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SYNTHESES AND REARRANGEMENTS OF $C_{11}H_{10}O$ KETONES DERIVED FROM HOMOOCTAVALENE - I[1]
COPPER-CATALYZED DECOMPOSITION OF HOMOOCTAVALENYLDIAZOMETHYLKETONE

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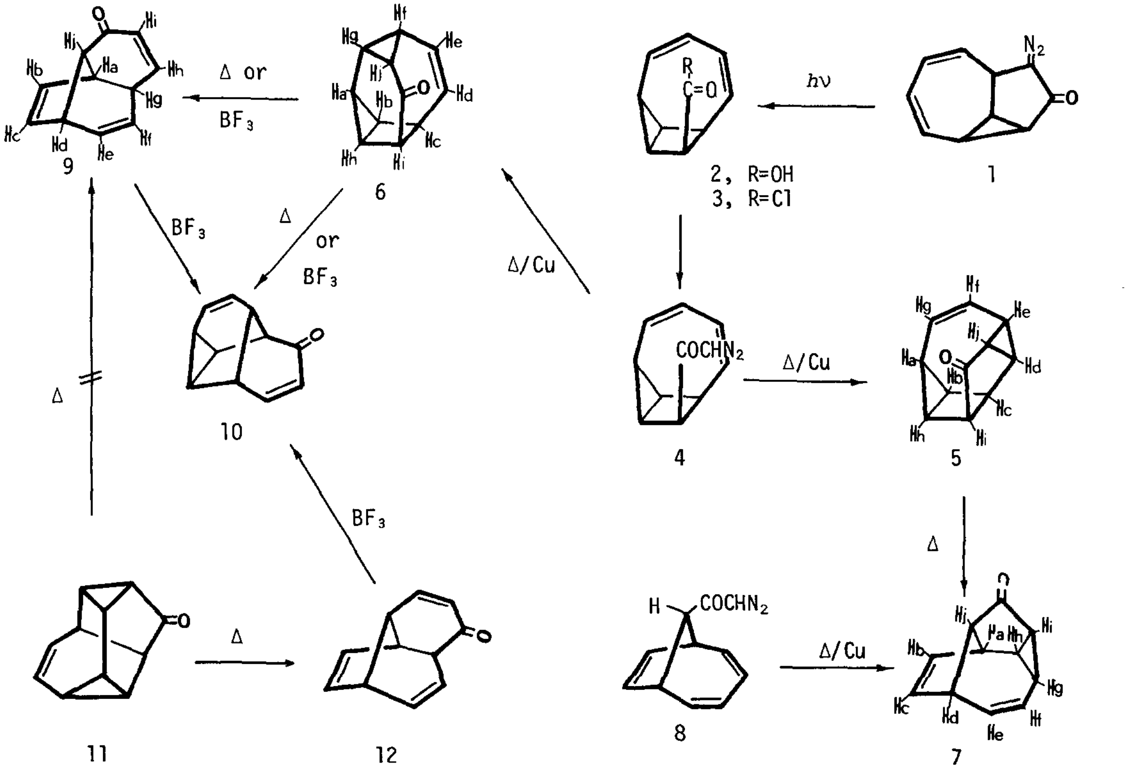
In recent years, much attention has been focused on syntheses and rearrangements of reactive $C_{11}H_{10}O$ ketones[2~9] which are of interest as potential precursors for $(CH)_{11}^{+}$ cations[10~13] and $(CH)_{12}$ hydrocarbons.[14] In the present and following[14] papers, we wish to report syntheses, thermal and BF_3-catalyzed rearrangements of several $C_{11}H_{10}O$ ketones derived from the readily accessible *endo*-8-carboxytricyclo[5.2.0.0^{2,9}]nona-3,5-diene (2).[15] In this paper, we also report the revised structure of the pyrolysis product of (11) which was previously assigned to (9).[16]

The carboxylic acid (2) was prepared by photolysis of the diazoketone (1)[15] in 45% yield. Chlorination of (2) with $SOCl_2$-HMPA was the most successful method to give (3) [ν_{max}^{neat}, 1800 cm^{-1}]

