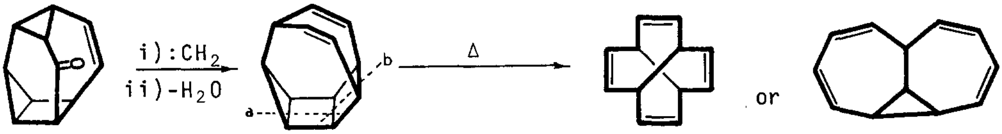
Tetrahedron Letters No. 2, pp 155 - 158.

0040-4039/79/0108-0155$02.00/0

SYNTHESES AND REARRANGEMENTS OF $C_{11}H_{10}O$ KETONES DERIVED FROM HOMOOCTAVALENE - II[1]
NOVEL SYNTHESIS AND THERMAL REARRANGEMENT OF 9-DEUTERIOTRICYCLO[5.4.0.$0^{2,11}$]UNDECA-3,5,9-TRIEN-8-ONE

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

As part of our synthetic approaches to an intriguing hitherto unknown $(CH)_{12}$ hydrocarbon, tricyclo[5.5.0.$0^{4,10}$]dodeca-2,5,8,11-tetraene (3),[3] an approach starting from the $C_{11}H_{10}O$ ketone (1)[2] is under our studies. One of important steps in this approach is whether a bond cleavage-a easily takes place or not in the hydrocarbon (2) since (4) expected by a bond cleavage-b has been presumed not to undergo the Cope rearrangement to give (3)[4] (Scheme I).



1 2 3 4

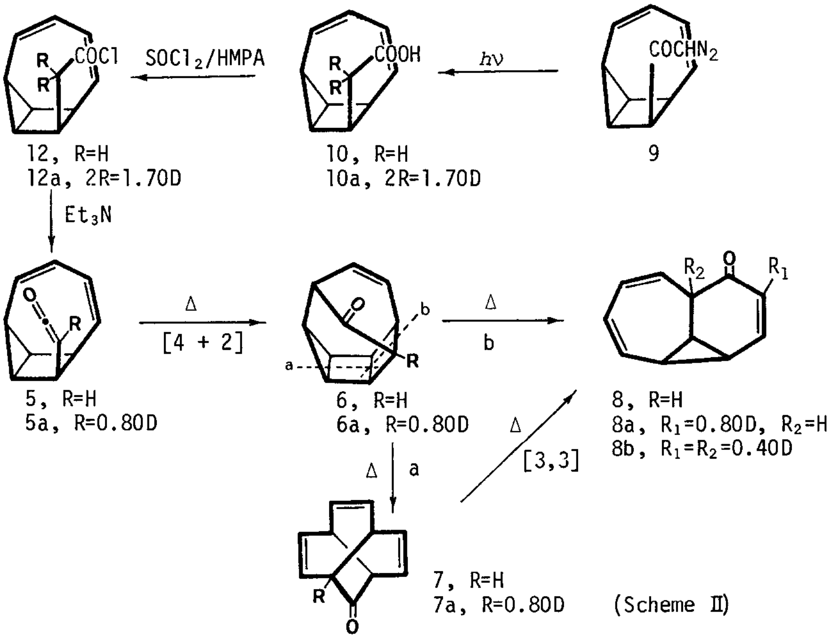
(Scheme I)

In order to test this possibility, model experiments were carried out in the $C_{11}H_{10}O$ ketone (6) which has structural similarities to (2) and is expected to be formed by an internal Diels-Alder reaction of the $C_{11}H_{10}O$ ketene (5) (Scheme II). Herein we wish to report our findings that the ketene (5) isomerizes with ease to tricyclo[5.4.0.$0^{2,11}$]undeca-3,5,9-trien-8-one (8)[5] possibly through an internal [4 + 2]-cycloaddition of (5) to (6) followed by a facile bond cleavage-b in (6), and also report the structural and energetic interrelationships in a family of the ketone(8).

The ketene (5) was prepared from the carboxylic acid (10)[6] which was synthesized by irradiation (350 nm) of the diazoketone (9)[2] in an aqueous dioxane in 30% yield together with a complex mixture of several neutral products.[7] The acid chloride (12) was prepared by treatment of (10) with $SOCl_2$-HMPA at 0°C. Treatment of (12) with triethylamine in refluxing ether afforded (8) in 70% yield from (10) which was proved to be identical with the authentic one[5] by comparisons of their spectral data.

