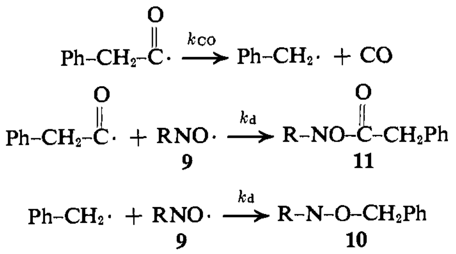

$$\mathrm{Ph{-}CH_2{-}\overset{O}{\overset{\|}{C}}\cdot \xrightarrow{k_{CO}} Ph{-}CH_2\cdot + CO}$$

$$\underset{}{\mathrm{Ph{-}CH_2{-}\overset{O}{\overset{\|}{C}}\cdot}} + \underset{\mathbf{9}}{\mathrm{RNO\cdot}} \xrightarrow{k_d} \underset{\mathbf{11}}{\mathrm{R{-}NO{-}\overset{O}{\overset{\|}{C}}{-}CH_2Ph}}$$

$$\mathrm{Ph{-}CH_2\cdot} + \underset{\mathbf{9}}{\mathrm{RNO\cdot}} \xrightarrow{k_d} \underset{\mathbf{10}}{\mathrm{R{-}N{-}O{-}CH_2Ph}}$$

By application of the steady-state approximation and several simplifying assumptions to this mechanism, it is possible to derive the following expression

$$\frac{[\mathrm{R{-}NO{-}CH_2Ph}]}{[\mathrm{R{-}N{-}O{-}C({=}O){-}CH_2{-}Ph}]} = \frac{2k_{CO}}{k_d[\mathrm{NO}\cdot]_0/2} + 1$$

Substituting the values found in this study, one calculates k_{CO} to be of the order of 10^8 sec^{-1}.

It is gratifying to note that this value is consistent with the failure of the tri-*n*-butyltin hydride to trap the phenylacetyl radical ($k_H[\mathrm{Bu_3SnH}] = 10^6$ sec^{-1}). Furthermore, since unimolecular *radical* reactions usually proceed at the same rate in nonpolar solvents and in the vapor phase,[14] the value for phenylacetyl radical decarbonylation calculated here may be compared with that found for the acetyl radical at room temperature in the vapor phase[15] ($k_{CO} \simeq 1$ sec^{-1}). Thus, one α-phenyl substitution increases the rate of decarbonylation by a factor of 10^8. This rate difference (10^8) corresponds to a ΔE_a which nearly matches the current benzyl resonance energy of $\sim$12.5 kcal/mol.[16]

As a result of these studies, we are confident that the photodecarbonylation of dibenzyl ketones in solution occurs *via* a two-step mechanism which is independent of cage effects.

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(14) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966.

(15) J. A. Kerr and J. G. Calvert, *J. Phys. Chem.*, **69**, 1022 (1965).

(16) R. Walsh, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 651 (1966).

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The Thermal Fragmentation of Cyclohexanone[1]

Sir:

Recently there has been interest expressed in parallels in the mechanism of fragmentation of molecules when induced, respectively, by light or electron impact.[2] In the case of cyclohexanone both photochemical (Norrish type I) and electron-impact fission take place in the α position.[3] Such thermolytic work as has been previously reported[4] suggested that this, too, involved α cleavage. We describe here evidence which indicates that the major pathway for thermolysis involves β cleavage.

The thermolyses were conducted in a flow system at 1050°,[4] and gave the following products: methyl vinyl ketone[6,7] (MVK, 25), ethylene (85), ethane (3), acetylene (5), propylene (16), allene (7), 1-butene (7),

Table I. Deuterium Distributions for Ethylene, Isoprene, and Methyl Vinyl Ketone from Pyrolysis of Specifically Labeled Cyclohexanones and Methylenecyclohexane[a]

