Polar Effects in Radical Reactions. V. Homolytic Aromatic Substitution by Methyl Radicals[1]

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Methyl radicals, produced by thermolysis of *tert*-butyl peracetate at 110°, effect substitution reactions with benzene and substituted benzenes. Partial rate factors were calculated using the relative reactivities of methyl radicals with substituted benzenes and the isomer distribution of the toluenes produced. A Hammett equation plot of the partial rate factors vs. σ gives $\rho = 0.1 \pm 0.1$, indicating that the methyl radical, like the phenyl radical, shows little polar character. This ρ value is very similar to the ρ found for reaction of methyl radicals with the methyl group of substituted toluenes, supporting the suggestion previously made by us that the ρ values are very similar for addition to benzenes and for abstraction from toluenes by any given radical. This similarity had not been noticed previously since in ionic or polar reactions, an electrophilic species which adds to aromatic rings generally does not also react as the benzylic position. The assumption which is inherent in most homolytic aromatic substitution studies, that the relative amounts of substituted benzenes formed are proportional to the relative rates of attack at the three positions of a monosubstituted benzene, is discussed and its limitations noted. The inadequacy of the correlation coefficient as a measure of goodness of fit of points to a line with a small slope is discussed.

The quantitative treatment of homolytic aromatic substitution reactions using the technique of partial rate factors[3,4a,5] provides insight into the nature both of the attacking radical[6,7] and of the aromatic system undergoing attack.[8] Radicals whose addition to benzene has been studied include the phenylethynyl,[9] benzoyloxy and substituted benzoyloxy,[10] isopropoxycarboxy,[11] and 1-cyclohex-1-enyl[12] radicals, and the oxygen atom,[13] all of which are electrophilic; the cyclohexyl,[14] *n*-propyldimethylsilyl,[15] and pentamethylsilanyl[15] radicals, which are nucleophilic; and the cyano,[16] cyclopropyl,[17] phenyl,[4b,9,18] and substituted phenyl[18] radicals and the hydrogen atom,[6] all of which are nearly electroneutral.

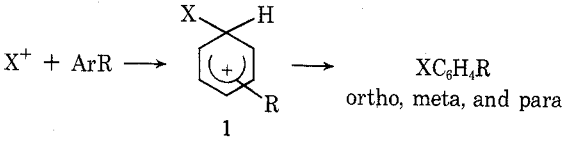
Homolytic substitution by methyl radicals has been the subject of numerous studies. The influence of substituents on reactivity in methylation was originally reported by Szwarc and coworkers[19] as a methyl affinity scale and later studied by Williams.[20] Substituent effects on orientation have been given by Eliel[21] (for toluene), Waters,[22] and Williams.[23] Surprisingly, however, no single reference describes the influence of a substituent on both reactivity and product distribution. Although Williams reported both types of data, he does not report a ρ value, and a Hammett correlation of his data is rather unsatisfactory.[24] We have studied substituent effects on both reactivities and orientations in the reaction of methyl radicals with five benzene derivatives and find $\rho \simeq 0.1$.

Our kinetic system involved the competitive reaction of methyl radicals, produced by thermolysis of *tert*-butyl peracetate at 110°, with either a substituted benzene or benzene.[28] The relative reactivities of methyl addition ($k_H{}^X$), determined from yields of the substituted toluene to toluene formed, are given in Table I. From these data and the isomer distribution of substituted toluenes listed in Table I, partial rate factors ($F_i{}^X$), given in Table II, were calculated from eq 1,[3,4a,5] where *s*, a statistical correction factor,

$$F_i{}^X = s(k_H{}^X)\text{ (fraction substitution at } i\text{th position in } XC_6H_4CH_3) \quad (1)$$

equals 6 for $F_p{}^X$ and 3 for $F_m{}^X$ and $F_o{}^X$, and $k_H{}^X$ is the total rate constant for the addition of methyl to all positions in C_6H_5X relative to the total rate constant for reaction with benzene.

