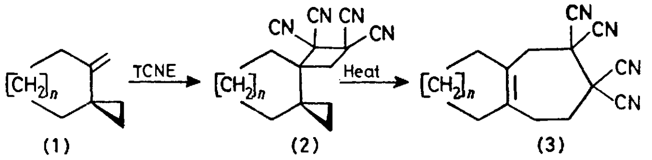
Bicyclic Cyclononadienes from 1,7-Cycloaddition of Tetracyanoethylene to Divinylcyclopropane Systems

By Shalom Sarel and Marcel Langbeheim

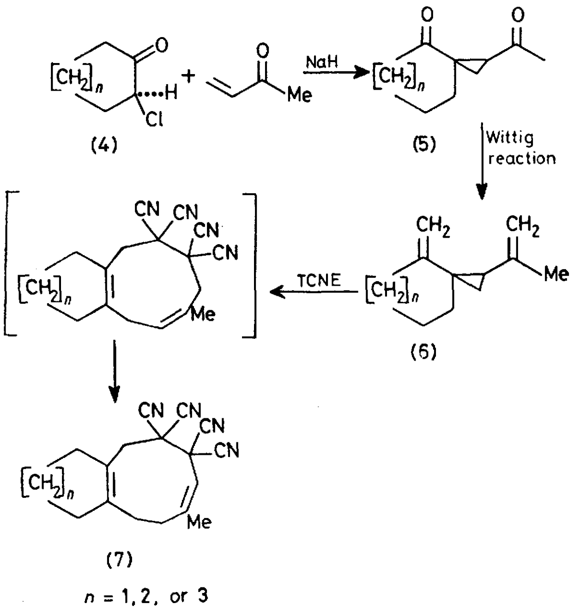
(Department of Pharmaceutical Chemistry, The Hebrew University School of Pharmacy, Jerusalem, Israel)

Summary A novel $[(2_\pi + 2_\sigma + 2_\pi) + 2_\pi]$ cycloaddition involving a divinylcyclopropane system and TCNE to form a nine-membered ring is described.

Our studies[1] of the 1,5-cycloaddition of tetracyanoethylene (TCNE) across the vinylcyclopropane system in 4-methylene-spiro[2.*x*]alkanes (**1**) to yield the corresponding cycloheptenes (**3**) indicated that the reaction is a two-stage process, giving at first the [2+2] cycloadduct (**2**) which on subsequent heating undergoes an internal [3+4] cycloaddition to form (**3**).



We report the first example of ring expansion sequences in which the divinylcyclopropane unit of the 4-methylene-1-vinyl-spiro[2.*x*]alkanes (**6**) reacts with TCNE to yield (88%) the bicyclic system (**7**) containing a cyclononadiene unit. The hitherto unknown diketone (**5**) was obtained (62%) from the α-chloroalkanone (**4**) following the method of Fraisse-Julien[2] and then converted into the spiro[2.6]-nonane (**6**), b.p. 32—34 °C at 0·04 mmHg,† by a modified Wittig reaction.[1]



The reaction between a solution of TCNE in acetonitrile and an equimolar quantity of (**6**) under N_2 at room temp. was fast and exothermic, affording a 1 : 1-adduct (88%), m.p. 150—153 °C (from C_6H_{12}). It was assigned structure (**7**) on the basis of elemental analyses, its mass spectrum (M^+, *m/e* 304), its i.r. spectrum (NaCl): 2185 (C≡N), 1640, and 1610 cm^{-1} (C=C), and its n.m.r. spectrum ($CDCl_3$): τ 2·21 (1H, vinyl), 7·35 (2H, AB, *J* 2 Hz), and 8·80 (3H, s, Me), complete absence of cyclopropane proton signals, and appearance instead of a new AB resonance (2H) typical for allylic methylene protons and a new (1H) vinylic proton absorption.

The reaction was general for substrates with *n* = 1, 2, or 3, giving rise to products exhibiting similar structural features.

(*Received*, 30*th May* 1977; *Com.* 526.)

---

† I.r.: 3080m (cyclopropane), 1640, 1620, and 880m cm^{-1} (C=C); n.m.r. ($CDCl_3$): τ 9·38—9·02 (m, cyclopropane), 8·14 (s, Me), 7·78—7·42 (m, 3-H), and 5·36 and 5·14 (finely split s, ratio 2 : 1, vinylic H); *m/e* 176 ($C_{13}H_{20}$).

[1] S. Sarel, A. Felzenstein and J. Yovell, *J.C.S. Chem. Comm.*, 1973, 859; 1974, 753.

[2] E. Bonavent, M. Causse, M. Guitard, and R. Fraisse-Julien, *Bull. Soc. chim. France*, 1963, 2462.