$\gg$ dimethylanilines > *t*-butylbenzenes. It is interesting to note that, while the use of σ^* often results in drastic changes in ρ, the ρ values obtained by different workers with different compounds are comparable.

Although the J–σ slopes indicate a slightly greater transmittivity for nitrogen relative to oxygen, the similarity of these values, the disparity in number of compounds used to evaluate ρ for both series, and the reversal of ρ order ($Y = O \gg N$) from the δ–σ lines argue for similar transmittivities for $Y = N$ and O.

The improvement in the correlations resulting from the use of σ^* values for certain electron-attracting groups is evidence for sizable resonance interactions in both the anisoles and dimethylanilines.

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Photolysis of 2-Methylcyclohexanone[1]

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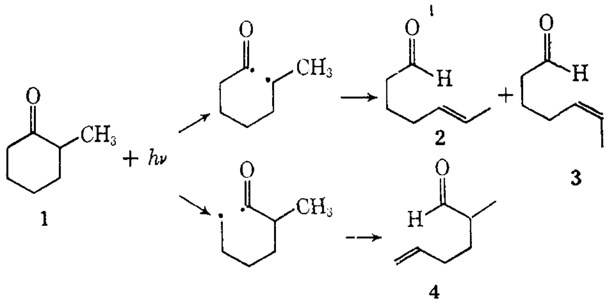
Abstract: The photolysis of 2-methylcyclohexanone at 3130 Å in both the gas and liquid phase has been critically reexamined. Contrary to an earlier report, both *trans*- and *cis*-5-heptenal are obtained as major products. Separate photolysis of various mixtures of the product aldehydes established that these geometric isomers are not readily interconverted under the reaction conditions. It can therefore be concluded that the unsaturated aldehydes are formed in both the gas and liquid phase by a nonstereospecific, presumably diradical, process. In photolysis of the ketone, a lower limit 50-fold preference for cleavage of the C_1–C_2 over the C_1–C_6 bond was established.

Although the photolysis of cyclic ketones has been extensively studied,[4] certain basic aspects of the mechanism of this reaction are still open to question. Srinivasan has suggested[5] a concerted pathway for formation of unsaturated aldehyde from 2-methylcyclohexanone and has reiterated this position in later work.[6] His evidence favoring a concerted mechanism consists of infrared data implying that only one isomer (*trans*) of 5-heptenal is formed in the liquid-phase reaction.[7] We have previously suggested[8,9] that this work is in error, based on our results with *cis*- and *trans*-2,6-dimethylcyclohexanone, both of which give the same *mixture* of unsaturated aldehydes in gas-phase photolyses. Frey[10] has also presented evidence for a diradical intermediate in the photolysis of *trans*-2,3-dimethylcyclopentanone, although aldehydic products were not examined in this instance. In reviewing this topic, Kan[11] has raised the question of variation in mechanism depending on whether the photolysis is carried out in the gas or liquid phase. We have, therefore, critically reexamined the reaction of 2-methylcyclohexanone in both phases.

Results and Discussion

In order to unequivocally identify the plausible aldehyde products from 2-methylcyclohexanone (**1**) (Scheme I), these materials (**2**, **3**, and **4**) were synthesized as shown in Scheme II. Vapor phase chromatography (vpc) conditions were established such that mutual separation of these aldehydes and starting ketone was accomplished.

Scheme I. Photolysis Pathways of 2-Methylcyclohexanone Leading to Unsaturated Aldehydes



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(1) This work was supported in part by the National Science Foundation.

(2) NDEA Title IV Predoctoral Fellow, 1965–1968.

(3) Alfred P. Sloan Fellow, 1967–1969.

(4) For a review of work prior to 1962, see R. Srinivasan, *Advan. Photochem.*, **1**, 84 (1963).

(5) R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 2601 (1959).

(6) R. Srinivasan and S. E. Cremer, *ibid.*, **87**, 1647 (1965).

