Allylic Carbonium Ions. Part I. Acetolysis of 1,1- and 3,3-Dimethylallyl 2,4-Dinitrophenyl Ether

By **K. Brian Astin** and **Mark C. Whiting**,* School of Chemistry, University of Bristol, Bristol BS8 1TS

The 2,4-dinitrophenyl ethers of 1,1- and 3,3-dimethylallyl alcohol were prepared by convenient new arylation techniques, and their acetolysis rates and reaction products are reported. The tertiary isomer undergoes concurrent rearrangement to the primary isomer by a process of ion-pair return. Experiments relating these solvolyses to similar processes already described, involving other leaving groups and solvents, are reported.

In their classical work on the solvolysis of 1,1-dimethylallyl chloride (Ia), Young *et al.*[1] observed extensive formation of a non-exchanging ion-pair (IIa) which in large part collapsed to give the less reactive 3,3-dimethylallyl chloride (IIIa). An intermediate of this type, (IIc), was originally proposed by Braude and Jones[2] to account for the precisely similar formation of hex-3-en-5-yn-2-ol (IIIc) when hex-4-en-1-yn-3-ol (Ic) was treated with ethanolic acid, although here its intervention was not rigorously proved. A rather remote analogy exists with intermediates (IId) postulated by Goering and

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[1] W. G. Young, S. Winstein, and H. L. Goering, *J. Amer. Chem. Soc.*, 1951, **73**, 1958.

[2] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 1944, 436.

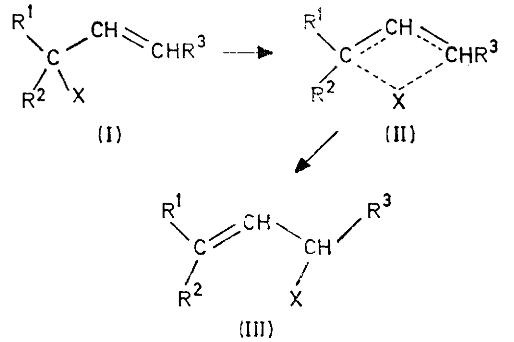
Pombo[3] in the degenerate rearrangement of an allylic ester. The Braude–Jones intermediate (II) is of importance in Sneen's recent theory of allylic solvolysis[4] and as an ionic analogue of a 1,3-sigmatropic shift transition-state; since case (IIa) can be formulated with hypervalent chlorine (IV), and there were ambiguities in cases (IIc and d), we have sought evidence for (IIb), an analogue of (IIa) with a leaving group having a single atom of a first-row element as charge centre. In all these cases, species (II) may in principle represent a transition-state rather than an energy minimum.

TABLE 1

Acetolysis data

Compound	t/°C	k/s^{-1} [b]	ΔH‡/kJ mol^{-1} (kcal mol^{-1}) at 100°	ΔS‡/J K^{-1} mol^{-1} (cal K^{-1} mol^{-1}) at 100°
Allyl picrate	93.0 ± 0.1	(3.79 ± 0.07) × 10^{-5}	97.9 ± 2.4	−67.7 ± 6.7
	93.0 ± 0.1	(4.05 ± 0.08) × 10^{-5}	(23.4 ± 0.6)	(−16.2 ± 1.6)
	82.55 ± 0.1	(1.39 ± 0.02) × 10^{-5}		
	82.55 ± 0.1	(1.56 ± 0.03) × 10^{-5}		
	71.4 ± 0.1	(4.70 ± 0.10) × 10^{-6}		
	71.4 ± 0.1	(4.84 ± 0.07) × 10^{-6}		
	100.0	(4.47 ± 0.18) × 10^{-5} [a]		
1,1-Dimethylallyl 2,4-dinitrophenyl ether	35.7 ± 0.05	(3.86 ± 0.04) × 10^{-5}	94.6 ± 1.2	−23.6 ± 3.6
	42.75 ± 0.05	(8.69 ± 0.03) × 10^{-5}	(22.6 ± 0.3)	(−5.6 ± 0.9)
	51.0 ± 0.05	(2.25 ± 0.15) × 10^{-4}		
	60.2 ± 0.05	(6.33 ± 0.03) × 10^{-4}		
	100.0	(2.64 ± 0.17) × 10^{-2} [a]		
3,3-Dimethylallyl 2,4-dinitrophenyl ether	66.2 ± 0.05	(1.62 ± 0.02) × 10^{-5}	120.2 ± 2.0	16.6 ± 5.7
	71.4 ± 0.05	(3.34 ± 0.08) × 10^{-5}	(28.7 ± 0.5)	(4.0 ± 1.4)
	76.5 ± 0.05	(6.16 ± 0.06) × 10^{-5}		
	90.95 ± 0.1	(3.22 ± 0.04) × 10^{-4}		
	100.0	(8.67 ± 0.40) × 10^{-4} [a]		

