Uncatalysed Olefin Metathesis Reaction

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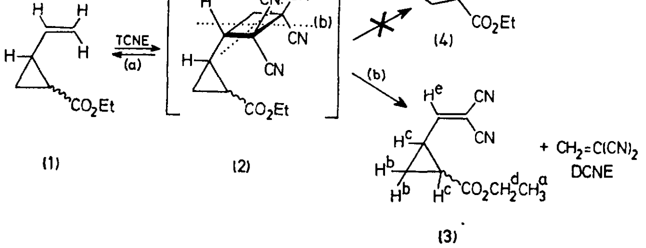
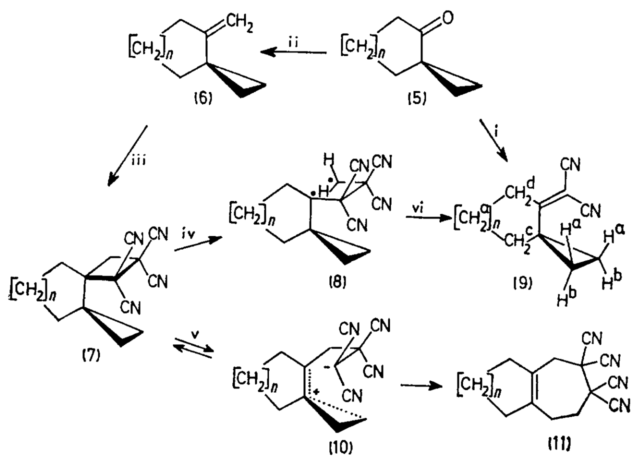
Summary. The 1,1,2,2-tetracyanodispiro[3.0.2.*x*]alkanes (**7a** and **b**) manifest two modes of thermal cleavage (180°C) of the 4-membered ring, giving rise to the respective 4-dicyanomethylene-spiro[2.*x*]alkanes (**9a** and **b**) with extrusion of vinylidenecyanide, and the respective intramolecular [3 + 4] cycloaddition products (**11a** and **b**) in a ratio depending on the solvent used; the formation of the respective olefin metathesis product (**3**) from the reaction of TCNE with (**1**) in $MeNO_2$ is explained in terms of an initial formation of the thermally unstable cyclobutane (**2**), undergoing ring-fusion to yield the products.

WE report a new uncatalysed olefin metathesis reaction involving cyclopropyl-olefins and tetracyanoethylene (TCNE). We found that heating of a *cis–trans* mixture of the cyclopropane[1] (1 mmol) (**1**) and TCNE (1 mmol) in $MeNO_2$ (sealed tube) at 100 °C for a few days provided after preparative g.l.c. separation (6 ft × $\frac{3}{8}$ in glass column, 5% DC-710, GCQ, 180 °C, 30 ml He/min) a liquid product (20%) (retention time 23 min), shown to be the dicyanoethylene (**3**).

This structure was inferred from its satisfactory elemental analysis and spectral data; ν_{max} (KBr) 2210 [=C(CN)] and 1725 cm^{-1} (ester); τ(60 MHz; CCl_4) 8·70 (3H, t, *J* 7·5 Hz, H^a),



8·87—8·03 (2H, m, H^b), 7·74—7·15 (2H, m, H^c), 5·85 (2H, q, *J* 7·5 Hz, H^d), and 2·57 (1H, d, H^e); λ_{max} (EtOH) 246 nm (ϵ 12,750); *m/e* 190 (M^+; 33%) and 145 (M^+ − OEt; 100%). The intermediacy of (**2**) (not isolated) was invoked to explain the formation of (**3**) following mode (b) cleavage of the four-membered ring with explusion of 1,1-dicyanoethylene (DCNE). Mode (a) cleavage of (**2**) represents the retrograde reaction, (**2**) → (**1**). We have also examined the solution-phase thermal behaviour of the previously described[2] [2 + 2] cycloadducts (**7a**) and (**7b**) resulting from the addition of TCNE to 4-methylenespiro[2.4]heptane (**6a**) and 4-methylenespiro[2.5]octane (**6b**).†



a; $n = 1$
b; $n = 2$

i, $CH_2(CN)_2$, β-alanine catalyst; ii, Wittig reaction; iii, TCNE, room temp.; iv, mode (b), solvent; v, mode (a), neat, heat; vi, loss of DCNE.

