Organic Anions. Part 3.[1a] Charge Control *versus* Product Stability Control in the Protonation of 1,3-Diarylpropenide Ions [1b]

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The kinetically controlled reaction of 1,3-diarylpropenide ions (I) in liquid ammonia with either ammonium chloride or methanol gives a mixture of alkenes [(II) and (III)]. The ratios of the products thus obtained can be correlated with the local charges at the benzylic sites as measured by n.m.r. spectroscopy (correlation coefficient $r = 0.961$—0.981) or, less well, with the relative stabilities of the two products ($r = 0.927$—0.931). The slope of the ' charge control ' graph corresponds to a critical interionic separation of 0.8 Å. The best correlation of all ($r = 0.989$—0.997) is obtained by using a two-parameter equation (7), but the statistical validity and theoretical justification for this remain somewhat obscure. A more limited study has been made for the reaction of the anions (I) with allyl chloride.

THE similar PMO treatments given by Fukui,[2,3] Salem,[4] Klopman,[5-7] and Hudson [5,8,9] show that the bonding part of a reagent–substrate interaction can often be divided into a coulombic term and an ' orbital ' term, *e.g.* equation (1).[6]

$$\Delta E \;=\; \underbrace{q_r q_s \Gamma_{rs}}_{\text{coulombic term}} \;+\; \underbrace{\sum_{j}^{\text{occ.}} \sum_{k}^{\text{unocc.}} \frac{2c_{rj}^{2}\, c_{sk}^{2}\, \beta_{rs}^{2}}{\alpha_j - \alpha_k}}_{\text{' orbital interaction ' term}} \qquad (1)$$

Sometimes one of these terms dominates over the other. Indeed, by considering the ' orbital ' term on its own, it is possible qualitatively to rationalise the course of many reactions.[3,7-9,10] On a semiquantitative level, superdelocalisabilities can be used to rationalise the site of attack in aromatic substitution [11,12] and more recently a similar ' orbital ' term has been shown to account *quantitatively* for the nucleophilicities of thiocarbonyl compounds.[13] The other extreme, domination by the coulombic term, is less well understood. Its importance in determining the rates of certain ionic, mainly inorganic, reactions has, however, been known for a long time.[14]

More recently it has been suggested [5,6,8] that the site of reaction in ambident anions is governed by the balance of the two terms in equation (1); an attractive suggestion which also provides a rationale for the earlier theories of ambident reactivity due to Kornblum [15] and to Pearson.[6,16] According to this suggestion the reaction of an ambident anion such as (I) with a suitable proton source

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[1] (*a*) Part 2, R. J. Bushby and G. J. Ferber, preceding paper; (*b*) preliminary communication, R. J. Bushby and G. J. Ferber, *J.C.S. Chem. Comm.*, 1973, 407.

[2] K. Fukui and H. Fujimoto, *Bull. Chem. Soc. Japan*, 1968, **41**, 1989; H. Fujimoto, S. Yamabe, and K. Fukui, *Tetrahedron Letters*, 1971, 439, 443.

[3] K. Fukui, *Fortschr. Chem. Forsch.*, 1970, **15**, 1; *Accounts Chem. Res.*, 1971, **4**, 57.

[4] L. Salem, *J. Amer. Chem. Soc.*, 1968, **90**, 543, 553.

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[6] G. Klopman, *J. Amer. Chem. Soc.*, 1968, **90**, 223.

[7] G. Klopman in ' Chemical Reactivity and Reaction Paths,' Wiley, New York, 1974.

[8] R. F. Hudson, *Angew. Chem. Internat. Edn.*, 1973, **12**, 36.

[9] R. F. Hudson, in ref. 7.

[10] R. B. Woodward and R. Hoffmann, ' The Conservation of Orbital Symmetry,' Academic Press, New York, 1970.

[11] J. Koutecky, R. Zahradnik, and J. Cizek, *Trans. Faraday Soc.*, 1961, **57**, 169; R. Zahradnik and C. Parkani, *Coll. Czech. Chem. Comm.*, 1965, **30**, 355; J. Kuthan, V. Skala, and J. Palecek, *ibid.*, 1969, **34**, 2223.

