Reactions of 4-Phenyl-1,2,4-triazoline-3,5-dione with Some Medium-ring Polyenes

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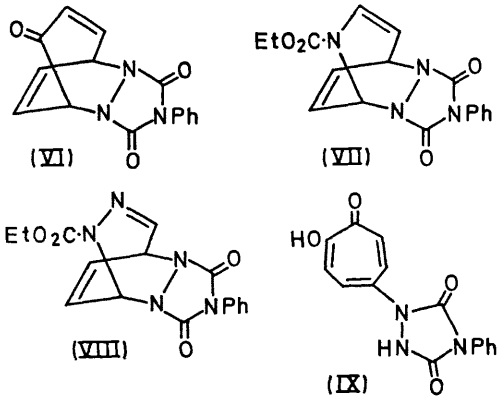
Summary Reaction of 4-phenyl-1,2,4-triazoline-3,5-dione with tropone, azepine, and diazepine gives normal (4 + 2)π cyclo-adducts, whereas reaction with tropolone gives compound (IX).

WE report the reactions of some medium-ring polyenes such as tropone (II), azepine (III), diazepine (IV),[1] and tropolone (V) with 4-phenyl-1,2,4-triazoline-3,5-dione (I) (*cis*-configuration about the nitrogen double-bond) which is a more powerful dienophile than tetracyanoethylene.[2] It reacts rapidly with (II), (III), and (IV) even at room temperature as evidenced by the immediate disappearance of the red colour in dioxan solutions, affording 1 : 1 adducts (VI), (VII), and (VIII), respectively, in high yields. The structures of (VI) (90% yield), (VII) (99%), and (VIII) (93%), have been established by spectral and chemical methods. The n.m.r. spectrum of compound (VI) at 60 MHz in $(CD_3)_2SO$ exhibited signals at τ 2·70 (1H, d,d) 2·95 (1H, d,d), 3·40 (1H, d,d) 4·02 (1H, d,d), 4·45 (1H, t), 4·65 (1H, d,d), and 2·55 (5H, C_6H_5). The mass spectrum showed a characteristic molecular ion (rel. int. 90%) and strong peak at $M - 175$ (*m/e* 106, rel. int. 94%) resulting from the loss of $C_8H_5N_3O_2$ from the molecular ion, originating



from a retro-Diels–Alder-type fragmentation. The n.m.r. spectra of (VII) and (VIII) were similar to that of (VI) in

the olefinic and aliphatic proton regions, and final assignments of these signals and coupling constants were confirmed by spin-decoupling experiments at 100 MHz. The mass spectrum of compound (VIII) showed a slightly different fragmentation pattern from those of (VI) and (VII): the ethoxycarbonyl group was readily eliminated from the molecular ion (rel. int. 42%) and then a fragmentation by a retro-Diels-Alder reaction was observed (*m/e* 94, rel. int. 93%). From this evidence, the compounds (VI), (VII), and (VIII) are normal $(4 + 2)\pi$ cyclo-adducts. The 2,6,7-triazabicyclo[3,2,2]nonadiene and 2,3,6,7-tetraazabicyclo[3,2,2]nonadiene ring systems present in (VII) and (VIII), respectively, have not been previously reported. More significantly, these ring systems are potential precursors to triaza- and tetra-aza-homobullvalene, molecules of considerable synthetic and theoretical interest.

When tropolone (V) is allowed to react with triazolinedione (I) under similar conditions, (IX) (87%) was obtained. The n.m.r. spectrum at 100 MHz in $(CD_3)_2SO$ exhibited signals at τ 2·45 (1H, s, OH), 2·49 (5H, C_6H_5), 5·00 (1H, bs, NH), and A_2B_2-type signals (2H, τ_A 2·31, τ_B 2·69, J_{AB} 12 Hz). The i.r. spectrum showed maxima at 3400, 3230, 1770, 1710, 1640, 1530, and 850 cm^{-1}, indicating the presence of the tropolone moiety. Compound (IX) is thus 5-(3,5-dioxo-4-phenyl-1,2,4-triazolidinyl)tropolone. This result is very similar to that reported by Kitahara *et al.* for the reaction of tropolone with ethyl azodicarboxylate,[3] but quite different from the reaction of cycloheptatriene with (I). The enhancement of the dienophilic reactivity of (I) relative to allylic reactivity is illustrated by the formation of the Diels–Alder adduct from cycloheptatriene, rather than the product of additive substitution as with diethyl azodicarboxylate.[4]

(*Received, November 11th*, 1969; *Com.* 1718.)

[1] For cycloaddition reactions of diazepine derivatives; see T. Sasaki, K. Kanematsu, and A. Kakehi, *Chem. Comm.*, 1969, 432.
[2] R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc.* (*C*), 1967, 1905.
[3] Y. Kitahara, I. Murata, and T. Nitta, *Tetrahedron Letters*, 1967, 3003.
[4] R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Letters*, 1962, 615.