

8-OXOHEPTAFULVENE. IV THE REACTION WITH 2-METHOXYTROPONES

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Recently we reported the formation of 8-oxoheptafulvene (I) and its reaction with olefins and carbonyl compounds including benzophenone, tropones and benzotropones to give various adducts which were mainly resulted from a chemical property of ketene moiety of I.^{1,3}

On the reaction of I with 2-methoxytropones, we isolated 1-oxaazulanones having a novel cyclohexa-1,4-diene moiety, together with heptafulvalenes and dihydro-1-oxaazulanone derivatives, the results will be reported herein.

Reaction of 2-methoxytropone (II) with 8-oxoheptafulvene (I) formed *in situ* by the reaction of tropyl-7-carboxylic acid chloride with NEt_3 in n-hexane, followed by chromatography on silicic acid afforded four products, (III), (IV), (V) and (VI) in the yields of 7, 11.4, 12.3 and 28 %, respectively.⁴ The compound (III) was identified as methyl tropyl-7-carboxylate by direct comparison of ir with authentic sample. The physical data of the compound (IV-VI) were shown in Table 1. From the facts that uv of (IV) was very similar to those of heptafulvalene and its derivatives⁵ and that the reaction of I with benzotropones gave benzoheptafulvalenes in good yield,³ the compound (IV) was found to be 2-methoxyheptafulvalene.

The compound (V) was assumed to be methoxydihydro-1-oxaazulanone containing norcaradiene moiety from the similarity of spectroscopic data with those of norcaradiene compounds obtained by the reaction of tropones and I.² The uv of VI was similar to those of 1-oxaazulanones,⁶ and the double resonance experiments of the nmr of VI indicated the presence of novel cyclohexa-1,4-diene moiety. The structure of the compound (VI) was finally determined as shown in the scheme by the X-ray crystallographic analysis of its bromo-derivative obtained in the following reaction.

The reaction of I with 5-bromo-2-methoxytropone (VII)⁷ also afforded the similar four products (III), (VIII), (IX) and (X) in the yields of 12.1, 19.8, 8.7 and 25.6 %, respectively.

Table 1. Physical Properties of the Products

| Compounds | Color, mp | uv (nm, log ϵ) | ir (cm ⁻¹) | nmr (in CDCl ₃) [δ (ppm), J (Hz)] |
|-----------|----------------------------------|---|---------------------------|--|
| (IV) | reddish oil | 234 (4.43) ^a 284 (4.14) 354 (4.35) | 1623 ^d 1585 | 3.6 (3H, -OCH ₃) 5.42 (1H, d, J = 6, Ha) 5.6-6.3 (10H, m) |
| (V) | colorless prisms 84-85°C | 245 ^{sh} (3.81) ^b 270 ^{sh} (3.76) 315 ^{sh} (3.37) | 1782 ^e 1660 | 1.78 (1H, d,d, J = 5.0, 2.0, Ha) 3.12 (1H, d,d, J = 8.0, 5.5, Hd or He) 3.37 (1H, d,d, J = 8.0, 5.5, He or Hd) 3.70 (3H, -OCH ₃) 4.95 (1H, d,d, J = 9.0, 5.0, Hb) 5.87 (1H, d,m, J = 9.0, Hc) 6.0-6.5 (6H, m) |
| (VI) | orange sticks 194-194.5°C | 244 (4.32) ^b 255 ^{sh} (4.27) 389 (4.03) 410 (3.96) 436 ^{sh} (3.38) 470 (3.16) 506 (2.92) 548 (2.80) | 1751 ^e 1730 | 3.96 (1H, t,t, J = 6.2, 1.2, Hd) 4.05 (1H, t,t, J = 6.2, 1.5, Ha) 6.04 (2H, d,d,d, J = 7.7, 6.2, 1.5, Hc) 6.39 (2H, d,d,d, J = 7.7, 6.2, 1.2, Hb) 6.6-7.1 (4H, m) |
| (VIII) | unstable reddish oil | 298 (ca. 3.8) ^{c*} 368 (ca. 4.0) | 1613 ^d 1570 | 3.57 (3H, -OCH ₃) 5.27 (1H, d, J = 7.6, Ha) 5.57 (1H, d, J = 11.9, Hd) 5.7-6.1 (6H, m) 6.18 (1H, d,d, J = 11.9, 1.5, Hc) 6.51 (1H, d,d, J = 7.6, 1.5, Hb) |
| (IX) | colorless prisms 130-131°C | 253 ^{sh} (3.72) ^b 274 (3.70) 315 ^{sh} (3.42) | 1788 ^e 1650 | 1.91 (1H, d, J = 5.4, Ha) 3.11 (1H, d,d, J = 8.0, 5.4, Hd or He) 3.34 (1H, d,d, J = 8.0, 4.0, He or Hd) 3.71 (3H, -OCH ₃) 5.18 (1H, d, J = 5.4, Hb) 6.0-6.5 (6H, m) |
| (X) | orange sticks 234-235°C | 225 ^{sh} (4.10) ^b 250 (4.31) 382 ^{sh} (4.04) 396 (4.11) 406 ^{sh} (4.04) 415 ^{sh} (4.16) 445 ^{sh} (3.52) 478 (3.34) 516 (3.17) 560 (3.03) | 1740 ^e | 3.93 (1H, t,t, J = 6.5, 1.1, Hd) 4.07 (1H, t,t, J = 6.5, 1.7, Ha) 6.05 (2H, d,d,d, J = 8.0, 6.5, 1.7, Hc) 6.43 (2H, d,d,d, J = 8.0, 6.5, 1.1, Hb) 6.49 (1H, d, J = 10, Hg) 7.23 (1H, d,d, J = 10, 1.5, Hf) 7.24 (1H, d, J = 1.5, He) |

