

8-OXOHEPTAFULVENE VI. FURTHER REACTIONS OF 8-OXOHEPTAFULVENE WITH SEVERAL
TROPONE DERIVATIVES

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We have reported that the reaction of 8-oxoheptafulvene with tropone and its derivatives afforded several products including (2 + 8)cycloadducts with cycloheptatriene and norcaradiene moieties, heptafulvalenes, and 1-oxaazulan-2-ones with cyclohexa-1,4-diene moiety at 3 and 4-positions, and we have also discussed the mechanisms of the formation of these products.^{1,2)}

Further reactions of 8-oxoheptafulvene with several tropone derivatives were studied and we have found that other new reactions concerning the adducts, the results will be reported in this communication.

The reaction of 2-acetoxytropone (2)³⁾ with 8-oxoheptafulvene (1) formed *in situ* by the reaction of tropyl-7-carboxylic acid chloride and triethylamine afforded 1-acetoxyheptafulvalene (3) (yield: 8.5%) and (2 + 8)cycloadduct (4) (44.4%). On the other hand, the reaction of 1 and 2-tosyloxytropone (5) gave 1-chloroheptafulvalene (6) (9.5%) and (2 + 8) cycloadduct (7) (49.2%). The compound (6) was identified by the direct comparison of nmr spectrum with that of 1-chloroheptafulvalene obtained from 2-chlorotropone as minor product.⁴⁾ The formation of (6) can be explained by the substitution of tosyloxy group of the initially formed 2-tosyloxyheptafulvalene (8) with chloride ion formed from tropyl-carboxylic acid chloride and triethylamine. An alternative explanation which consists of the initial formation of 2-chlorotropone from 2-tosyloxytropone⁵⁾ followed by the reaction with 8-oxoheptafulvene (1) can be ruled out because the reaction of 2-chlorotropone with 1

has been known to give (2 + 8)cycloadduct substituted with chlorine atom as major product.^{1,4)} The nucleophilic substitution is the first example in heptafulvalene series although the detailed reaction mechanism is not clear.

The pattern of the reaction of 2-dimethylaminotropone (9) with 1 was found to be completely different from those of 2 and 5, and the reaction gave 3-phenyl-1-oxaazulan-2-one (10) (21.8%) and a cage molecule (11) (7.4%), both compounds were identified by direct comparison of the spectroscopic data with those of the authentic specimens.²⁾

The direct formation of 10 is the first example in the reaction of tropones and 1, and the mechanism can be explained by the elimination of dimethylamine involving a cleavage of cyclopropane ring from the (2 + 8)cycloadduct (12) which is formed by the cycloaddition between the C-2 and carbonyl oxygen of 2-dimethylaminotropone (9) with 1 as shown in the scheme. All the hitherto known (2 + 8)cycloadducts were formed between C-7 and carbonyl oxygen of 2-substituted tropones. The same intermediate (12) can be possibly formed from (2 + 2)cycloadduct (13) by [1,7]rearrangement of C-C bond of β -lactone.^{2,6)}