When a solution of (**7b**) (m.p. 115 °C) in decalin was refluxed for 30 min and then subjected to preparative g.l.c. separation (6 ft × ¼ in glass column, 5% OV on GCQ at 220 °C, 40 ml He/min) two products in a 14:86 ratio (75% conversion) were obtained. The minor product of higher retention time (19·5 min) was identified as the previously described tetracyano-homo-octalin of structure (**11b**),[2] probably *via* route (**7b**) → (**10b**) → (**11b**). The major product (retention time 4·5 min) was assigned the 4-dicyanomethylenespiro[2.5]octane (**9b**) structure on the basis of its elemental analysis ($C_{11}H_{12}N_2$ product), spectroscopic data [ν_{max} (KBr) 2220 cm^{-1}; τ (CCl_4) 9·08 (2H, m, H^a), 8·83 (2H, m, H^b), 8·62—7·80 (6H, m, H^c), and 7·58—7·10 (2H, m, H^d); λ_{max} (EtOH) 242 nm (ϵ 12,340); *m/e* 172·1015 (57%) (calc. 172·1000) and 144·0687 (100%) (calc. 144·0687; $M^+ - C_2H_4$)], and comparison with an authentic specimen prepared (in 53% yield) from a condensation between malononitrile and the spiroketone (**5b**) in the presence of β-alanine,[3] (**5b**) → (**9b**).

A dramatic reversal in (**9b**):(**11b**) ratio occurs upon changing to more polar solvents. Thus, at 180 °C a 28:72 ratio of (**9b**) to (**11b**) was observed on conducting the reaction in nitrobenzene or bromobenzene.

A similar study of (**7a**) revealed that the (**9**):(**11**) ratio depends not only on solvent but also on ring size. Thus, at 180 °C the ratio of (**9a**) to (**11a**) for bromobenzene or nitrobenzene solvent is 6:94 (*cf.* 44:56 for decalin). The minor product (**9a**) was obtained alternatively in 24% yield from the route (**5a**) → (**9a**) described above (retention time 9 min, 170 °C, 40 ml He/min). It analysed as a $C_{10}H_{10}N_2$ product, ν(C≡N) 2220 cm^{-1}; τ (CCl_4) 8·66 (2H, m, H^a), 8·13 (2H, m, H^b), 8·30—7·85 (4H, m, H^c), and 7·23—6·86 (2H, m, H^d); λ_{max} (EtOH) 270 nm (ϵ 11,770); *m/e* 158·0822 (84%) (calc. 158·0845) and 130·0659 (100%) ($M^+ - H_2CN$). The behaviour of (**9a**) under electron impact is significantly different from that of (**9b**).

The data presented here clearly suggest that unlike the thermolysis in the neat state or in polar solvents which induces the intramolecular cycloaddition route, (**7**) → (**10**) → (**11**), the reaction in the presence of nonpolar solvents gives rise to an alternative mode of cleavage (b) of the 4-membered ring, providing (**9**) and DCNE (not isolated). The intermediacy of a di-radical species (**8**) is invoked to rationalise the prevalance of the metathesis products in the reaction mixture. The non-observance of formation of (**4**) in the reaction of (**1**) with TCNE could be explained in terms of inability of the cyclopropane to stabilize the analogous zwitterionic species (**10**) owing to the ethoxycarbonyl substituent which suppresses the (**2**) → (**4**) in favour of the (**2**) → (**3**) route.

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† Polar solvents strongly augment rates of the cycloaddition of TCNE to electron-rich olefins, favouring charge separation in the rate-determining step with a charged intermediate. (J. K. Williams, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, 1962, **84**, 2210; F. Effenberger and O. Gerlach, *Chem. Ber.*, 1974, **107**, 278). It was reported in the former reference that TCNE was unreactive towards styrene at room temperature but in refluxing xylene benzylidene malononitrile (15% yield) could be obtained as the sole reaction product. Furthermore, the [2+2]cycloadduct between *p*-$MeOC_6H_4CH{=}CHMe$ and TCNE slowly cracks at 177 °C, yielding *p*-methoxybenzylidenemalonitrile (1%).

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