

SYNTHESIS AND AQUEOUS REACTIVITY OF
N-ADAMANTYLIDYLCARBINYL-N,N-DIMETHYL-4-CYANOANILINIUM BROMIDE

Barry L. Knier* and Carmen L. Rodríguez

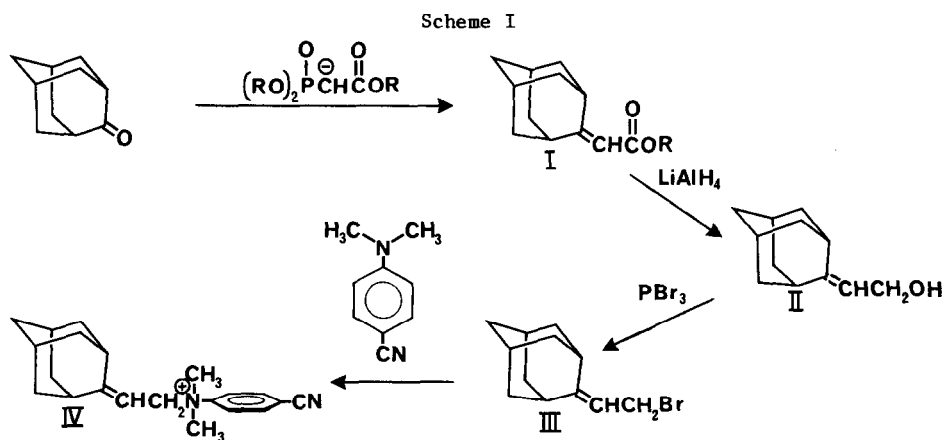
Department of Chemistry, University of Puerto Rico, Río Piedras, PR¹

Summary: The aqueous decomposition of the title allyl compound, whose synthesis is also described, is strongly indicative of concurrent S_N1 and S_N2 reactivity.

The allyl structure plays an important role in synthetic, theoretical, and biological chemistry. The reason for this importance is largely due to its enhanced reactivity in both S_N1 and S_N2 reactions.^{2,3} The S_N1 activity can readily be explained in terms of carbocation stability using Hammond postulate reasoning. No similar logic can be applied to the S_N2 reactivity since these reactions are not necessarily very endo- or exothermic nor do they involve any intermediates to which analogies can be made. The S_N2 reactivity of this structural type is further complicated by the potential intervention of 1-3 substitution (S_N2')⁴ and by ion pair mechanisms.⁵

In order to study this reaction directly we have synthesized N-adamantylidylcarbinyln-N,N-dimethyl-4-cyanoanilinium bromide (IV). This compound sterically disfavors concerted 1,3 substitution and, because after bond cleavage the leaving group is neutral, the coulombic interaction required for ion pair stability is absent.

The synthesis of IV was performed as in Scheme I.



Synthesis: Methyl-(2-adamantylidenyl)acetate (I) was prepared in 84% yield from adamantanone and trimethylphosphonoacetate anion in glyme. It was obtained as a mobile oil which was Kugelrohr distilled (bulb-to-bulb) bp 145-155°C/0.1 torr: ^1H NMR: 5.58 (s, 1H), 3.65 (s, 3H), 2.42 (s, 2H) and 1.90 (s, 12H); ^{13}C NMR: 171.5, 166.5, 107.8, 49.9, 40.9, 39.6, 38.6, 36.4, 32.3, 27.5.

The alcohol (II) was prepared by reduction of I with LiAlH_4 in 1,4-dioxane. We have observed on two occasions that this reaction involves an exotherm that occurs after about two hours of stirring at room temperature when working on a 0.1 molar scale in 250 ml of solvent. Furthermore, acidic conditions must be avoided in the work-up since the alcohol easily couples to the ether. Work up was performed using basic conditions as described by Mićović and Mihailović⁶. The product was obtained in 93% yield as a colorless oil which was Kugelrohr (bulb-to-bulb) distilled. Bp = 150°C/0.4 torr: ^1H NMR: 5.31 (t, 1H), 4.08 (d, 2H), 2.85 (s, 1H), 2.35 (s, 1H) 1.83 (s, 12H); ^{13}C NMR: 150.3, 115.5, 57.0, 39.9, 39.1, 38.4, 36.7, 31.8, 28.2. Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{O}$: C, 80.90; H, 10.11. Found: C, 80.66; H, 10.21.

