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REARRANGEMENTS OF $C_{11}H_{10}O$ KETONES CATALYZED BY BORON TRIFLUORIDE

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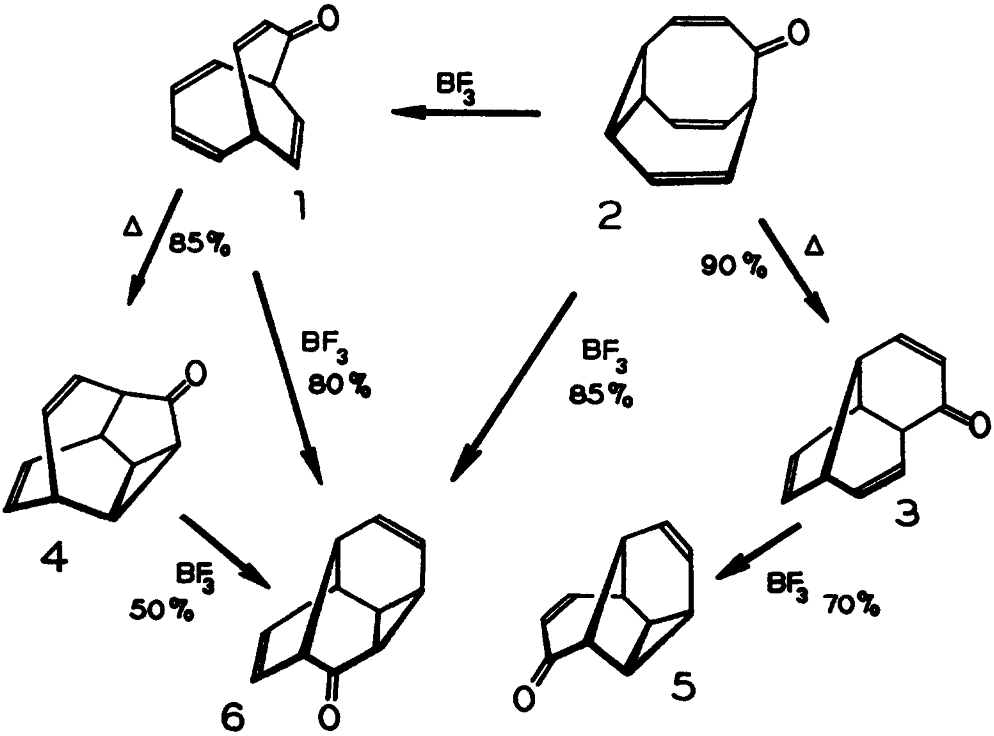
We[1] and others[2] have been elaborating the structural and energetic interrelationships among the family of $C_{11}H_{10}O$ ketones 1^{2d}, 2^{2a}, 3^{1a}, 4^{1b}, and 5^{2b}. We report here several new interconversions catalyzed by boron trifluoride and a new isomer, 6, which appears to be one of the most stable members described to date.

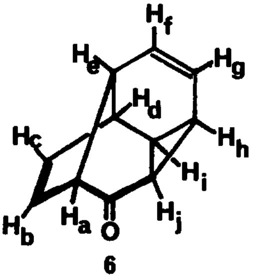
Scheme I



Treatment of homobullvalenone (**2**) with boron trifluoride etherate at room temperature for three hours afforded an 85% yield of an isomeric ketone **6** after initial formation of **1**. The structure of **6** became apparent after scrutiny of its spectral data[3]. Particularly definitive was the Eu(fod)$_3$-shifted[4], 100 MHz pmr spectrum (Table I) which revealed the proximity of the carbonyl function to a bridgehead hydrogen (H_a) and a cyclopropyl hydrogen (H_j). Spin decoupling of the normal and shifted spectra led to unambiguous assignment of the skeletal bond connectivity. In addition, the observed intra-vinyl hydrogen coupling constants, $J_{b,c}$=5.8 Hz and $J_{f,g}$=9.4 Hz, are characteristic of five- and six-membered rings, respectively[5].

