Intramolecular [3+4] Cycloaddition in Substituted Dispiro[2,3,x]Alkanes. A New Pathway to Polycyclic Olefins containing Cycloheptene

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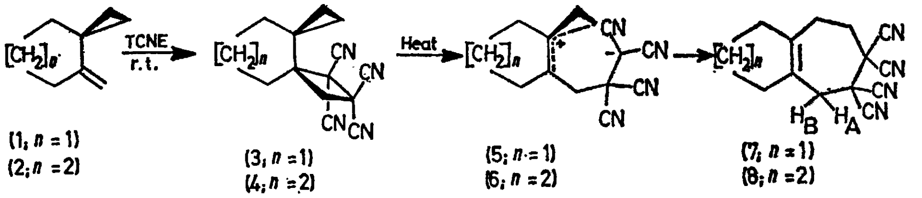
Summary A novel cycloreaction involving intramolecular addition of cyclopropane to a tetrasubstituted cyclobutane contained in a dispiro-system to form a seven-membered ring is described.

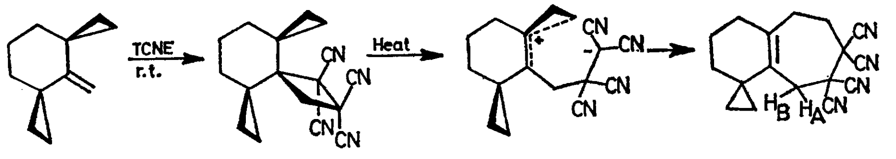
During our studies on tetracyanoethylene (TCNE) addition to rigid vinylcyclopropane systems we have found that the previously reported[1] [2 + 5] cycloaddition ('homodienic' synthesis) is, in fact, a two-stage process. A [2 + 2] addition at the initial stage of the reaction (**2**) → (**4**) is followed by a novel thermally induced intramolecular [3 + 4] cycloaddition to yield the 7-membered ring product (**4**) → (**8**).

This was shown in a study of a lower homologue of the spirovinylcyclopropane series. We prepared the hitherto unknown 4-methylenespiro[2,4]heptane (**1**) from spiro[2,4]-heptan-4-one[2] *via* a modified Wittig reaction.[1,†] Compound (**1**) was allowed to react with TCNE in MeCN at room temp. under N_2 for 1 h. The resulting 1:1 adduct (78%), m.p. 135—136° (from CCl_4,) ($C_{14}H_{12}N_4$, *m/e* 236), was proved to be a [2 + 2] cycloadduct (**3**); τ 9·84—8·72 (4H, m, cyclopropane) and 7·44 (2H, AB $\Delta\nu$ 20·0 *J* 13·0 Hz, cyclobutane). Heating of (**3**) for a short time (180—200°) provided a higher-melting isomer (m.p. 159—160°), the n.m.r. spectrum of which indicated the complete disappearance of the cyclopropane group and the appearance of a different AB resonance (τ 7·27 2H, $\Delta\nu$ 15·4 Hz, *J* 14·3 Hz) assigned to the isolated allylic methylene, in agreement with formulation (**7**). This suggested that thermolysis of (**10**) might similarly generate (**12**), and that formation of (**8**) is also preceded by a [2 + 2] cycloadduct of structure (**4**).

Indeed, heating of (**10**) at 200° for a short period provided a single $C_{17}H_{16}N_4$ compound, m.p. 135°, shown to have structure (**12**) from its n.m.r. spectrum in which one of the cyclopropyl resonances was absent and an AB pattern appeared at τ 7·20.



(1, *n* = 1) (2; *n* = 2)
(3, *n* = 1) (4; *n* = 2)
(5; *n* = 1) (6; *n* = 2)
(7; *n* = 1) (8; *n* = 2)



(9) (10) (11) (12)

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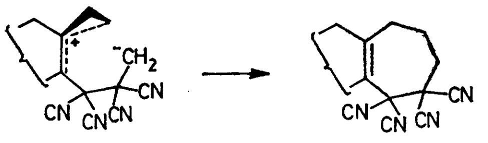
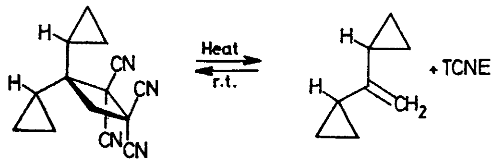
† The new hydrocarbon showed *m/e* 108 (M^+), and τ 5·54 and 5·83 (each 1 vinylic H), 7·33—7·76 (2 allylic H), 8·06—8·43 (4 cyclopentane H) and 9·32 (s, 4 cyclopropane H).

The reaction of (**2**) with TCNE at room temp. leads to a [2 + 2] cycloadduct (88%; 95% pure; semisolid $C_{15}H_{14}N_4$) which did contain a cyclopropane group (τ 9·90—8·75, 4H, m) and a tetracyanocyclobutane unit (i.r.: 2240 cm^{-1} (CN); τ 7·63, 2H, s). Thermally induced intramolecular [3 + 4] cycloaddition (**4**) → (**8**) could easily be effected, and the resulting product (m.p. 94°) was identical with that previously recorded.[1,‡]



(13) (14)



(16) (15)

A priori one can envisage two distinct modes for the thermal intramolecular isomerization, depending on whether the cyclobutane ring is cleaved at the carbon atom bearing two cyano-groups, as in (**5**), (**6**), and (**11**), or else at the methylene group, as in (**13**). Since none of the compounds of type (**14**) could be detected in any of the reaction mixtures it is highly likely that the cycloreaction involves a dipolar intermediate species of the former type. This intermediate is indeed the preferred one, since both ends of the dipole are considerably stabilized by neighbouring substituents. The positive charge occurs on the carbon atom linked to a cyclopropane unit fixed in the bisected conformation, conferring extensive stabilization to the system. The importance of this is reflected by the ready thermal fragmentation of compound (**16**) into (**15**) and TCNE under similar conditions.§ The negative site is stabilized by the electron-withdrawing cyano-groups.

These are the first examples of a hitherto unknown cycloaddition involving strained and polarisable σ bonds, which are transformed into new σ and π bonds in a seven-membered ring. The two-stage cycloaddition of tetracyanoethylene across the vinylcyclopropane system of methylenespiro[2,*x*]alkanes described here provides a novel route towards synthesis of polycyclics containing the cycloheptene ring.

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‡ The data at hand clearly suggest that the tendency towards intramolecular cycloreaction increases in the order (**10**) → (**12**) < (**3**) → (**7**) < (**4**) → (**8**).

§ It is generally conceded that the bisected conformation of the cyclopropylcarbinyl cation is the most stable. (C. U. Pittman, Jr. and G. A. Olah, *J. Amer. Chem. Soc.*, 1965, **87**, 2998, 5123.). MO calculations indicate extremes of stabilization of 9—26 kcal/mol between bisected and perpendicular conformations. (P. v. R. Schleyer and V. Buss, *J. Amer. Chem. Soc.*, 1969, **91**, 5880). Cyclopropyl cations in which the bisected conformation is precluded have been observed to have decreased stability. (T. Sharp and J. C. Martin, *J. Amer. Chem. Soc.*, 1966, **88**, 1817; H. C. Brown and J. D. Cleveland, *ibid.*, p. 2054.)

[1] S. Sarel, A. Felzenstein, and J. Yovell, *J.C.S. Chem. Comm.*, 1973, 859.
[2] P. Leriverend and J. M. Conia, *Bull. Soc. chim. France*, 1966, 121.