(7) Srinivasan and Cremer[6] have also cited as evidence for a concerted mechanism the observation that 2-methylcyclohexanone yields no 6-heptenal, and 2-ethylcyclopentanone yields no 5-heptenal on photolysis. However, these results can also be taken as support for a diradical mechanism; the transfer of hydrogen would involve an eight- (rather than six-) membered ring in the former case, and a seven- (rather than five-) membered ring in the latter. The simple rationale that five- and six-membered cyclic transition states are favored over larger rings can explain other related photochemical results as well, for example, the observations of T. Matsui, *Tetrahedron Letters*, 3761 (1967).

(8) B. Rickborn, R. L. Alumbaugh, and G. O. Pritchard, *Chem. Ind.* (London), 1951 (1964).

(9) R. L. Alumbaugh, G. O. Pritchard, and B. Rickborn, *J. Phys. Chem.*, **69**, 3225 (1965).

(10) H. M. Frey, *Chem. Ind.* (London), 947 (1966).

(11) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, p 85.

Scheme II. Syntheses of the Unsaturated Aldehydes

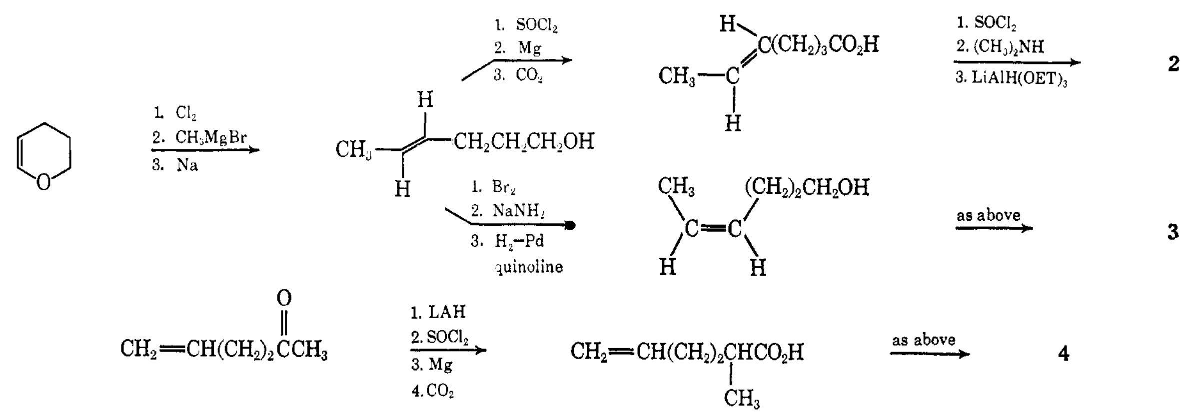

Table I. Photolysis of **1** (Neat Liquid, 3130 Å, 25°)

Time, hr	~% reaction	2/3
3.0	...	3.42
5.0	...	3.42
25.5	7.6	3.56
36.5	10.5	3.23
59.0	12.9	3.18
73.0	15.2	3.06
4.0	5.2	2.50
52.0	19.2	3.17
72.0	21.2	3.00
3.0	1.7	3.00
10.0	6.6	3.27
24.5	12.2	3.00
51.0	18.0	2.60
68.5	22.9	2.80
90.5	23.6	3.33
36.0	15.9	3.05
		Av 3.10

As shown in Table I, both **2** (75 ± 4%) and **3** (25 ± 4%) are formed in the liquid-phase photolysis of 2-methylcyclohexanone. Although there is some scatter in the data (within the limits indicated), there is no clear trend in the ratio of these products with length of photolysis. The identity of **2** and **3** from photolysis was established by coinjection of known samples on various vpc columns, and by comparison of spectra. The ir spectrum of a vpc collected sample of **2** and **3** (combined) closely resembles that of its major constituent (**2**). The nmr spectrum contained a multiplet at 9.6 ppm (aldehydic proton) which was partially resolved into two triplets (J = 1.65 and 1.75 cps), with relative areas in agreement with the product ratio established by vpc analysis.

