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Facile Carbon-Carbon Bond Heterolysis. S_N1-$E1$ Reactions of t-Cumyl and t-Butyl Substituted Tricyanomethanes

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The tricyanomethanide ion $C(CN)_3^-$ was found to serve as an efficient leaving group anion to generate unstable carbocations such as t-cumyl and t-butyl cations, the ability of carbon-terminated leaving groups so far examined being in the order $C(CN)_2N{=}NC_6H_4NO_2\text{-}p \ll C(CN)_3 \ll C(CN)_2NO_2$.

Whereas S_N1-$E1$ reactions constitute a dominant subject in organic reaction mechanisms, the method of generation of unstable carbocations was restricted almost exclusively to the heterolytic cleavage of carbon-hetero-atom bonds, and little effort had been devoted to the study of carbon-carbon bond heterolysis itself. Recently, we achieved the first generation of typical unstable carbocations such as t-cumyl[1)] and t-butyl[2)] cations via carbon-carbon bond heterolysis, as shown in reactions (1) and (2).

(1) $PhCMe_2\text{-}C(CN)_2N{=}NC_6H_4NO_2\text{-}p \longrightarrow PhCMe_2^+ + (NC)_2C{=}NN^-C_6H_4NO_2\text{-}p$

(2) $t\text{-}BuC(CN)_2NO_2 \longrightarrow t\text{-}Bu^+ + {}^-C(CN)_2NO_2$

We now report that alkyl(tricyano)methanes are useful substrates for S_N1-$E1$ reactions via carbon-carbon bond heterolysis, and discuss the relative ability of carbon-terminated leaving groups which we have developed. The decomposition of $PhCMe_2C(CN)_3$ (**1**)[3)] in dimethyl sulfoxide (DMSO) at 33.5 °C was found to afford α-methylstyrene in almost quantitative yield (96% along with t-cumyl alcohol of 4% yield), while that in methanol gave not only t-cumyl methyl ether (90%) but also an adduct with a solvent molecule (**2**; 10%).[4,5)] When dissolved in pyridine, **1** gave the pyridinium salt $PhCMe_2\text{-}Py^+\ C(CN)_3^-$ in 83% yield, which was converted quantitatively to α-methylstyrene upon heating the reaction mixture at 115 °C for 2 h. The result clearly indicates that the heterolysis reaction (3) to give an intermediate t-cumyl cation is the major process in the decomposition of **1** in polar solvents.

(3) $R\text{-}C(CN)_3 \longrightarrow R^+ + {}^-C(CN)_3$

1: R = $PhCMe_2$; **3**: R = t-Bu

$RC(CN)_2C(OMe)\text{=}NH$ **2**: R = $PhCMe_2$; **4**: R = t-Bu

The rates were determined by ^1H NMR spectroscopy. The heterolysis of **1** at 33.5 °C proceeds faster in DMSO-d_6 (476×10^{-5} s^{-1}) than in methanol-d_4 (k_{obs} = 99.0×10^{-5} s^{-1}; k_{het} = 89×10^{-5} s^{-1}), reflecting the hydrogen-bond-insusceptible nature of the reaction as seen in heterolysis reactions (1) and (2) (Tables 1 and 2)[1,2] and in pericyclic reactions via dipolar transition states.[6,7] In contrast, $PhCMe_2Cl$ exhibits a reverse propensity and a much lower reactivity in DMSO (k = 11.0×10^{-5} s^{-1} in DMSO-d_6; k = 1250×10^{-5} s^{-1} in methanol[8] at 33.5 °C). As shown in Table 1, the tricyanomethanide ion acts as a much more efficient leaving group anion than the *p*-nitrophenylazo(dicyano)methanide ion produced in the reaction (1).