2-Adamantylidylcarbinylbromide (III) was prepared from II using PBr_3 /pyridine in pentane at -20°C in 81% yield. It was obtained as a heat sensitive oil that was purified by flash chromatography on silica gel using hexane as eluent. ^1H NMR: 5.44 (t, 1H), 3.98 (d, 2H), 2.91 (s, 1H), 2.35 (s, 1H), 1.83 (s, 12H); ^{13}C NMR: 155.6, 112.6, 40.2, 39.4, 38.5, 36.8, 32.0, 28.4, 28.2.

4-Cyano-N,N-dimethylaniline was prepared by the method of Vowinkel, et al.⁷

N-(2-adamantylidylcarbiny1)-N,N-dimethyl-4-cyanoanilinium bromide (IV) using 1.2 g. (0.005 mol) adamantylidylcarbiny1bromide (III) and 0.75 g (0.005 mol) 4-cyano-N,N-dimethylaniline in 10 mL of anhydrous benzene. The solution was allowed to stand at room temperature for 72 hours, during which time a crystalline mass precipitated from solution. The solid was filtered, washed with anhydrous Et_2O (10 mL) and dried in a vacuum dessicator. Obtained were 1.82 g (yield 94.0 %) of white crystals, mp = 160°C: ^1H NMR: 7.52, 7.42, 6.70, 6.60, (aromatic AB, 4H), 5.64 (t, 1H), 4.05 (d, 2H), 3.05 (s, 6H), 2.36 (s, 2H), 1.83 (s, 12H). Anal. Calcd. for $\text{C}_{21}\text{H}_{27}\text{BrN}_2$: C, 65.13; H, 6.98; N, 7.24. Found: C, 65.01; H, 7.01; N, 7.20.

Aqueous reactivity: Reactions were followed spectrophotometrically by the appearance of the leaving aniline at 291 nm. Temperature was maintained by water flow through jacketed cell holders. Infinity points were determined experimentally from the absorbance values at times greater than ten half-lives. For the reactions of nucleophilic agents with IV pseudo-first order conditions were normally employed. Initial [IV] was always less than 10^{-4} M. and [Nu] in excess of 0.1 M. First order rate constants were determined from the slopes of semi-log plots which were linear for at least five half-lives. Ionic strength was maintained at 1.0 molar with KCl and, except in the cases of NaOH and NaI, pH was maintained by self buffering with Nu-NuH^+ . Under these conditions the reactions are forced to display first order kinetics where $k_{\text{obs}} = k_{\text{hyd}} + k_2[\text{Nu}]$. Thus plots of k_{obs} v.s. [Nu] yield intercepts of k_{hyd} , the hydrolysis rate constant, and slopes of k_2 , the second order rate constant for the reaction with nucleophile.

Table 1

								k_2^d
[HO-Et-S ⁻] ^a	0.9	0.72	0.54	0.45	0.36	0.27	0.18	
$10^5 k_{obs}^b$	295	236	179	153	120	86.8	51.7	326
[NaOH]	0.4	0.3	0.2	0.15	0.1			
$10^5 k_{obs}$	19.8	15.1	11.9	8.62	7.36			42.3
NaI	1.0	0.8	0.6	0.4	0.2			
$10^5 k_{obs}$	13.26	11.14	9.41	7.06	4.84			10.46
DABCO ^a	0.9	0.72	0.54	0.36	0.18			
$10^5 k_{obs}$	13.3	11.0	8.98	6.76	4.46			11.56
Propylamine ^c	0.88	0.66	0.44	0.22	0.088			
$10^5 k_{obs}$	4.20	3.65	3.39	2.99	2.89			1.65
Ethanolamine ^a	0.9	0.675	0.45	0.225	0.090			
$10^5 k_{obs}$	3.20	3.08	2.97	2.91	2.81			0.45
Hydrolysis ^e	2.67×10^{-5}							

^a Self buffered 90% basic form. ^b Units are sec^{-1} . ^c Self buffered 88% basic form. ^d From the least squares slopes of k_{obs} v.s. [Nu]. Units are $\text{M}^{-1}\text{sec}^{-1}$. ^e Average of the least squares intercepts. Range less than 5%.