Injection of the possible alternate cleavage product, 2-methyl-5-hexenal (**4**), showed that it had a considerably shorter retention time on vpc, and hence would not interfere with the spectral analysis discussed above. In fact, only a trace amount, if any, of **4** is formed in the liquid-phase photolysis. The material could have accounted for at most 2% of the total aldehyde products. Unless the C_1–C_6 cleavage diradical behaves very differently than the C_1–C_2 intermediate (*i.e.*, different extents of reversal to ketone or decarbonylation), these data imply that the latter cleavage is favored by a factor of 50 or more. This behavior is in keeping with the relative thermodynamic stabilities of secondary *vs.* primary radicals.[12] However, it is not obvious that the cleavage should be a thermodynamically controlled process, since the initially excited molecule contains more than sufficient energy to cause the scission of either bond. An analogy may be drawn with the photolysis of methyl ethyl ketone,[13,14] which undergoes C_2–C_3 cleavage 20–40 times more readily than C_1–C_2 cleavage at 3130 Å. This ratio decreases to 5.5:1 at 2654 Å and 2.6:1 at 2537 Å.

The results of gas-phase photolysis of 2-methylcyclohexanone are shown in Table II. In agreement

Table II. Vapor-Phase Photolysis of **1** (3130 Å)

Temp, °C	Time, min	Pressure, mm	% reaction	(2 + 3)/ total product[a]	2/3
150	180	221	25	0.66	2.71
156	20	17	39	0.23	1.99
156	15	1.0	...	...	1.91
100	60	38	71	0.22	2.60
100	30	32	14	0.56	2.64
100	20	20	20	0.47	2.24
100	40	20	42	0.41	1.98
100	20	20	22	0.52	2.05
100	15	20	20	0.48	2.12
100	10	20	13	0.51	2.15
100	10	20	12	0.54	2.13
100	5	20	6.4	0.57	2.15
100	15	12	16	0.50	2.17
100	30	6.8	9.2	0.66	2.46
100	15	5.0	18	0.43	2.02
100	120	5.0	6.9	0.51	2.10[b]
100	10	2.0	16	0.38	1.80
100	10	1.0	32	0.14	2.09
100	25	1.0	2.9	0.22	1.82[b]
100	60	1.0	5.0	0.33	1.83[b]
100	20	0.4	8.1	0.27	1.81
100	10	0.2	...	...	1.78
100	40	0.2	6.0	0.22	1.82[b]
100	20	0.11	4.6	0.16	1.71[b]
56	77	34	37	0.54	2.80
100	45	14	14	0.65	2.23
100	20	2.0	25	0.34	1.89
100	30	9.0	36	0.31	2.04

[a] This ratio represents the area of vpc peaks for **2** and **3** divided by the total area for all products. [b] These runs were carried out in the 2-l. cell described in the Experimental Section.

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(12) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 815–830.

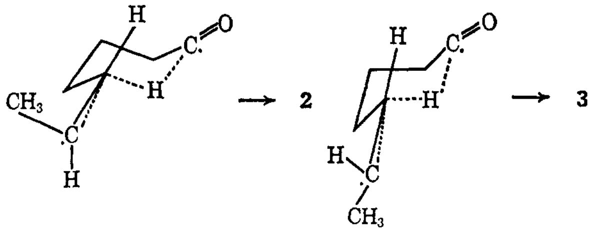
(13) J. N. Pitts, Jr., and F. E. Blacet, *J. Am. Chem. Soc.*, **72**, 2810 (1950).

(14) G. R. Martin and H. C. Sutton, *Trans. Faraday Soc.*, **48**, 823 (1952).

with earlier work, it is seen that the proportion of decarbonylated product increases at lower pressures.[9,15] As in the liquid phase, no measurable product (**4**) from C_1–C_6 cleavage was observed.

Although there is some scatter in the vapor-phase data, an interesting trend in the *trans/cis* ratio is apparent. As the pressure of starting ketone is lowered, this ratio decreases. Thus, as decarbonylation becomes more favored (less collisional deactivation of an excited precursor), the selectivity of the hydrogen-abstraction process leading to aldehyde is diminished. The ratios of **2** to **3** observed in this work are very similar to the ratios obtained earlier[9] in the photolysis of *cis*- and *trans*-2,6-dimethylcyclohexanone and further substantiate the identity of the unsaturated aldehydes formed in the previous work. We suggest that the **2**/**3** ratio may be determined by a conformational preference in the six-membered H-bridging transition state (Scheme III) proposed for aldehyde formation, and that this conformational effect becomes relatively less important as the excess vibrational energy of the system is increased. One would not expect a 6-methyl group to appreciably affect the product distribution.

