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UNUSUAL CYCLOADDITIONS OF 4-PHENYL-1,2,4-TRIAZOLIN-3,5-DIONE TO *ENDO*- AND *EXO*-TRICYCLO$[3.2.1.0^{2,4}]$OCT-6-ENES

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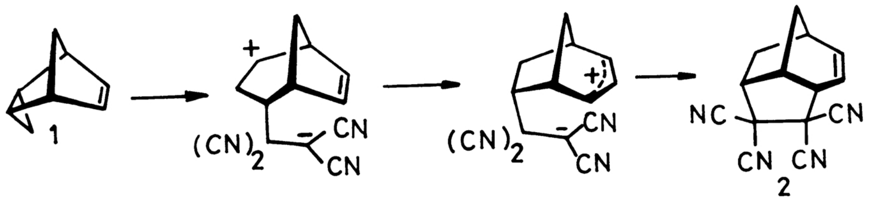
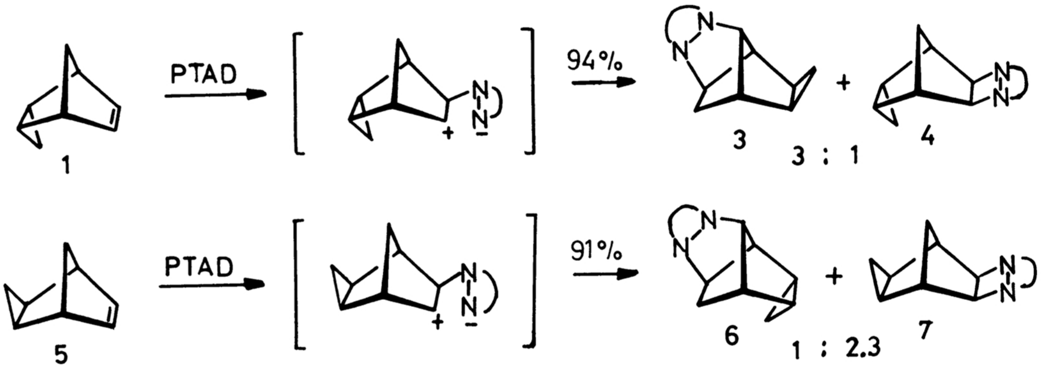
4-Phenyl-1,2,4-triazolin-3,5-dione readily cycloadds to endo- and exo-tricyclo-$[3.2.1.0^{2,4}]$oct-6-enes to give Δ^1-1,2-diazetines besides skeletally rearranged products. All adducts can be converted to the respective azo compounds which exhibit some unusual thermal and photochemical behavior.

Tetracyanoethylene reacts with endo-tricyclo$[3.2.1.0^{2,4}]$oct-6-ene (1) with cyclopropane ring opening and subsequent 1,2-alkyl shift to give the adduct 2 1). On the other hand, 4-phenyl-1,2,4-triazolin-3,5-dione (PTAD) was reported to react with 1 only at elevated temperatures to afford complex product mixtures, which could not be characterized 1). We have previously shown that PTAD cycloadds to certain strained polycyclic olefins via dipolar intermediates to supply cyclic urazoles with skeletal rearrangements in high yields 2,3,4). In order to gain more insight into the mechanistic features of this intriguing cycloaddition reaction, it is of interest to establish whether and to what extent a cyclopropyl group, annelated to a bicyclic framework, affects the fate of the initial zwitterionic intermediate.



