# An Easy Vinylcyclobutane–Cyclohexane Rearrangement

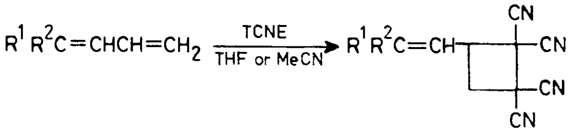
By NOBUJIRO SHIMIZU and SHINYA NISHIDA*

(*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido* 060, *Japan*)

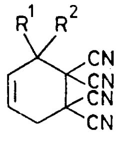
*Summary* 1-(2,2-Dicyclopropylvinyl)-2,2,3,3-tetracyanocyclobutane (**2a**), which was obtained in the reaction of 1,1-dicyclopropylbuta-1,3-diene (**1a**) with tetracyanoethylene, rearranged smoothly to the cyclohexene (**3a**) in a polar solvent, whereas 1-(2,2-di-isopropylvinyl)-2,2,3,3-tetracyanocyclobutane (**3d**) fragmented into methylenemalononitrile and the diene (**4**).

1,1-DISUBSTITUTED buta-1,3-dienes are known to react with tetracyanoethylene (TCNE) preferentially in a 2 + 2 manner.[1–3] We have found that compounds (**1a**—**d**)† reacted similarly, to give compounds (**2**), however, particularly in the reaction of (**1a**), a formally 4 + 2 cycloadduct (**3a**) was produced after longer reaction times in polar solvents. These findings could be explained by assuming that the rearrangement of (**2**) to (**3**) would occur easily in a polar solvent if the vinylcyclobutane were substituted by cyclopropyl group(s) at C-2 of the vinyl group and cyano-groups at C-2 of the ring. Thus the present results provide a rare example of a ready vinylcyclobutane–cyclohexene rearrangement.‡

Since the rearrangement of (**2a**) took place so readily (completed after 3 h at room temperature in acetonitrile), immediate work-up was required for the isolation of (**2a**) in high yield. A solution of (**1a**) (5·0 mmol) in 30 ml of tetrahydrofuran (THF) was added to a cold solution of TCNE (5·0 mmol) in 20 ml of THF. The resultant purple colour faded almost instantly. Immediate work-up gave a crystalline 1 : 1 adduct (m.p. 99—100 °C; 90%), which was characterized as the cyclobutane (**2a**).§ The same reaction in refluxing acetonitrile for 30 s produced a second 1 : 1 adduct (m.p. 103—104 °C; 88%), which was found to be the cyclohexene (**3a**).§ Reactions in benzene (20 s) or cyclohexane (4 min) at room temperature gave a mixture of (**2a**) and (**3a**) with the former predominating (>95%). Similarly, the reactions of (**1b**),¶ (**1c**), and (**1d**) in THF or acetonitrile yielded (**2b**) (m.p. 74—75 °C; 75%), (**2c**) (m.p. 158—159 °C, lit.[2] 153—155 °C; 95%), and (**2d**) (m.p. 140—141 °C; 98%), respectively.



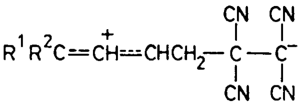
(1) (2)



(3)

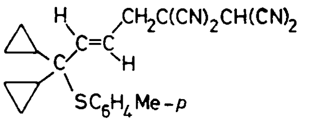
$Pr^{i}_{2}C{=}CHCH{=}C(CN)_2$

(4)



$R^1R^2C{=}\overset{+}{C}H{=}CHCH_2{-}\underset{CN}{\overset{CN}{C}}{-}\underset{CN}{\overset{CN}{C^-}}$

(5)



(6)

**a**; $R^1{=}R^2{=}$cyclopropyl
**b**; $R^1{=}$cyclopropyl, $R^2{=}$Me
**c**; $R^1{=}R^2{=}$Ph
**d**; $R^1{=}R^2{=}$Pr$^i$

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† F. Effenberger and O. Gerlach (*Chem. Ber.*, 1974, **107**, 278) reported a different result in that 4-cyclopropyl-5-methylhexa-1,3-diene and 4-cyclopropyl-6-methylhepta-1,3-diene produced Diels–Alder adducts in their reaction with TCNE. However, the n.m.r. data reported by them suggest that the adducts they obtained are in fact vinylcyclobutanes like (**2**).