[a] Extrapolated from ΔH‡ and ΔS‡ values at 100°. [b] These refer to the formation of 2,4-dinitrophenol. At 100.0° the total rate of reaction of the 1,1-dimethylallyl compound will be (3.1 ± 0.2) × 10^{-2} s^{-1}, allowing for concurrent isomerisation, with $k_R = 0.16\ k_T$.



(I) (II)

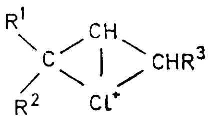
(III)

(a) $R^1 = R^2 = CH_3$, $R^3 = H$, $X = Cl$

(b) $R^1 = R^2 = CH_3$. $R^3 = H$, $X = OC_6H_3(NO_2)_2$

(c) $R^1 = H$, $R^2 = C{\equiv}CH$, $R^3 = CH_3$, $X = OH$,

(d) $R^1 = H$, $R^2 = R^3 = CH_3$, $X = OCOC_6H_4NO_2$



(IV)

The primary ether (IIIb) was prepared from the alcohol, 1-fluoro-2,4-dinitrobenzene, and diaza[2.2.2]bicyclo-octane in tetrahydrofuran or ether, a new variant of our picrate synthesis[5] which is probably the method of choice for the dinitrophenylation of reactive alcohols, as the reaction is self-indicating. The tertiary isomer (Ib) was obtained in variable yield by the phenyl-lithium method of Page *et al.*[6] A new method for tertiary alcohols, which worked well in this case, was found in the preparation of the alkoxide,[7] ROK, from a molar equivalent of potassium hydride in tetrahydrofuran, and its reaction with 1-fluoro-2,4-dinitrobenzene; in contrast, metallic potassium gives only ROK, ROH, which appears to be less reactive. Both ethers were crystalline.

Solvolysis in acetic acid led to good first-order behaviour in each case with a rate ratio of 71 at 65° (compared with 6.1 for the chlorides at 25°, leading to complicated kinetics for the tertiary chloride because of concurrent isomerisation[1]). The rate constants, k_T, and activation parameters are presented in Table 1. The tertiary isomer gave a product mixture after eight half-lives which did indeed contain the primary ether (14% yield, *i.e.* $k_R = 0.16\ k_T$), as assayed by spectrophotometry and confirmed by its rate of acetolysis at a higher temperature. The other products were the primary and tertiary acetates and (we presume) isoprene, and are given in Table 2; they show, as is usually observed in such reactions,[8] a similar product mixture from both isomers, the formation of more of the tertiary than the primary acetate, and a superimposed small preference for the isomer corresponding to the starting material.

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[3] H. L. Goering and M. M. Pombo, *J. Amer. Chem. Soc.*, 1960, **82**, 2515.

[4] (*a*) R. A. Sneen and W. A. Bradley, *J. Amer. Chem. Soc.*, 1972, **94**, 6995; (*b*) R. A. Sneen and P. S. Kay, *ibid.*, p. 6983; (*c*) R. A. Sneen and J. C. Carter, *ibid.*, p. 6990.

[5] M. L. Sinnott and M. C. Whiting, *J. Chem. Soc.* (*B*), 1971, 965.

