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8-OXOHEPTAFULVENE. II THE REACTION WITH BENZOPHENONE AND TROPONES

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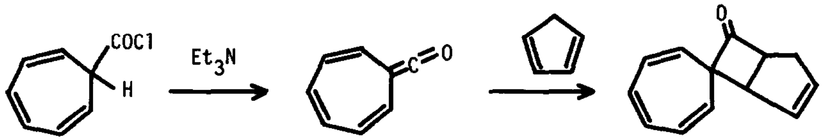
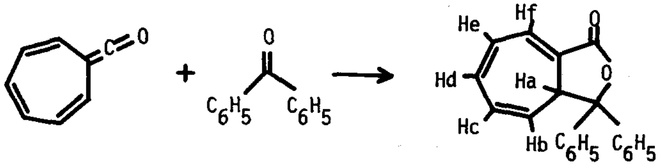
In previous paper,[2] we have reported the formation of 8-oxoheptafulvene (I) and its reaction with some olefins in 2 + 2 cycloaddition process giving spiro compounds having four-membered cyclic ketone and cycloheptatriene moieties.



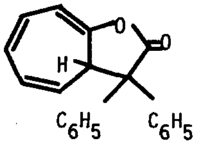
I

In the present communication, the reaction of I with some carbonyl compounds will be reported.

Reaction of cycloheptatriene-7-carboxylic acid chloride with triethylamine in the presence of excess of benzophenone in refluxing n-hexane afforded a compound (II),[3] m.p. 164~165°C in ca. 10% yield based on the chloride used. The compound II shows M^+, 300; ir (KBr) νC=0, 1780 cm^{-1}; uv λ_{max}^{MeOH}, 226.5 nm (logε 4.01), 275 (3.63) and 316 (3.53), suggesting that it is a 1 : 1 addition



I II



III

product containing a conjugated γ-lactone formed by 8 + 2 cycloaddition of 8-oxoheptafulvene formed *in situ* and benzophenone. Furthermore, the nmr spectroscopic data indicate the structure II for the product. The proton assignments and coupling constants (Table 1) have been confirmed by decoupling techniques. The nmr pattern is similar to those of isomeric compound III, addition product of tropone and diphenyl ketene,[4] however, the chemical shift of Hf of II is remarkably shifted to low field by anisotropy of carbonyl group.

TABLE 1. Chemical Shifts (δ in ppm) and Coupling Constants (in Hz) of the Adducts in $CDCl_3$.[5]

	II	V	V (Δppm)*	VII	VIII
Ha	3.42 d,d,d	1.70 d,t	1.27	1.79 m	1.92 d,d
Hb	4.83 d,d	4.68 d,d	1.10	4.83 d,d	4.88 d,d
Hc	6.1 d,m	5.9 m	<1.0**	5.9 d	5.93 d,m
Hd, He	6.8 m	6.0~6.5 m	<1.0**	6.0~6.5 m	6.0~6.5 m
Hf	7.15 d,m	5.75~5.9 m	<1.0**		
Hg, Hh		3.09 d,d 3.33 d,d	2.73	3.13 d,d 3.37 d,d	3.12 d,d 3.35 d,d
Hi~Hl		6.0~6.5 m	<1.0**	6.0~6.5 m	6.0~6.5 m
CH_3				1.94 d	
Jab	4.1	4.8		4.8	4.8
Jac	2.2	1.7		1.7	1.8
Jaf	1.2	1.7			
Jbc	9.5	9.8		9.3	9.5
Jgh		7.5		7.8	8.0
$JaCH_3$				1.5	