Inherent in our analysis is the requirement that the relative amounts of substituted toluenes formed are proportional to the relative rates of attack at the three positions of a monosubstituted benzene. Although this assumption is made in all homolytic aromatic substitution studies[3,4a,5] and appears to be satisfactorily fulfilled,[4c,29] it is probably not strictly true in all these systems. It should be noted that in *ionic* electrophilic aromatic substitution, a reaction which generally is excellently correlated by linear free energy relations (LFER),[30] the analogous assumption is surely valid. The rate of attack by the electrophile X^+ at meta or para positions would be expected to closely parallel the ultimate yield of meta- or para-substituted products since the substituent R in intermediate **1** does not divert intermediate **1** from its expected aromatization to XC_6H_4R (eq 2). Similarly, in abstraction of hydrogen atoms from substituted toluenes by the radical X·, the conversion of the intermediate radicals **2** to the ultimate products would not be expected to be influenced markedly by the substituent R (eq 3). However, in homolytic aromatic substitution (eq 4), the nature and position of the substituent R in intermediate radicals **3a**, **3b**, or **3c** probably exerts an influence on the relative rates at which these radicals dimerize, disproportionate, or are oxidized to ortho, meta, or para XC_6H_4R by a radical present in the system.[4c,7,31]



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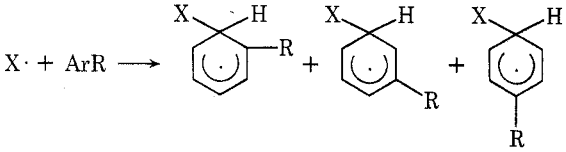
(2)

$$X\cdot + RC_6H_4CH_3 \longrightarrow XH + \underset{\mathbf{2}}{RC_6H_4CH_2\cdot} \quad (3)$$



3a **3b** **3c**

(4)

In our system, we tested this assumption that the substituent R does not influence the partition of intermediates **3a–c** by varying the rate of production of intermediates **3** and **3** (R = H), and consequently their concentrations, and observing the effect on $k_H{}^X$ and isomer distribution. The constancy of both $k_H{}^X$ (Table I) and isomer distribution

Table I
Relative Rates and Isomer Distributions of Methylation of C_6H_5X at 110°

				$\%XC_6H_4CH_3$		
X	[TBA][a]	$[C_6H_6]/[C_6H_5X]$	k_H^X [b]	Ortho	Meta	Para
NO_2	0.05	1.1	4.3	71	6	23
	0.05	3.4	3.8	70	7	22
	0.05	5.7	4.2	70	8	21
	0.1	1.1	4.6	69	7	23
	0.1	3.4	6.1	68	9	23
	0.1	5.7	5.4	71	6	23
		Av[c]	4.6 ± 1.0	70	7	22
CN	0.05	1.1	4.2	58	10	32
	0.05	3.4	6.0			
	0.05	5.7	4.9	61	11	29
	0.1	1.1	5.2	57	12	32
	0.1	3.4	5.3			
	0.1	5.7	5.3			
		Av[c]	5.1 ± 0.6	59	11	31
Br	0.05	1.2	1.4	66	22	12
	0.05	3.5	1.6			
	0.05	5.9	1.6	66	23	11
	0.1	1.2	1.8	65	24	11
	0.1	3.5	1.7			
	0.1	5.9	1.9	66	22	12
		Av[c]	1.7 ± 0.2	66	23	12
Cl	0.05	1.2	1.2	69	20	11
	0.05	3.5	1.5			
	0.05	5.8	1.6			
	0.1	1.2	1.7	69	21	10
	0.1	3.5	1.6			
	0.1	5.8	1.5			
		Av[c]	1.5 ± 0.2	69	20	10
CH_3	0.1	*d*	0.8			
	0.1	*d*	1.2			
	0.1	0		53	31	15
	0.1	1.0		51	32	15
		Av[c]	1.0 ± 0.2	52	32	15

[a] Molar concentration of *tert*-butyl peracetate. [b] Relative reactivity of C_6H_5X to C_6H_6 toward methyl addition. [c] Average k_H^X ± one standard deviation, and average isomer distribution. [d] Indirectly determined. See Experimental Section for discussion.

