JOURNAL
OF THE AMERICAN CHEMICAL SOCIETY

Registered in U. S. Patent Office. © Copyright, 1969, by the American Chemical Society

VOLUME 91, NUMBER 3 FEBRUARY 4, 1969

Physical and Inorganic Chemistry

Nuclear Magnetic Resonance Studies of the Bonding in Aromatic Systems. A Correlation of Hammett σ Constants with Methyl C^{13}–H Coupling Constants and Chemical Shifts

Claude H. Yoder, Richard H. Tuck, and Ronald E. Hess

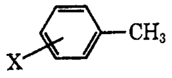
Contribution from the Departments of Chemistry, Franklin and Marshall College, Lancaster, Pennsylvania 17604, and Ursinus College, Collegeville, Pennsylvania 19426. *Received August 5, 1968*

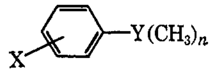
Abstract: Methyl C^{13}–H coupling constants were measured for a series of substituted toluenes, *t*-butylbenzenes, N,N-dimethylanilines, and anisoles. A linear relationship between coupling constants and Hammett σ constants of substituents was found, and the relative slopes of these lines (toluenes > dimethylanilines > anisoles > *t*-butylbenzenes) were interpreted in terms of the mode of transmission of substituent effects to the methyl site. Methyl chemical shifts also exhibit a linear correspondence to the σ constants, with a slightly different order of relative slopes (toluenes > anisoles $\geqslant$ dimethylanilines > *t*-butylbenzenes). The use of σ^* values for those substituents capable of direct resonance interactions in the dimethylanilines and anisoles greatly improved the linear consistency of the correlations for these series.

The magnitude of the C^{13}–H coupling constant is generally believed to be related to the hybridization and polarity of the C–H bond. Evidence for this relationship has come from studies of the dependence of coupling constants on valence angles,[1] bond lengths,[1] and electronegativity[2] of substituents. The present study is concerned with the dependence of coupling constants in substituted aromatic systems on the nature of the substituent.

It is well known that many properties, reaction rates, equilibrium constants, infrared absorption intensities, chemical shifts, etc., of substituted aromatics are linearly related to the Hammett σ constant of *meta* and *para* substituents. The effect of these substituents on various side-chain reactions and physical properties of benzene derivatives must depend, at least in part, upon the manner in which they modify the electronic structure of the molecule. It is, therefore, to be expected that any physical measurement which is dependent upon the electron distribution in such an aromatic system should reflect differences in electronic structure brought about by the presence of different substituents. Since both the coupling and reactivity constants are some function of the electron distribution, it seems reasonable to inquire whether these constants are related to one another.

Thus, the objectives of the present work were (a) to determine whether methyl C^{13}–H coupling constants in systems of the types I and II, where Y equals carbon


I


II

(n = 3), nitrogen (n = 2), or oxygen (n = 1), are linearly related to the Hammett σ constant of the substituent X, and (b) to determine whether the slopes (ρ) of such relations, if they exist, are indicative of the ability of Y to transmit the electrical effects of the sub-

---

[1] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1965, Chapters 5 and 12.

[2] D. M. Grant and W. M. Litchman, *J. Am. Chem. Soc.*, **87**, 3994 (1965); R. M. Hammaker, *J. Chem. Phys.*, **43**, 1843 (1965); L. Lunazzi and F. Taddei, *Spectrochim. Acta*, **23A**, 841 (1967).

stituent. It was hoped that such relations would prove of value in studying the bonding between Y and the aromatic ring and that a comparison of types I and II would indicate how those compounds in which the C–H bond involved in the coupling is bonded to the aromatic ring (I) differ from those with intervening Y atoms (II).

Experimental Section

Compounds. Most of the compounds studied were commercial samples whose purity probably exceeded 95% as indicated by the absence of any spurious signals in their nmr spectra. These samples were used without further purification. The following compounds were synthesized.