[6] I. D. Page, J. R. Pritt, and M. C. Whiting, *J.C.S. Perkin II*, 1972, 906.

[7] C. A. Brown, *J. Amer. Chem. Soc.*, 1973, **95**, 982.

[8] (*a*) R. H. DeWolfe and W. G. Young, *Chem. Rev.*, 1956, **56**, 793; (*b*) R. E. Robertson and J. M. W. Scott, *J. Chem. Soc.*, 1961, 1596.

Some additional work was needed to link these results to those already published.[1,4,9,10] A comparison of the rate of solvolysis of 3,3-dimethylallyl 2,4-dinitrophenyl ether and that of the corresponding allyl compound would be useful, but proved impracticable because of the low reactivity of the latter; allyl picrate was therefore acetolysed, with results given in Table 1. Assuming a ratio of $1:10^4$ for the two leaving groups,[5] one can observe strong acceleration by $\gamma\gamma$-substitution. However, the acetolysis of allyl picrate is bimolecular in character, showing a negative $\Delta S^{\ddagger}$ value similar to that of ethyl picrate.[5] The behaviour of the corresponding chloride is analogous.[8]

TABLE 2

Solvolysis products of 1,1- and 3,3-dimethylallyl X

DMA X [a]	t/°C	Solvent	k_R/k_T	Substitution (%)	Tertiary (%)	Primary (%)	Ref.
1,1-DMA 2,4-dinitrophenyl ether	65.0	HOAc	0.16 [b]	54	60.7	39.3	This work
3,3-DMA 2,4-dinitrophenyl ether	92.5	HOAc		75	57.6	42.4	This work
1,1-DMA propionate	104.5	HOAc	0.17	68 [c]	69.7	30.3	This work
1,1-DMA p-nitrobenzoate	100	70% acetone	0.41				9
1,1-DMA 3,5-dinitrobenzoate	100	70% acetone		28	71	29	10
3,3-DMA 3,5-dinitrobenzoate	100	70% acetone		49	75	25	10
1,1-DMA chloride	32	80% acetone	0.36		78	22	4 [b]
1,1-DMA chloride	25	HOAc	2.7				1

[a] Dimethylallyl. [b] Ratio measured at 70°. [c] Acetates + propionates.

To bridge these experiments on acetolysis with ' one-atom ' leaving groups and the aqueous solvolysis of carboxylate esters,[9,10] we examined the acetolysis of the tertiary propionate; the corresponding primary propionate might well have reacted mainly by acyl–oxygen fission and was not examined. G.l.c. was used to ascertain products and an approximate rate constant, $k_R + k_T = (4.9 \pm 0.1) \times 10^{-4}\ s^{-1}$ at 104.5° was obtained. The products (Table 2) show that this process is better regarded as unimolecular solvolysis, giving an ion-pair of which the anion is EtCO·Ō · · · HOAc, than as an acid-catalysed variant of the usual 3,3-sigmatropic shift of allylic esters. The 2,4-dinitrophenyl ether : propionate rate ratio, 89, is similar to those observed (20—63) in the acetolysis of saturated tertiary derivatives;[11] thus there is no sign of the large difference in rate of reaction usually found between suprafacial 3,3- and 1,3-sigmatropic shifts under non-solvolytic conditions,[12] and the description in terms of ion-pairs applied to similar alcoholyses by the Wisconsin school[3] is confirmed and extended to acetolysis.

In general, then, Braude–Jones intermediates or transition-states of type (II) exist for X = 2,4-dinitrophenyl ether, and therefore are not restricted to, or greatly favoured by, the availability of d or π-orbitals for X.