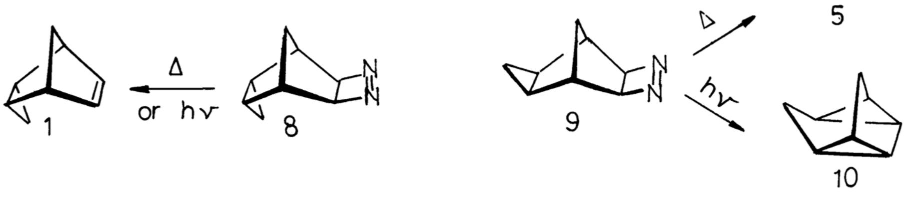
Endo-tricyclo$[3.2.1.0^{2,4}]$oct-6-ene (1) in methylene chloride reacted with PTAD at room temperature within 8 hours to give an almost quantitative yield (94%total) of a 3:1 mixture of two products which were separated by column chromatography (SiO_2, CH_2Cl_2). They were unequivocally characterized on the basis of their 270 MHz ^{1}H-NMR spectra (see Table 1) and their chemical transformations (see below). The surprising formation of the [2+2]- adduct 4 suggests a certain stabilization of the carbenium ion in the initial ionic intermediate through the remote cyclopropane ring, since $[\pi^{2s}+\pi^{2s}]$-cycloaddition is precluded by the orbital symmetry rules of Woodward and Hoffmann5). Examination of the photoelectron spectra of homonorbornadienes reveals a considerably stronger interaction of the cyclopropyl group with the remote double bond



in the *exo*-isomer than in the *endo*-isomer6). Hence, *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (5) should supply considerably more [2+2]-adduct than 1. Indeed, reaction of PTAD with 5 afforded a 1:2.3 mixture of 6 and 7. The dramatic change of the ratio of the products in favor of the [2+2]-adduct in the *exo*-isomer 5 points to a more effective homoconjugative interaction of the *exo*-cyclopropane ring with the developing carbenium ion, which suppresses the 1,2-alkyl shift to a greater extent and hence favors the 1,2-addition7).

Alkaline hydrolysis and decarboxylation of the adducts in isopropanol with potassium hydroxide, oxidation of the respective hydrazides with Cu(II) chloride, and subsequent treatment of the brick-red Cu(I) complexes with aqueous alkali8) furnished in high yields the 1,2-pyrazolines 11 and 12, and the Δ^1-1,2-diazetines 8 and 9, respectively. For further studies they were purified by preparative gas chromatography.

Photolysis of 8 (ether, Corex filter), as well as thermolysis in a sealed tube at 130°C in CCl_4, gave 1 as the sole product. In contrast, photolysis of 9 gave rise to 10 quantitatively, whereas thermolysis (130°C, CCl_4) led to 5. These latter reactions parallel the reported transformations of 3,4-diaza[4.2.1.$0^{2,5}$]nona-3,7-diene9).



The pyrazolines 11 and 12 proved to be considerably more stable thermally. Thus, gas phase pyrolysis of 11 (350°C, 0.01 Torr) gave rise to a mixture of 10 and 5 in a ratio of 96:4 (total

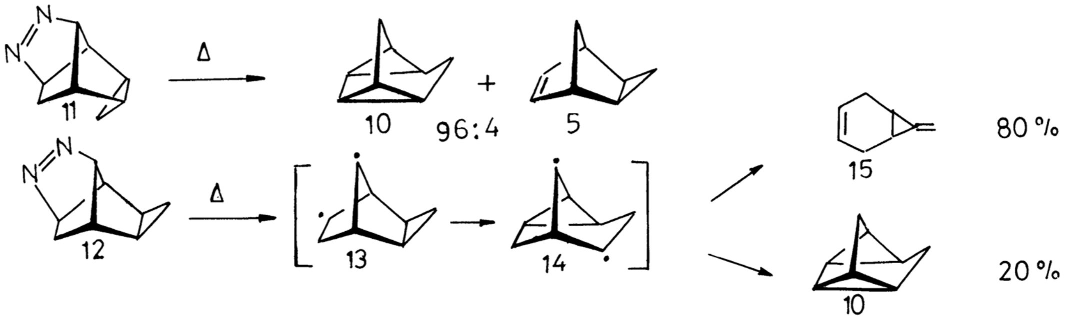
Table 1. Spectroscopic data of new compounds[a)]