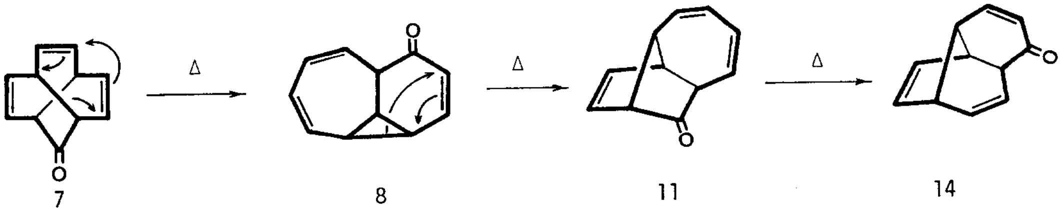
For this facile formation of (8) from (5), two mechanisms can be considered. One is a bond cleavage-a in (6) to give (7) followed by the retro-Cope rearrangement[5] to (8). On the other hand, an alternative bond cleavage-b gives (8) directly (Scheme II). In connection with our approach to (3) from (2), it is inevitable to know which bond cleavage, a or b, actually took place in (6). For this purpose, the labeled carboxylic acid (10a) (2R=1.70D) was prepared by deuteriation of the methyl ester of (10) with $NaOCH_3$ in CH_3OD followed by hydrolysis with NaOD

in CH_3OD-D_2O.
Integration of the signals appearing in the shifted spectra[8] of the product (8a) showed the location of 0.80D only at the C_9 position. This fact suggests the remarkably facile bond cleavage-b in (6) since an alternative bond cleavage-a leading to (7a) followed by the retro-Cope rearrangement must give the disubstituted analog (8b). If this mechanism[9] is correct, the direct formation of (3) from (2) seems unfeasible, but instead one of (4) is encouraged.



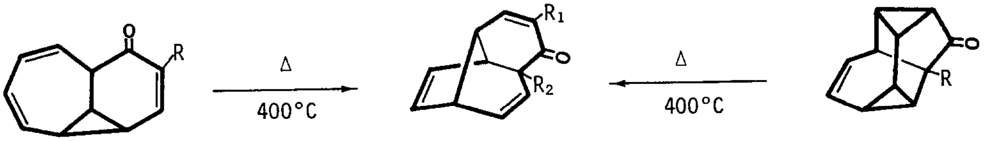
(Scheme II)

In addition to this novel synthesis of (8), pyrolysis of the labeled ketone (8a) is also of interest in connection with the structural and energetic interrelationships in a family of the ketone (8). Concerning the structural one, the thermal rearrangements, (7) → (8) → (11), has been reported by Aumann.[5] Additionally, we found the further rearrangement of (11) to (14)[11] when (11) was prrolyzed at 400°C.



(Scheme III)

This structural interrelationship among (7), (8), (11) and (14) reminds us of one presumption that (7), (8) and (11) may serve as intermediates during the rearrangement of (15) to (14) reported in our previous report.[2] In order to know this possibility, pyrolysis of (8a) was carried out at 400°C. The shifted nmr spectra[8] of the pyrolysis product (14a) reveals the deuterium distribution at two positions, i.e., 0.37D at C_7 and 0.53D at C_9.



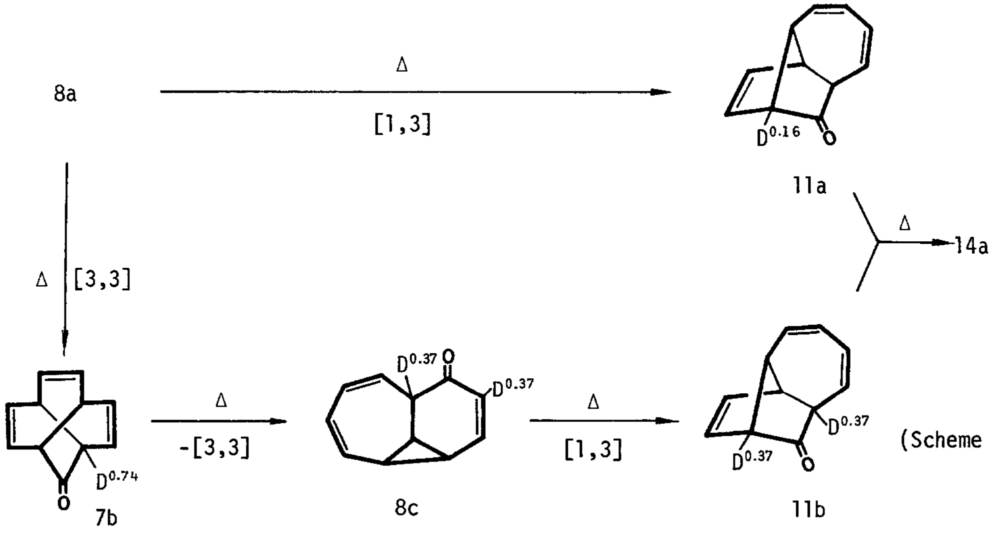
8a, R=0.80D

14a, R_1=0.53D
R_2=0.37D
14b, R_1=0.77D
R_2=0.21D

15, R=H
15a, R=0.96D

(Scheme IV)

