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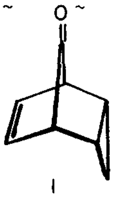
SYNTHESIS AND THERMAL DECARBONYLATION OF *ENDO*-6,7-BENZOTRICYCLO-[3.2.1.$0^{2,4}$]OCTEN-8-ONE

Merle A. Battiste* and Melean Visnick
Department of Chemistry, University of Florida
Gainesville, Florida 32611

The first definitive evidence for the marked stereoelectronic effect exerted by a cyclopropane ring in thermal chelotropic reactions was reported from this laboratory in 1967.[1] *endo*-Tricyclo[3.2.1.$0^{2,4}$]octen-8-one (1) was observed to thermally extrude carbon monoxide with surprising ease compared to the corresponding exo-isomer 2 which did not differ materially in reactivity from 7-norbornenone (3).[2] Subsequent kinetic investigation[3] established the 1/2 (or 1/3) rate factor to be *ca.* 10^6. It was also noted[1] that the *exo*-benzotricyclooctenone (4) underwent decarbonylation only with great difficulty (70% reaction after 1 hr. at 400°).[1,4] These observations were rationalized on the basis of the orbital topography of C_2-C_4 bond which is appropriate for stabilization of the decarbonylation transition state for ketone 1, but not for the exo cases 2 and 4.



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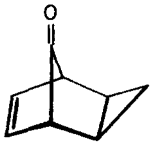

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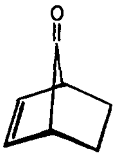

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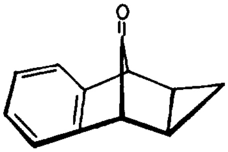
	1	2	3
$\Delta G^{\ddagger}$ (kcal/mole)	23.5_4	32.6_8	31.9_5
Solvent	C_6D_6	$(C_6H_5)_2O$	C_6D_6
$k^{35°}_{rel}$	$10^{6.5}$	1.0	3.3

In subsequent years other examples of cyclopropyl assisted extrusion reactions have been reported, most notably, the tricyclic azo compounds 5[5] and 6[6]. Compared to their respective model systems 7 and 8 nitrogen extrusion from 5 and 6 is remarkably facile exhibiting rate factors of 10^{11} (5/7)[5] and 10^{17} (6/8).[6] The magnitude of the rate enhancements observed for 5 and 6 was surprising at first considering the more modest (10^6) rate enhancement for ketone 1. The nitrogen extrusion reaction would appear to provide a more sensitive measure of cyclopropyl assistance than carbonyl extrusion, however the azo systems are saturated while ketones 1-3 contain a π-center. It is possible, then, that the double bond in 1 exerts a leveling effect on the extent of cyclopropyl participation in decarbonylation. To test this suggestion we have prepared endo-6,7-benzotricyclo[3.2.1.0^{2,4}]octen-8-one (**9**) and measured its rate of thermal decarbonylation for comparison with the corresponding exo ketone **4**.



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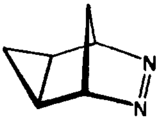

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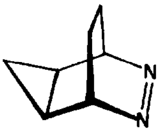

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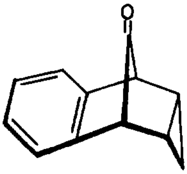

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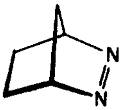

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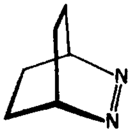

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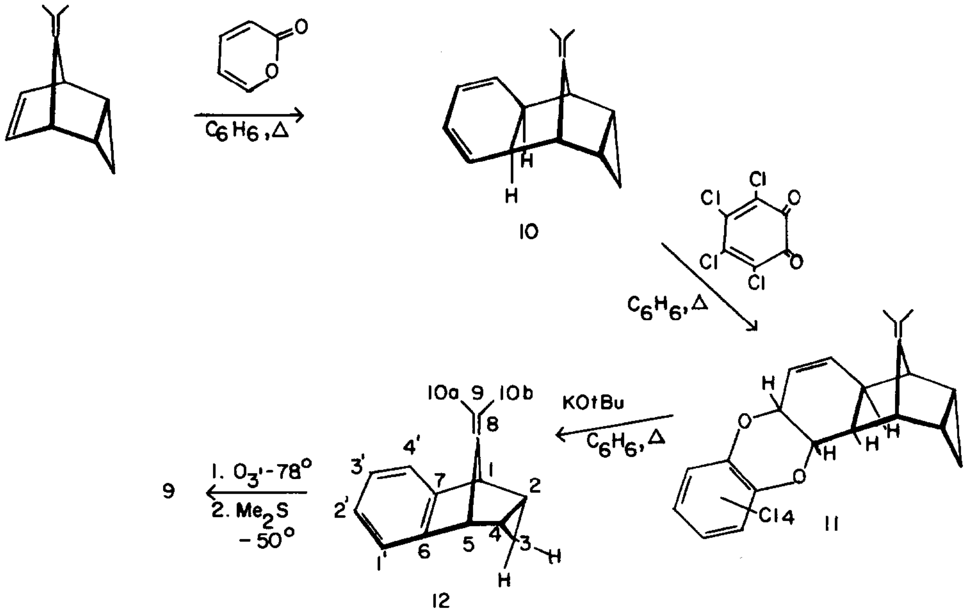
Synthetic entry into the endo-benzotricyclo[3.2.1.0^{3,4}]octene skeleton has previously been achieved for the parent hydrocarbon only, and then in very low yields from cuprous halide-diazomethane cyclopropanation of benzonorbornadiene (exo/endo ratio 10-20).[7,8] Our synthetic route to **9** is outlined in Chart I. The starting material for this synthesis is the endo adduct of 6,6-dimethylfulvene and cyclopropene.[9] Reaction of this adduct with α-pyrone in refluxing benzene afforded hydrocarbon **10**[10] in 70% yield.