Table 1. Relative Rates of Heterolysis Reactions of $PhCMe_2X$ at 33.5 °C

X	k_{rel} In DMSO-d_6	k_{rel} In Methanol-d_4	$k_{DMSO}/k_{Methanol}$
Cl	1	1[a]	0.01
$C(CN)_2N\text{=}NC_6H_4NO_2\text{-}p$ [b]	4	0.003	12
$C(CN)_3$	43	0.07	5.4

a) The rate determined in undeuteriated methanol (Ref. 8).

b) Reference 1.

In order to examine the ability of tricyanomethanes to generate more unstable carbocations, t-$BuC(CN)_3$ (**3**; mp 119 °C)[4] was prepared according to the literature procedure described for the preparation of **1**.[3] Heating of the tricyanomethane **3** in DMSO-d_6 at 80 °C gave isobutene (55%) as a product arising from a t-butyl cation, and t-butylmalononitrile (30%) which would be formed via an adduct with water inevitably included in the solvent. Although the latter is a product formed via a bimolecular process, the decomposition of **3** obeys apparently the first-order rate law, and thus allows an estimation of the rate of heterolysis (k_{obs} = 2.48×10^{-5} s^{-1}; k_{het} = 1.4×10^{-5} s^{-1}), comparable to the rate of decomposition of t-BuCl

($k = 2.07\times10^{-5}$ s^{-1} in DMSO-d_6 at 80 °C).

On the other hand, the decomposition of **3** in methanol gave exclusively **4**, an adduct with the solvent molecule like **2**.⁵⁾ Unfortunately, the decomposition rate in methanol-d_4 could not be measured because the difference in the chemical shift of t-butyl signals between **3** and **4** was not discernible. The fact that none of the S_N1-$E1$ products was observed suggests the lack of the ability of methanol to generate a t-butyl cation from the tricyanomethane **3**. The formation of the adducts **2** in **1** as well as the formation of **4** and t-butylmalononitrile in **3** is unavoidable, since tricyanomethane derivatives are prone to lose a cyano group when treated with protic solvents.⁹⁾

In the case of the reaction (2), we presented definitive evidence that isobutene as a major product in DMSO is formed via a t-butyl cation but not via a retro-ene-type reaction, which was based on the product analysis of the reactions in DMSO-methanol.²⁾ Such an examination was impossible for the tricyanomethane **3** because of the very facile formation of **4** in methanol. A retro-ene-type reaction as another possibility of the olefin formation requires a hydrogen acceptor in the substrate molecule t-BuC(CN)$_3$. However, the reaction (2), which was also carried out at 80 °C, lends strong confirmation to the view that neither NO_2 nor CN in a substrate molecule is able to serve as a hydrogen acceptor under the reaction conditions used.

Table 2. Relative Rates of Heterolysis Reactions of t-BuX at 80 °C

X	k_{rel} In DMSO-d_6	k_{rel} In Methanol-d_4	$k_{DMSO}/k_{Methanol}$
Cl	1	1	0.05
C(CN)$_3$	0.7	-	-
C(CN)$_2$NO$_2$ a)	11	0.01	50

a) Reference 2.

As compared in Table 2, the nitromalononitrile t-BuC(CN)$_2$NO$_2$ produces a t-butyl cation more easily than the tricyanomethane t-BuC(CN)$_3$, in agreement with the view that carbon acids bearing a nitro group instead of a cyano group exhibit higher acidities.¹⁰⁾ We therefore conclude that the ability of carbon-terminated leaving groups increases in the order shown below.

$$C(CN)_2N{=}NC_6H_4NO_2\text{-}p \ll C(CN)_3 \ll C(CN)_2NO_2$$

This, however, does not imply the order of the yield of heterolysis products, since the extent of reaction paths other than heterolysis depends on the reaction conditions as well as the nature of carbocations produced.

