ± 0·03) × 10^{-4}		
	105·6 ± 0·2	(2·03 ± 0·04) × 10^{-3}		
	100·0	(1·15 ± 0·03) × 10^{-3} [b]		
1α-Methyl-4β-t-butylcyclohexan-1β-ol	73·10 ± 0·05	(1·89 ± 0·01) × 10^{-5}	120·1 ± 1·7	10·0 ± 5·0
	74·40 ± 0·05	(2·23 ± 0·02) × 10^{-5}	(28·7 ± 0·4)	(2·4 ± 1·2)
	78·65 ± 0·05	(4·00 ± 0·05) × 10^{-5}		
	99·7 ± 0·2	(4·05 ± 0·10) × 10^{-4} [a]		
	100·0	(4·17 ± 0·08) × 10^{-4} [b]		
1α-Methyl-4α-t-butylcyclohexan-1β-ol	73·05 ± 0·05	(2·97 ± 0·02) × 10^{-5}	118·0 ± 2·1	8·8 ± 5·9
	74·85 ± 0·05	(3·67 ± 0·04) × 10^{-5}	(28·2 ± 0·5)	(2·1 ± 1·4)
	76·75 ± 0·05	(5·04 ± 0·04) × 10^{-5}		
	78·85 ± 0·05	(6·69 ± 0·05) × 10^{-5}		
	99·7 ± 0·2	(6·25 ± 0·15) × 10^{-4} [a]		
	100·0	(6·44 ± 0·19) × 10^{-4} [b]		
2-Methyladamantan-2-ol	50·00 ± 0·05	(9·59 ± 0·04) × 10^{-6}	109·6 ± 0·4	−1·7 ± 1·3
	64·85 ± 0·05	(6·02 ± 0·03) × 10^{-5}	(26·2 ± 0·1)	(−0·4 ± 0·3)
	69·50 ± 0·05	(1·04 ± 0·01) × 10^{-4}		
	72·20 ± 0·05	(1·45 ± 0·01) × 10^{-4}		
	78·40 ± 0·05	(2·82 ± 0·03) × 10^{-4}		
	100·0	(2·64 ± 0·04) × 10^{-3} [b]		
2-Phenylpropan-2-ol *	30·80 ± 0·05	(2·48 ± 0·01) × 10^{-5}	100·1 ± 0·4	−4·2 ± 1·3
	36·80 ± 0·05	(5·45 ± 0·03) × 10^{-5}	(23·9 ± 0·1)	(−1·0 ± 0·3)
	48·30 ± 0·05	(2·32 ± 0·01) × 10^{-4}		
	59·10 ± 0·05	(8·22 ± 0·05) × 10^{-4}		
	73·10 ± 0·05	(3·56 ± 0·02) × 10^{-3}		
	100·0	(4·83 ± 0·07) × 10^{-2} [b]		
Diphenylmethanol	48·95 ± 0·05	(2·77 ± 0·01) × 10^{-5}	104·3 ± 5·9	−8·8 ± 1·7
	54·75 ± 0·05	(5·68 ± 0·03) × 10^{-5}	(24·9 ± 1·4)	(−2·1 ± 0·4)
	59·10 ± 0·05	(9·82 ± 0·07) × 10^{-5}		
	64·95 ± 0·05	(1·92 ± 0·01) × 10^{-4}		
	72·75 ± 0·05	(4·42 ± 0·03) × 10^{-4}		
	77·75 ± 0·05	(7·59 ± 0·03) × 10^{-4}		
	100·0	(6·76 ± 0·13) × 10^{-3} [b]		
Diphenylmethyl 2-nitro-4-cyanophenolate	49·85 ± 0·05	(1·630 ± 0·008) × 10^{-5}	104·7 ± 0·4	−12·6 ± 0·8
	65·25 ± 0·05	(1·004 ± 0·002) × 10^{-4}	(25·0 ± 0·1)	(−3·0 ± 0·2)
	77·40 ± 0·05	(3·83 ± 0·02) × 10^{-4}		
	100·0	(3·16 ± 0·03) × 10^{-3} [b]		

* From the three-parameter equation, $\Delta H^{\ddagger} = 93{\cdot}8 \pm 0{\cdot}08$ kJ mol^{-1} ($22{\cdot}41 \pm 0{\cdot}02$ kcal mol^{-1}), $\Delta S^{\ddagger} = -20{\cdot}9 \pm 0{\cdot}4$ J K^{-1} mol^{-1} ($-5{\cdot}0 \pm 0{\cdot}1$ cal K^{-1} mol^{-1}), $\Delta C_p^{\ddagger} = -131{\cdot}9 \pm 34{\cdot}3$ J K^{-1} ($-31{\cdot}5 \pm 8{\cdot}2$ cal K^{-1}), $k = (4{\cdot}27 \pm 0{\cdot}05) \times 10^{-2}$ s^{-1}, all at 100°. † See also ref. 1*a*.