EXPERIMENTAL

Materials.—Tetrahydrofuran was dried by distillation from lithium aluminium hydride, diethyl ether by shaking vigorously overnight with freshly prepared sodium wire, and acetic acid by distillation of commercial glacial acetic acid from freshly prepared tetra-acetyl diborate, yielding a product containing <0.02% (w/w) water. 1,1-Dimethylallyl alcohol was obtained from Air Products Ltd. 3,3-Dimethylallyl alcohol was prepared by the lithium aluminium hydride reduction of 3,3-dimethylacrylic acid, affording the alcohol (51%), b.p. 138—140° at 750 mmHg (lit.,[13] 140—142°), with the expected n.m.r. and i.r. spectra.

3,3-*Dimethylallyl* 2,4-*dinitrophenyl ether* was prepared by the reaction of 3,3-dimethylallyl alcohol with 1-fluoro-2,4-dinitrobenzene and diaza[2.2.2]bicyclo-octane[5] in dry tetrahydrofuran in 51% yield, m.p. 52—54° (Found: C, 52.4; H, 4.9; N, 11.1. $C_{11}H_{12}N_2O_5$ requires C, 52.4; H, 4.75; N, 11.1%), τ ($CDCl_3$) 4.5 (1 H, t, vinyl, J 7 Hz), 5.2 (2 H, d, J 7 Hz), and 8.2 (6 H, s, 2Me), $\lambda_{max.}$ (iso-octane) 284 nm (ε 13 500).

1,1-*Dimethylallyl* 2,4-*dinitrophenyl ether*. (a) This was prepared by the reaction of the lithium salt of 1,1-dimethylallyl alcohol at −78° with 1-fluoro-2,4-dinitrobenzene[6] affording 40 and 9% yields in separate experiments, m.p. 38—40°.

(b) The potassium hydride method.[7] Potassium hydride (0.2 g, 5 mmol) was suspended in dry tetrahydrofuran (10 ml). 1,1-Dimethylallyl alcohol (0.44 g, 5 mmol) in dry tetrahydrofuran was added slowly under nitrogen. After the hydride had reacted, the alkoxide solution was added by syringe to a solution of 1-fluoro-2,4-dinitrobenzene in dry tetrahydrofuran under nitrogen, and stirred for 30 min. The solution was then filtered. This was washed with saturated sodium hydrogen carbonate solution and water and dried ($MgSO_4$), organic material was taken into ether, and solvent was removed under reduced pressure. The residue was crystallised from ether–n-hexane and stored at 0°. Recrystallisation from ether–n-hexane gave 1,1-*dimethylallyl* 2,4-*dinitrophenyl ether* (0.9 g, 70%), m.p. 39—41° (Found: C, 52.1; H, 5.0; N, 11.2. $C_{11}H_{12}N_2O_5$ requires C, 52.4; H, 4.75; N, 11.1%), τ ($CDCl_3$) 3.8 (1 H, q, vinyl, J_{12} 10, J_{13} 16 Hz), 4.65 (2 H, two d, J_{21} 10, J_{31} 16 Hz), and 8.4 (6 H, s, 2Me), $\lambda_{max.}$ (iso-octane) 283 nm. This product was stable for some weeks, then rapidly decomposed to dinitrophenol and isoprene.

Allyl picrate was prepared by the method of Sinnott and Whiting,[8] m.p. 86° (lit.,[14] 90°). 1,1-Dimethylallyl acetate

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[9] S. Winstein, G. Valkanas, and C. F. Wilcox, jun., *J. Amer. Chem. Soc.*, 1972, **94**, 2286.

[10] G D. Sargent, T. J. Mason, M. J. Harrison, and J. A. Hall, *J. Amer. Chem. Soc.*, 1973, **95**, 1849.

[11] J. R. Pritt, Ph.D. Thesis, University of Bristol, 1972.

[12] M. J. Goldstein and M. R. DeCamp, *J. Amer. Chem. Soc.*, 1974, **96**, 7356; M. J. Goldstein and W. A. Haily, *ibid.*, p. 7358.

[13] A. I. Lebedeva and L. L. Shchkovskaya, *Zhur. obshchei. Khim.*, 1951, **21**, 1132 (*Chem. Abs.*, 1952, **46**, 1958).