Table II
Partial Rate Factors for Methylation of C_6H_5X at 110°

X	F_o^X	F_m^X	F_p^X	Registry no.
NO_2	9.7	0.97	6.1	98-95-3
CN	9.0	1.7	9.5	100-47-0
Br	3.4	1.2	1.2	108-86-1
Cl	3.1	0.90	0.90	108-90-7
H	(1.0)	(1.0)	(1.0)	71-43-2
CH_3	1.6	0.96	0.90	108-88-3

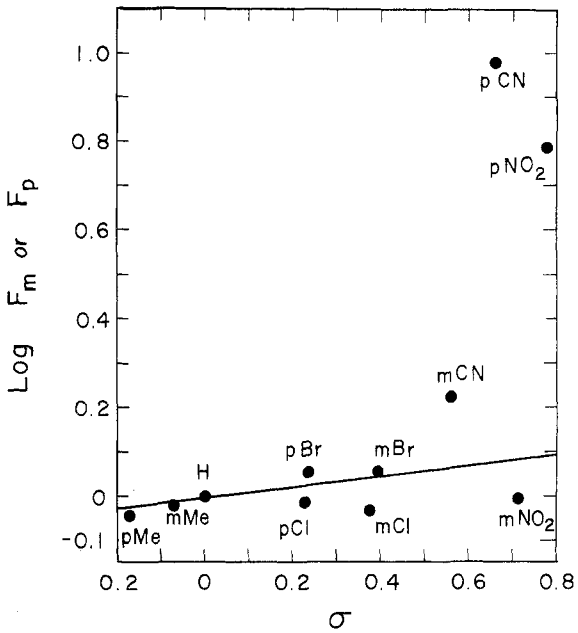


Figure 1. A plot of the partial rate factors for substitution by methyl radicals in monosubstituted benzenes at 110° vs. σ constants. The least-squares treatment gives $\rho = 0.1 \pm 0.1$ for meta substituents only and $\rho = 0.14 \pm 0.9$ for all points except *p*-CN and *p*-NO_2.

(Table I) as the initiator concentration and ratio of reactants are varied over the limited range studied supports the assertion that this assumption is satisfactorily obeyed in our system.[32] However, this is negative evidence and does not establish the general applicability of the partial rate factor approach in radical systems. Furthermore, in our system, as in most others that have been studied, the range over which the variables can be altered to test the constancy of the partial rate factors is rather narrow. At present, it appears that an adequate test of the assumption that the rates of formation of **3a–c** parallel the rates of formation of final ortho-, meta-, and para-substituted products may not be possible. In theory, the direct measurement of the rates of formation of **3a–c** is possible using pulse techniques; however, the one application of this technique of which we are aware found that the absorption peaks of three isomers of **3** could not be resolved so that only the sum of the three could be determined.[33] In the final analysis, the most striking testimonial to the utility of the partial rate factor method is the fact that it works. This is not totally satisfactory because, among other things, it may work because of the fortuitous cancellation of influences from several factors. We suspect that this probably is the case: LFER correlations of homolytic aromatic substitution generally are not as satisfactory as those of hydrogen abstraction from toluenes; for one thing, they appear more susceptible to the influence of "extra" resonance.[6,34]

A Hammett treatment (Figure 1) of the partial rate factors of Table II vs. σ gives the following: meta substituents only, $\rho = 0.1 \pm 0.1$ (six points); meta and para substituents $\rho = 0.1 \pm 0.1$ (nine points).[35,36] The *p*-NO_2 and *p*-CN points are not included in this analysis because these points lie far from the least-squares lines. In fact, in homolytic aromatic substitution reactions, the *p*-NO_2 and *p*-CN groups always have partial rate factors which are much different from the values predicted by the linear regression line.[4b,6,14,17–19,22] Apparently these deviations arise because the "extra" resonance of these groups is far beyond that accommmodated by their σ constants.[34] A "σ-dot" scale is needed, but the reaction series on which to base this scale remains a mystery.[6]

Since the methyl radical is considered to be nearly electroneutral, the ρ for homolytic aromatic methylation, like that for phenylation,[4b,9,18] should be about zero. However, the values which can be obtained from the literature are surprisingly large; the ρ calculated by combining data of Szwarc,[19] Eliel,[21] and Waters[22] is 1.4 ± 0.4[6] and the value obtained from the data of Williams[20,23] is 0.8 ± 0.4.[24] The data on which both these ρ values are based suffer from the fact that relative rates and isomer distributions were measured at different temperatures, and often in different laboratories. Furthermore, the isomer distributions were determined by ir analyses of fractions obtained by subjecting the reaction mixtures to distillation and preparative VPC,

