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METHYL SUBSTITUENT PROBE OF THE TRANSITION STATE FOR THERMAL DECARBONYLATION OF ENDO-TRICYCLO[3.2.1.$0^{2,4}$]OCTAN-8-ONE

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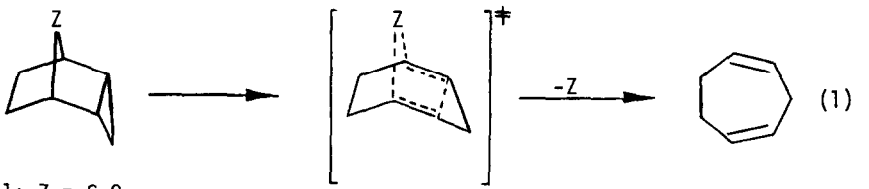
Summary. Methyl substituent probes at the C-2 and C-2,C-4 positions of endo-tricyclo[3.2.1.$0^{2,4}$]octan-8-one(1) have provided kinetic evidence confirming the simultaneity of C-2,C-4 cyclopropane bond cleavage in the rate-determining step for thermal extrusion of carbon monoxide.

The extraordinary stereoelectronic effect of the cyclopropyl ring in thermal cheletropic and related extrusion processes has been increasingly documented since the original quantitative evidence reported in 1967.[1] In the correct molecular topography the kinetic influence of a cyclopropyl group can be dramatic as revealed in the extrusion reactions of ketone 1[2] and its aza-analog 2.[3] Thus 1 extrudes carbon monoxide at a rate only a factor of 10 less than that of its unsaturated homolog, 7-norbornenone, while the rate factor for nitrogen extrusion from 2 compared to its appropriate model, 2,3-diazabicyclo[2.2.2]oct-2-ene, is an impressive 10^{17}.

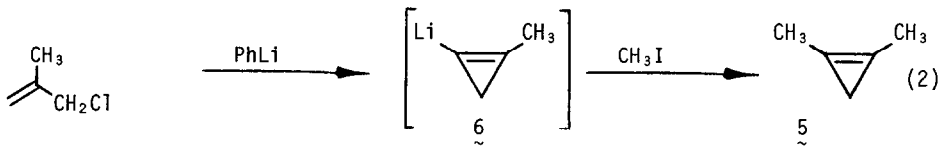


(1)

1; Z = C=O
2; Z = -N=N-

As indicated in equation (1) loss of the small molecule (CO or N_2) from 1 or 2 is generally considered to proceed by a linear cheletropic or cycloreversion pathway with synchronous opening of the cyclopropane ring in the transition state.[2,3] Although reasonable on theoretical grounds, there are almost no experimental data to support this conclusion. Using methyl substituent probes at the C-2 and C-2,C-4 positions of ketone 1 we have now obtained confirmatory kinetic evidence for the simultaneous cleavage of the C-2,C-4 cyclopropane bond in the rate determining step for carbon monoxide extrusion.

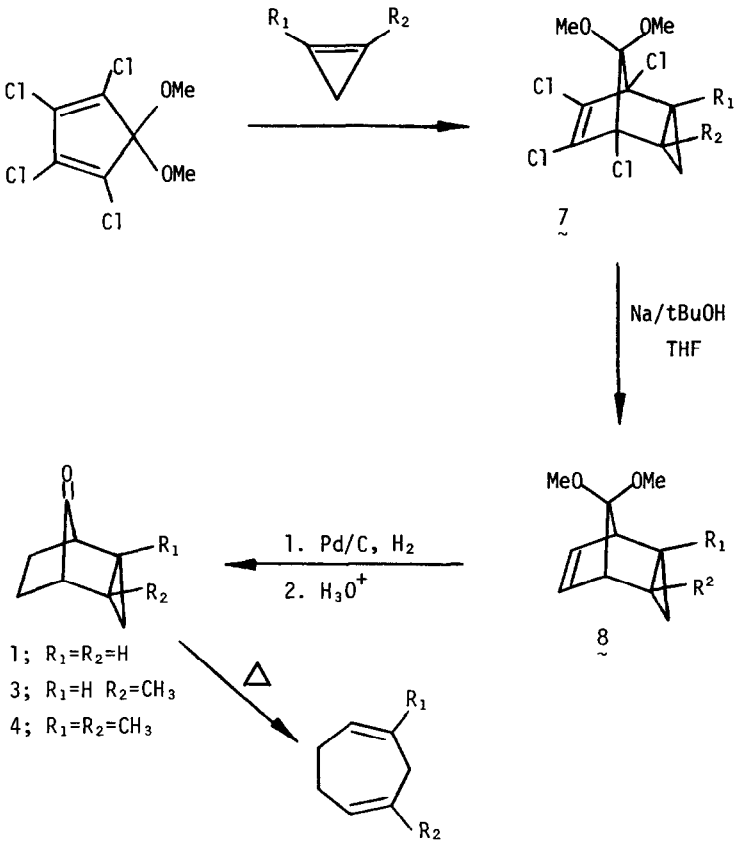
The requisite ketones, 2-methyl-endo-tricyclo[3.2.1.$0^{2,4}$]octan-8-one(3) and 2,4-dimethyl-endo-tricyclo[3.2.1.$0^{2,4}$]octan-8-one(4), were synthesized by an analogous route to that previously reported for the parent ketone (1) (Scheme I).[4,5] The critical feature in the synthesis of 4 was the development of a convenient and efficient synthesis of 1,2-dimethylcyclopropene (5). This was accomplished as indicated in equation (2). Treatment of 3-chloro-2-methylpropene with two equivalents of freshly prepared and recrystallized phenyllithium[6] in ether affords the lithio methylcyclopropene (6).[7] Immediate reaction of 6 with methyliodide in