[12] A. Streitwieser, ' Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961.

[13] M. Arbelot, J. Metzger, M. Chanou, C. Guimon, and G. Pfister-Guillouzo, *J. Amer. Chem. Soc.*, 1974, **96**, 6217.

[14] V. K. La Mer, *J. Franklin Inst.*, 1938, **225**, 709; K. J. Laidler, ' Chemical Kinetics,' McGraw-Hill, New York, 1965, ch. 5.

[15] N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Amer. Chem. Soc.*, 1955, **77**, 6269.

[16] R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, 1967, **89**, 1827.

should provide another example of control by the coulombic term. Such 'charge control' qualitatively accounts for the course of protonation of most delocalised organic anions.[12,17,18] On this qualitative level a few exceptions are known (*e.g.* methylallyl Grignard reagent in ether solvents [19]) but these are in systems where contact ion pairs or aggregates are probably the dominant and possibly the reactive species (*N.B.* the effect of added hexamethylphosphoramide on the Grignard reagent mentioned above [19]). In this paper the theory is tested on a quantitative level by using the diarylpropenide ions (I). It is known that the sodium salts of these anions in liquid ammonia exist as free ions or solvent-separated ion pairs [1a] and, if we assume that they react in one or other of these forms,[20,*] then to a first approximation the effect of counter-ion can be ignored. If it is assumed that there is an exponential relationship [14,18] between the rates of protonation at sites 'a' and 'b' and the charges at these sites q_a and q_b (which should be virtually the same for free anion and solvent separated ion pair) then the product ratio (III) : (II) is given by equation (2), where a is a constant. If it is further

$$\log([(\mathrm{III})]/[(\mathrm{II})]) = \mathrm{a}\,(q_b - q_a) \tag{2}$$

assumed that there is a linear relationship between the charges q_a and q_b and the corresponding n.m.r. chemical shifts δ_a and δ_b [equation (3),[16,†] where b and c are constants] then equation (2) can be reduced to the experimentally verifiable form (4), where A and C are constants.

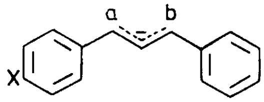
$$\delta = \mathrm{b}q + \mathrm{c} \tag{3}$$

$$\log([(\mathrm{III})]/[(\mathrm{II})]) = \mathrm{A}(\delta_b - \delta_a) + \mathrm{C} \tag{4}$$

An older theory of ambident reactivity, also investigated in the present paper, is its relationship to product stability. For ambident reactions involving a 'late' transition state, product stabilities (or in the case of aromatic substitution localisation energies [11,12]) are known to be a good criterion for the site of attack. In ambident reactions involving an 'early' transition state, however, product stability appears to be a much less reliable guide. In the case of protonation of ambident anions, for example, many cases are known both of systems which follow the Hughes–Ingold Rule and give the least stable product [21] and of those which break the Rule and give the most stable product.[22] These differences are not readily explained in terms of ion-pairing effects. Despite these gross differences in 'sign', however, it is not unreasonable to suppose that *within a limited series*, such as that investigated in the present paper, there may be a linear relationship between the energy barrier to protonation and the energy difference between the anion and alkene. This leads to a relationship between the product ratio obtained under kinetic control, (III) : (II), and the equilibrium constant, K,[23] of the form given in equation (5) (where B and C are constants).

$$\log([(\mathrm{III})]/[(\mathrm{II})]) = \mathrm{B}\log K + \mathrm{C} \tag{5}$$

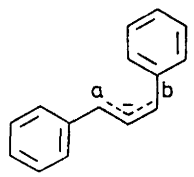
(I)



(II) $XC_6H_4\cdot CH{=}CH\cdot CH_2Ph$

(III) $XC_6H_4\cdot CH_2\cdot CH{=}CHPh$

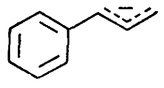
(IV)



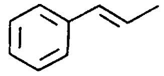
(V) $XC_6H_4\cdot CH{=}CH\cdot CHRPh$

(VI) $XC_6H_4\cdot CHR\cdot CH{=}CHPh$

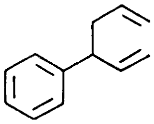
(VII)