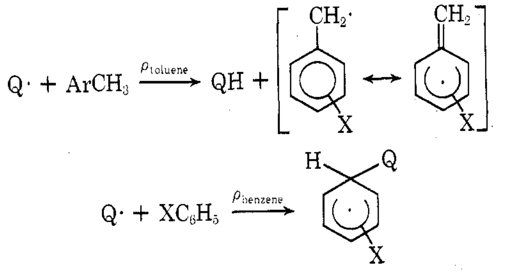
Table III
Comparison of ρ Values for Hydrogen Abstraction from Ring-Substituted Toluenes and for Addition to Substituted Benzenes[a]

	H abstraction from toluenes		Addition to benzenes	
Radical	ρ	Temp, °C	ρ	Temp, °C
Methyl	-0.2^{b}	100	0.1^{c}	110
Hydrogen atom	-0.1^{d}	35	-0.3^{e}	40
Phenyl	-0.5^{f}	60	0.1^{h}	80
Phenyl	-0.2^{g}	60	0.0^{i}	*i*
Phenyl			0.1^{j}	20
p-$CH_3C_6H_4\cdot$	-0.1^{f}	60	0.0^{j}	20
p-$XC_6H_4\cdot$	$-0.3^{f,k}$	60	$-0.3^{j,l}$	20
p-$NO_2C_6H_4\cdot$	-0.6^{f}	60	-0.7^{j}	20
Cyclopropyl	$0.2^{m,n}$	100	0.1^{m}	100
Cyclohexyl			1.1^{o}	90
3-Heptyl	0.7^{p}	80		
Isopropyl	0.9^{q}	35		

[a] This correlation is based on meta substituents, except for a few cases in which an insufficient number of meta derivatives were studied. In those instances the ρ values are based on both meta- and para-substituted compounds. [b] W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969). [c] This work. [d] R. W. Henderson and W. A. Pryor, submitted for publication. [e] W. A. Pryor, T. H. Lin, J. P. Stanley, and R. W. Henderson, *J. Am. Chem. Soc.*, **95**, 6993 (1973). [f] W. A. Pryor, J. T. Echols, and K. Smith, *J. Am. Chem. Soc.*, **88**, 1189 (1966). [g] R. F. Bridger and G. A. Russell, *ibid.*, **85**, 3754 (1963). [h] Data summarized by G. H. Williams, *Chem. Soc., Spec. Publ.*, **24**, 36 (1970). [i] G. Martelli, P. Spagnolo, and M. Tiecco, *J. Chem. Soc. B*, 1413 (1970) (temperature not given). [j] R. Itô, T. Migita, N. Morikawa, and O. Simamura, *Tetrahedron*, **21**, 955 (1965). [k] X is bromine. [l] X is chlorine. [m] T. Shono and I. Nishiguchi, *Tetrahedron*, **30**, 2183 (1974). [n] Value for 2-phenylcyclopropyl radical. [o] J. R. Shelton and C. W. Uzelmeier, *Intra-Sci. Chem. Rep.*, **3**, 293 (1969). [p] R. W. Henderson, *J. Am. Chem. Soc.*, **97**, 213 (1975). [q] W. A. Pryor and W. H. Davis, Jr., unpublished results.

rather than by analytical VPC of the reaction mixture itself as we have done. The ρ value we report here, 0.1, certainly is more indicative of the expected electroneutrality of the methyl radical.

Our interest in the Hammett ρ value for the homolytic methylation of benzenes was kindled not by the failure of previous ρ values to reflect the methyl radical's nonpolar character but rather by the failure of these values to substantiate a proposal we made. We suggested that for a given radical, Q·, the ρ for hydrogen abstraction from the side chain of substituted toluenes (ρ_{toluene}) is very similar to ρ for additions to benzenes (ρ_{benzene}).[6] At the time we made this suggestion, the most significant difference in ρ_{toluene} and ρ_{benzene} was for the methyl radical; $\rho_{\text{toluene}} = -0.2$[39] and $\rho_{\text{benzene}} \sim 1$. However, the ρ we report here, $\rho_{\text{benzene}} = 0.1$, is very close to that for reaction of methyl with toluene, and thus supports our suggestion. Table III lists radicals for which both ρ_{toluene} and ρ_{benzene} are known. Although it is not obvious that there need be a relation between these sets of ρ values, evidently, $\rho_{\text{toluene}} \simeq \rho_{\text{benzene}}$.