ether gave 1,2-dimethylcyclopropene (5) which was volatilized and trapped with 5,5-dimethyoxy-1,2,3,4-tetrachlorocyclopentadiene at 0°C to give 7 (R_1=R_2=CH_3)[8], m.p. 135-136°. Dechlorination of this adduct gave the unsaturated ketal 8 (R_1=R_2=CH_3)[8] which on hydrogenation and hydrolysis with 2.5% aqueous sulfuric acid gave ketone 4[8]; bp 82-84° (12mm); νC=O 1770 cm^{-1}; nmr ($CDCL_3$; ref$CHCl_3$) δ 1.95-1.19 (6H,m), 1.17 (6H,s), 0.76 (2H, AB quart., J=8.2 Hz).

The kinetic parameters for the thermal decarbonylation of ketones 1, 3 and 4 in 1,2,4-trimethylbenzene as solvent are given in Table I. At the outset one might have anticipated that the observed rate ratio 1:3:4 would permit a distinction between a statistical (1:x:2x) or multiplicative (1:y:y^2) effect of each successive methyl substitution; however, inspection of the data clearly reveals that this is not the case. Rather, the observed rate ratio (1:6:152)

SCHEME I



strongly implicates steric relief of methyl-methyl compressional strain in the transition state for decarbonylation of ketone 4. Other interpretations of the observed ratio for 1, 3 and 4 are not apparent and we thus conclude that cleavage of the cyclopropane intercyclic bond in the rate determining step is simultaneous with bridge bond(s) cleavage. While we prefer the symmetrical transition state structure depicted in equation (1) the data do not exclude involvement of an unsymmetrical (diradical) transition state in which the C-2,C-4 bond is involved.

Table I. Kinetic Parameters for Thermal Decarbonylation of endo-Tricyclo[3.2.1.$0^{2,4}$]octan-8-ones

Ketone	T,°C	$10^4 k(sec^{-1})$[a]	$\Delta H^{\ddagger}$(kcal/mole)	$\Delta S^{\ddagger}$(e.u.)	$k_{rel}^{145°}$
1	165	1.96 ± 0.02			
	152.5	0.293[b]	32.3[b]	3.3[b]	
	145	0.317[c]			1
3	165	11.9 ± 0.2	32.5 ± 1.3	1.5	
	155	5.12 ± 0.04			
	145	1.90 ± 0.02			6
4	145	48.2 ± 1.8	27.8 ± 0.5	-3.2	152
	135	21.1 ± 0.7			
	125	8.51 ± 0.34			

[a]Rate constants are the average of at least two runs and were determined in 1,2,4-trimethylbenzene utilizing sealed micro-ampules with Glpc monitoring of the increasing response of the respective 1,4-cycloheptadiene products relative to an internal standard. Diene production is essentially quantitative under these conditions.

[b]Reference 2. [c]Extrapolated value.

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References and Footnotes

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5. The methyl ketone 3 has been previously prepared by the approach outlined in Scheme I; see P. K. Freeman, T. A. Kardy, R. S. Raghavan, and D. G. Kupu, J. Org. Chem., 42, 3882 (1977)
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8. Satisfactory elemental analysis and/or exact mass molecular weights were obtained on all new compounds reported. Spectral data were in accord with assigned structures and stereochemistry The endo stereochemistry of ketone 4 was further confirmed by lanthanide shift reagent studies of the corresponding syn and anti alcohols derived from 4.

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