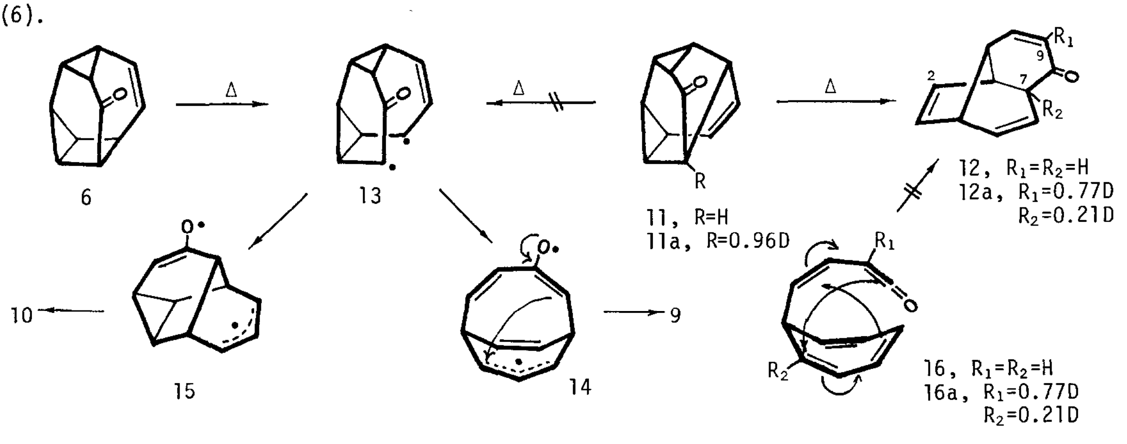


and diazomethylation gave (4) (85% yield from (2)) [mp 59°C; ν_{max}^{KBr}, 2100, 1630 cm^{-1}; λ_{max} (cyclohexane), 250 nm (log ε, 4.04), 275 (3.98), 380 (1.43); nmr, see ref. 17]. Copper-catalyzed decomposition of (4) in refluxing THF gave two new $C_{11}H_{10}O$ ketones, (5) [mp 58°C; ν_{max}^{KBr}, 1710 cm^{-1} ; λ_{max} (cyclohexane), 250 nm (log ε, 2.94)] and (6) [mp 79°C; ν_{max}^{KBr}, 1668 cm^{-1}] in 35.3 and 46.7% yields, respectively. The structures of these ketones were determined by spin decouplings in normal and shifted nmr spectra shown in Table I.

In order to know the structural interrelationship among the hitherto known $C_{11}H_{10}O$ ketones, thermal and BF_3-catalyzed rearrangements of (5) and (6) were studied. Treatment of (5) with BF_3 etherate resulted in the formation of an extremely complex mixture of unseparable several products. Pyrolysis of (5) in benzene at 200°C, however, gave the isomeric new ketone (7)[18] in 95% yield as a sole product [mp 64°C; ν_{max}^{KBr}, 1725 cm^{-1}; λ_{max} (cyclohexane), 225 nm (log ε, 3.35)], which structure was confirmed by its nmr spectrum shown in Table I and the independent synthesis from the diazoketone (8).[19] The ketone (7), however, appears to be very stable both to BF_3 and heating even at 450°C.

On the other hand, the ketone (6) was found to be more labile both to BF_3[21] and heating as compared with (5). Thus, upon treatment with BF_3 etherate, (6) spontaneously isomerized to the new ketone (9) (15%) [ν_{max}^{neat}, 1670 cm^{-1}; λ_{max} (cyclohexane), 220.5 nm (log ε, 3.72), 270.5 (3.13)] and the known ketone (10) (75%).[6~10] Furthermore, the ketone (9) was found to isomerize slowly to (10) upon prolonged treatment with BF_3 etherate via a similar mechanism[8] in the rearrangement of (12) to (10). Similarly, pyrolysis of (6) at 160°C in benzene gave (9) and (10) in 28 and 60% yields, respectively. The thermal interrelationship between (9) and (10), however, was not observed. The structure of the new ketone (9) was unambiguously determined by spin decouplings of normal and shifted nmr spectra (Table I). In connection with the structure of (9), we previously reported that pyrolysis of (11) gave (9).[16] However, the comparison[22] of the nmr spectrum of the pyrolysis product of (11) with those of (9) and the authentic (12)[3] provides that the pyrolysis product of (11) is not (9) but (12).

For the rearrangement of (6) to (9) and (10), the initial bond cleavage leading to a diradical (13) followed by further rearrangements to (9) and (10) through respectively diradicals (14) and (15) is most plausible. Similarly, zwitter ion intermediates corresponding to diradicals (14) and (15) probably generate and isomerize to (9) and (10) in the BF_3-catalyzed rearrangement of (6).



On the other hand, evidence that the structurally related ketone (11) does not afford either (9) or (10) suggests that a bond cleavage takes place in an entirely different manner from (6). One possible mechanism would involve the formation of the vinylketene (16)[3] either from (11) directly or from any isomeric intermediate(s) generated during the rearrangement of (11) to (12). In order to gain some insight into the mechanism, the labeled ketone (11a)[2,3] was synthesized and pyrolyzed at 400°C. Integrations and spin decouplings of the signals appearing in shifted nmr spectra showed that 0.21D and 0.77D locate at the C_7 and C_9 positions, respectively. If the vinylketene mechanism[3] which was established by Goldstein in the rearrangement of homobullvalenone to (12) operates in this case, a vinylketene such as (16a) must be generated and cyclize only at the designated sites in (16a) in a completely regiospecific manner which is impossible to occur. The fact that deuteriums locate only at the C_7 and C_9 positions suggests the generation of a certain symmetrical intermediate other than the vinylketene (16) during the rearrangement. Full details of further studies to elucidate this rearrangement will be reported soon elsewhere.