Scheme III. Proposed Transition States for Formation of Unsaturated Aldehydes



With regard to the stereospecificity (or lack thereof) of unsaturated aldehyde formation, one final point remains to be examined. As noted earlier,[8,9] a mixture of aldehydes could result if some particularly facile isomerization pathway, *e.g.*, intramolecular triplet transfer from the carbonyl group to the olefin, were available. The data in Table III show that no such reaction occurs, at least not at a rate sufficient to explain the product distribution obtained from photolysis of the ketone. The aldehydes do undergo photodegradation, and a somewhat faster reaction of **3** can account for the slight relative increase in *trans* material observed in Table III. This same effect presumably operates during photolysis of the ketone, but its bearing on the ratio of **2** to **3** apparently is not important (*cf.* Table II) at relatively low conversions.

Table III. Vapor-Phase Photolysis of *cis*- and *trans*-5-Heptenal Mixtures (100°, 3130 Å)

Time, min	Pressure mm	~% reaction[a]	**2/3** (init)	**2/3** (final)
5	40	7	0.88	0.89
10	40	9	0.88	0.90
30	40	~25	0.88	0.97
20	40	25	0.84	0.94
60	40	40	0.84	1.09
35	1.0	6.3	0.06	0.07
90	1.0	3.0	0.06	0.06

[a] This figure represents the percentage area of all product peaks that appeared in the vpc.

The evidence presented here taken in conjunction with that discussed earlier[9,10] demonstrates conclusively that neither the unsaturated aldehydes nor the decarbonylated products of cyclic ketone photolysis (gas or liquid phase) are formed by a concerted process. It appears most logical to postulate that both processes arise *via* a common diradical intermediate, as originally suggested by Benson and Kistiakowsky[16] and Blacet and Miller.[17,18]

Recent work[20,21] with cyclopentanone has led to the suggestion that the triplet state is the precursor of the unsaturated aldehyde product and that decarbonylated products may arise from an excited singlet. Lee[21] performed some excellent experiments using singlet and triplet benzene as a diagnostic sensitizer; he has also described[22] a similar dependence of the dissociative pathway upon multiplicity for cyclobutanone. We have briefly examined the triplet mercury sensitized photolysis of 2-methylcyclohexanone and find that *all* of the normal 3130-Å photolysis products are formed. In fact, decarbonylated material comprises a larger fraction of the total products than is formed in the direct photolysis.[23,24]

Summary

The role that multiplicity plays in determining the dissociative modes of cyclic ketones is thus not clearly established. The apparent conflict with the data of Lee[21,22] may be associated with the greater transferable energy (about 112 kcal/mole) of triplet mercury compared with triplet benzene (85 kcal/mole).[21,22] The main determining factor appears to be the "energy content" (unspecified electronic and vibrational) of the species while it is undergoing reaction, as the effects of wavelength, temperature, and pressure have previously established.[4,9] The decomposition in the liquid phase is due, in the main, to molecules that have undergone

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(15) R. Srinivasan, *J. Am. Chem. Soc.*, **83,** 4344, 4348 (1961).

(16) S. W. Benson and G. B. Kistiakowsky, *ibid.*, **64,** 80 (1942).

(17) F. E. Blacet and A. Miller, *ibid.*, **79,** 4327 (1957).

(18) It would seem needless to assume "that the aldehyde might be formed in an excited state capable of undergoing geometrical isomerization": R. B. Cundall and A. S. Davies, *Progr. Reaction Kinetics*, **4,** 149 (1967). Further, since the completion of this work H. M. Frey and D. H. Lister (Eighth Informal Conference on Photochemistry, University of Ottawa, June 17–19, 1968) have reported the observation of both *cis*- and *trans*-4-methyl-4-hexenal in the photolysis of *trans*-2,3-dimethylcyclopentanone. Srinivasan and Cremer[6,19] have claimed the exclusive formation of only the *trans* aldehydes in the photolysis of 2-methyl-, 2-ethyl-, and 2-*n*-propylcyclopentanones.