[14] L. C. Raiford and D. M. Birosel, *J. Amer. Chem. Soc.*, 1929, **51**, 1778.

was prepared from the reaction of 1,1-dimethylallyl alcohol with acetic anhydride in dry pyridine for 12 h at 80° in 33% yield, b.p. 120—124° (lit.,[15] 120—122°). 3,3-Dimethylallyl acetate was prepared by the reaction of 3,3-dimethylallyl alcohol with acetic anhydride in dry pyridine for 1 h at room temperature in 48% yield, b.p. 145—150° (lit.,[15] 149—151°). 1,1-Dimethylallyl propionate was made in a manner analogous to the corresponding acetate, using redistilled propionic anhydride, in 35% yield, b.p. 135—140° (lit.,[16] 48—51° at 8 mmHg).

Product Analyses.—(a) *Acetate substitution products.* These were determined by acetolysing the 2,4-dinitrophenyl ethers for short periods, involving 5—10% reaction, and quenching with alkaline phosphate solution.[17] The organic material was extracted with ether and dried ($MgSO_4$). The ether solution was concentrated under reduced pressure and analysed by g.l.c. (50 ft SCOT Carbowax 20M at 95°).

(b) *Determination of* 3,3-*dimethylallyl* 2,4-*dinitrophenyl ether in the acetolysis product of* 1,1-*dimethylallyl* 2,4-*dinitrophenyl ether.* 1,1-Dimethylallyl 2,4-dinitrophenyl ether was acetolysed at 70° for *ca.* 8 half-lives. The reaction mixture was quenched with 4 volumes of water and the organic material was extracted with benzene. The extract was washed with water, 2N-sodium hydroxide, and water, and dried ($MgSO_4$). The benzene solution was concentrated under reduced pressure and the residue applied to an alumina column (grade II; 50 : 1 ratio). Elution with 20% ether in light petroleum afforded 2,4-dinitrophenyl ether free from 2,4-dinitrophenol, monitored by u.v. Assay of the product indicated a yield of 14% rearranged ether (assumed to be 3,3-dimethylallyl 2,4-dinitrophenyl ether). Acetolysis of this ether at 93° afforded a first-order rate constant of 2.7×10^{-4} s^{-1}.

Kinetics.—All acetolyses were followed spectrophotometrically at 350 nm. Repetitive u.v. scans of acetolysing allylic 2,4-dinitrophenyl ethers indicated the largest optical density change at this wavelength (*ca.* ×2). The majority of kinetic runs were followed on a Unicam SP 1700 spectrophotometer, interfacing with a Solartron digital transfer unit producing printed output on a Kode teletype, using specially adapted 10 mm u.v. cells.[18] The cell block was thermostatted to ±0.1° using a Paratherm water bath. The temperature of the bath was measured with an N.P.L. calibrated thermometer and the temperature difference between the bath and the cell block was measured using a calibrated copper–constantan thermocouple and galvanometer. Other spectrophotometers used were Cary 14, Unicam SP 800, and Unicam SP 1800 models.

First-order rate constants were determined by the method of Guggenheim.[19] The gradients and standard errors of the resulting linear plots, comprising at least 10 points, were determined by a computerised least-squares technique. Activation parameters were determined from the computerised least-squares plot of log (rate constant) *versus* $1/T$, comprising at least 4 points over a temperature range of at least 20 °. Absence of curvature in these plots was confirmed visually.

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[15] I. N. Nazarov and I. N. Azerbaev, *Zhur. obshchei. Khim.*, 1948, **18**, 414 (*Chem. Abs.*, 1949, **43**, 114).

[16] F. J. Soday, U.S.P. 2,246,545 (*Chem. Abs.*, 1951, **35**, 5915).

[17] M. Pánková, J. Sicher, M. Tichý, and M. C. Whiting, *J. Chem. Soc.* (*B*), 1968, 365.

[18] P. A. Bristow and R. G. Coombes, *Chem. and Ind.*, 1969, 1509.

[19] E. A. Guggenheim, *Phil. Mag.*, 1926, **7**(2), 538.