	Cyclohexanone, %	Ethylene, %	Methyl vinyl ketone, %
α deuterated[b,f]	d_1 0.2	d_0 4.5	d_0 0.3
	d_2 0.6	d_1 9.9	d_1 1.0
	d_3 8.0	d_2 22.6	d_3 3.4
	d_4 91.2	d_3 1.8	d_3 25.7
		d_4 1.2	d_4 69.6
	3.90 atoms of D/molecule	0.65 atom of D/molecule	3.63 atoms of D/molecule
β deuterated[c,f]	d_0 0.1	d_0 7.4	d_0 2.4
	d_1 1.1	d_1 23.8	d_1 21.4
	d_2 8.0	d_2 64.3	d_2 75.0
	d_3 28.9	d_3 4.5	d_3 1.2
	d_4 61.8		
	3.51 atoms of D/molecule	1.66 atoms of D/molecule	1.75 atoms of D/molecule
γ deuterated[d,f]	d_0 49.8	d_0 68.5	d_0 99.2
	d_1 50.2	d_1 31.5	d_1 0.8
	0.50 atom of D/molecule	0.32 atom of D/molecule	0.008 atom of D/molecule
	Methylenecyclohexane-d_4, %	Ethylene, %	Isoprene, %
α deuterated[e,f]	d_0 0.1	d_0 58.7	d_0 0.6
	d_1 0.4	d_1 13.7	d_1 1.6
	d_2 0.2	d_2 21.4	d_2 9.6
	d_3 5.1	d_3 4.9	d_3 31.8
	d_4 87.1	d_4 1.3	d_4 47.9
	d_5 6.1		d_5 7.4
	d_6 1.1		d_6 1.1
	4.02 atoms of D/molecule	0.76 atom of D/molecule	3.51 atoms of D/molecule

[a] Average of duplicate runs. [b] The recovered cyclohexanone had 3.82 atoms of D/molecule distributed as follows: d_0, 0.0; d_1, 0.9; d_2, 1.7; d_3, 12.8; d_4, 84.7. This indicates a minor amount of equilibration. [c] Recovered, 3.50 atoms of D/molecule. [d] Recovered, 0.5 atom of D/molecule. [e] Recovered, 4.00 atoms of D/molecule. [f] Distribution essentially unchanged from starting material.

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(1) (a) Flash Thermolysis. Part IV. (b) This work was supported by the Petroleum Research Fund administered by the American Chemical Society.

(2) Photochemical Cleavage: R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963); R. G. Shortridge and E. K. C. Lee, *J. Amer. Chem. Soc.*, **92**, 2228 (1970), and references therein cited. Mass Spectrometric Cleavage: H. Budziekiewicz, C. Djerassi, and D. H. Williams in "The Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, p 19.

(3) C. D. Hurd, H. Greengard, and A. S. Roe, *J. Amer. Chem. Soc.*, **61**, 3359 (1939); E. Ibuki, *Nippon Kagaku Zasshi*, 71, 96 (1950); *Chem. Abstr.*, **45**, 7025 (1950).

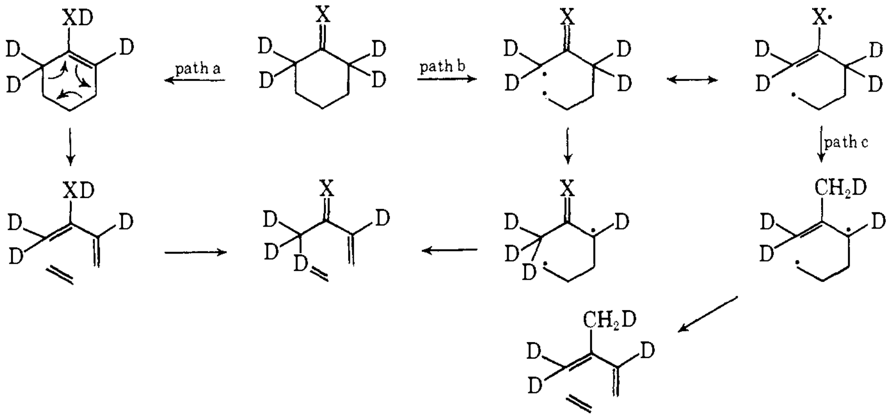
(4) The flow system consisted of a heated empty ceramic tube leading to a liquid nitrogen cold-finger.[5] The thermolyses were carried out at 60 μ with calculated contact times of about 10 msec. The technique follows that pioneered for mass spectrometry over the last decade by F. P. Lossing (see, for instance, R. F. Pottie, A. G. Harrison, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 3204 (1961)) and developed by Hedaya for isolation purposes (see E. Hedaya and D. McNeil, *ibid.*, **89**, 4213 (1967)).

(5) J. F. King, P. de Mayo, C. L. McIntosh, K. Piers, and D. J. H. Smith, *Can. J. Chem.*, in press. A similar apparatus has been described by E. Hedaya, *Accounts Chem. Res.*, **2**, 367 (1969).

(6) Mole per cent yield based on decomposed cyclohexanone. The products were identified by retention time on gas–liquid chromatography and by mass spectra.

(7) Dr. E. Hedaya (Union Carbide Research Institute) informs us that he has also observed the formation of methyl vinyl ketone from the thermolysis of cyclohexanone.

Scheme I



1,3-butadiene (3), 1,5-hexadiene (3), cyclopentane (3), cyclopentadiene (2), acrolein (2), and benzene (1). The thermal stability of the products at 1050° was not extensively examined, but it was found that MVK itself decomposed to the extent of about 50% to give all the products observed from cyclohexanone except the last four.