(VIII)



(IX)



The kinetically controlled protonation of the anions (I) was investigated in two different ways. In the first case a solution of the anion in liquid ammonia–ether (85 : 15) and a solution of ammonium chloride in liquid ammonia, both at room temperature, were rapidly mixed. In the second case methanol was rapidly added by syringe to a

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[*] As barriers to ion-pair type interconversion are frequently lower than the energy barriers for chemical reactions the dominant ion pair type in solution is not necessarily the reactive form. As however the normal (but not invariable) order of reactivities is aggregate < contact ion pair < solvent-separated ion pair < free ion it seems unlikely that when solvent-separated ion pairs or free ions dominate, as in the present case, reaction will occur through one of the other forms. *A posteriori* this assumption is justified by the close similarity in products from the sodium and lithium salts of the dimethylamino-substituted anion (Table 4).

[17] E. Huckel, 'International Conference on Physics, London,' 1934, Vol. II, p. 9; A. J. Birch, *Discuss. Faraday Soc.*, 1947, **2**, 246; *J. Chem. Soc.*, 1950, 1551; *Quart. Rev.*, 1950, **4**, 69; M. J. S. Dewar, *Discuss. Faraday Soc.*, 1947, **2**, 261.

[18] G. J. Hoijtink and J. van Schooten, *Rec. Trav. chim.*, 1952, **71**, 1089; 1953, **72**, 691.

[19] G. Courtois and G. Miginiac, *J. Organometallic Chem.*, 1974, **69**, 1.

[20] 'Ions and Ion pairs in Organic Reactions,' vol. 2, ed. M. S. Wiley, New York, 1974.

[21] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca, New York, 1953, ch. 10 and references therein.

[22] R. J. Bushby and G. H. Whitham, *J. Chem. Soc.* (*B*), 1969, 67; 1970, 563; D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965, ch. 5.

[23] Part 1, R. J. Bushby and G. J. Ferber, *J.C.S. Perkin II*, 1976, 1683.

TABLE 1

trans-Alkene ratios from acid quenching and equilibration experiments

X	NH_4Cl; 25 °C log ([(III)]/[(II)])	MeOH; −42 °C log([(III)]/[(II)])	Equilibration; 25 °C log([(III)]/[(II)])
p-Me_2N	$\bar{1}.362 \pm 0.009$	$\bar{1}.176 \pm 0.009$	$\bar{1}.602 \pm 0.013$
p-MeO	$\bar{1}.657 \pm 0.030$	$\bar{1}.555 \pm 0.030$	$\bar{1}.778 \pm 0.043$
p-Bu^t	$\bar{1}.833 \pm 0.013$	$\bar{1}.740 \pm 0.013$	$\bar{1}.897 \pm 0.017$
p-Me	$\bar{1}.826 \pm 0.043$	$\bar{1}.720 \pm 0.043$	$\bar{1}.939 \pm 0.052$
p-F	$\bar{1}.968 \pm 0.013$	0.100 ± 0.013	0.053 ± 0.013
p-Cl	0.243 ± 0.009	0.389 ± 0.009	0.025 ± 0.013
m-F	0.362 ± 0.013	0.544 ± 0.013	0.086 ± 0.017

TABLE 2

Fits of experimental data to equations (4), (5), and (7)

Eqn.	Proton source	Temp. (°C)	δ_a, δ_b	A	B	C	Correl. coeff.	r_{AB}/Å
(4)	NH_4Cl	25	^{13}C	0.109		−0.050	0.967	0.8
(4)	NH_4Cl	25	^1H	2.423		−0.004	0.961	0.6
(4)	MeOH	−42	^{13}C	0.156		−0.032	0.981	(0.6) [a]
(4)	MeOH	−42	^1H	3.412		0.031	0.963	(0.4) [a]
(5)	NH_4Cl	25			1.825	0.046	0.931	
(5)	MeOH	−42			2.554	0.101	0.927	
(7)	NH_4Cl	25	^{13}C	0.072	0.769	−0.006	0.989	1.3
(7)	NH_4Cl	25	^1H	1.535	0.833	0.027	0.991	0.9
(7)	MeOH	−42	^{13}C	0.111	0.924	0.020	0.997	(0.8) [a]
(7)	MeOH	−42	^1H	2.217	1.122	0.073	0.990	(0.6) [a]

[a] On the assumption that the proton source carries a charge of +1.