(5)

The correlation coefficient, r, of our data ($r = 0.4$[35]) is much smaller than 0.9, which is the minimum value which has been recommended as acceptable.[27,38b] The value of r, however, is a poor measure of the "goodness of fit" of the experimental points to the least-squares line in linear free energy relations, since r is related to the slope of the line, ρ.[40] The numerators of r and ρ are the same (eq 6), where

$$r = \frac{\Sigma xy}{(\Sigma x^2 \Sigma y^2)^{1/2}} \qquad (6)$$

$$\rho = \frac{\Sigma xy}{\Sigma x^2}$$

$x = X_i - \bar{X}$, $y = Y_i - \bar{Y}$, and the averages of the coordinates of the points (X_i, Y_i) are $\bar{X}$ and $\bar{Y}$.[26b] Lines of zero slope ($\rho = 0$ and $\Sigma xy = 0$) give $r = 0$ regardless of whether all points lie on the line or are widely scattered from it. It is not surprising, therefore, that when Hammett correlations result in small ρ values, small r's have been obtained even though the points fall close to the line; e.g., see Figure 1 of ref 9, in which $\rho = 0.03 \pm 0.03$ but $r = 0.17$; and Figure 1 of ref 17, in which $\rho = 0.09 \pm 0.07$ but $r = 0.57$.

Experimental Section

Benzene (MCB Chromatoquality) and toluene (Baker Ultrex) were used as received. No toluene in the benzene was observed by VPC. The other substituted benzenes were vacuum distilled before use. Benzene-free *tert*-butyl peracetate (TBA, Lucidol) was obtained by vacuum distillation. All VPC analyses were performed on a Varian 1440 flame ionization gas chromatograph using a 10 ft × 2 mm glass column of 10% OV-1 on 100/120 Chromosorb W AW-DMCS (column A) or a 10 ft × 2 mm glass column consisting of 8 ft of 15% 4,4′-azoxydianisole on 100/120 Chromosorb W AW with 1 ft of 10% OV-1 on 100/120 Chromosorb W AW-DMCS on each end (column B). Liquid crystals, such as 4,4′-azoxydianisole, are excellent stationary phases to affect the VPC separation of ortho, meta, and para isomers of disubstituted benzenes.[41]

General Procedure. Solutions of various benzene/substituted benzene ratios (1, 3, and 5 to 1 by volume) and different TBA concentrations (0.1 and 0.05 *M*) were prepared in glass ampoules. After degassing by three freeze–pump–thaw cycles, the tubes were sealed and heated at 110 ± 0.5° for 10 hr. The ampoules were opened and samples were analyzed by VPC. Column A was employed to determine the substituted toluene to toluene ratio (relative reactivity) for all the substituted benzenes (except toluene) and to determine the isomer distribution of nitrotoluene from nitrobenzene. The other isomer distributions (ortho-, meta-, para-substituted toluenes) were measured using column B. Since methylation of benzene gives toluene, the relative reactivity of toluene to benzene, k_H^{Me}, cannot be evaluated by direct competition. Instead, the relative reactivity of toluene to bromobenzene, k_{Br}^{Me}, was determined from the amount of xylene to bromotoluene produced in a competition experiment involving toluene and bromobenzene. Multiplying this value, k_{Br}^{Me}, by the relative reactivity of bromobenzene to benzene, k_H^{Br}, gives k_H^{Me}.

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(24) Methyl affinities obtained at 85°[20] were combined with isomer distributions from studies at 84–115°[23] to give partial rate factors which were statistically analyzed to give these data: meta only, $\rho = 0.78 \pm 0.37$ (five points, $r = 0.77$, $s_{yx} = 0.16$); meta and para, $\rho = 0.82 \pm 0.37$ (nine points, $r = 0.64$, $s_{yx} = 0.22$).[25] These correlation coefficients are low for ρ values of these sizes,[27] and plots of the data show that the experimental points are widely scattered from the least-squares line.