As seen in in Table 1 there is significant bimolecular reactivity with HO-CH₂CH₂-S⁻, HO⁻, I⁻, and 1,4-diazabicyclo[2.2.2]octane (DABCO). For each of these reagents a linear dependence is observed between the observed pseudo-first order rate constant and the nucleophile concentration. With the less nucleophilic reagents hydroxyl amine and propyl amine, however, the dependence on [Nu] is so small that it cannot be distinguished from a non-specific effect. These reagents apparently cannot effectively compete with the water reaction even though they are much stronger bases and nucleophiles. This suggests a mechanistic difference between the water and nucleophile reactions because if both involved nucleophilic attack the water reaction would be much slower comparatively (even correcting for concentration differences). To test this idea the nucleophile DABCO was used in an Arrhenius analysis of both the k_{hyd} and k_2 (Table 2). The large positive entropy of activation observed for the hydrolysis reaction is strong evidence that that component of the reaction does not involve nucleophilic attack by water but rather is consistent with simple dissociative (S_N1) process. This idea is also supported by the observation that the ratio of k_2 to k_{hyd} is extremely small for each of

Table 2

Temp °C	20.0	25.0	30.0	34.0	38.2	43.0	E_a (kcal)	S^\ddagger (eu)
$k_2 \times 10^5 \text{ M}^{-1}\text{sec}^{-1}$	8.36	11.53	23.2	38.7	50.6	110.9	32.3	29.1
$k_{\text{hyd}} \times 10^5 \text{ sec}^{-1}$	0.59	2.67	4.18	9.63	21.1	38.4	21.2	-5.6

the nucleophiles. Iodide, for example, is normally considered to be about 10^5 times better as a nucleophile than water⁸; in this case it is better by only a factor of five. If both were behaving as nucleophiles in the decomposition of IV then the sensitivity of the reaction to nucleophilicity would have to be remarkably low (Swain Scott $m < .05$).

If this hypothesis is correct it has several implications in solvolysis chemistry. First, the idea that the addition of nucleophile has no effect on the rate of an S_N1 reaction needs to be modified with the recognition that S_N1 and S_N2 reactions can apparently proceed concurrently and competitively in the same reaction mixture. Second, it complicates some of the ideas of mechanistic selection. It had been tacitly assumed (at least by us) that S_N2 mechanisms only obtained when the intermediate produced by the S_N1 pathway was too unstable to exist as a solvent equilibrated species. (This instability might result from reaction conditions, eg. solvent, etc. or it might be inherent in the structure of the molecule.) These results indicate that this is not necessarily the case but rather that an S_N1 reaction may be diverted into an S_N2 mechanism if sufficiently powerful nucleophiles are used.

- (1) Supported by a grant from la Oficina de Coordinacion de Estudios Graduados e Investigaciones, University of Puerto Rico.
- (2) Vernon, C. A. J. Chem. Soc., 1954, 423.
- (3) Vernon, C. A. J. Chem. Soc., 1954, 4462.
- (4) (a) Bordwell, F.G. Acc. Chem. Res., 1970, 3, 281. (b) DeWolf, R.H.; Young, W.G. Chem. Rev., 1956, 56, 753.
- (5) (a) Young, W. G.; Winstein, S.; Goering, H. L. J. Am. Chem. Soc., 1951, 73, 1958.
(b) Goering, H.L.; Linsay, E.C. J. Am. Chem. Soc., 1969, 91, 7435.
(c) Goering, H. L.; Koermer, G. S.; Lindsay, E. C. J. Am. Chem. Soc., 1971, 93, 1230. (d) Goering, H. L.; Pombo, M. M.; McMichael, K. D. J. Am. Chem. Soc., 1963, 85, 965. (e) Goering, H. L.; Anderson, R. P. J. Am. Chem. Soc., 1978, 100, 6469.
- (6) Mičovič, V.M.; Mihailović, M.L.J. J. Org. Chem., 1953, 18, 1190.
- (7) Vowinkel, E.; Bartel, J. Chem. Ber., 1974, 107, 1221.
- (8) Swain, C. G; Scott, C. B. J. Am. Chem. Soc., 1953, 75, 146.

(Received in USA 2 January 1985)