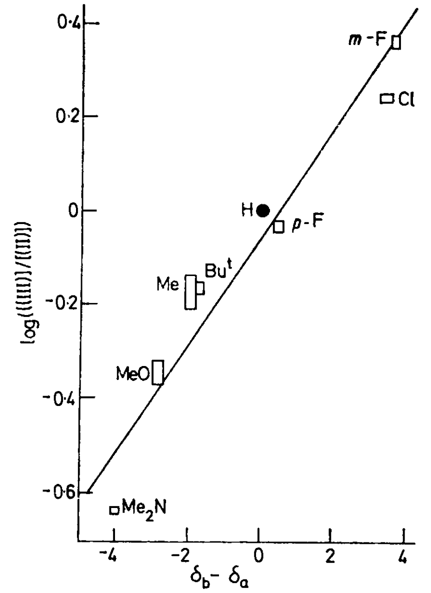

FIGURE 1 Fit of the ammonium chloride quenching data to the charge control equation (4)

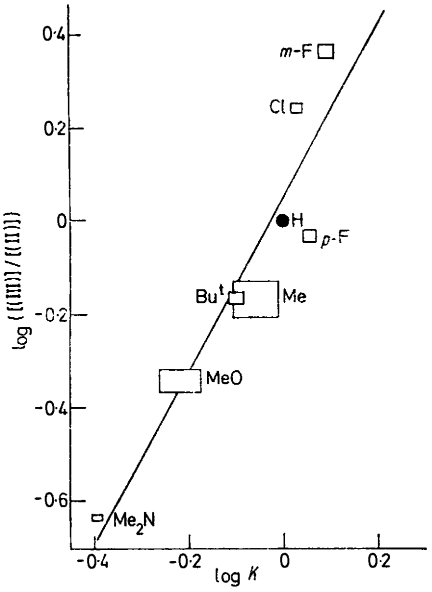

FIGURE 2 Fit of the ammonium chloride quenching data to the product stability control equation (5)

stirred solution of the anion in liquid ammonia–ether (85 : 15) maintained at −42 °C. The results of these acid quenchings together with estimates of the corresponding experimental errors are given in Table 1. This Table also includes values for the logarithm of the equilibrium constant. These latter values are based on the results given in Part 1 except that a small correction has been made to allow for the *ca.* 3% product in the equilibration studies arising from kinetic control. Figure 1 shows a plot of log (product ratio) from the room temperature–ammonium chloride reaction against $(\delta_b - \delta_a)$ [1a] as measured by ^{13}C n.m.r. [equation (4)]. Figure 2 shows the same results plotted against log *K* [equation (5)]. In both graphs the sizes of the boxes indicate the approximate limits of errors associated with the experimental measurements. Both equations give reasonably good linear correlations [hardly surprising in view of the earlier observation that both log *K* [23] and $(\delta_b - \delta_a)$ [1a] correlate with σ!] but the correlation for the charge-control equation (4) is the better of the two. This pattern is unaffected by the use of ^1H instead of ^{13}C n.m.r. data or by the use of methanol instead of ammonium chloride as the proton source (Table 2). It seems therefore, that for these particular systems the initial stages of the energy profile (as represented by the coulombic interaction) and the latter stages (as represented by the product stabilities) are both related to the position of the energy maximum and hence that all the energy profiles are similar in shape. As might be expected for such an ' early ' transition state process, however, the position of the energy maximum is more accurately reflected by the initial shape of the profile. This complements the situation in electrophilic aromatic substitution. Here, at least for alternant systems, both superdelocalisability (reflecting the initial shape of the energy profile) and localisation energy (reflecting the shape of the latter part of the profile) are acceptable criteria for the position of attack [11,12] but overall, in these reactions involving a 'later' transition state, localisation energies more accurately reflect the position of the energy maximum.[24] For example the aromatic substitution data given by Streitwieser [12] can be correlated by using superdelocalisabilities (for 'σ_r' correlation coefficient, $r = 0.937$, 25 points; for deuteriodeprotonation, $r = 0.967$, 14 points; for nitration $r = 0.896$, 18 points) but a better correlation [12,24] is obtained by using localisation energies ('σ_r', $r = 0.959$; deuteriodeprotonation, $r = 0.971$; nitration, $r = 0.912$) or Dewar reactivity numbers ('σ_r', $r = 0.969$; deuteriodeprotonation, $r = 0.965$; nitration, $r = 0.949$).