***o*-, *m*-, and *p*-N,N-dimethylchloroanilines, N,N-dimethyl-*p*-methoxyaniline, N,N-dimethyl-*p*-ethylaniline, and N,N-dimethyl-*p*-*t*-butylaniline** were obtained by methylation of the appropriate anilines with trimethyl phosphate following the procedure of Thomas, Billman, and Davis.[3] Boiling or melting points for these derivatives were found to be: *o*-Cl, bp 80° (15 mm) (lit.[3] 205–206° (740 mm)); *m*-Cl, bp 105° (15 mm) (lit.[3] 231–232° (740 mm)); *p*-C(CH$_3$)$_3$, bp 129–131° (20 mm) (lit.[4] bp 124–126° (16 mm)); *p*-Cl, mp 34–35° (lit.[3] 32–33.5°); *p*-OCH$_3$, mp 47–48.5° (lit.[3] 37–38.5°). The *p*-Cl and *p*-OCH$_3$ derivatives were recrystallized twice from ethanol.

N,N-Dimethyl-*m*-nitroaniline was prepared by nitration of N,N-dimethylaniline according to the procedure in *Organic Syntheses*.[5] The compound melted at 57.5–59° (lit.[5] 59–60°).

***p*-Nitro-*t*-butylbenzene** was prepared by the nitration of *t*-butylbenzene with fuming nitric acid (sp gr 1.5) according to the procedure of Shoesmith and Mackie.[6] The product boiled at 134–139° (20 mm) (lit.[6] bp 125–130° (10 mm)). However, this fraction appeared to be a mixture of isomers, since the nmr spectrum showed the principal absorption in the methyl region to be at τ 8.69 with a moderately intense band at τ 8.65.[7] An nmr spectrum of the material remaining in the distillation pot indicated essentially none of the τ 8.65 absorption, and so this material was assumed to be the pure *para* isomer.

***p*-*t*-Butylaniline** was prepared by the reduction of *p*-nitro-*t*-butylbenzene with tin and hydrochloric acid.

***p*-Chloro- and *p*-bromo-*t*-butylbenzene** were prepared by the method of Rueggeberg, Cushing, and Cook,[8] which involved the condensation of *t*-butyl alcohol with the halobenzene in the presence of chlorosulfonic acid. The boiling points were found to be: *p*-Cl, bp 80–85° (11 mm) (lit.[8] bp 211° (759 mm)); *p*-Br, bp 113–114° (20 mm) (lit.[9] bp 103° (10 mm)).

Nmr Parameters. Coupling constants were determined by standard side-banding techniques on a Varian A-60A or A-60 nmr spectrometer with Hewlett-Packard Model 200 CD audiooscillator and Model 521C or 522B electronic counter. The probe temperature was 40 ± 3°. Recorded values are averages of at least four and in most cases five or six traces. Values for the toluene and *t*-butylbenzene series were obtained at 100-cps sweep width and are believed accurate to within ±0.3 cps; values for the other series were obtained at 50-cps sweep width and are believed accurate to within ±0.2 cps.

Chemical shifts were recorded at 500-cps sweep width and are believed accurate to ±0.5 cps. All chemical shifts measured in CCl$_4$ were obtained by extrapolating values from three concentrations below 10% to infinite dilution.

Solvents used were spectroquality grade CCl$_4$ and chemical grade CHCl$_3$, shaken three times with alumina to remove ethanol.

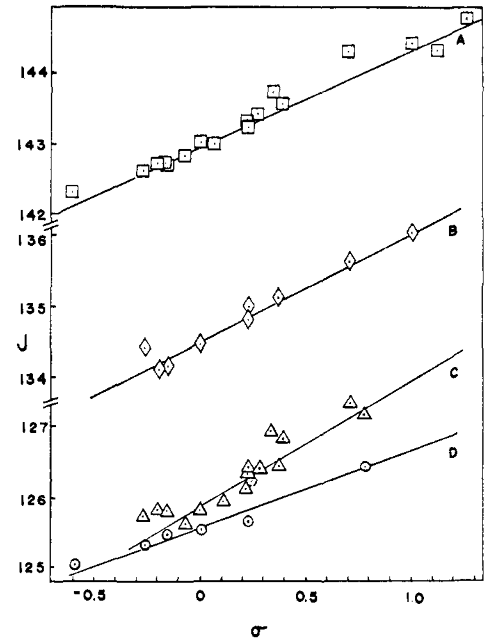


Figure 1. Plots of $J_{C^{13}-H}$ (CCl$_4$ solution) *vs.* σ for the four series: (A) anisoles, (B) dimethylanilines, (C) toluenes, and (D) *t*-butylbenzenes.

