

Thermal Decomposition of *t*-Butyl(nitro)malononitrile: Evidence for the Generation of a *t*-Butyl Cation *via* Facile Carbon–Carbon Bond Heterolysis

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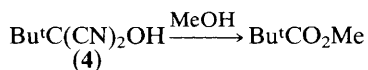
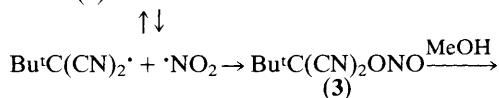
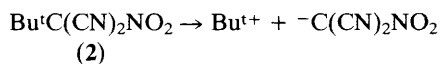
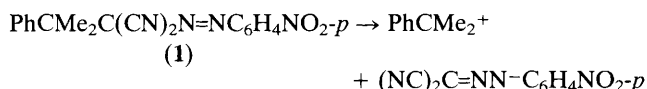
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The decomposition of *t*-butyl(nitro)malononitrile in dimethyl sulphoxide at 80 °C gives isobutene (65%) as a product arising from a *t*-butyl cation generated *via* carbon–carbon bond heterolysis which proceeds eleven times faster than the carbon–chlorine bond heterolysis of *t*-butyl chloride.

Recently we reported the first example of the generation of unstable carbocations *via* the heterolysis of an open-chain quaternary carbon–carbon bond, *i.e.*, the decomposition of the azo compound (1) giving a *t*-cumyl cation,¹ which revealed a unique solvent effect different from those on common S_N1 – $E1$ reactions.^{1,2} However, an attempt to generate a *t*-butyl cation, the most archetypal tertiary carbocation, by means of the decomposition of a similar azo compound was unsuccessful. The generation of a *t*-butyl cation *via* heterolysis needs a much higher activation energy than that of the *t*-cumyl cation: *e.g.*, the difference in free energy of activation for ethanolysis between Bu^tCl and $PhCMe_2Cl$ amounts to about 20 kJ mol⁻¹.³ Herein we report that a *t*-butyl cation can be produced by the decomposition of *t*-butyl(nitro)malononitrile (2) in the dipolar aprotic solvent dimethylsulphoxide (DMSO), although there is little cation generation in the protic solvent methanol.

Compound (2) was prepared by the dropwise addition of $Mn(NO_3)_2 \cdot 6H_2O$ to a solution of *t*-butylmalononitrile in acetic anhydride at 53 °C⁴ (m.p. 110 °C).[†] When heated in [²H₆]DMSO at 80 °C, (2) gave isobutene in 65% yield, whereas the decomposition in methanol afforded methyl pivalate (61%) as the major product along with a very small amount of *t*-butyl methyl ether (3%). We have confirmed that methyl pivalate results from the nitrite (3), a recombination product in the homolytic fission of (2).⁵ The treatment of the nitrite (yellow oil), obtained as the major product in CCl_4 , with a very small amount of water gave the alcohol (4) (m.p. 35 °C),[†] which was converted quantitatively to methyl pivalate when heated in methanol.

Analysis of the products in DMSO–methanol furnishes definitive evidence that isobutene is formed *via* heterolysis, and methanol is an inefficient solvent for the heterolysis (Figure 1): in the presence of methanol, the S_N1 product (the maximum yield, 20%) was obtained at the expense of the $E1$ product but the sum of the S_N1 and $E1$ products decreased on



increasing the quantity of methanol. There are some unidentified products, whose *t*-butyl peaks appear in the NMR spectrum of each reaction mixture, which are probably due to homolysis products other than methyl pivalate. We ignored these products, because it was assumed that the extent of generation of *t*-butyl cation can be estimated exactly by determining yields of the S_N1 and $E1$ products only.

The observed first-order rate coefficient in [²H₆]DMSO at 80 °C, determined by ¹H NMR spectroscopy, ($k_{obs} = 37.3 \times 10^{-5} s^{-1}$) shows that its heterolysis ($k = 24 \times 10^{-5} s^{-1}$) proceeds much more rapidly than that of Bu^tCl ($k = 2.07 \times 10^{-5} s^{-1}$), while the heterolysis in [²H₄]methanol ($k_{obs} = 15.1 \times 10^{-5} s^{-1}$; $k_{het} = 0.5 \times 10^{-5} s^{-1}$) is much slower than that of Bu^tCl ($k = 42 \times 10^{-5} s^{-1}$). The high DMSO/methanol rate ratio (*ca.* 50) in the heterolysis of (2) is typical of the hydrogen bond-insusceptible reaction.^{1,2,6}

In the light of the standard reactions of solvent and substituent effects,^{7,8} generation of both *t*-butyl and *t*-cumyl cations is of historical significance in the area of S_N1 – $E1$ reactions. Our results clearly indicate that the carbon–carbon bonds geminally tri-substituted by strongly electron-withdrawing groups have the distinct ability to generate these unstable carbocations. The observed hydrogen bond-insusceptible behaviour is attributed to the 'three-fold delocalization' of negative charge of the leaving group anion⁹ and is now recognised as a common feature of this type of heterolysis.

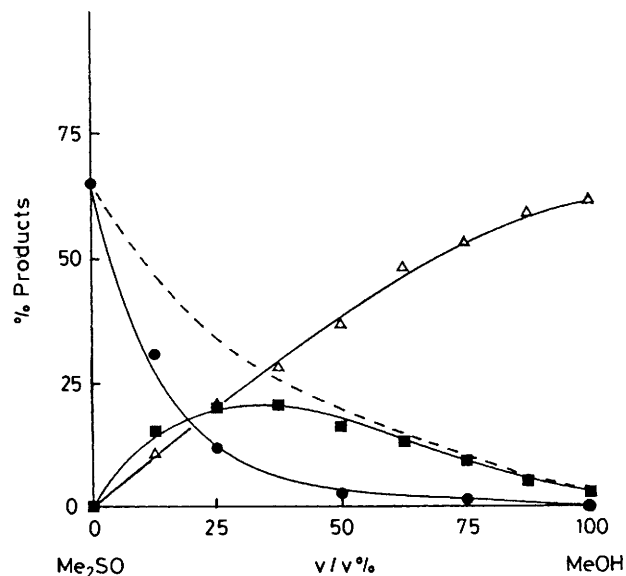


Figure 1. Product distribution in the decomposition of (2) in DMSO–methanol at 80 °C: ■ *t*-butyl methyl ether (S_N1 product); ● isobutene ($E1$ product); --- the sum of the S_N1 and $E1$ products; △ methyl pivalate (homolysis product).

[†] Satisfactory elemental analyses were obtained.

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