‡ The vinylcyclobutane–cyclohexene rearrangement is known to occur at elevated temperature (R. J. Ellis and H. M. Frey, *Trans. Faraday Soc.*, 1963, **59**, 2076; G. S. Hammond and C. D. DeBoer, *J. Amer. Chem. Soc.*, 1964, **86**, 899; L. Eisenhuth and H. Hopf, *Tetrahedron Letters*, 1976, 1265).

§ All adducts described gave appropriate microanalytical and spectral (i.r., n.m.r., and mass) data. Compounds (**2**) and (**3**) were characterised unambiguously by n.m.r. spectroscopy: *e.g.* (**2a**) ($CCl_4$) δ 5·12 (d, *J* 8 Hz, 1H), 4·46 (d of t, *J* 10 and 8 Hz, 1H), 3·16 (d of d, *J* 12 and 8 Hz, 1H), 2·90 (d of d, *J* 12 and 10 Hz, 1H), 1·6 (m, 1H), and 0·4—1·1 (m, 9H); (**3a**) ($CCl_4$) δ 5·88 (d of t, *J* 11 and 4 Hz, 1H), 5·25 (d of t, *J* 11 and 2 Hz, 1H), 3·13 (d of d, *J* 4 and 2 Hz, 2H), 1·25 (m, 2H), and 0·6—0·8 (m, 8H).

¶ A mixture of *E*- and *Z*-(**1b**) (5 : 1) was used. The adduct (**2b**) may have the *E* configuration.

The rates of the rearrangement were markedly affected by the substituents. Thus, (**2a**) rearranged most rapidly whereas (**2c**) rearranged rather slowly [(**2a**): (**2b**): (**2c**) = 30 : 1 : <0·001]. The cyclopropyl group appears to exert an anomalous influence. In contrast, (**2d**) did not rearrange in a similar manner, but fragmented into the hexadiene (**4**) and methylenemalononitrile (120 °C in acetonitrile). Although the rearrangement proceeded more rapidly in a polar solvent [for (**2a**), $k_1$ (MeCN) : $k_1$ ($CDCl_3$) = 6·4 : 1], the same was not true for the fragmentation [for (**2d**), $k_1$ (MeCN) : $k_1$ ($CDCl_3$) = 1 : 1]. Therefore, it may be concluded that the rearrangement is a heterolytic process involving a zwitterionic intermediate (**5**) whereas the fragmentation is not. A large rate-enhancing effect of the cyclopropyl group is in accord with such a process.

The possibility that the formation of (**3**) from (**2**) is a consequence of regeneration of (**1**) and TCNE followed by their recombination in a 4 + 2 manner[2] was ruled out by studies of the cycloaddition and the rearrangement in the presence of toluene-*p*-thiol. When an equimolar mixture of (**1a**) and toluene-*p*-thiol was added to a solution of TCNE in THF, $(NC)_2CHCH(CN)_2$ (39%), $(p\text{-}MeC_6H_4S)_2$ (50%), and (**2a**) (40%) were obtained. In contrast, the rearrangement of (**2a**) in the presence of an equimolar amount of toluene-*p*-thiol gave the adduct (**6**) (m.p. 94—95 °C; 92%)** and (**3a**) (4%). Failure to observe $(NC)_2CHCH(CN)_2$ or $(p\text{-}MeC_6H_4S)_2$ in the latter reaction provides good evidence for the absence of free TCNE in the rearranging mixture. Thus, the rearrangement appears to be intramolecular.

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** The *E* configuration was deduced from the coupling constant of the two olefinic protons (16 Hz). Only toluene-*p*-thiol was effective for trapping (5). *p*-Cresol and methanol simply accelerated the rearrangement.

[1] C. A. Stewart, Jr., *J. Amer. Chem. Soc.*, 1962, **84**, 117; *cf. J. Org. Chem.*, 1963, **28**, 3320.
[2] J. J. Eisch and G. R. Husk, *J. Org. Chem.*, 1966, **31**, 589.
[3] P. D. Bartlett, *Quart. Rev.*, 1973, **24**, 473.