It it is assumed that the ion atmosphere contributions to the rates of protonation at sites 'a' and 'b' are equal [25] then the slope, A, of the 'charge control' graph should be given by equation (6), derived simply from

$$\mathrm{A} = q_\mathrm{A}e^2/2.503\mathrm{bD}r_\mathrm{AB}kT \qquad (6)$$

consideration of the coulombic interactions. In this equation e is the charge of the electron. If D, the dielectric constant of the medium, is assumed to be that for pure ammonia; [26] q_A the charge of the attacking acid, is assumed to be $+1$; and b, the proportionality constant from equation (3), to be 160 p.p.m. per electron for ^{13}C n.m.r. and 10 p.p.m. per electron for ^{1}H n.m.r.; [27] then values of the critical interionic separation r_AB, can be calculated, and these are included in Table 2. Ammonium chloride is almost certainly aggregated in liquid ammonia,[28] and as a Grotthus chain-type mechanism of proton transfer is thought not to be important in this solvent [29] a reasonable theoretical estimate for r_AB would seem to be the sum of the ionic radii of the ammonium ion and the carbon atom (*ca.* 2.2 Å).[26] The values calculated from equation (6) are smaller than this but the error is not much worse than that for values calculated in a similar manner for other ionic reactions.[14] The values from the methanol data are particularly interesting. It was anticipated that for methanol MeOH would be the reactive species as this is probably the dominant species in solution.[30] This data suggests rather that NH_4^+ or ion pair NH_4^+ MeO^- is involved.

Errors in the calculated values of r_AB and deviations from linearity 'outside of experimental error' which are apparent in Figure 1 probably arise from the following factors: (i) the use of the macroscopic dielectric constant in applying equation (6); as usual this is probably a gross overestimate; [31] (ii) deviations from linearity in the charge–chemical shift correlation [equation (3)]; [1a,27] (iii) consideration of the coulombic interaction with only one centre; (iv) the assumption that all the *trans*-products (II) and (III) arise from the *trans,trans*-anion (I). In fact the spectroscopic studies [1a] had indicated the presence of *ca.* 7—10% *cis,trans*-anion in solution and this is consistent with the finding that 3—11% *cis*-alkenes were among the quenching products (Table 4). The problem is how much of the *trans*-alkenes arise from *cis,trans*- rather than *trans,trans*-anion. CNDO II calculations [32] suggest that for the unsubstituted *cis,trans*-anion (IV) the charge at 'a' is greater than that at 'b' (Pople–Segal parameter and standard bond lengths [33]). Hence protonation of (IV) should give mainly the *cis*-product. This probably also applies to the substituted *cis,trans*-anions as the calculated charge difference in (IV) (0.067e) is greater than the perturbation in charge distribution produced by any of the substituents [up to 0.025e in (I) as estimated by n.m.r.]. If this is so then the errors in log ([(III)]/[(II)]) from this source should not be very great. Whilst these factors are quite sufficient to explain deviations from equation (4) the experimental data were also used to test the suggestion of Rogers that protonation is controlled by a combination of coulombic and product stability factors.[34] Equation (4) then becomes equation (7) (where A, B, and C are

$$\log([(\mathrm{III})]/[(\mathrm{II})]) = \mathrm{A}\,(\delta_\mathrm{b} - \delta_\mathrm{a}) + \mathrm{B}\log K + \mathrm{C} \quad (7)$$

constants). The theoretical justification for this equation is not wholly clear but it has been suggested * that the 'orbital interaction' term of equation (1) is related to the strength of the developing covalent bond and hence to product stability. If this is so (and it is certainly consistent with the previously mentioned linearity [11,12] between superdelocalisability and localisation energy) then equation (7) may be seen as a special form of equation (1). The results of fitting the experimental data to equation (7) are included in Table 2, and Figure 3 shows the resultant plot for the ammonium chloride quenching data, with ^{13}C n.m.r. values used for δ_a and δ_b. As might be expected the correlation obtained by using the two-parameter equation (7) is better than that with either of the single parameter equations [(4) or (5)] but whether this improvement in correlation is significant is questionable.