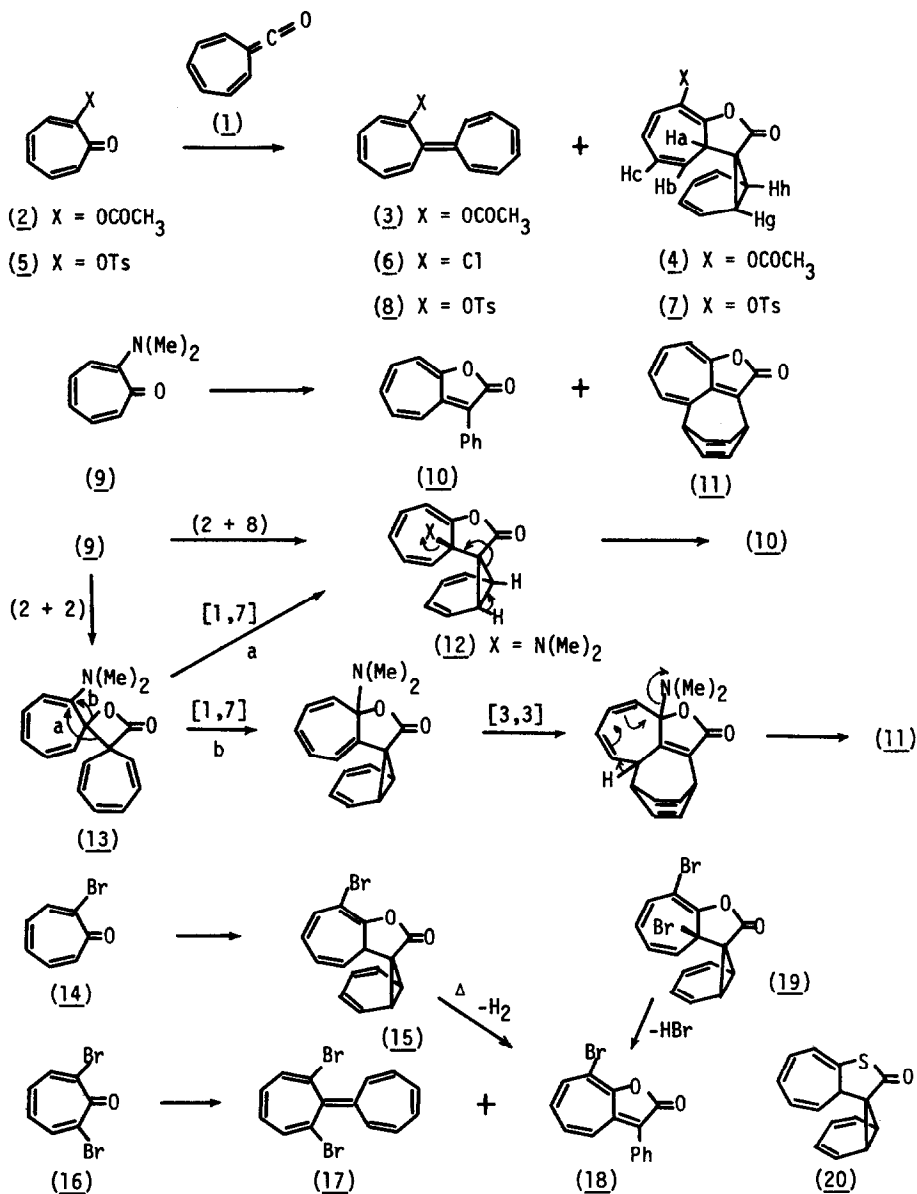
The formation of (11) is also explained by the mechanism which consists of the [1,7] rearrangement of C-O bond of β -lactone of the intermediate (13) followed by Cope rearrangement and elimination of dimethylamine as has been observed in the reaction of 2-methoxytropone and 1.²⁾

The reaction of 2-bromotropone (14) with 1 afforded only (2 + 8)cycloadduct (15) in a quantitative yield. However, 2,7-dibromotropone (16) yielded 1,6-dibromoheptafulvalene (17) (8.4%) and 8-bromo-3-phenyl-1-oxaazulan-2-one (18) (57%),⁷⁾ the latter compound was also obtained by the heating of compound 15 at around 150°C in an air which involved an antarafacial [1,7] sigmatropic rearrangement followed by a dehydrogenation.⁸⁾ Compound (18) is considered to be formed by the dehydrobromination from the initially formed (2 + 8)cycloadduct (19) as in the case of 2-dimethylaminotropone. 1,6-Dibromoheptafulvalene (17) was so unstable that it was not completely characterized.

The reaction of troponethione with 1 afforded only (2 + 8)cycloadduct (20) (15.3%).

From the above results as well as from the results already been reported,²⁾ it is clear that 8-oxoheptafulvene (1) reacts with tropones as 2π component similarly to ketenes, and all of the products could be rationalized by the initial formation of (2 + 2)cycloadducts and successive [1,7]rearrangements of various bonds.

Physical data of the new compounds are shown below; see structure (4) for abbreviations.



(3): unstable reddish oil. Ir (neat), 1760 cm⁻¹; λ_{max} (EtOH), 233 nm (log ε, 4.32), 351 (4.25); nmr (CCl₄), δ 2.01 (s, CH₃), 5.6-6.3 (m, 11H).

(4): colorless micro needles, mp 164-165°C. Ir (KBr), 1786, 1760 cm⁻¹; nmr (CDCl₃), δ 1.96 (dd, J=4.5, 1.5 Hz, Ha), 2.20 (s, CH₃), 3.09 (ddm, J=8.0, 5.5 Hz, Hg or Hh), 3.32 (ddm, J=8.0, 5.5 Hz, Hh or Hg), 4.92 (dd, J=10.0, 4.5 Hz, Hb), 5.94 (dddd, J=10.0, 5.0, 2.0, 0.5 Hz,

Hc), 6.05-6.5 (m, 6H).