[a] Mean of two ampoule kinetic runs. [b] Extrapolated using $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ values at 100°.

Alcohols used for 2,4-dinitrophenylations were either commercially available or were synthesised by literature routes (see Table 1).

Phenyl-lithium.—This compound was prepared by the method of Gilman and Morton[19] and estimated by the method of Clifford and Olsen.[20]

General Methods of 2,4-*Dinitrophenylation*.—(a) *Caesium fluoride method* (cf. *ref*. 3). The alcohol (10 mmol), 1-fluoro-2,4-dinitrobenzene (10 mmol), and caesium fluoride (20 mmol; freshly ignited at 400°, cooled, and powdered), together with a small magnetic follower were sealed into a stout ampoule under dry nitrogen and heated to 80—90° with vigorous stirring for 4 h or until the contents solidified and their colour changed from red-brown to yellow. The contents were distributed between dichloromethane and water; the organic layer was dried over calcium chloride and the solvent was removed under reduced pressure at 25°. The residue was dissolved in the minimum amount of dry ether and quickly eluted with dry ether from a column of 50 g of 5% sodium hydroxide on alumina,[21] which removed unchanged 1-fluoro-2,4-dinitrobenzene. If the parent alcohol was liquid at room temperature, recrystallisation from carbon tetrachloride or ether–light petroleum gave the required ether. If the parent alcohol was solid at room temperature the eluted solid from the sodium hydroxide–alumina column was chromatographed on alumina (grade II, 200 : 1 ratio), elution with 20% ether in light petroleum (b.p. 30—40°) separating the ether from unchanged parent alcohol. The appearance of the ether was monitored by its characteristic u.v. spectrum.

(b) *Potassium method*. Freshly cut potassium (1 mg-atom) was added to the alcohol (2 mmol), if necessary dissolved in a small quantity of dry toluene or tetrahydrofuran, and the solution was refluxed until all the metal had dissolved (1—4 h). An aliquot of the solution was removed and weighed in a tared flask under nitrogen. Water was then added and the total equivalent was estimated with 2N-hydrochloric acid using phenolphthalein as indicator. The alkoxide solution was then added dropwise under nitrogen with vigorous agitation to a solution of a 5% excess of 1-fluoro-2,4-dinitrobenzene in dry tetrahydrofuran (2 ml). On entering the solution each drop turned red-black then rapidly went yellow; with time a yellow precipitate of potassium fluoride and potassium 2,4-dinitrophenolate formed which was filtered off. The filtrate was washed twice with 5% sodium hydrogen carbonate solution, then with water and treated as for method (a).

(c) *Phenyl-lithium method*. The alcohol (0·5 mmol) was dissolved in a small quantity of dry tetrahydrofuran in a nitrogen-filled flask with a magnetic follower and septum cap, and cooled to −78°. Phenyl-lithium solution in ether (0·45 mmol) was added by syringe and the solution was allowed to warm to room temperature; it was then stirred for 15 min, after which time a white precipitate of alkoxide had appeared. An aliquot of the solution was tested with Mischler's ketone to ensure the absence of phenyl-lithium; the solution was then cooled to −78°. Sufficient 1-fluoro-2,4-dinitrobenzene was added in a small quantity of dry tetrahydrofuran to react with all the lithium alkoxide present, and the solution was allowed to warm, the deep red clear colour of the Meisenheimer complex appearing at different temperatures and reaction times according to the alkyl group. At this stage the reaction was quenched by the addition of two volumes of ice-cold dry light petroleum (b.p. 60—80°). The solution became brown and cloudy, depositing (after 30 min) a yellow-brown precipitate which was filtered off. The solvent was removed *in vacuo* and dry cold piperidine (3 ml) was added to the residue; the mixture was then stirred at room temperature for 10 min to convert phenyl 2,4-dinitrophenolate and remaining 1-fluoro-2,4-dinitrobenzene into 2,4-dinitrophenylpiperidine. Light petroleum (50 ml) was added, and the solution was washed with water, 2N-hydrochloric acid, 5% sodium hydrogen carbonate solution, and water again. The petrol solution was dried ($MgSO_4$), the petrol was removed under reduced pressure, and the residue was taken up in the minimum amount of dry light petroleum (b.p. 30—40°) and applied to an alumina column (grade II, 200 : 1 ratio). Petrol elution removed the small amount of biphenyl present, then 20% ether in petrol eluted the alkyl 2,4-dinitrophenolate (monitored by u.v.) ahead of 2,4-dinitrophenylpiperidine which gave a broad yellow band on the column. Further elution with ether gave unchanged alcohol. The 2,4-dinitrophenolate was recrystallised from carbon tetrachloride or light petroleum (b.p. 60—80°) and stored away from light.

