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# PYROLYSES OF THE $C_{11}H_{10}O$ AND $C_{12}H_{12}O$ KETONES[1]
## TWO TYPES OF THERMAL 6-π ELECTRON REARRANGEMENTS OF THE PENTACYCLIC BIS-HOMOTROPILIDENES

Tsutomu Miyashi, Heizan Kawamoto and Toshio Mukai*
Department of Chemistry, Faculty of Science, Tohoku University,
Sendai, 980 Japan

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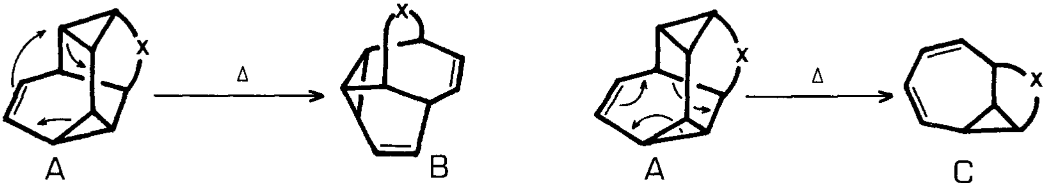
In general, cyclic compounds containing the cyclopropyl-vinylcyclopropane ring system, upon thermolysis, undergo an internal [2π + 2σ + 2σ] cycloaddition reaction,[2] regardless of whether the second cyclopropane ring conjugates with the double bond or not. The pyrolysis of one of bis-homotropilidenes, pentacyclo[$5.5.0.0^{2,12}.0^{6,8}.0^{3,9}$]dodeca-4,10-diene (A, X = -C=C-)[2b] is unexceptional and undergoes the homo Cope rearrangement[3] of the cyclopropyl-vinylcyclopropane system to afford the tetracyclic hydrocarbon, tetracyclo[$5.5.0^{2,4}.0^{3,10}$]dodeca-5,8,11-triene (B, X = -C=C-) even though the retro-Diels-Alder reaction would be expected to give the tricyclic hydrocarbon, tricyclo[$5.5.0.0^{2,12}$]dodeca-3,5,8,10-tetraene (C, X = -C=C-C=C-) which is of interest as a potential precursor of tricyclo[$5.5.0.0^{4,10}$]dodeca-2,5,8,11-teraene.[4] This recent communication[2b] prompts us to report our results on the investigation of pyrolyses of the skeletally related bis-homotropilidenes (1 and 2).

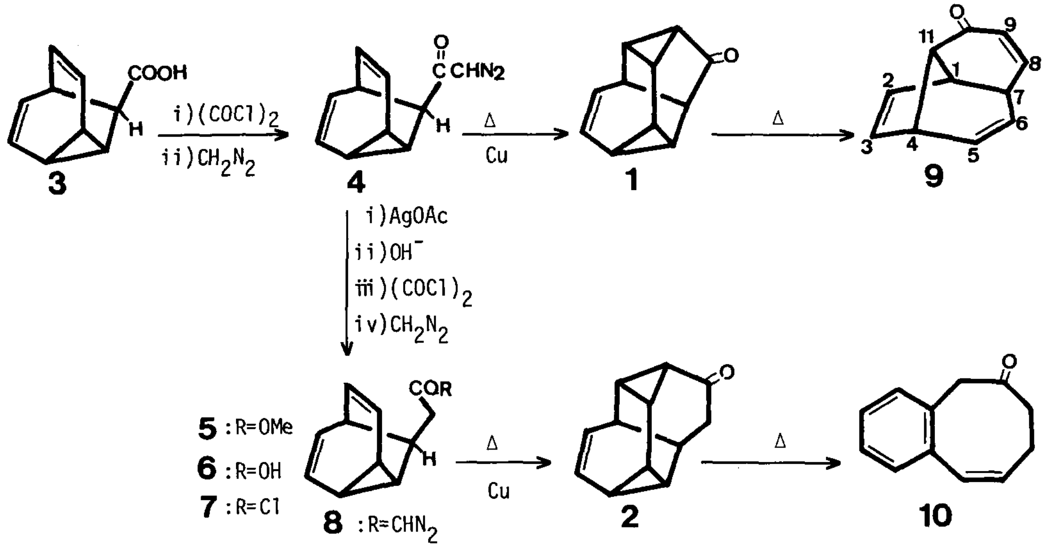


We wish to report here a marked difference in thermal behavior between these two compounds that the $C_{11}H_{10}O$ ketone (1) containing the cyclopentanone ring undergoes the retro-Diels-Alder reaction such as A → C, while the cyclohexanone homologue, the $C_{12}H_{12}O$ ketone (2) behaves differently and instead, undergoes the homo Cope rearrangement such as A → B.

