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8-OXOHEPTAFULVENE V. THE MECHANISTIC CONSIDERATION OF THE REACTION OF 8-OXOHEPTAFULVENE WITH 2-METHOXYTROPONES[1)]

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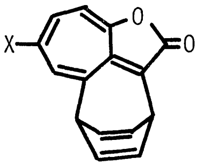
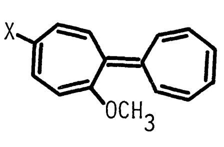
The results of the reactions of 4-isopropyl-, 3-deuterio-, and 7-deuterio-2-methoxytropones with 8-oxoheptafulvene support a mechanism of the formation of 1-oxaazulan-2-one containing cyclohexa-1,4-diene moiety at C-3 and C-4, which involves [2 + 2] cycloaddition, [1, 7] oxygen migration, [3, 3] rearrangement, and elimination of methanol.

We recently reported the formation of 1-oxaazulan-2-ones (1) containing cyclohexa-1,4-diene moiety, together with heptafulvalenes (2), dihydro-1-oxaazulan-2-ones (3) having norcaradiene moiety at 3-position, and methyl tropilidene-7-carboxylate (4) in the reaction of 8-oxoheptafulvene with 2-methoxytropones.[1)]



(1) X = H, Br



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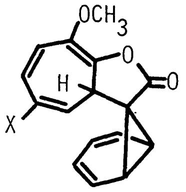

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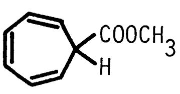
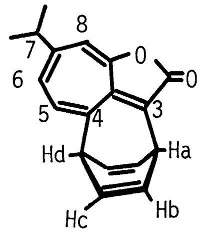


(4)

This observation of an unprecedented reaction has led us to investigate further the mechanism of the formation of (1).[2)] The reaction of 4-isopropyl-, 3-deuterio-, and 7-deuterio-2-methoxytropones with 8-oxoheptafulvene provide some evidence in support of our earlier mechanistic postulates.[1)]

Reaction of 4-isopropyl-2-methoxytropone[3)] (4.7 mmol) with 8-oxoheptafulvene,[4)] formed *in situ* by the reaction of tropilidene-7-carbonyl chloride (4.7 mmol) with triethylamine (6.0 mmol) in boiling n-hexane resulted in the formation of four products, (4)~(7) in 15.2, 19.8, 23.8, and 14.5%



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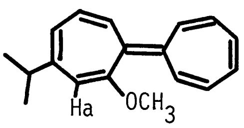

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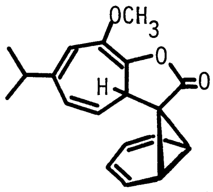

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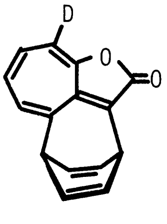

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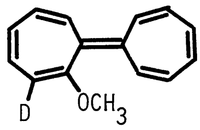

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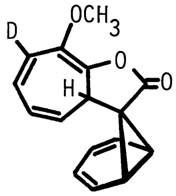

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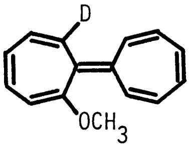

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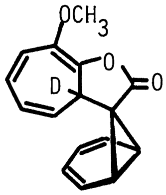

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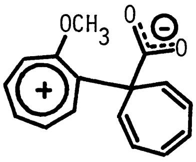

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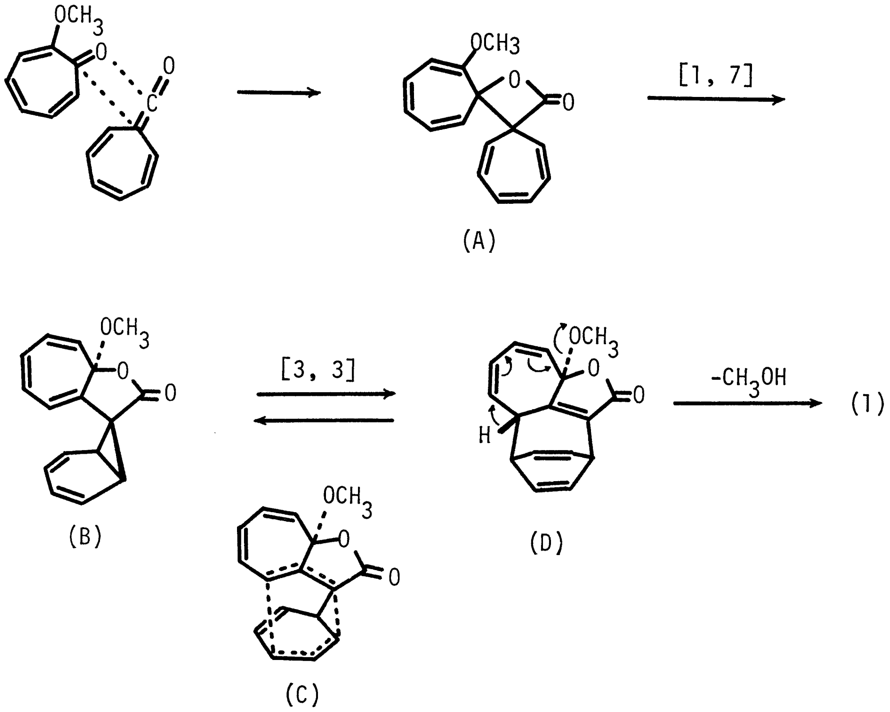

