The Reaction of 1,2,4-Triazoline-3,5-diones with Mono-olefins

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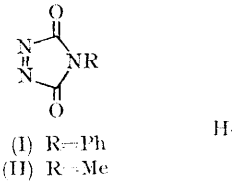
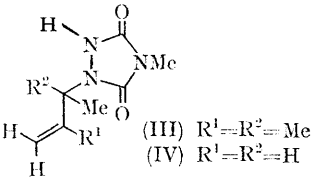
ONE of the most reactive dienophiles is 4-phenyl-1,2,4-triazoline-3,5-dione (I); solutions of this red dione are decolorized instantaneously at −78° by cyclopentadiene.[1,2] We now report that 1,2,4-triazoline-3,5-diones are also extremely reactive toward mono-olefins having allylic hydrogens. A methylene chloride solution (0·01M) in (II)[3] and 1·0M in cyclohexene is decolorized at 25° within 6 min. after mixing. Ethyl azodicarboxylate also reacts with olefins having allylic hydrogens[4] but far more slowly; a comparable solution of this ester in an evacuated sealed tube is incompletely reacted even after 3 weeks at 50°. Thus dione (II) is at least thirty thousand times more reactive toward cyclohexene than is ethyl azodicarboxylate.

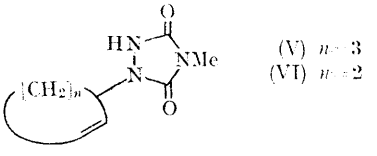
The olefin–dione reaction results in the quantitative formation of a 1 : 1 adduct of the additive-substitution type (III—VI) first noted by Diels and Alder[5,6] and more recently by Thaler and Franzus.[7] The structures of the adducts arising from the aliphatic olefins, (III) and (IV), indicate that a



(I) R=Ph
(II) R=Me



(III) $R^1=R^2=Me$
(IV) $R^1=R^2=H$



(V) $n=3$
(VI) $n=2$

shift in the position of the double bond has occurred; however, one cannot conclude from the structures of the alicyclic olefin addition products, (V) and (VI), whether or not a migration of the double bond has occurred.

The Table indicates the structures of the adducts arising from the various mono-olefins. All adducts have the correct elemental composition and have i.r. and n.m.r. spectra consistent with the suggested structures.

TABLE

Products from the reaction of 4-methyl-1,2,4-triazoline-3,5-dione with mono-olefins

Mono-olefin	Product	M.p. (°C)
2,3-Dimethylbut-2-ene	(III)	95·0—96·0
cis-But-2-ene	(IV)	72·0—73·0
trans-But-2-ene	(IV)	71·0—72·0
Cyclohexene	(V)	149·0—149·6
Cyclopentene	(VI)	118·5—119·5

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