The planar structure of leaving group anions is needed to cause extensive charge delocalization responsible for the hydrogen-bond-insusceptible nature of reactions, and has been confirmed by X-ray analysis for $(NC)_2C{=}NN^{-}C_6H_4NO_2$-*p*,[11] $C(CN)_3^{-}$,[12] and $C(CN)_2NO_2^{-}$.[13] Interesting studies of carbon-carbon bond heterolysis using the equilibrium system involving stable carbocations have been reported by the Arnett[14] and Okamoto-Takeuchi[15] groups. Although solvent effects on the rate have not been examined in these cases, the heterolytic process of their reaction systems may be hydrogen-bond-insusceptible as well, since extensive charge delocalization is expected in the leaving group anions used.

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References

1) T. Mitsuhashi, *J. Am. Chem. Soc.*, **108**, 2394 (1986); T. Mitsuhashi, "Structure and Reactivity," Chap. 5, J. F. Liebman and A. Greenberg, Eds., VCH Publishers, New York (1988); Y. Kondo, S. Kusabayashi, and T. Mitsuhashi, *J. Chem. Soc., Perkin Trans. 2*, **1988**, 1799.
2) T. Mitsuhashi and H. Hirota, *J. Chem. Soc., Chem. Commun.*, **1990**, 324.
3) J. K. Williams, E. L. Martin, and W. A. Sheppard, *J. Org. Chem.*, **31**, 919 (1966).
4) Satisfactory elemental analyses were obtained.
5) **2**: mp 103 °C; NMR($CDCl_3$) δ 1.70(s, 6H), 3.57(s, 3H), 6.35 (br s, 1H), 7.2-7.4(m, 5H); IR(KBr, cm^{-1}) 3260(m, NH), 2260(s, CN), 2210(s, CN), 1595(vs, O-C=N). **4**: oil; NMR(CCl_4) δ 1.28(s, 9H), 3.87(s, 3H), 7.9 (br s, 1H); IR(neat, cm^{-1}) 3325(m, NH), 2200(vw, CN), 1665(vs, O-C=N).
6) T. Mitsuhashi, *J. Am. Chem. Soc.*, **108**, 2400 (1986).
7) T. Mitsuhashi and G. Yamamoto, *Bull. Chem. Soc. Jpn.*, **63**, 643 (1990).
8) Y. Okamoto, K. Inukai, and H. C. Brown, *J. Am. Chem. Soc.*, **80**, 4972 (1958).
9) A. Hantzsch and G. Osswald, *Chem. Ber.*, **32**, 641 (1899).
10) R. G. Pearson, and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953); H. Yamabe, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jpn.*, **43**, 2702 (1970).
11) T. Mitsuhashi, G. Yamamoto, M. Goto, and Y. Kondo, unpublished data.
12) P. Andersen and B. Klewe, *Nature*, **200**, 464 (1963); C. Biondi, M. Bonamico, L. Torelli, and A. Vaciago, *J. Chem. Soc., Chem. Commun.*, **1965**, 191; P. Andersen, B. Klewe, and E. Thom, *Acta Chem. Scand.*, **21**, 1530 (1967); J. R. Witt, and D. Britton, *Acta Crystallogr.*, **B27**, 1835 (1971).
13) Y. M. Chow and D. Britton, *Acta Crystallogr.*, **B30**, 147 (1974).
14) E. M. Arnett, E. B. Troughton, A. T. McPhail, and K. E. Molter, *J. Am. Chem. Soc.*, **105**, 6172 (1983); E. M. Arnett and K. E. Molter, *Acc. Chem. Res.*, **18**, 339 (1985); E. M. Arnett, N. G. Harvey, K. Amarnath, and J.-P. Cheng, *J. Am. Chem. Soc.*, **111**, 4143 (1989).
15) K. Okamoto, T. Kitagawa, K. Takeuchi, K. Komatsu, and K. Takahashi, *J. Chem. Soc., Chem. Commun.*, **1985**, 173; K. Okamoto, K. Kitagawa, K. Takeuchi, K. Komatsu, and A. Miyabo, *ibid.*, **1988**, 923; K. Komatsu, S. Aonuma, K. Takeuchi, and K. Okamoto, *J. Org. Chem.*, **54**, 2038 (1989).

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