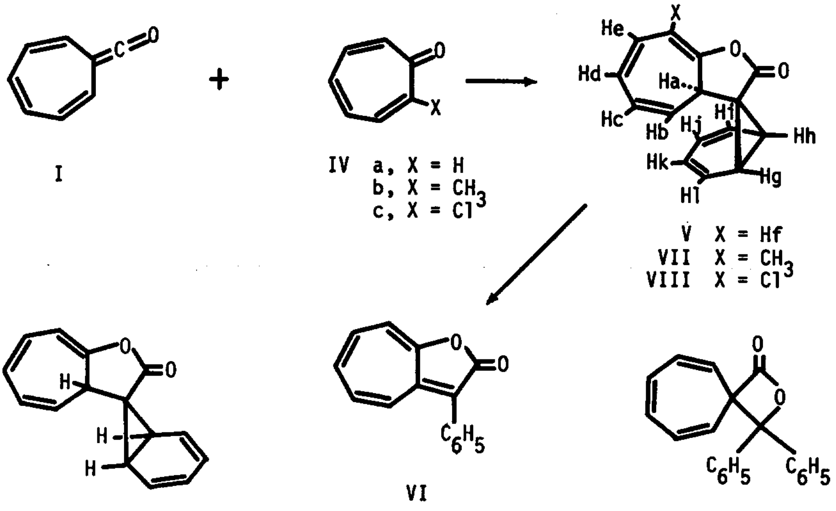
* Values (Δ ppm) in the presence of 0.59 molar equivalents of $Eu(DPM)_3$.

** Accurate values could not be determined, however, it is obvious that the values are less than 1.0 ppm.

The reaction of 8-oxoheptafulvene with tropone (IVa) gave a 1 : 1 addition product (V), m.p. 87~87.5°C in 80% yield. The structure was established as shown in scheme having a novel norcaradiene and cycloheptatriene moieties in a molecule from the spectroscopic evidence as well as thermal reaction in refluxing xylene to give 3-phenyl-1-oxaazulan-2-one (VI)[6] involving rearrangement and dehydrogenation. Such aromatization is common to most norcaradienes and cycloheptatrienes.[7]

The compound V shows M^+, 224; ir (KBr), $\nu C=O$ 1785 cm^{-1}; uv λ_{max}^{MeOH} 247 nm (log ε 3.65) and

269 (3.66), which indicate the presence of an unconjugated γ-lactone. Analysis of the nmr spectrum of the compound V with the aid of decoupling techniques provided definite assignments of protons and the coupling constants as shown in Table 1.



I

IV a, $X = H$
b, $X = CH_3$
c, $X = Cl$

V $X = Hf$
VII $X = CH_3$
VIII $X = Cl$

IX

VI

X

2-Methyltropone (IVb) and 2-chlorotropone (IVc) react with 8-oxoheptafulvene to give the similar norcaradiene type compound (VII), m.p. 112~113°C, $\nu C{=}O$ 1792 cm^{-1} and (VIII), m.p. 159~160.5°C, $\nu C{=}O$ 1780 cm^{-1}, in the yield of 84.5% and 62.6%, respectively. Nmr data of these compounds were also shown in Table 1. In both cases, the substituents are exclusively located at Hf-position and not at Hb-position of V.

An alternative structure (IX) for the adducts are also considered. The nuclear Overhauser effects between Hb (or Ha) and any protons of norcaradiene moiety could not be observed, however, the structure IX can be excluded by the application of shift reagent for the nmr. The differences in ppm on the nmr of the compound V in the presence of paramagnetic chelate complex $Eu(DPM)_3$ are also shown in Table 1. It is clear from the Table that cyclopropane ring protons (Hg and Hh) show the largest shift which indicate these protons located at the nearest position from the carbonyl oxygen.[8]

It is interesting the reaction modes of 8-oxoheptafulvene with benzophenone and tropones are completely different. The thermal 8 + 2 cycloaddition of tropone to unsaturated molecules has been known as well as 6 + 4 and 4 + 2 additions,[4,9] and it seems to common for 8-oxoheptafulvene to react as 2π component at 7,8 position[2] similar to ketenes. Therefore, it is considered that the adducts (V, VII and VIII) are concerted 8 + 2 cycloaddition products, but that the adduct (II) might be an isomerized product of 2 + 2 cycloaddition product (X) as in the case of the product of I and cyclopentadiene,[2] although the compound X could not be isolated. The similar 1,7-rearrangement has been postulated for the isomerization of spiro[2.6]nona-2,4,6-triene derivative to indane derivative.[10]

Norcaradiene compounds (V, VII and VIII) arouse our interest in the fact that they are new class of norcaradiene type compounds.[7,11] The study of norcaradiene cycloheptatriene tautomer of these compounds is in progress.

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