Table I. Normal and Shifted[a] NMR Spectra of (5), (6), (7) and (9) (100 MHz)

	(5)		(6)		(7)		(9)		
	δ and J^b	s^e	δ and J^c	s	δ and J^c	s	δ and J^d	δ and J^c	s
Ha	1.28(ddd) ab:6.0 ag:8.5	2.4	0.95(ddd) ab:5.0 ag:8.5	3.6	3.63(m) ah:7.0 aj:7.5	5.1	2.62(m) ab:3.0 aj:6.0	2.60~2.83	4.0
Hb	1.84~2.35 bc:6.0 bh:6.0	2.4	1.25(ddd) bc:4.0 bh:5.0	3.6	5.90(m) bc:6.0	3.8	5.42(dd) bc:5.5	5.70(dd)	1.7
Hc	3.40(ddd) ci:12.0 cd:6.0	3.2	2.79(m) ci:10.0 cd:8.0	5.2	5.70(dd) cd:3.0	3.2	6.32(dd) cd:2.5	6.63(dd)	1.8
Hd	1.84~2.35 dj:9.0	3.2	5.40(dd) de:11.0	3.6	3.65(m) dj:7.0 de:3.0	5.1	2.74~2.84 de:7.0 dj:6.0	2.83~3.10	5.8
He	1.84~2.35 ej:6.0	3.2	5.72(ddd) ef:7.0 ec:1.5	3.6	5.80(dd) ef:6.0	2.3	5.73(dd) ef:9.5	5.98(dd)	2.7
Hf	5.82(dd) ef:6.0 fg:12.0	2.8	1.41(ddd) fg:8.0 fj:9.0	4.0	5.90(dd) fg:3.0	3.8	5.14(dd) fg:4.5	5.41(dd)	2.5
Hg	5.60(dd)	2.8	1.66(ddd) gj:8.5	4.0	2.00(m) gi:7.0	4.9	2.13(m) ag:2.5 gh:7.0	2.60~2.83	2.7
Hh	1.84(ddd) ah:6.0 hi:6.0	3.2	1.80(ddd) hi:4.0 ha:5.0	4.4	2.00(m) hi:7.0	4.9	6.78(dd) hi:9.5	7.35(dd)	2.6
Hi	3.04(ddd) ij:2.0	9.6	3.18(ddd) ij:1.0	14.8	2.30(dd)	11.2	5.99(dd) ig:1.5	5.98(dd)	9.8
Hj	2.36(ddd)	7.2	1.95(ddd)	14.8	3.00(dd)	14.8	2.74~2.84	2.83~3.10	10.5

[a] Eu(fod)$_3$; [b] in $CDCl_3$; [c] in CCl_4; [d] in C_6D_6; [e] slope of Δppm/([Eu(fod)$_3$]/[substrate])

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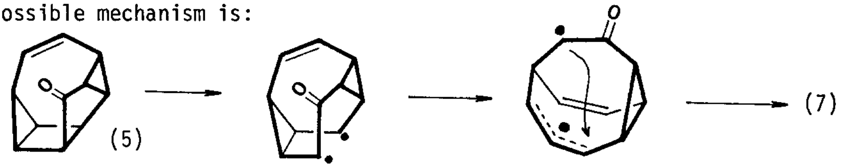
17) (4): δ 2.06~2.20 (C_1 and C_9-H, J_{19}=5.0 Hz, J_{12}=5.0, J_{29}=5.0), 1.72 (ddd, C_2-H, J_{23}=5.0), 6.16 (dd, C_3-H, J_{34}=11.0), 5.60~6.0 (C_4, C_5, C_6-H), 3.25~ 3.60 (C_7 and C_8), 5.32 (s, $-C\underline{H}-N_2$).

18) One possible mechanism is:



19) The diazoketone (8) was prepared from the corresponding carboxylic acid.[20]
20) J. B. Press and H. Schechter, *J. Org. Chem.*, **40**, 2446 (1975).
21) For instance, (5) rapidly isomerized to (9) and (10) even in $CDCl_3$.
22) The authors are indebted to Professor M. J. Goldstein for the comparison of the nmr spectrum of (12) with that of the authentic sample and also for helpful suggestions relating to the structure of the pyrolysis product from (11).
23) The labeled ketone (11a) was prepared from 9-deuterio-9-carboxybarbaralane by the same procedure reported in our previous report.[16]

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