Results

Methyl C^{13}–H coupling constants for the four series studied are given in Table I. Liquids were measured neat and in CCl$_4$. Constants for solids were determined in CHCl$_3$ and CCl$_4$. A variety of liquids were also measured in CHCl$_3$.

Many of the compounds were measured at two or more concentrations in CCl$_4$, and in most cases the values were the same within experimental error (the recorded value is an average). In a few instances the constants appeared to vary monotonically with concentration, and the value recorded for these compounds is the value at the lowest concentration.

Plotting coupling constants for *meta* and *para* derivatives *vs.* Hammett σ constants[10] resulted in straight-line relationships for each series. The slope (ρ), intercept (C), standard deviation (S), and correlation coefficient (r) as determined by a least-squares analysis[10] for the neat and CCl$_4$ values for each series are given in Table II. The least-squares plot for the CCl$_4$ values are shown in Figure 1. The scatter of points is considerably worse for the neat values in each series as indicated by the correlation coefficients. In the anisole and dimethylaniline series the correlation was improved by using σ^* values[10] for the *p*-CN, *p*-CHO, and *p*-NO$_2$ groups; ordinary Hammett values for these groups were used in the other two series.

Table III contains the methyl chemical shifts for the *t*-butyl and dimethylamine series in CCl$_4$ at infinite dilution. Chemical shifts for the toluene,[11] anisole,[12] and *t*-butylbenzene[13] series in CCl$_4$ and the dimethyl-

---

[3] D. G. Thomas, J. H. Billman, and C. E. Davis, *J. Am. Chem. Soc.*, **68**, 895 (1946).

[4] D. I. Legge, *ibid.*, **69**, 2079 (1947).

[5] H. M. Fitch, *Org. Syn*, **27**, 62 (1947).

[6] J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 2335 (1928).

[7] Although Shoesmith and Mackie report this reaction to yield only *p*-nitro-*t*-butylbenzene, it appears from nmr data that the crude product is a mixture of isomers, in which the *para* compound is predominant. The same result was obtained when the reaction was repeated.

[8] W. H. C. Rueggeberg, M. L. Cushing, and W. A. Cook, *J. Am. Chem. Soc.*, **68**, 191 (1946).

[9] W. C. Davies and F. L. Hulbert, *J. Soc. Chem. Ind.*, **57**, 349 (1938); *Chem. Abstr.*, **33**, 1682 (1939).

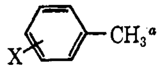
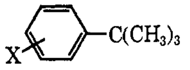
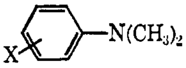
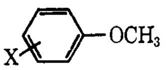
[10] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[11] S. H. Marcus, W. F. Reynolds, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966).

[12] C. Heathcock, *Can. J. Chem.*, **40**, 1865 (1962).

[13] H. Sakurai and M. Ohtsuru, *J. Organometal. Chem.*, **13**, 81 (1968).

Table I. Methyl C^{13}–H^1 Coupling Constants (±0.2 cps)