(19) R. Srinivasan and S. E. Cremer, *J. Phys. Chem.*, **69,** 3145 (1965).

(20) P. Dunion and C. N. Trumbore, *J. Am. Chem. Soc.*, **87,** 4211 (1965).

(21) E. K. C. Lee, *J. Phys. Chem.*, **71,** 2804 (1967).

(22) H. O. Denschlag and E. K. C. Lee, *J. Am. Chem. Soc.*, **89,** 4795 (1967); see also T. H. McGee, *J. Phys. Chem.*, **72,** 1621 (1968).

(23) At low conversion levels, the small relative difference in ketone and aldehyde quenching cross sections does not allow for formation of decarbonylated material by subsequent reaction of the aldehyde.

(24) The reaction of Hg^3P_1 with cyclobutanone, cyclopentanone, and cyclohexanone has also been studied by F. P. Lossing and J. B. Homer (unpublished data, 1964–1965). They found that decarbonylated products accounted for 70–80% of the decomposition yields, *e.g.*, 25% c-C_4H_8 + CO and 55% $2C_2H_4$ + CO with cyclopentanone. Aldehydes were not observed, but they would not be expected at the low pressures used. We are indebted to Dr. Lossing for the communication of his unpublished data.

intersystem crossing to a low-lying triplet energy state.[20]

We are conducting further experiments using Hg^3P_1 sensitization to establish the ratio of the isomeric aldehydes formed in the primary reaction. The formation of decarbonylated products using Hg^3P_1 does not allow for a concerted mechanism, since there is insufficient energy for the CO or the cyclic hydrocarbon to be formed in their triplet states if the spin conservation rule is obeyed.[25] Pathways are available for the formation of singlet product molecules from triplet biradical intermediates.[25]

Experimental Section

The majority of vapor-phase photolytic runs were carried out in a conventional system with greased stopcocks, with the cell isolated by a metal bellows valve. The cell had a double quartz wall with reaction volume of 156 ml, with temperature (including that of dead space) maintained by a vapor bath. The condensable products were frozen into a cold finger at −195° for analysis. Illumination was provided by a British-Thomson-Houston (B-T-H) high-pressure mercury arc (Type ME/D, 250 W). The light was collimated by a single quartz lens, passed through a Corning 9863 blue glass filter, and fully illuminated the cell volume.

Low-pressure runs (*cf.* Table II) were performed in a mercury and grease-free vacuum system using Westef Teflon stopcocks. The cell, isolated by a metal diaphragm valve, was a quartz cylinder, 82.5 mm in diameter and 400 mm long, volume 2150 cc. Illumination, collimated and filtered as described above, was obtained from a PEK Model 210 high-pressure short-arc lamp (200 W). The beam illuminated about 30% of the cell face.

Liquid-phase photolyses were carried out in 3-ml (6-mm path length) Vycor cells, using the B-T-H lamp described above.

2-Methylcyclohexanone. Commercial material was carefully fractionated, with the middle cut, bp 160°, used for photolyses; analysis by vpc indicated purity >99.5%. The uv spectrum obtained in hexane solution showed λ_{max} 293 nm (ϵ 16.9), ϵ_{313} 9.2.

2-Methyl-5-hexenal. Reduction of 68 g (0.7 mole) of 5-hexen-2-one (Aldrich) by 8.1 g of lithium aluminum hydride in ether gave the corresponding alcohol. The crude material was treated with thionyl chloride to give 39 g (47%) of 5-chloro-1-hexene, bp 56–58° (100 mm), which was converted to the Grignard reagent in the usual manner and treated with excess solid carbon dioxide. The acid was not purified, but treated directly with thionyl chloride to form the acid chloride, which was subsequently treated with ethereal dimethylamine. The distilled 2,N,N-trimethyl-5-hexenoamide, bp 109–110° (17 mm), weighed 32.9 g. This amide, 18.3 g (0.12 mole), was subjected to the Brown and Garg[26] reduction procedure using 0.12 mole of lithium triethoxyaluminum hydride; hydrolysis and vacuum distillation gave 7.0 g of 2-methyl-5-hexenal, bp 52–54° (31 mm). The 2,4-dinitrophenylhydrazone had mp 93.7–94° (lit.[27] 87–88°).