Table I· PMR Spectrum of **6**[a]

δ	H_a	H_b	H_c	H_d	H_e	H_f	H_g	H_h	H_i	H_j	Apparent Multiplicity	Δ^b_{Eu}
H_a	3.06	3.8			3.8						t	3.4
H_b		6.05	5.8								d, d	1.4
H_c			6.75	3.0							d, d	0.76
H_d				2.32	4.8				8	1.5	t, m	0.54
H_e					3.06	8.2			1.8		q, m	0.81
H_f						6.04	9.4	1.7			d, d	0.85
H_g							6.32	5.8			d, d	0.81
H_h								2.49	4.5	6.7	t, m	0.67
H_i									2.13	6.7	d, m	0.85
H_j										2.13	t	3.3



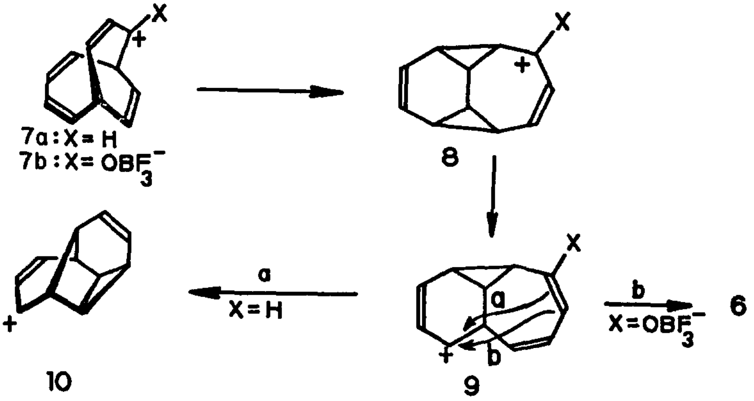
6

a) Diagonal elements are chemical shifts (δ) obtained in CDCl$_3$; off diagonal elements are coupling constants (Hz) assigned by selective decoupling, b) for Eu(fod)$_3$ in CDCl$_3$.[6]

Examination of ketones 1, 3, and 4 under similar reaction conditions revealed the transformations 1 → 6, 3 → 6, and 4 → 5 (Scheme I) in good to moderate yields.[7] The conversion of 1 to 6 upon treatment with BF_3 is particularly surprising since the parent carbonium ion (7a) has been reported to afford 10,[2b] a carbonium ion corresponding to 5. A convenient explanation for this behaviour may be obtained from the known chemistry of 1.[1b] Intramolecular Diels-Alder addition of 7 and cyclopropylcarbinyl homoallyl rearrangement of the resulting ion leads to 9. In the absence of a directing group, transannular alkylation of 9 would be expected to follow path a affording the known ion 10 as observed. In contrast, path b should be preferred when the diene has a pendant oxygen ($X{=}OBF_3^-$) and the rearrangement is thus diverted to 6 That the intramolecular cycloaddition 7 → 8 should occur at room temperature in the presence of BF_3 while the thermal reaction requires more stringent conditions ($\tau_{1/2}$=4.75 Hr)[1b] is intriguing and suggestive of a lowering of the energy barrier for addition[2d] by virtue of the proximate allylic cation[8]

Reasonable carbonium rearrangements of BF_3 adducts of 3 and 4 also lead to ion 9, differing only in the position of oxygen substitution[9] Again the expected oxygen directive effect leads to 6 from 4 and to 5 from 3, as observed. The details of these and other $C_{11}H_{10}O$ transformations and the inferred generality of intermediate 9 are under continued study.

Scheme II



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3. Tetracyclo[5.4.0.0^{2,11}. 0^{4,8}]undeca-5,9-dien-3-one (6) m.p. 66.5-67°; *M/e* 158.0731±0.0004, calcd for $C_{11}H_{10}O$ 158.07316, (relative intensity) (45 eV) 158(19.4), 130(100), 115(65.8), ir(CCl_4) 3042, 2932, 1702, 1127, 922, 926, 889, 699, 681 cm^{-1}, UVλ_{max} (cyclohexane) 203 (304), 214(752), 222(1152), 239(464), 298(64) nm

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7. Given the synthetic economy of these transformations and the ready availability of 7^{1b}, reasonable quantities of all of these isomers, 1—6, are now accessible.

8. The driving force for the conversion of 7 to 8 may derive from electronic stabilization of 8 which is a bishomotropilium ion, c.f. P. Ahlberg, D. L. Harris, S. Winstein, *J. Amer. Chem. Soc.*, 92, 2146 (1970).

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