In order to ascertain the primary thermal process involved, three specifically deuterated cyclohexanones were prepared and thermolyzed. The deuterium distribution in some of the products was obtained and part of the results are summarized in Table I.

Cyclohexanone-*2,2,6,6-*d_4 gave MVK with 93% overall retention of deuterium. The fragmentation spectrum clearly showed the presence of the retained deuterium in the methyl group. The deuterium content of the MVK from cyclohexanone-*3,3,5,5-*d_4 was half that of the starting material, while essentially no deuterium was present in the MVK from cyclohexanone-*4-d*.

The observations require that, following β cleavage, a hydrogen atom (or ion) α to the carbonyl be intramolecularly transferred to the other α position. Two mechanisms, at least, can be envisaged (Scheme I). One (path a, X = O) requires prior enolization, perhaps on the walls, followed by a reverse Diels–Alder reaction and subsequent ketonization. The second (path b, X = O) involves initial homolysis of the β carbon–carbon bond, hydrogen atom migration, and collapse of the 1,4 biradical in the expected manner (or *vice versa*). Relevant evidence was obtained as follows. Thermolysis of methylenecyclohexane-*2,2,6,6-*d_4 gave isoprene, the equivalent of MVK in this system, in 12% yield with 87.4% total deuterium retention. Path a (X = CH_2) is evidently inapplicable[8] here, and path b (and path c) must be operative. In view of the parallel results we favor, but essentially by analogy, the view that path b (X = O) be that followed in MVK formation.

The results permit a quantitative check. The mechanism demands that equimolar amounts of ethylene and MVK be formed, but analysis was complicated by the fact that the decomposition of MVK also produced ethylene. The monodeuterated ethylene produced from cyclohexanone-*4-*d_1 gave the amount of ethylene formed by path b (X = O) as 63%. There should be the amount of unlabeled ethylene from the *2,2,6,6-*d_4 material:[9] the observed value was 64.5%. Since the total isolated yield of ethylene was actually 85% then the actual yield of MVK (equivalent to unlabeled ethylene) may be computed at 54%, *i.e.*, a figure about twice the actual yield, but in good agreement with the 50% recovery of MVK under the same conditions in the control experiment mentioned earlier.

The β cleavage to give MVK is thus the major pathway followed in cyclohexanone thermolysis. It represents a minimum of the total β-cleavage products, and reveals this fission as the primary thermal process.[10,11]

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[8] To follow this route prior rearrangement to methylcyclohexene would be required. Since <0.1% of this hydrocarbon was obtained from the thermolysis of methylenecyclohexene this explanation would require the complete decomposition of methylcyclohexene under these conditions. Experimentally, it was found that about 15% of methylcyclohexene was recovered in the thermolysis of this substance, together with about 50% isoprene.

[9] Any ethylene from MVK should surely have contained at least one deuterium atom.

[10] Crandall has suggested such a cleavage in his study of the photolysis and thermolysis of cyclooct-4-enone: J. K. Crandall, J. P. Arrington, and R. J. Watkins, *Chem. Commun.*, 1052 (1967).

[11] The thermolysis of cyclopentanone has been reported to give α-cleavage products resembling those of photochemical fission (F. M. Delles, L. T. Dodd, L. F. Lowden, F. J. Romano, and L. G. Daignavet, *J. Amer. Chem. Soc.*, **91**, 7645 (1969)). We intend to study this substance under our conditions.

[12] Holder of N.R.C. Scholarship, 1967–present.

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Facile Conversion of Alkyl Bromides into Aldehydes Using Sodium Tetracarbonylferrate(–II)

Sir:

We wish to report that the d^{10} dianion derived from iron pentacarbonyl is an effective reagent for the conversion of primary bromides into corresponding aldehydes containing an additional carbon atom. Reduction of iron pentacarbonyl in THF by sodium amalgam followed by treatment of the resulting dianion, sodium tetracarbonylferrate(–II)[1] (**1**), with primary bromides in the presence of triphenylphosphine at 25° gives, after quenching with acetic acid, the corresponding aldehyde in high yield.[2] Results using typical alkyl bromides are

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[1] V. W. Hieber and G. Braun, *Z. Naturforsch.*, **146**, 132 (1959).

[2] (a) Aromatic aldehydes have been obtained previously by the reaction of aryllithium reagents with iron pentacarbonyl; see M. Ryang, I. Rhee, and S. Tsutsumi, *Bull. Chem. Soc. Jap.*, **37**, 341 (1964). (b) It