This pyrolytic result, in particular, the location of deuteriums, provides a similar result observed in pyrolysis of (15a) to (14b)[2] and can not be accounted for either by the vinylketene mechanism[11] or by a simple transformation such as (8) → (11) → (14).[12] One of intriguing features in this labeling experiment is the ratio of deuterium at the C_7 and C_9 positions which is not unity and can not be explained by a single mechanism. A plausible mechanism for this involves two reaction pathways, a minor one of the direct formation of (11a)[4,5] and a sequence of the Cope rearrangement of (8a) to (7b) and the retro-Cope rearrangement[5] of (7b) leading to (8c) followed by the rearrangement of (8c) to (11b)[5] as a major pathway. Then, (11a) and (11b) rearrange to (14a) (Scheme V). This result provides an unexceptional Cope rearrangement of *cis*-divinylcyclopropane in the tricyclo[5.4.0.0^{2,11}]undeca-3,5,9-triene system.[4] More detail studies on the thermal rearrangement of (8a) and the structural and energetic interrelationships among (7), (8), (11) and (14) will be reported soon elsewhere.



(Scheme V)

References

1) Organic Thermal Reactions, Part XLVI. Part XLV, see Ref. 2.

2) T. Miyashi, T. Nakajo, H. Kawamoto, K. Akiyama, and T. Mukai, the proceeding paper. see also, T. Miyashi, T. Sugiyama, T. Nakajo, and T. Mukai, *Tetrahedron Lett.*, 3903 (1976).

3) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., Germany, 1970, p 106.

4) E. Vedejs, W. R. Willer, and R. Twieg, *J. Org. Chem.*, 42, 401 (1977).

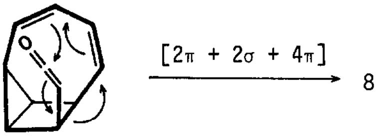
5) R. Aumann, *Chem. Ber.*, 110, 1434 (1977).

6) (10): mp 78°C; ν_{max}^{KBr}, 3100-2900, 1720 cm^{-1}; λ_{max}^{EtOH}, 276 nm (ε, 2011); m/e, 176 (M^+, 3.7%), 131, 118 (100%); nmr (100 MHz, in $CDCl_3$), δ1.87 (C_1-H, ddd, *J*=6.0, 4.0, 6.0Hz), 1.48 (C_2-H, ddd, *J*=6.0, 6.0, 5.0Hz), 6.30 (C_3-H, ddd, *J*=6.0, 11.0, 1.5Hz), 5.75 (C_4-H or C_5-H, ddd, *J*=7.0, 11.0, 1.5Hz), 5.97 (C_5-H or C_4-H, ddd, *J*=7.0, 11.0, 1.5Hz), 5.63 (C_6-H, ddd, *J*=11.0, 8.0, 1.5 Hz), 3.35 (C_7-H, ddd, *J*=8.0, 10.0, 4.0Hz), 3.19 (C_8-H, ddt, *J*=10.0, 4.0, 7.0Hz), 2.03 (C_9-H, ddd, *J*=6.0, 5.0, 4.0Hz), 2.52 (C_{10}-H, dd, *J*=7.0, 1.5Hz), 10.8 (-COO$\underline{H}$, s).

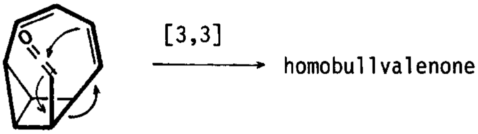
7) One of those was proved to be identical with tricyclo[5.4.0.0^{2,9}]undeca-3,5,10-trien-8-one (11)[5] (6%) by comparisons of their spectral data.

8) Shift reagent experiments were carried out by means of 100 MHz using Eu(fod)$_3$ in $CDCl_3$.

9) The third mechanism, a direct formation of (8) from (5) through a [2π + 2σ + 4π] process,[11] can not be ruled out completely. However, this mechanism seems unfeasible since another low energy pathway expected in this system, the Cope rearrangement[10] of (5) leading to homobullvalenone[11] should take place more rapidly than or at least in an enough rate to compete with this process.



5



5

10) T. Miyashi, A. Hazato, and T. Mukai, *J. Am. Chem. Soc.*, 100, 1008 (1978).

11) M. J. Goldstein and S. -H. Dai, *J. Am. Chem. Soc.*, 95, 933 (1973). In this mechanism, the C_2 position in (14) must be also deuteriated.

12) In this mechanism, deuterium locates only at the C_9 position.

(Received in Japan 6 October 1978)