												
X	Neat	$CHCl_3$^{b}	CCl_4^{b}	Neat	$CHCl_3$^{b}	CCl_4^{c}	Neat	$CHCl_3$^{b}	CCl_4^{b}	Neat	$CHCl_3$^{d}	CCl_4^{d}
p-NO_2		127.3	127.15	126.0		126.4					144.9	144.75
m-NO_2	127.4	127.7	127.3	126.2					135.6		144.4	144.3
o-NO_2	128.9											
p-CN									136.0			144.4
p-CHO			126.1							144.6		144 3
p-I		126.6	126.4								144.3	143.4
m-I										143.7		143.7
o-I										144.1		
p-Br	126.7		126.4	125.6		126.2		135.6	135.0	144.3	144.2	143.2
m-Br	126.5		126.8							143.6		143.55
o-Br	127.7									144.3		
p-Cl	126.4		126.3	125.5		125.6		135.75	134.8	143.4		143.3
m-Cl	126.5		126.4				135.4		135.1			
o-Cl	127.7						134.55					
p-F										143.8		143.0
m-F	126.3		126.9									
o-F										144.2		
p-H	125.8		125.8	125.2	125.5	125.5	135.1	134.7	134.45	143.1		143.0
p-CH_3	125.7	125.8	125.45	125.8		125.5				142.8	143.0	142.7
m-CH_3	125.4		125.6							143.0		142.8
o-CH_3										142.85		
p-C_2H_5	125.7		125.8				134.2		134.15	142.85		142.7
p-$C(CH_3)_3$	125.4		125.8		125.8	125.45	134.2		134.1	143.4	143.1	142.7
p-OCH_3	126.2	126.1	125.7	125.8	125.4	125.3				143.6		142.6
m-OCH_3	126.5	126.2	125.9									
o-OCH_3	127.3											
p-$N(CH_3)_2$				125.1		125.0					142.6	142.3

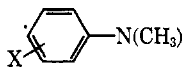
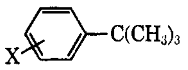
^{a} ±0.3 cps. ^{b} 0.53–0.83 g/ml (all concentrations will be expressed as grams of solute/ml of solvent). ^{c} 0.20–0.27 g/ml. ^{d} 0.40–0.83 g/ml.

Table II. Coupling Constant Regression Analysis Parameters

		ρ, cps/σ^b	C, cps^b	r^c	S^d	n^e
Toluenes	Neat	1.67	126.0	0.836	0.332	13
	CCl_4	1.72	125.9	0.925	0.227	16
t-Butylbenzenes	Neat	0.568	125.6	0.705	0.293	8
	CCl_4	1.03	125.6	0.928	0.186	8
Dimethylanilines	Neat^a	2.68	134.8	0.901	0.333	6
	CCl_4	1.74	134.5	0.945	0.229	9
	CCl_4^{f}	1.49	134.5	0.974	0.158	9
Anisoles	Neat	1.08	143.4	0.750	0.384	12
	CCl_4	1.83	143.1	0.915	0.308	12
	CCl_4^{g}	1.38	143.0	0.970	0.184	17

^{a} Includes one chloroform value. ^{b} Parameters of the equation $J = \rho\sigma + C$. ^{c} Correlation coefficient. ^{d} Standard deviation of residuals. ^{e} Number of compounds. ^{f} σ* used for p-CHO. ^{g} σ* used for p-NO_2, p-CN, and p-CHO.

Table III. Chemical Shifts in CCl_4^{a} (±0.5 cps)

X		
p-NO_2		82.4
m-NO_2	182.5	
p-CN	182.3	
p-CHO	184.9	
p-Br	174.7	78.0
p-Cl		
m-Cl	176.6	
p-H	175.3	78.8
p-CH_3	172.5	78.0
p-C_2H_5		
p-$C(CH_3)_3$	173.5	77.0
p-OCH_3	169.3	77.2
p-$N(CH_3)_2$		75.7

^{a} Extrapolated to infinite dilution; obtained at 60 Mcps.

aniline[14] series in $CHCl_3$ have been reported. The values in each series show linear relationships to the σ constants. Marcus, *et al.*,[11] report the results of a least-squares analysis of the anisole values (10% in CCl_4; ordinary σ constants used) and their own toluene values (0.1 *M* in CCl_4; ordinary σ constants used). Recently Sakurai and Ohtsuru[13] found $\rho = 5.38$, and $S = 0.990$ for the t-butyl series (5% in CCl_4; ordinary σ constants used), while Rae and Dyall[14] found $\rho = 10.1$, $r = 0.965$, and $S = 1.07$ for the dimethylanilines (0.2% in $CHCl_3$; σ* values used for 8 of 15 compounds).[14] Table IV presents the least-squares parameters of the δ–σ relationships for the four series; the t-butyl and dimethylamino values are from the present study, and normal Hammett σ constants were used for all groups except p-CN and p-CHO in the dimethylaniline series. This table also contains the results of a least-squares analysis of the anisole data[12] (excluding