(6): unstable reddish oil. λ_{\max} (EtOH), 238 nm (log ϵ , 4.31), 353 (4.25); nmr (CCl₄), δ 5.5-6.4 (m).

(7): colorless needles, mp 143-144°C. Ir (KBr), 1790 cm⁻¹; nmr (CDCl₃), δ 1.72 (dd, J=4.5, 1.7 Hz, Ha), 2.43 (s, CH₃), 2.97 (dd, J=8.0, 5.7 Hz, Hg or Hh), 3.26 (dd, J=8.0, 5.0 Hz, Hh or Hg), 4.78 (dd, J=9.5, 4.5 Hz, Hb), 5.92 (ddt, J=9.5, 4.5, 1.7 Hz, Hc), 6.15-6.55 (m, 6H), 7.3 and 7.76 (broad AB-quartet, 4H).

(15): colorless needles, mp 152-153°C. Ir (KBr), 1796 cm⁻¹; nmr (CDCl₃), δ 1.90 (dd, J=4.5, 1.5 Hz, Ha), 3.11 (dd, J=8.0, 5.6 Hz, Hg or Hh), 3.35 (dd, J=8.0, 5.0 Hz, Hh or Hg), 4.84 (dd, J=9.0, 4.5 Hz, Hb), 5.8-6.6 (m, 7H).

(17): unstable reddish oil. λ_{\max} (EtOH), 240 nm, 350.

(18): scarlet needles, mp 197-198°C. Ir (KBr), 1770 cm⁻¹; λ_{\max} (EtOH), 240 nm (log ϵ , 4.30), 270^{sh}, 279 (4.27), 400 (4.23); nmr (CDCl₃), δ 6.55 (ddd, J=11.7, 8.5, 1.0 Hz, 1H), 6.87 (ddd, J=11.0, 8.5, 1.0 Hz, 1H), 7.18 (dt, J=11.7, 1.0 Hz, 1H), 7.3-7.7 (m, 6H).

(20): colorless plates, mp 131-132°C. Ir (KBr), 1645 cm⁻¹; nmr (CCl₄), δ 1.70 (dm, J=5.5 Hz, Ha), 2.90 (dd, J=9.0, 5.5 Hz, Hg or Hh), 3.28 (dd, J=9.0, 5.5 Hz, Hh or Hg), 4.73 (dd, J=9.0, 5.5 Hz, Hb), 5.8-6.6 (m, 8H).

References and Footnotes

- 1) N. Morita, T. Asao, and Y. Kitahara, *Tetrahedron Lett.*, 869 (1972); T. Asao, N. Morita, and Y. Kitahara, *Synthetic Commun.*, 2, 353 (1972).
- 2) T. Asao, N. Morita, C. Kabuto, and Y. Kitahara, *Tetrahedron Lett.*, 4379 (1972); N. Morita, T. Asao, N. Iwagame, and Y. Kitahara, *Chem. Lett.*, 67 (1973).
- 3) Recently rapid and reversible migrations of acyl groups between two oxygen atoms have been found for 2-acyloxytropone derivatives: S. Masamune, A. V. Kemp-Jones, J. Green, D. L. Rabenstein, M. Yasunami, K. Takase, and T. Nozoe, *Chem. Commun.*, 283 (1973); V. I. Minkin, L. P. Olekhovich, Yu. A. Zhdanov, Z. N. Budarina, and V. P. Metlusenko, *Tetrahedron Lett.*, 563 (1974).
- 4) We have reported that 2-chlorotropone reacts with 8-oxoheptafulvene to give only (2 + 8) cycloadduct, however we found the reaction afforded a very minute amount of 1-chloroheptafulvalene besides the adduct.
- 5) It has been known that the reaction of 2-tosyloxytropones with hydrochloric acid afforded 2-chlorotropones: W. von E. Doering and C. F. Hiskey, *J. Amer. Chem. Soc.*, 74, 5688 (1952); T. Nozoe, T. Asao, E. Takahashi, and K. Takahashi, *Bull. Chem. Soc. Japan*, 39, 1310 (1966).
- 6) E. E. Waali and W. M. Jones, *J. Amer. Chem. Soc.*, 95, 8114 (1973).
- 7) The reactivity of 2,7-dibromotropone to 1 is less than that of 2-bromotropone, and about half of the starting tropone was recovered.
- 8) N. Morita, T. Asao, and Y. Kitahara, in preparation.