Both bis-homotropilidenes (1 and 2) were prepared starting from the readily accessible carboxylic acid (3)[5] in good yields. Chlorination with oxalyl chloride followed by diazomethylation afforded the diazoketone (4)[7] in 83% yield from (3). Copper-catalyzed decomposition of (4) in refluxing tetrahydrofurane yielded the novel $C_{11}H_{10}O$ ketone, tetracyclo-[$5.4.0.0^{2,11}.0^{6,8}$]undeca-3-en-9-one (1), mp 68°C, in 73% yield. The structure of (1) was unequivocally determined by the spectral properties [$\nu_{max}^{KBr}$, 1725 $cm^{-1}$; m/e, 158 ($M^+$), 130, 129 (100%), 115, 78; NMR ($\delta$ in $CDCl_3$), 6.30 (ddd, 10.0, 6.8, 1.0 Hz, 1H), 6.04 (dd, 10.0, 6.8 Hz, 1H), 3.0 (m, 1H), 1.90 ~ 2.20 (m, 4H), 1.55 ~ 1.80 (m, 3H)].

Similarly, the $C_{12}H_{12}O$ ketone, tetracyclo[$5.5.0^{2,11}.0^{6,8}$]dodeca-3-en-9-one (2)(mp 115°C)[2b] was prepared from the diazoketone (8)[8] which was, however, derived from (4) by the different way from the previous one[2b] as shown in Scheme I.

(Scheme I)

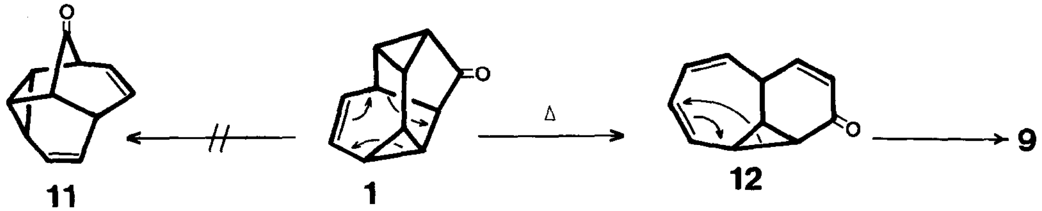


The $C_{11}H_{10}O$ ketone (1) was relatively stable to heating around at 300°C, but the isomeric trienone, tricyclo[$5.4.0.0^{4,11}$]undeca-2,5,8-trien-10-one (9) was obtained as the sole product in 84% yield upon thermolysis at 400°C in a flow system. The structure of (9) was discerned from its spectral data [$\nu_{max}^{CHCl_3}$, 1680 $cm^{-1}$; $\lambda_{max}^{EtOH}$, 214.5 nm (log $\varepsilon$ = 3.90); m/e, 158 ($M^+$), 130, 129 (100%), 115, 78], and definitively, spin decoupling of individual resonance provided the complete assignment of the nmr spectrum (Table I). The fact that neither a homo Cope rearrangement product such as (11) nor its secondary pyrolysis product was found indicates that

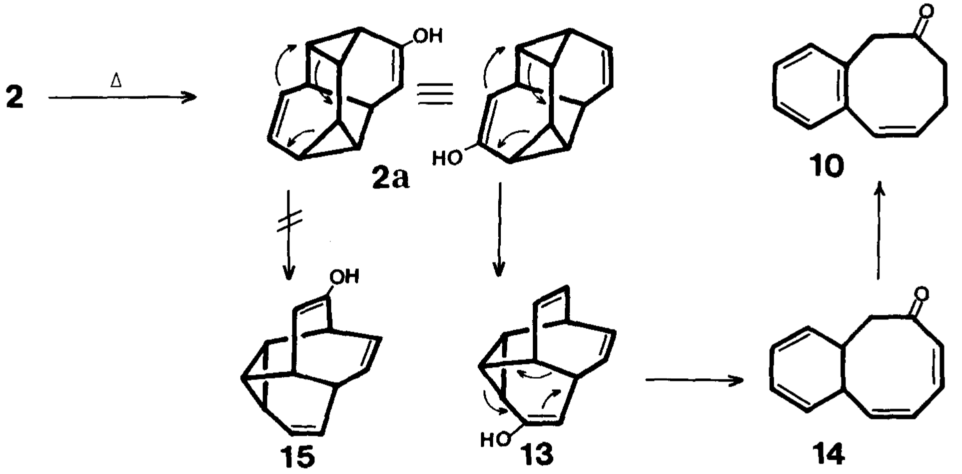
Table I. NMR Spectrum of (9)

| Assignment | $\delta$ (ppm) | Appearance (Hz) | Assignment | $\delta$ (ppm) | Appearance (Hz) |
|---|---|---|---|---|---|
| $C_1$-H | 2.70-3.15 | multiplet | $C_7$-H | 2.70-3.15 | multiplet |
| $C_2$-H | 5.66 | ddd(d=6.0,3.0,1.0) | $C_8$-H | 6.80 | ddd(J=10.0, 5.0, 1.0) |
| $C_3$-H | 6.58 | dd(J=6.0,3.0) | $C_9$-H | 6.06 | dd(J=10.0,0.8) |
| $C_4$-H | 2.70-3.15 | multiplet | $C_{11}$-H | 2.70-3.15 | multiplet |
| $C_5$-H | 6.13 | ddd(J=9.0,6.0,1.0) | | | |
| $C_6$-H | 5.40 | dddd(J=9.0,6.0,1.6,1.0) | | | |