4-*Fluoro*-3-*nitrobenzonitrile*.—4-Fluorobenzonitrile (400 mg, 3·3 mmol) was added to an ice-cold solution of 15 ml of concentrated sulphuric acid and 5 ml of concentrated nitric acid. The mixture was stirred at 50° for 10 min and was then poured onto crushed ice (250 g) and set aside for 2 h. The solid was separated and added to the dichloromethane extract of the filtrate, which was then washed twice with normal sodium hydrogen carbonate solution and once with water; it was then dried ($MgSO_4$). After removal of solvent, sublimation at 100° (water pump pressure) gave 4-fluoro-3-nitrobenzonitrile (320 mg, 58%), m.p. 91—92° (lit.,[22] 91—92°).

Diphenylmethyl 2-*Nitro*-4-*cyanophenyl Ether*.—4-Fluoro-3-nitrobenzonitrile (108 mg, 0·65 mmol), diphenylmethanol (120 mg, 0·65 mmol), anhydrous caesium fluoride (205 mg, 1·30 mmol), and a magnetic follower were sealed into a stout ampoule under nitrogen, and heated at 100° for 25 min with vigorous stirring. The ampoule contents had then set into a yellow solid which was extracted with ether; the solution was concentrated and applied to the top of a column of 10 g of 5% sodium hydroxide on alumina. Ether elution gave the products free of unchanged 4-fluoro-3-nitrobenzonitrile. The products were chromatographed on alumina (grade II, 200 : 1 ratio), the alkyl ether being eluted with 10% ether in light petroleum (b.p. 30—40°), and its appearance being monitored by its characteristic u.v. spectrum. Recrystallisation from light petroleum–carbon tetrachloride gave diphenylmethyl 2-nitro-4-cyanophenolate (43 mg, 20%), m.p. 170—172° (Found: C, 72·6; H, 4·45. $C_{20}H_{14}N_2O_3$ requires C, 72·7; H, 4·25%).

Cleavage of the 1-*Methyl*-4-*t-butylcyclohexyl* 2,4-*Dinitrophenyl Ethers with Piperidine*.—Either of the isomeric 2,4-dinitrophenolates (3 mg, 0·01 mmol) and dry piperidine (0·1 ml) were sealed into an ampoule and heated at 100° for 1 h. The ampoule contents were extracted between water and light petroleum (b.p. 60—80°), and the petrol extract was washed with 0·1N-hydrochloric acid, 5% sodium hydrogen carbonate solution, and water; it was then dried ($MgSO_4$).

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G.l.c. analysis of the solution (50 ft S.C.O.T. Carbowax 20M, 110°) showed total retention of configuration in the product alcohol.

Kinetics.—All solvolyses were followed spectrophotometrically. In acetic acid 2,4-dinitrophenolates show an absorption maximum at 290—300 nm with a typical extinction coefficient of $1\cdot1 \times 10^4$ at 25°. Repetitive u.v. scans of solvolysing 2,4-dinitrophenolates revealed that the biggest optical density increase occurred at 350 nm (×2·2) in acetic acid and at 370 nm (×8) in aqueous buffered solvents, and the solvolyses were followed at these wavelengths. The addition of sodium acetate did not change the u.v. spectrum of 2,4-dinitrophenol in acetic acid, but produced the spectrum of sodium 2,4-dinitrophenolate ($\lambda_{max.}$ 370 nm) in aqueous solvents. In acetic acid diphenylmethyl 2-nitro-4-cyanophenolate showed an absorption maximum at 315 nm; repetitive u.v. scans at 70° showed the biggest optical density increase (×4) to occur at 340 nm, and solvolyses were followed at this wavelength.

Kinetic runs at less than 80° were followed on a Cary 14 spectrophotometer with digital tape output, using specially adapted 10-mm u.v. cells.[23] The cell-block was heated by water circulation from a ' Tamson ' water-bath thermostatted to ±0·02. The temperature of the bath was measured with an N.P.L. calibrated thermometer and the temperature difference between the bath and cell-block was measured using a calibrated thermocouple and galvanometer. Kinetic runs at more than 80° were followed by sealing the solvolysis solution in glass ampoules which were placed in a ' Tamson ' oil-bath thermostatted to ±0·2° and withdrawn after suitable intervals for spectral assay on a Unicam SP 800 spectrophotometer.

For *in situ* kinetics first-order rate constants were determined by the method of Guggenheim,[24] and for ampoule kinetics from a normal first-order plot, made with the aid of multiply determined infinity readings. The gradients and standard errors of the resulting linear plots, comprising at least 17 points for *in situ* kinetics and 9 points for ampoule kinetics, were determined by a computerised least-squares technique.

Activation parameters were determined from the least-squares plot of log (rate constant) *versus* 1/absolute temperature, comprising at least 4 points over a temperature range of at least 25°. Absence of curvature in these plots was confirmed visually. Data for 2-phenyl-2-propyl dinitrophenolate were also fitted to a 3-parameter equation [17] by Dr. G. Kohnstam, whom we thank for this work.

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