a, in EtOH; b, in isooctane; c, in CCl₄; d, neat; e, KBr disk

* Accurate intensity values could not be determined.

The structures of these compounds were determined as shown in the scheme from the similarity of the spectroscopic data (Table 1) with the corresponding compounds (IV-VI).

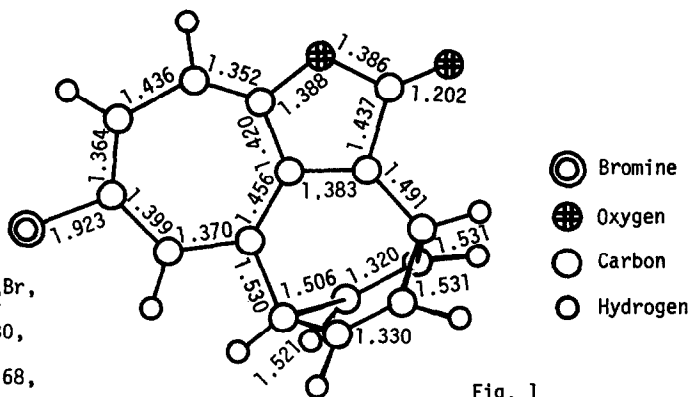
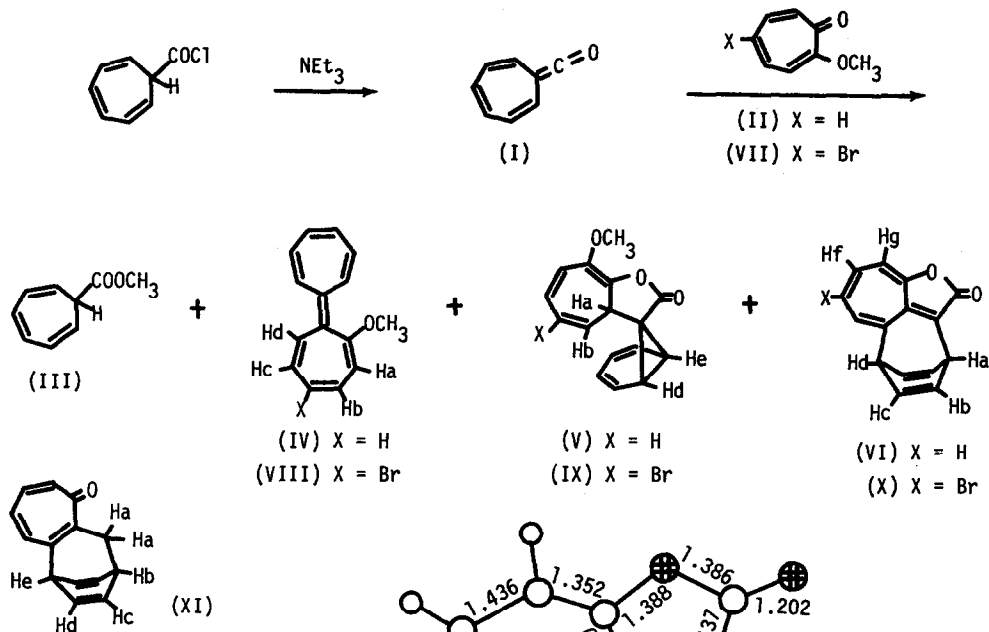