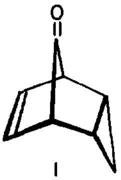
Chart I



The dihydroaromatic 10 was surprisingly resistant to direct aromatization attempts using DDQ, chloranil, *o*-chloranil, sulfur, and palladium-on-charcoal. Decomposition and/or recovery of starting material was observed for all attempts with exception of the tetrachlorobenzoquinone reactions in which crystalline (4+2) cycloadducts were obtained. The precise stereochemistry of both of these adducts has not been rigorously established, but the *o*-chloranil adduct 11, obtained in quantitative yield, clearly has the 1,4-dioxene structure shown.[11]

Despite the failure of the dehydrogenation attempts adduct 11 proved to be a useful precursor of the desired hydrocarbon 12 by virtue of the labile allylic aryl ether grouping. Thus treatment of 11 with excess potassium tert-butoxide in refluxing benzene afforded 12[10] in 60% yield. The stereochemistry of 12 was confirmed by the exceptionally high field position of the *endo*-C-3 proton which appeared as a sharply defined pentet at δ-0.70. The conversion of 10 into 12 via adduct 11 therefore constitutes a novel alternative to dehydrogenations utilizing high-potential quinones.

Ozonization of 12 in ethyl acetate at -78°C followed by quenching with excess dimethyl sulfide at -50° to -60°C afforded, after workup and alumina chromatography, a 60% yield of ketone 9,[10] m.p. 44-45°. Ketone 9 is reasonably stable towards decarbonylation having a half-life of 5-6 hrs. at 95°. The kinetic parameters for thermal decarbonylation of 9 are given in Table I. Compared to ketone 1 and its saturated analog 13, the annelated ketone (9) has intermediate activity. The reactivity series 1:9:13 provides a useful quantitative demonstration of the annelation effect in a chelotropic reaction. Finally a comparison of the rate of decarbonyltion of 9 with that estimated for the corresponding *exo* ketone 4 (ca. 3.5 x 10^{-4} sec^{-1} at 400°;



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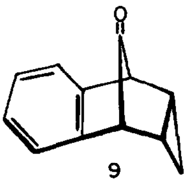

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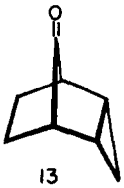

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ΔG‡	23.5_4	29.2_3	33.4_1
solvent	C_6D_6	C_6D_6	1,2,4-$Me_3C_6H_3$
$k^{35°}_{rel}$	10^7	10^3	1.0

Table I. Kinetic Parameters for Thermal Decarbonylation of *endo*-6,7-Benzotricyclo[3.2.1.$0^{2,4}$]-octen-8-one (9) in Benzene-d_6^a

T°,C	10^5k(sec^{-1})	ΔG‡(kcal/mol)	ΔH‡(kcal/mol)	ΔS‡(e.u.)
95.4	3.29 ± 0.05	29.28		
100.4	6.16 ± 0.03	29.22	32.0	7.3
106.1	11.6 ± 0.2	29.19		

[a] Kinetic points were obtained by nmr integration of the well separated and decreasing bridgehead proton multiplet of 9 against the increasing methylene triplet of 3,4-benztropilidene. Use of an internal standard established that the formation of 3,4-benztropilidene from 9 was essentially quantitative.

$\Delta G^{\ddagger} \cong 51$ kcal/mol) leads to a 9/4 rate factor of about 10^{15} which is well within the range of *endo*-cyclopropyl acceleration reported for azo compounds 5 and 6. The true magnitude of cyclopropyl assistance to carbon monoxide extrusion has thus emerged in the reactivity of ketone 9 while it is partially masked by the double bond in 1. The nature of this leveling effect in 1 apparently has its origin in the maximum allowed accumulation of bonding at the original C-1, C-5 bridgehead carbons.

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References and Footnotes

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10. Correct elemental analyses were obtained for all new compounds. If not otherwise mentioned nmr, mass, and infrared spectra were in accord with assigned structures.
11. (a) Although tetrahalogen o-quinones are known to function as carbodienes as well as oxadienes[11b] it is interesting to note that no 1,2-diketone adduct was detected in the reaction of 10 with *o*-chloranil. (b) For a review see G. Pfundt and G. O. Schenk in "1,4-Cycloaddition Reactions", Ed. J. Hamer, Academic Press, Inc., New York, 1967, pp. 345-417.
12. Cf. R. E. Keay and G. A. Hamilton, *J. Am. Chem. Soc.*, 97, 6876 (1975), and references cited therein.

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