(25) The ρ values are reported as follows: $\rho = b \pm s_b$ (n points, r, s_{yx}), where b is the slope of the least-squares line, s_b is the standard deviation of the slope, n is the number of points, r is the correlation coefficient, and s_{yx} is the standard deviation from regression.[26a]

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(28) (a) Since the reactions were only run for 1 initiator half-life, the yield of toluenes must be less than 0.05 *M*. After decomposition of 0.1 *M tert*-butyl peracetate in chlorobenzene and benzene ($[C_6H_6]/[C_6H_5Cl] = 3.5$), the total concentration of the toluenes formed in this reaction was 0.031 *M*. Once formed, these toluenes are not significantly consumed by benzylic hydrogen abstraction by methyl radicals because the ratio of rate constants for this abstraction to addition to the aromatic ring is less than 10[28b] while the concentration ratio [toluenes]/[benzenes] is less than 0.005. (b) W. A. Pryor, D. L. Fuller, and J. P. Stanley, *J. Am. Chem. Soc.*, **94,** 1632 (1972); M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry", Kekule Symposium, Butterworths, London, 1958, p 262; S. H. Wilen and E. L. Elliel, *J. Am. Chem. Soc.*, **80,** 3309 (1958).

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(35) The complete analysis of our methylation data gives, for meta only, $\rho = 0.1 \pm 0.1$ (six points, $r = 0.37$, $s_{yx} = 0.1$); meta and para, $\rho = 0.1 \pm 0.1$ (nine points, $r = 0.44$, $s_{yx} = 0.09$).[25]

(36) Partial rate factors for *p*-nitro and *p*-cyano substituents are not included in these correlations because they lie far off the line determined by the meta substituents alone. The suggestion of van Bekkum and Taft[37,38a] has been followed; meta substituents are used to determine a line and the fit of para substituents to this line is examined. Also see discussion in ref 6.

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Stable Carbocations. CLXXVIII. Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study of Protonated and Diprotonated Acyclic and Cyclic Diketones in FSO_3H-SbF_5-SO_2 Solution[1]

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The carbon-13 NMR chemical shifts for a series of protonated acyclic and cyclic diketones were determined in FSO_3H-SbF_5-SO_2 solution at −60° together with those of their parent diketones. Phenyl-substituted diketones were studied in FSO_3H-SO_2ClF solution at −80° to avoid protonation of the aromatic ring. Protonation of acyclic and cyclic diketones results in deshielding of the carbonyl resonances of the order of 10 ppm and the carbons α to the carbonyl carbons by 5 ppm. The results are discussed in view of other substituent effects and provide an insight into the extent of keto–enol tautomerism operating for the ions and precursors at low temperatures. Diprotonated diketones can also serve as model systems for carbodications.

Keto–enol tautomerism is well recognized in 1,2- and 1,3-dicarbonyl compounds.[4] Physical measurements of the extent of keto–enol tautomeric equilibria of acyclic and cyclic diketones is of interest since both tautomers can be observed under suitable conditions. Extensive research efforts have been carried out along these lines utilizing bromine titrations,[5] infrared[6] and ultraviolet spectroscopy,[7] and proton[8] and ^{17}O nuclear magnetic resonance.[9] ^{13}C NMR carbonyl chemical shifts for some acyclic diketones were reported by Stothers and Lauterbur.[10] Proton magnetic resonance studies of protonated 1,3-diketones have been reported by Brouwer.[11]

In our previous investigation of protonated heteroaliphatic compounds, we reported a proton NMR study of protonated diones in FSO_3H-SbF_5-SO_2 solution.[12] We felt it, therefore, of interest to extend this study by undertaking a systematic ^{13}C NMR investigation of protonated 1,2-, 1,3- and 1,4-diketones (as well as their parent compounds) using the Fourier transform method. As protonated ketones can serve as model compounds for carbenium ions, diprotonated diketones are expected to provide similar information about carbodicationic systems. The study of these ions is being reported in detail in a forthcoming paper.

Results and Discussion

We undertook the ^{13}C NMR study of a series of protonated diketones in the FSO_3H-SbF_5-SO_2 superacid system, and for comparison also studied their neutral parent compounds. FSO_3H-SO_2ClF solution was used for aromatic diketones sensitive to the stronger "Magic Acid" system.