Compound (m.p.)	^{1}H-NMR (270 MHz, CDCl$_3$, TMS)	IR (KBr or film) ($\mathrm{cm^{-1}}$)
3 (176°C)	0.28(m,1H);0.55(m,1H); 1.01(m,2H); 1.59(m,2H); 2.66(br.s,1H); 2.70(br.s,1H); 3.83(br.s,1H); 4.40(br.s,1H); 7.17-7.42(m,5H).	3050,2940(C-H) 1770,1700(C=O)
4 (205.5°C)	0.64(m,2H); 1.44(m,2H); 2.28(d,J=9.6 Hz,1H); 2.61(d,J=9.6 Hz, 1H); 2.65(br.s,2H); 4.28(s,2H); 7.19-7.47(m,5H).	3050,2960(C-H) 1780,1715(C=O)
6 (182°C)	0.99(m,1H); 1.58(m,1H); 1.71-1.87(m,3H); 1.91(m,1H); 2.13(m,1H); 2.60(m,1H); 4.22(m,1H); 4.67(m,1H); 7.21-7.56(m,5H).	3045,2965(C-H) 1772,1710(C=O)
7 (192°C)	0.29(m,1H); 0.57(m,2H); 0.71(m,1H); 1.22(d, J=11.6 Hz,1H); 1.91(d,J=11.6 Hz,1H);2.75(s,2H); 4.48(s,2H); 7.23-7.58(m,5H).	3050,2970(C-H) 1780,1710(C=O)
8	0.51(m,2H); 1.48(m,2H); 1.55(d,J=10.0 Hz,1H); 1.61(d,J=10.0 Hz, 1H); 2.42(br.s,2H);4.38(s,2H).	3055,2970(C-H) 1540(N=N)
9	0.21(m,1H); 0.58(m,1H); 0.67(d,J=12.0 Hz,1H); 0.70(m,2H); 0.91(d,J=12.0 Hz,1H); 2.52(s,2H); 4.44(s,2H)	3060,2980(C-H) 1550(N=N)
11	0.74(m,1H); 1.36(m,1H); 1.51(m,1H); 1.64(m,2H); 1.91(m,2H); 2.24(m,1H); 4.69(m,1H); 4.94(m,1H).	3045,2955(C-H) 1535(N=N)
12	0.30(m,1H); 0.55(m,1H); 1.00(m,2H); 1.20(m,2H); 2.28(m,2H); 4.50(m,1H); 4.87(m,1H).	3050,2960(C-H) 1530(N=N)
16	0.10(m,1H); 0.25(m,1H); 0.92(m,1H); 1.10(m,1H); 1.33(m,1H); 1.46(m,1H); 1.61(m,2H); 2.25(m,1H); 2.46(m,1H).	3070,3040,2960 2925(C-H)

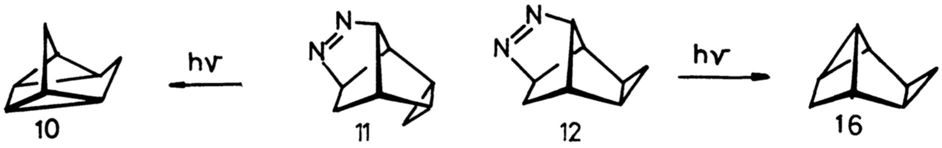
a) All the new compounds gave satisfactory elemental analysis and/or mass spectrometrically determined molecular weights.

yield 92%).

Under the same conditions, however, **12** behaved very differently, giving 7-methylene bicyclo-[4.1.0^{1,6}]hept-3-ene (**15**)[10)] predominantly (80%) plus 20% of **10** (total yield 82%).



This result can be rationalized by the intermediacy of the diradicals 13 and 14.



The different arrangement of the cyclopropane ring in 11 and 12 made itself noticable also in the photochemical decomposition of both compounds: whereas 12 (ether, Corex filter) smoothly afforded the novel tetracyclic compound 16, the isomeric 11 gave exclusively 10.

References and Notes

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7) It has been suggested by Prof.M.A.Battiste, University of Florida, that the observed change in the product ratio is also consistent with the known lesser tendency of 5,6-exo-cycloalkyl fused norbornyl cations to undergo Wagner-Meerwein rearrangements.

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