Cycloaddition Reactions of Tropone with Enamines

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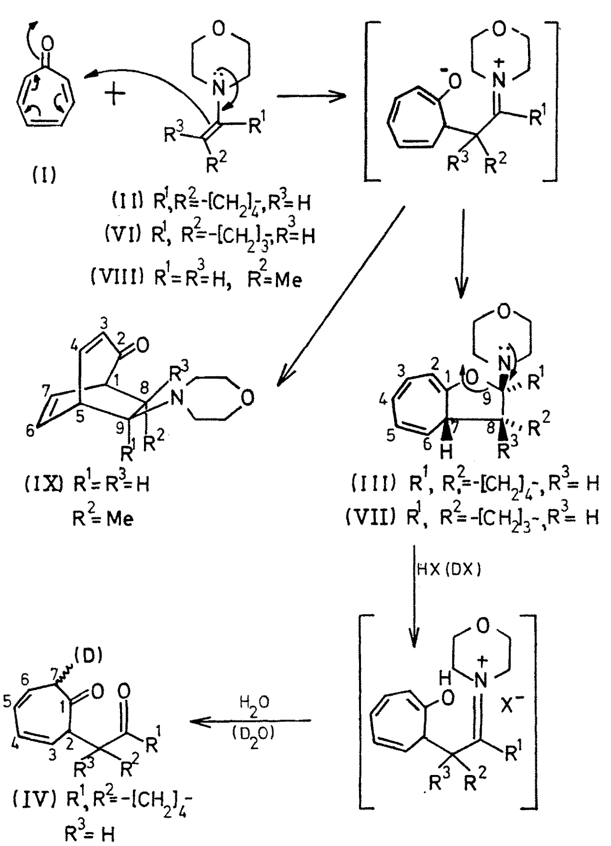
WE report on the reactions of tropone (I) with enamines. Reaction with 1-morpholinocyclohexene (II) without solvent (or in EtOH, C_6H_6 or tetrahydrofuran) at room temperature gave a 1 : 1 addition product (III) (77% yield), m.p. 103—104°, ν_{max} (KBr) 3030, 3015, 1631, 1617, 1196, 1118, 790, and 702 cm.$^{-1}$, λ_{max} (cyclohexane) 213 (ϵ 21,900) and 307 (4140) nm. The i.r. and u.v. data are comparable with those of 1-ethoxycycloheptatriene,[1] indicating the presence of a 1-alkoxycycloheptatriene moiety in (III). The n.m.r. spectrum (Table) further confirmed the structure. The large coupling constant (9·2 Hz.) between 7-H and 8-H suggests a *cis*-relationship between these protons. 8-H and the morpholino-group are probably *cis*, as the *trans*-form cannot be constructed from Dreiding models. Compound (III) was easily hydrolysed by dilute mineral acids to give a diketone 2-(2′-oxocyclohexyl)cyclohepta-3,5-dien-1-one (IV) (89% yield), m.p. 108—109°, ν_{max} (KBr) 3025, 1705, 1597, and 705 cm.$^{-1}$; λ_{max} (EtOH) 235 (ϵ 5350) and 285 (550) nm.; n.m.r. (100 MHz., $CDCl_3$) τ 3·76 (m, 4-H, 5-H), 4·22 (ddd, 11·0, 6·7, 3·8, 6-H), 4·52 (dd, 10·5, 5·2, 3-H), 6·4—7·1 (m, 7a- and 7b-H, 2-H, 1-H) and 7·5—8·9 (m, 8H). Hydrogenation (Pd/C) of (IV) gave a tetrahydro-compound (V); colourless liquid; i.r., carbonyl at 1715 (six-membered) and 1698 cm.$^{-1}$ (seven-membered). Hydrolysis of (III) with

TABLE

N.m.r. spectral data (100 *MHz*, $CDCl_3$)

Compound	Proton assignment	Chemical shift (τ)	Multiplicity	Coupling constants (Hz.)
(III)	2-H	4·40	dt	$J_{2,3}$ = 6·2
	3—5-H	3·60—4·05	m	$J_{2,4}$ = $J_{2,7}$ = 1·5
	6-H	5·14	ddd	$J_{5,6}$ = 10·0
	7-H	*ca.* 7·2	—	$J_{6,7}$ = 3·5
	8-H	7·48	ddd	
		7·8—8·7	m (8H)	$J_{4,6}$ = 1·5
	Morpholino-group	6·35	m (4H)	
		7·20	m (4H)	$J_{7,8}$ = 9·2
(IX)	1-H	6·85	ddd	$J_{1,3}$ = 2·3, $J_{5,9}$ = 3·0
	3-H	4·25	ddd	$J_{3,4}$ = 11·3, $J_{7,8}$ = 1·0
	4-H	3·10	dd	
	5-H	6·60	dddd	$J_{4,5}$ = 8·7, $J_{8,9}$ = 7·0
	6-H	3·43	ddd	
	7-H	4·01	dddd	$J_{3,5}$ = 0·5, $J_{8,Me}$ = 6·8
	8-H	8·06	bq	$J_{5,6}$ = 7·0
	9-H	7·56	dd	
	CH_3	8·83	d	
	Morpholino-group	6·35	m(4H)	$J_{6,7}$ = 8·2
		7·2—7·8	m(4H)	$J_{1,7}$ = 7·2
				$J_{1,6}$ = $J_{5,7}$ = 1·0
				$J_{1,8}$ *ca.* 0·5

Abbreviations: d, doublet; t, triplet; m, multiplet; b, broad; q, quintet.



D_2O–D_2SO_4 (5°, 5 min.) resulted in the introduction of one deuterium at C-7 of (IV), the n.m.r. signals of 6-H changing to double-doublet from doublet-doublet-doublet, and the integrated area at τ 6·4—7·1 (4H) decreasing to 3H. Under the same conditions, deuterium exchange in (IV) was negligible. This result suggests that the mechanism of the hydrolysis is as shown in the Scheme.

With 1-morpholinocyclopentene (VI), (I) also gave a 1 : 1 addition product (VII) in high yield.

However, with 1-morpholinopropene (VIII) under the same conditions, (I) gave another type of 1 : 1 addition product (IX) (66% yield), m.p. 129—130°, ν_{max} (KBr) 3040, 1660 and 1626 cm.$^{-1}$, λ_{max} (EtOH) 215, (sh) (ϵ 6400) and 291 (2480) nm.; λ_{max} (EtOH–0·2N-HCl) 224 (6580) and 258 (sh) (1260) nm. The i.r. data indicate the presence of an $\alpha\beta$-unsaturated carbonyl group in (IX). The change of the u.v. spectrum in acidic solution from that in neutral solution (the former is typical for the bicyclo[3,2,2]nona-3,6-dien-2-one (8,9-dihydrohomobarrelenone) structure),[2] suggests spatial interaction of the morpholino-group with the $\alpha\beta$-unsaturated carbonyl group. The exact structure was elucidated by 100 MHz. n.m.r. and double-resonance spectra (Table). The coupling constants, J_{8-9} 7·0, J_{1-8} *ca.* 0·5 and J_{5-9} 3·0 Hz. suggest† that 8-H (exo) and 9-H (endo) are *trans*. In this configuration, the nitrogen of the morpholino-group and C-4 are near enough (2·50 Å in the Dreiding model) to interact, accounting for the u.v. spectra.

Possible mechanisms for these addition reactions are shown in the Scheme.

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