Reversible Additions of an Enamine to 8,8-Disubstituted Heptafulvenes

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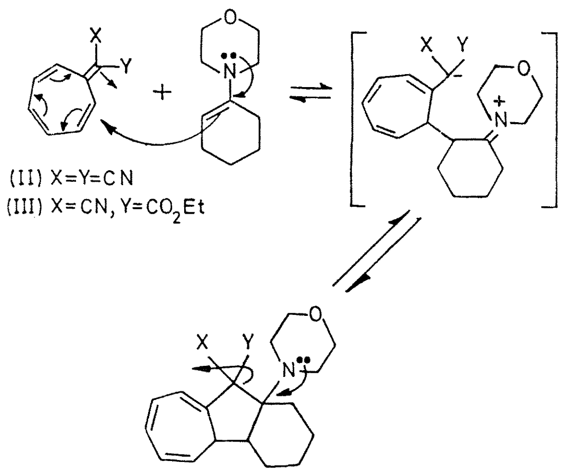
WE have reported cycloaddition reactions of enamines to tropone.[1] We describe here an analogous and ready reversible cycloaddition of 1-morpholinocyclohexene (I) to 8,8-dicyano- and 8-cyano-8-ethoxycarbonyl-heptafulvene,[2] (II) and (III), which are more polar than tropone.

Reaction of (II) with an excess of (I) (3 eq.) in absolute ethanol at room temperature gives a 1 : 1 addition product (IV), m.p. 106° d., in 95% yield. The cyano-groups in (IV) absorb weakly at 2250 cm.$^{-1}$, indicating the cyano-group is not conjugated. Solutions of (IV) in organic solvents were red even when cooled in ice and the heptafulvene (II) was recovered quantitatively. Because of this ready reversibility, we could not obtain u.v. and n.m.r. spectra. From the i.r. data and a consideration of probable reaction mechanisms we thought that (IV) was a 1,8-cycloaddition product as shown in the Scheme and that the ready reversibility is due to electron withdrawal by the cyano-group. Therefore, we performed the reaction with a less polar heptafulvene (III) and again obtained 1 : 1 addition product (V) (room temperature, EtOH, 3 hr., 89%), m.p. 119—122° d., i.r. ν_{max} (KBr) 3030, 2950, 2860, 2260, 1740, 1620, 1230, 1118, and 708 cm.$^{-1}$, u.v. λ_{max} (EtOH) 282 nm. (log ϵ 3·53), n.m.r. (60 MHz., CCl_4) τ 3·60 (m, 3H), 3·98 (m, 1H), 4·87 (dd, 1H *J* 9·2, 4·0 Hz.), 5·82 (q, 2H 6·8 Hz.), 6·5 (m, 4H), 6·6—7·3 (m, 5H), 7·35—7·90 (m, 3H), 8·0—8·8 (m, 6H) and 8·65 (t, 3H 6·8 Hz.). The spectral data are consistent with the structure indicated, but the stereochemistry is not yet certain. Compound (V) is stable, as expected, in solution at room temperature and gradually dissociates to the starting material above 65°.



(II) X=Y=CN
(III) X=CN, Y=CO_2Et

(IV) X=Y=CN
(V) X=CN,Y=CO_2Et

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[1] M. Oda, M. Funamizu, and Y. Kitahara, preceding communication.

[2] T. Nozoe, T. Mukai, K. Osaka, and N. Shishido, *Bull. Chem. Soc. Japan*, 1961, **34**, 1384.