Reaction of the anion (I) with an alkyl halide gives a mixture of alkylated alkenes (V) and (VI). This is a reaction in which 'orbital interaction' [equation (1)] or

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* This idea was first suggested to the present authors by N. A. J. Rogers but it seems to be implicit in parts of recent papers by Hudson and Klopman (refs. 7 and 9).

[24] A. Streitwieser, *Tetrahedron*, 1963, **19**, Suppl. 2, 379; M. J. S. Dewar, *Adv. Chem. Phys.*, 1965, **8**, 65.

[25] C. H. Bamford and C. F. H. Tipper, 'Comprehensive Chemical Kinetics,' vol. 2, Elsevier, Amsterdam, 1969, pp. 381 *et seq.*

[26] 'Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland, Ohio, 1971—1972.

[27] D. G. Farnum, *Adv. Phys. Org. Chem.*, 1975, **11**, 123.

[28] J. J. Lagowski and G. A. Moczygemba in 'The Chemistry of Non-Aqueous Solvents,' Academic Press, New York, 1967, vol. II, p. 319.

[29] W. L. Jolly and O. J. Hallada in 'Non-aqueous Solvent Systems,' Academic Press, New York, 1965, p. 1.

[30] M. Herlem, *Bull. Soc. chim. France*, 1970, 383 and previous papers.

[31] K. J. Laidler, *Canad. J. Chem.*, 1959, **37**, 138.

[32] Program written by R. F. Weaver (1971) and modified (1973).

[33] J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

[34] T. N. Huckerby, N. A. J. Rogers, and A. Sattar, *Tetrahedron Letters*, 1967, 1113.

product stability [equations (5) and (7)] should be of greater importance. For simple alkyl halides the relative stabilities of products (V) and (VI) are difficult to measure. When, however, R is allyl these two compounds may be equilibrated *via* the Cope rearrangement. The results of treating the methoxy- and dimethylamino-substituted anions with allyl chloride are summarised in Table 3 together with the results for equilibrating the products at 205 °C. For these particular systems the products could be analysed by the n.m.r. shift reagent method.[23] For other systems (for example X = Cl) the product was hydrogenated and an attempt was made to analyse the resultant mixture of tetrahydro-derivatives by g.l.c. This was not, however, very satisfactory.

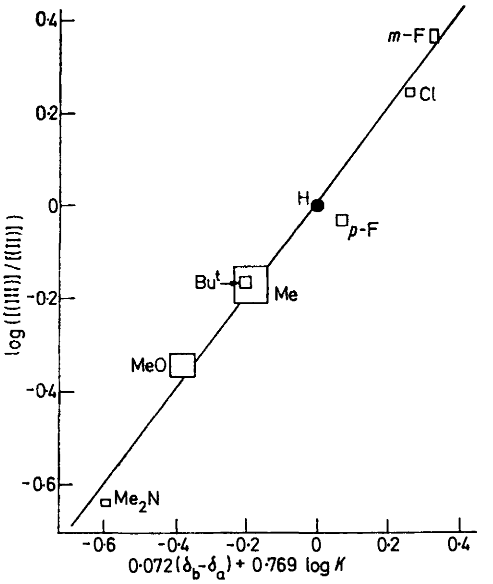

FIGURE 3 Fit of the ammonium chloride quenching data to the two-parameter equation (7)

TABLE 3

trans-Alkene product ratios from the reactions of the anions (I) with allyl chloride and the results of thermal equilibration of (V) and (VI).