Table IV. Chemical Shift Regression Analysis Parameters

	ρ, cps/σ	C, cps	r	S	n	Ref
Toluenes	12.8	138.9	0.884	2.56	22	7
t-Butylbenzenes	4.56	78.3	0.946	0.752	7	a
Dimethylanilines^c	9.59	173.9	0.964	1.502	9	a
Anisoles	16.2	6.35^b	0.891	0.0442^b	15	7
Anisoles^d	10.1	6.36^b	0.916	0.0392^b	14	7, a

^{a} This study. ^{b} In τ (ppm) units. ^{c} σ* used for p-CHO and p-CN. ^{d} σ* used for p-NO_2, p-CHO, p-COOH, p-$COOCH_3$, and p-CN.

---

(14) I. D. Rae and L. K. Dyall, *Aust. J. Chem.*, 19, 835 (1966).

p-NH_2) using σ^* values for 5 of the 14 derivatives. It is to be noted that the use of σ^* values produces a marked change in slope and a small improvement in correlation coefficient and standard deviation.

Examination of the data in Tables II and IV reveals that the $J_{C^{13}-H}$ *vs.* σ slopes with the highest correlation coefficients (CCl_4 values and use of σ^* for Y = N and O) vary as toluenes > dimethylanilines > anisoles > *t*-butylbenzenes, whereas δ–σ slopes vary as toluenes > anisoles $\geqslant$ dimethylanilines > *t*-butylbenzenes.

Discussion

The amount of s character in the C–H bonds of the methyl groups in the system X-Ph-Y$(CH_3)_n$ can be related by Bent's isovalent hybridization model[15] to the effective electronegativity of Y: the greater this electronegativity, the greater the amount of s character. The magnitude of the C^{13}–H coupling constant has been shown to be a function of the amount of s character in the carbon–hydrogen bond and the effective nuclear charge of carbon. Since both of these parameters are directly related to the effective electronegativity of Y, one must conclude that the coupling constant itself is a function of the effective electronegativity of Y: the greater this electronegativity, the greater the coupling constant. That such is the case is readily seen from an examination of Table I. In dilute CCl_4 solution, the methyl C^{13}–H coupling constants for *t*-butylbenzene, dimethylaniline, and anisole are 125.5, 134.45, and 143.0 cps, respectively. This increase in the magnitude of the coupling constants follows the order of increasing electronegativity of Y.

As is obvious from the results presented above, the methyl C^{13}–H coupling constants and proton chemical shifts in the substituted aromatic system studied are directly proportional to the Hammett σ constants of the substituents. This result can be rationalized quite nicely using the Bent model. The presence of an electron-donating substituent, *i.e.*, one whose σ constant is negative, on the ring decreases the effective electronegativity of the entire system to which the methyl group is bonded. Such a decrease in electronegativity results in decreased s character for the C–H bonds as well as decreased effective nuclear charge of carbon in the O-methyl group and a smaller C^{13}–H coupling constant, relative to the unsubstituted parent. The converse, of course, applies to electron-attracting substituents. The chemical shift data can be explained in an analogous fashion.

Two notable exceptions to the observed linearity are the *p*-CN derivatives in the dimethylanilines and the anisoles; the observed C^{13}–H coupling constants in these cases are considerably greater than would be predicted on the basis of the substituent Hammett σ values. If, however, the σ^* values are accepted as a more accurate representation of the electron-withdrawing ability of these groups and are plotted against C^{13}–H coupling constants, plots with better linear consistency are obtained for the anisoles (neat and in CCl_4) and for the dimethylanilines (in CCl_4). The coupling constant of *p*-nitroanisole likewise appears anomalous until the σ^* value of the nitro group is employed. The coupling constant of *p*-nitrodimethylaniline could not be determined owing to its insolubility. However, it should exhibit the same behavior.