Fig. 1

Crystal data of λ : $C_{15}H_9O_2Br$,

$M = 301.14$, triclinic, $a = 10.680$,

$b = 8.184$, $c = 7.064$ Å, $\alpha = 100.68$,

$\beta = 89.56$, $\gamma = 110.00^\circ$, $D_c = 1.70$, $D_o = 1.72$ g/cm³,

$Z = 2$, space group $P1\bar{1}$. Three dimensional intensity data were collected on Rigaku-automated

controlled four circle diffractometer using Mo-K α radiation. The structure was solved by heavy

atom method. After block-diagonal least-squares refinements, final R factor is 0.063 for hy-

drogen atoms with isotopic thermal parameters and the other atoms with anisotropic. Perspec-

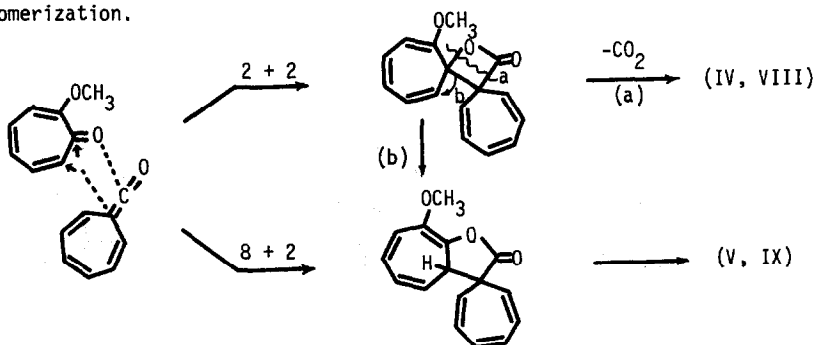
tive drawing of the molecule is shown in Fig. 1. A part of the diagram is quite similar to those of 1-oxaazulane derivatives.⁸

Alkaline hydrolysis of the compound (VI) followed by decarboxylation afforded tropone derivative (XI), mp 102-103°C, condensed with homobarrelene at 2 and 3 positions of tropone.

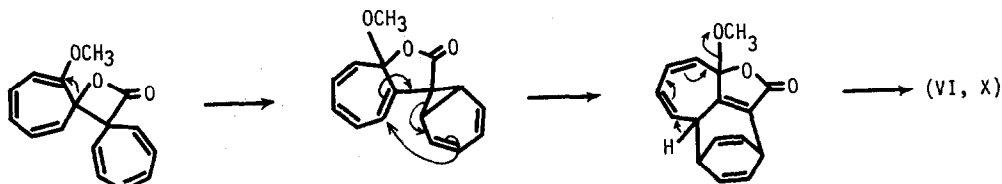
The spectroscopic data of XI are as follows, M^+ 196 (MS), ir (KBr) 1630 (m), 1550 (vs) and 1500 (s) cm⁻¹, uv $\lambda_{max}^{cyclohexane}$ 228 nm ($\log \epsilon$ 4.17), 314 (3.68), nmr (in CDCl₃) δ 2.71 ppm (2H,

d, $J = 3.8$ Hz, Ha), 3.30 (1H, m, Hb), 3.73 (1H, t,t, $J = 6.0, 1.5$ Hz, He), 6.30 (2H, d,d,d, $J = 8.0, 6.0, 1.5$ Hz, Hc), 6.48 (2H, d,d,d, $J = 8.0, 6.0, 2.0$ Hz, Hd) and 6.89 (4H, m).

The mechanism of the formation of heptafulvalenes and norcaradiene type compounds can be explained by 2 + 2 and/or 8 + 2 cycloaddition processes followed by decarboxylation or valence bond isomerization.



For the mechanism of the formation of (VI and X) involving novel rearrangement, we tentatively propose the following scheme starting from 2 + 2 cycloadduct followed by rearrangement of tropilidene and elimination of methanol, and the study of the mechanism is now progressive. It is obvious that the compound (III) is derived from the reaction of I or starting chloride with the eliminated methanol.



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