	Reaction with allyl chloride		Equilibration	
X	[(VI)]/[(V)] [a]	log([(III)]/[(II)])	[(III)]/[(II)] [a]	log([(III)]/[(II)])
Me$_2$N	0.46	$\bar{1}.66$	0.76 [b]	$\bar{1}.88$
Mc$_2$N	0.45		0.75 [c]	
MeO	0.63	$\bar{1}.79$	0.88 [b]	$\bar{1}.95$
MeO	0.61		0.90 [c]	

[a] ±5%. [b] 2.5 h. [c] 4 h equilibration time.

With the limited amount of data obtained it is difficult to draw any definite conclusions although there appears to be a linear relationship (3 points only including X = H) between log (product ratio) (Table 3) and log (equilibrium constant) [Table 3, equation (5)] or chemical shift difference [equation (4)] and also a linear relationship between the stabilities of the alkenes (II) and (III) and the corresponding alkylated alkenes (V) and (VI) (R = allyl). The present work shows that for these systems protonation and alkylation occur preferentially at the same carbon atom. This appears to contrast with the report that protonation of the anion (VII) in liquid ammonia gives mainly (VIII),[35] but that the reaction with allyl chloride gives mainly (IX).[36] However the method used for protonation [35] of this anion may have produced the thermodynamic rather than the kinetic product. The results for the anion (VII) may also be affected by steric effects which are absent in the anion (I).

EXPERIMENTAL

Reactions of the Anions (I) *with Ammonium Chloride.*—An apparatus shaped like an inverted U was connected to the vacuum line *via* a B-10 joint attached to the same adaptor as was used in the spectroscopic studies (Part 2). One arm of the apparatus contained ammonium chloride (0.4 g, 7.5 mmol) and a solution of the anion (1.0 mmol) in liquid ammonia (*ca.* 8 cm^3); ether (0.6 cm^3) was prepared in the other arm.[1a] After a single freeze–pump–thaw cycle the connection to the vacuum line was sealed off and the apparatus detached. Approximately half the ammonia was carefully distilled onto the ammonium chloride. Both chambers were allowed to warm to room temperature with gentle swirling to dissolve the ammonium chloride. After 15 min at room temperature to ensure thermal equilibration, the apparatus was rapidly tilted and shaken to pour the carbanion solution onto the acid solution. The cherry-red carbanion colour appeared to be dissipated instantly. The quenched solution was immediately frozen in liquid nitrogen, the apparatus cut open, and water–ether (1 : 1) added to the frozen ammonia. When the ammonia had thawed the ether layer was separated, washed with water, dried, and evaporated under reduced pressure. When the product could not be analysed instantly it was stored in frozen benzene solution.

The results are summarised in Table 4, which also summarises the methods used to analyse the mixtures.[23]

In order to check against the (unlikely) possibility of equilibration during the time of quenching the duplicate reactions reported in Table 4 were performed with 0.2 g instead of 0.4 g of ammonium chloride. This had no detectable effect on the result.

Isolation of the monomeric products of the ammonium chloride reaction by preparative t.l.c. gave 91—96% recoveries of alkene.

Reaction of the Anions (I) *with Methanol.*—A long-necked 10 cm^3 pear-shaped flask containing a magnetic stirrer was connected to the vacuum line as before and a solution was prepared in this of the anion (0.50 mmol) in ammonia (4 cm^3) and ether (0.3 cm^4). The apparatus was surrounded in solid CO$_2$–diethyl ketone (−42 °C). After 15 min stirring at −42 °C to allow thermal equilibration, dry methanol [37] (0.5 cm^3) was rapidly added from a syringe. The carbanion colour appeared to be dissipated instantly. This was at once followed by water and ether and the product separated

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[35] T. W. Campbell and W. G. Young, *J. Amer. Chem. Soc.*, 1947, **69**, 688.

[36] W. G. Young, M. Kosmin, R. Y. Mixer, and T. W. Campbell, *J. Amer. Chem. Soc.*, 1952, **74**, 608.

[37] A. Vogel, 'A Textbook of Practical Organic Chemistry,' 3rd edn., Longmans, London, 1948, p. 167.

and analysed as before. The results are summarised in Table 4.