the pathway to give (9) is exclusive in the pyrolysis of (1). Thus, the formation of (9) can be rationalyzed by the initial retro-Diels-Alder reaction to give tricyclo[5.4.0.0$^{2,11}$]undeca-3,5,8-trien-10-one (12) followed by the 1,3-sigmatropic rearrangement of (12) to (9). Although the trienone (12) was not isolated, thermolabile character of (12) would be feasible, considering thermal behavior of its isomeric ketone, tricyclo[5.4.0.0$^{2,11}$]undeca-3,5,9-trien-8-one.[9] The rearrangement of (12) to (9) also provides sharp contrast to the low energy thermal process observed in the 8-carboethoxyl derivative of (12).[10]



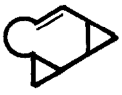
On the contrary to the $C_{11}H_{10}O$ ketone (1), the homologated ketone (2) exhibited the different type of the rearrangement upon thermolysis at 400°C to afford benzocyclooctenone (10) in 80% yield [$\nu_{max}^{neat}$, 1705 cm$^{-1}$; $\lambda_{max}^{EtOH}$, 243 nm (log ε = 2.92); m/e, 172 ($M^+$), 144, 129 (100%); NMR (δ in $CDCl_3$), 6.64 (d, J=12.0 Hz, 1H), 6.00 (m, 1H), 3.80 (s, 2H), 2.42 (m, 4H), 7.20 ( m, 4H)]. The exclusive formation of (10) from (2) suggests that the homo Cope rearrangement observed in the pyrolysis of (A, X = -C=C-)[2b] takes place regiospecifically in the enol form (2a). The subsequent retro-Diels-Alder reaction[2b] of (13) to (14) followed by the succesive 1,5-hydrogen shifts result in the formation of (10).



A remarkable difference in thermal behavior observed in the pyrolyses of bis-homotropilidenes (1 and 2) could be ascribed to the difference of the ring strain imposed. Thus, the retro-Diels-Alder reaction involving cleavage of the inner α,β-bond of the cyclopentanone ring becomes operatative in the more strained $C_{11}H_{10}O$ ketones. The rearrangements of the $C_{11}H_{10}O$ ketones (1 and 12) are also intriguing from a stand points of the energy surface of the increasing number of thermolabile $C_{11}H_{10}O$.[11]

## References and Notes

1) Organic Thermal Reactions XXXIX, Part XXXVIII, T. Miyashi, A. Hazato, and T. Mukai, J. Am. Chem. Soc., **99**, (1977).
2) a) The typical example is the retro-Diels-Alder reaction of bis-homobenzenes.
   H. M. Whitlock, Jr., and P. F. Schatz, J. Am. Chem. Soc., **93**, 3837 (1971). See also Ref. 2b, references cited therein.
   b) E. Vedejs and R. A. Shepherd, J. Org. Chem., **41**, 742 (1976).
3) In order to distinguish the rearrangement of the cyclopropyl-vinylcyclopropane system (16) in which the second cyclopropane ring does not conjugate with the double bond from the retro-Diels-Alder reaction of the bis-homobenzene system (17), the rearrangement of (16) is termed the homo Cope rearrangement in this report since that is rather resemble the Cope rearrangement of the cis-divinylcyclopropane system.


(16)


(17)

4) R. B. Woodward and R. Hoffman, "The Consrvation of Orbital Symmetry", Verlag Chemie GmbH, Weinheim/Berg str., 1970, p 106.
5) The carboxylic acid (3)(mp 109°C) was prepared by oxidation ($Ag_2O$) of 9-aldehydetricyclo-[3.3.1.$0^{2,8}$]nona-3,6-diene$^6$ in 92% yield.
6) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones,Jr., G. Klump, R. M. Rubin and M. Saunders, Tetrahedron, **23**, 3943 (1967).
7) The diazoketone (4) was prepared by chlorination with oxalyl chloride (88.5%) followed by diazomethylation (93.7%).
8) The diazoketone (8) was prepared by following procedures. Silver acetate-catalyzed Wolff rearrangement of (4) in methanol gave (5) in 71.8%. Hydrolysis of (5) by sodium hydroxide in aqueous methanol gave (6) in quantitative yield. Chlorination of (6) with oxalyl chloride (67%) followed by diazomethylation (90%) gave (8). Copper-catalyzed decomposition of (8) gave (2) in 60% yield [$\nu_{max}^{KBr}$, 1670 $cm^{-1}$; m/e, 172 ($M^+$, 38%), 144, 129 (100%), 115, 94; NMR (δ in $CDCl_3$), 2.69 (dd, 18.0, 3.0 Hz, 1H), 2.60 (dd, 18.0, 4.0 Hz, 1H), 2.00 (broad s, 1H), 1.20-1.90 (m, 6H), 6.00-6.15 (m, 2H)].
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10) E. Vedejs and W. R. Wilber, Tetrahedron Lett., 2679 (1975).
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