***trans*-5-Heptenal.** *trans*-4-Hexen-1-ol (bp 74–75° (23 mm)) was prepared in 95% yield (98% pure by vpc) by sodium cleavage of 3-chloro-2-methyltetrahydropyran.[28] The alcohol (0.5 mole) was converted to the chloride, bp 74–75° (97 mm), by treatment with thionyl chloride in pyridine; this in turn was converted to the Grignard reagent and carboxylated. The crude acid was treated as described above to give 13.9 g of *trans*-N,N-dimethyl-5-heptenoamide, bp 122–125° (15 mm). Reduction of 13.0 g with lithium triethoxyaluminum hydride[26] gave 2.6 g of *trans*-5-heptenal, bp 65–66° (31 mm). Vpc analysis showed the presence of 89% *trans* and 11% *cis* material. The following spectral data were obtained: nmr, triplet 9.70 (J = 1.55 cps), multiplet 5.55–5.23, multiplet 2.58–1.33 ppm; ir, 2710 (m), 1730 (s), 1630 (w), 966 (m) cm^{-1}; uv, λ_{max} 295 nm (ϵ 18.4), ϵ_{313} 15.1. The 2,4-dinitrophenylhydrazone, recrystallized from methanol, had mp 107–107.5° (lit.[29] 109.5–110°).

***cis*-5-Heptenal.** Bromine, 99 g (0.62 mole), was added to 61.5 g (0.61 mole) of *trans*-4-hexen-1-ol, and the resulting dibromide was dehydrobrominated using 100 g (2.7 moles) of sodamide in ether-liquid ammonia. Distillation of the residue gave 20.1 g (33%) of 4-hexyn-1-ol, bp 98–100° (37 mm), which was 80% pure by vpc analysis. Partial hydrogenation of this material was accomplished by treatment in 40 ml of methanol at 1 atm of hydrogen pressure, using 0.5 g of 5% palladium on barium sulfate and 0.5 g of quinoline as the catalyst poison. When 102% of the theoretical amount of hydrogen had been absorbed, the catalyst was removed and the residue distilled to give 19.0 g of impure (84%) *cis*-4-hexen-1-ol, bp 75–77° (32 mm).

This material was converted to the homologated aldehyde, as described for the *trans* isomer, to give 1.67 g of material, bp 65–66° (30 mm). Analysis indicated 5% of the *trans* aldehyde as the only impurity. The following spectral data were obtained: nmr, triplet 9.69 (J = 1.6 cps), multiplet 5.67–5.00, multiplet 2.56–1.42 ppm; ir, 2705 (m), 1725 (s), 1660 (w), 708 (m) cm^{-1}; uv, λ_{max} 295 nm (ϵ 20.4), ϵ_{313} 15.2. The 2,4-dinitrophenylhydrazone, recrystallized from methanol, had mp 93.7–94.7° (lit.[29] 94–95°).

A Carbowax 4000 vpc column, among others, gave good separation of the isomeric aldehydes and was used for photolysis product analyses.

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(25) O. P. Strausz, P. J. Kozak, G. N. C. Woodall, A. G. Sherwood, and H. E. Gunning, *Can. J. Chem.*, **46**, 1317 (1968).

(26) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **86**, 1085 (1964).

(27) A. Viola, E. J. Iorio, K. K. Chen, G. M. Glover, U. Nayak, and P. J. Kocienski, *ibid.*, **89**, 3462 (1967).

(28) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1707 (1950).

(29) N. A. LeBel, M. E. Post, and J. J. Whang, *J. Am. Chem. Soc.*, **86**, 3759 (1964).