TABLE 4

Reaction of sodium salts of the anions (I) with acid

X	Quenching agent	Expt. no.	% (II)		% (III)		% Impurities
			trans	*cis*	*trans*	*cis*	
p-Me_2N [a]	NH_4Cl; 25 °C	1	74.8	7.3	16.9	0.9	
		2 [b]	73.7	9.0	16.1	0.1	
		3 [c]	74.2	7.5	16.8	1.4	
	MeOH; −42 °C	1	77.6	10.5	11.7	0.2	
		2	77.3	11.1	11.4	0.2	
p-MeO [d]	NH_4Cl; 25 °C	1	63.0	~8.0	28.5	~0.5	
		2 [b]	63.5	~7.0	28.9	~0.5	
	MeOH; −42 °C	1	67.6	~8.2	24.2	~0.1	
		2	67.2	~8.7	24.1	~0.1	
p-Bu^t [e]	NH_4Cl; 25 °C	1	51.3	5.9	34.2	0.7	8.0 [f]
		2 [b]	50.5	6.7	34.6	1.3	6.9 [f]
	MeOH; −42 °C	1	53.0	7.1	29.5	1.3	9.1 [f]
		2	54.3	7.4	28.9	1.2	8.2 [f]
p-Me [g]	NH_4Cl; 25 °C	1	53.4	(7.2) [h]	35.8	(7.2) [h]	3.6 [f]
		2 [b]	51.8	(9.0) [h]	34.7	(9.0) [h]	4.5 [f]
	MeOH; −42 °C	1	61.3	(2.7) [h]	33.3	(2.7) [h]	2.7 [f]
		2	62.8	(2.9) [h]	31.7	(2.9) [h]	3.4 [f]
H [i]	NH_4Cl; 25 °C		95.8	4.1	95.8	4.1	
	MeOH; −42 °C		94.7	5.3	94.7	5.3	
p-F [j]	NH_4Cl; 25 °C	1	49.9		45.7	4.4	
		2 [b]	47.5	0.3	44.2	7.9	
	MeOH; −42 °C	1	40.4	0.3	50.9	8.4	
		2	40.3	0.4	50.5	8.8	
p-Cl [i]	NH_4Cl; 25 °C	1	34.0	2.0	59.1	4.9	
		2 [b]	34.4	0.3	59.9	5.4	
	MeOH; −42 °C	1	27.2	1.2	66.6	5.0	
		2	28.6	1.8	68.9	2.6	
m-F [j]	NH_4Cl; 25 °C	1	27.7		66.1	6.2	
		2 [b]	28.3		66.8	4.9	
	MeOH; −42 °C	1	20.9	0.2	75.1	3.8	
		2	22.1		75.5	2.4	

[a] Products analysed by g.l.c. and checked by ^1H n.m.r. ($CHCl_3$ + added shift reagent). [b] Half quantity of ammonium chloride (four-fold rather than eight-fold excess). [c] Lithium salt. [d] Product analysed by ^1H n.m.r. ($CHCl_3$ + added shift reagent) and checked by g.l.c. [e] Products analysed by g.l.c. and checked by ^1H n.m.r. (C_6F_6). [f] Approximately this percentage of impurity was present in the alkene from which the anion was generated (see Part I). [g] Products analysed by ^1H n.m.r. (C_6F_6); *cis* : *trans* ratio determined by g.l.c. [h] Total *cis*-product [(II) and (III) not distinguishable]. [i] Products analysed by g.l.c. only. [j] Products analysed by g.l.c. and checked by ^{19}F n.m.r.

Reactions of the Anions (I) *with Allyl Chloride*.—The same procedure was employed as in the methanol reaction, and allyl chloride (0.6 cm^3) [38] was added from a syringe. The products were isolated as before and the results are summarised in Table 3. Details of and properties of the products are available as Supplementary Publication No. SUP 21828 (5 pp.).*

Equilibration of the Alkylated Products.—Two samples of the purified alkylated products were sealed under vacuum in Carius tubes which were placed in an oven at 205 °C (mercury thermometer). One sample was removed after 2.5 and the other after 4 h. N.m.r. and t.l.c. indicated that only starting materials were recovered.

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* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin II*, 1975, Index issue.

[38] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' Pergamon, Oxford, 1966, p. 65.