yield, respectively, whose separation was performed by column chromatography on silica gel. Physical data of the products are as follows; (5), orange prisms, mp 143~143.5°C, ir (KBr) 1725, 1745 cm^{-1}, uv $\lambda_{max}^{isooctane}$ 244 nm (logε 4.36), 253 (4.35), 394 (4.09), 410 (4.06), 454^{sh} (3.32), 490^{sh} (2.93), and 530^{sh} (2.32), nmr ($CDCl_3$) δ 3.93 (t,t, J = 6.4, 1.4 Hz, Hd), 4.04 (t,t, J = 6.4, 1.5 Hz, Ha), 6.05 (d,d,d, J = 7.5, 6.4, 1.4 Hz, Hc), and 6.39 (d,d,d, J = 7.5, 6.4, 1.5 Hz, Hb); (6), reddish oil, uv $\lambda_{max}^{isooctane}$ 235 nm (logε 4.30), 287 (3.80), and 352 (4.23), nmr (CCl_4) δ 3.55 (s, CH_3), 5.37 (bs, Ha), and 5.5~6.1 (m, 9H); (7), colorless oil, ir (neat) 1780 cm^{-1}.

The structures of these products were determined by the comparison of spectroscopic data with those of the compounds1,5) obtained from tropone or 2-methoxytropone as well as elemental analyses and mass spectra. The chemical shift and coupling constant of aromatic ring protons of the compound (5), ($CDCl_3$) δ 6.84 (d, J = 1.8 Hz, H-8), 6.67 (d,d, J = 9.5, 1.8 Hz, H-6), and 6.99 (d, J = 9.5 Hz, H-5), show that isopropyl group locates at C-6 or C-7 rather than at C-5. Furthermore, the position of C-6 can be excluded by the fact that 6-bromo derivative (1, X = Br), whose structure was determined by X-ray analysis,1) was obtained from 5-bromo-2-methoxytropone.

From the above result, it is found that cyclohexa-1,4-diene moiety of (5) is formed between the positions of carbonyl oxygen and C-7 of 4-isopropyl-2-methoxytropone. However, it would be possible that the cyclization occurred at C-7 due to steric influence of isopropyl group at C-4, therefore, the similar reaction was studied using monodeuterated 2-methoxytropones.

Reaction of 3-deuterio-2-methoxytropone6) with 8-oxoheptafulvene afforded the corresponding four products; (4) and (8)~(10), and 7-deuterio-2-methoxytropone6) also gave (1), (4), (11), and (12). The structures of these products were determined by the comparison of spectroscopic data with those of (1)~(4) (R = H), as well as mass spectra. Especially, the position of a deuterium atom in the compound (8) was determined to be C-8 by the analysis of 300 MHz nmr as shown in Fig. 1.

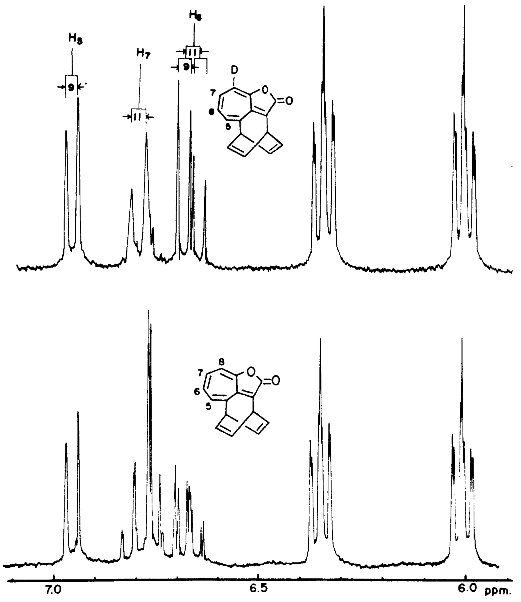

Fig. 1. Nmr spectra (partial) of compounds (1) and (8) in $CDCl_3$ at 300 MHz.

From the spectra, the chemical shifts and coupling constants of aromatic protons of compound (1, X = H) are determined as follows; H-5, δ 6.95, H-6, 6.67, H-7, 6.80, H-8, 6.75, $J_{5,6}$ = 9.0 Hz, $J_{5,7}$ = 1.0 Hz, $J_{6,7}$ = 11.0 Hz, $J_{6,8}$= 2.0 Hz, and $J_{7,8}$ = 9.0 Hz.

Above results are consistent with the fact that cyclohexa-1,4-diene moiety was formed between the positions of carbonyl oxygen and C-7 of 4-isopropyl-2-methoxytropone. They also provide the evidence to support a tentatively proposed mechanism for the formation of (1),$^{1)}$ involving [2 + 2] cycloaddition to (A), [1, 7] oxygen migration to norcaradiene intermediate (B), and [3s, 3s] sigmatropic shift to (D) followed by elimination of methanol. It is known that Cope rearrangement easily undergoes even at low temperature in sterically favorable system.$^{7)}$ The intermediate (B) would be ideally disposed to rearrange via quasi-boat transition state (C). Therefore, it is assumed that (B) could not be isolated contrary to the case of norcaradiene compound (3) which is formed by another pass; [1, 7] carbon migration of (A).$^{2)}$ However, we can not decide that the [1, 7] oxygen migration proceeds via either doubly concerted 1,5-shifts or ionic mechanism involving a intermediate (13). Recently, the similar [1, 7] migrations are also observed in tropilidene system.$^{4,8)}$

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