This effect is very likely a consequence of resonance interactions between the lone pairs on nitrogen and oxygen and the multiple bonds of the substituents. For example, a structure such as IIIb probably contributes significantly to the ground state of such molecules as *p*-cyanoanisole (Y = O, n = 1) and *p*-cyanodimethylaniline (Y = N, n = 2). Such charge-separated contributors would tend to increase the s character (or the sp^2 character) of the Y atom and, therefore, lead to an enhanced C^{13}–H coupling constant. This effect is, of course, absent in the toluene and *t*-butylbenzene series.

IIIa IIIb

Several secondary trends in the coupling constant deserve mention: first, for almost every compound with a complete set of *ortho*, *meta*, and *para* isomers, the *ortho* neat value is the highest. This is very likely a result of the high inductive effect in this position.

Second, the *p*-NO_2 value is higher than the *m*-NO_2 value in the anisole series, but the reverse is true in the toluene series and probably the *t*-butyl (an accurate *m*-NO_2 CCl_4 value could not be obtained). This is probably a consequence of resonance interaction between NO_2 and OCH_3 in the *para* isomer, and, if so, the order *para* > *meta* should also prevail in the dimethylaniline series (*vide supra*).

Several workers[16] have postulated a linear relationship between C^{13}–H coupling constants and proton chemical shifts in systems in which anisotropy effects are approximately constant. The higher correlation coefficients for the J–σ relationships as opposed to the δ–σ relations and the consequent rather *crude* J–δ relation may be an indication of some anisotropy effects in the chemical shift data.

A linear relationship between the C^{13}–H coupling constants and Hammett σ constants having been established, it was hoped that the relative abilities of carbon, oxygen, and nitrogen to transmit electronic effects could be determined through an examination of the slopes of these plots (Table II).

The relative slopes of the J–σ lines (CCl_4 values with highest r) for the four series indicate that substituent effects are transmitted most effectively to the methyl group in the toluenes. Transmission to the methyls in the *t*-butylbenzene series is least effective, and the anisole and dimethylaniline series fall in between. The greater transmission in the toluenes is easily rationalized by the inductive or field effects; the methyl group in the toluenes is one atom closer to the benzene ring than it is in the other series. The order of slopes Y = N > O > C for the other compounds is quite probably a result of overlap between the lone pairs of oxygen or nitrogen and the aromatic π system.

The relative ρ values (CCl_4 values with highest r) obtained from the chemical shift data argue for essentially the same order of transmission: toluenes > anisoles

---

[15] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

[16] H. Goldstein and G. S. Reddy, *J. Chem. Phys.*, **36**, 2644 (1962); N. Matwiyoff and R. S. Drago, *ibid.*, **38**, 2583 (1963).

$\geqslant$ 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 ($Y = O \geqslant N$) 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.

Acknowledgment. The authors are indebted to The University of Pennsylvania and to Elizabethtown College for use of their nmr facilities and to the Research Corporation for financial support of this project through a Frederick Gardner Cottrell Grant.

Photolysis of 2-Methylcyclohexanone[1]

C. C. Badcock,[2] M. J. Perona, G. O. Pritchard, and B. Rickborn[3]

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106. *Received September 5, 1968*

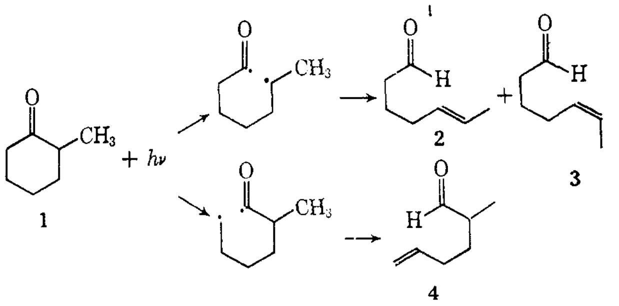
Abstract: The photolysis of 2-methylcyclohexanone at 3130 Å in both the gas and liquid phase has been critically reexamined. Contrary to an earlier report, both *trans*- and *cis*-5-heptenal are obtained as major products. Separate photolysis of various mixtures of the product aldehydes established that 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



---

[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.