Structural Effects in Solvolytic Reactions. 16. The Effect of Conformation of the Cyclopropyl, Phenyl, and Isopropyl Substituents on Their Electronic Contributions to the Electron-Deficient Center

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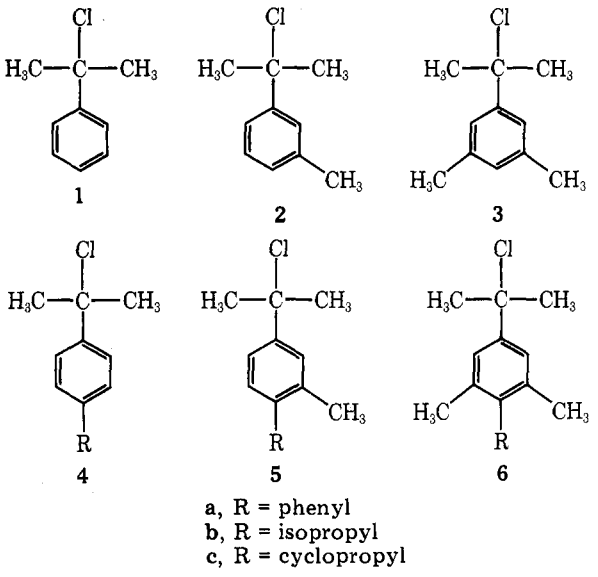
The effect of conformation on the electronic contribution of the cyclopropyl, phenyl, and isopropyl substituents to an electron-deficient center was examined by placing these substituents in the para position of the *tert*-cumyl chloride molecule and determining the rates of solvolysis of these *tert*-cumyl chlorides with no, one, and two *m*-methyl groups flanking the para substituent. The results reveal that there is only a small influence of conformation on the electronic contribution of the isopropyl substituent to the electron-deficient center. On the other hand, there are significant effects of the flanking *m*-methyl groups on the electronic contributions of the cyclopropyl and phenyl substituents to the electron-deficient center. An examination of molecular models indicates that the two flanking *m*-methyl groups compel rotation of the phenyl substituent from the coplanar arrangement of the two aromatic rings believed to favor maximum electronic supply. On the other hand, these models indicate that the two flanking *m*-methyl groups allow, indeed, force the cyclopropyl substituent to assume a quasi-coplanar arrangement with the electron-deficient center. It is therefore concluded that in contrast to the phenyl substituent, such a conformation is not conducive to favorable electronic supply. Therefore, the bisected conformation of the cyclopropyl substituent, which is possible both in the monomethyl and unmethylated derivatives, strongly facilitates electronic contributions to the electron-deficient center.

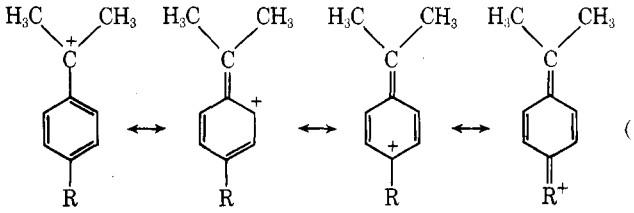
The effect of conformation on the maximum orbital overlap of a group with an adjacent p orbital has been the subject of numerous investigations over the years by experimental and theoretical chemists.[2] In particular, the effects of conformation of phenyl,[2c-e,3] cyclopropyl,[4] and alkyl[2a,b,4g,5] groups on the stability of adjacent carbonium ions have been extensively studied.

We have measured the effect of conformation on the electronic contributions of cyclopropyl, phenyl, and isopropyl substituents to the electron-deficient center of the developing *tert*-cumyl cation. This examination required the synthesis and measurement of the rate of solvolysis of the series of compounds **1–6.** In compounds **4–6,** solvolysis affords a carbonium ion of which a resonance structure places a positive charge in the para position where the group R may satisfy the electron deficiency generated (eq 1).

Inasmuch as no resonance interactions are possible in the meta positions, the inductive contributions of the *m*-methyl groups are constant throughout the series **2, 3, 5,** and **6.** However, the rate of a para-substituted *tert*-cumyl chloride relative to unsubstituted *tert*-cumyl chloride (**1**) measures both the inductive and conjugative (either resonance or hyperconjugation) contribution of a given substituent. Evidence is available which demonstrates that the inductive effect of a group is nearly the same in the meta and para positions of benzene derivatives.[6] Thus any difference in rate of a para- vs. a meta-substituted *tert*-cumyl chloride relative to **1** is a measure of the additional conjugative contributions of a given substituent.

Each of the substituents (cyclopropyl, phenyl, and isopropyl) whose total electronic contribution is measured in **4a–c,** is forced into a definite conformation with respect to the electron-deficient center in the series **5a–c** and **6a–c.** The inductive effects of the *m*-methyl groups are small and are taken to be additive throughout the series **2, 3, 5,** and **6.** It is usually found that the combined effect of two substituents can be represented by the product of their individual rates relative to the unsubstituted parent compound. Indeed, data are available for many reactions to confirm this additivity relationship.[7-13] Thus the additivity relationship predicts that the rates of the series **5a–c** and **6a–c** will be equal to the product of the rates of the individual substituents relative to





(1)

tert-cumyl chloride. The difference between predicted and observed rates in the series **5a–c** and **6a–c** measures the effect of conformation on the electronic contribution of each of the three substituents in carbonium ion reactions.

Special interest is centered in the series **4c–6c,** where solvolysis affords carbonium ions, resonance structures of which give species analogous to cyclopropylcarbinyl cations. Cyclopropylcarbinyl cations exhibit special behavior. To account for such behavior, several theoretical models with definite conformational requirements for their existence have been proposed. The conformational limitations imposed upon the cyclopropyl substituent in **5c** and **6c**[4k] permit a choice to be made among the various proposed theoretical models by

Table I. Rate Constants and Derived Data for the Solvolysis of *tert*-Cumyl Chlorides in 90% Aqueous Acetone

Registry no.	Substituents	k_1, $s^{-1} \times 10^5$ 0.0 °C	k_1, $s^{-1} \times 10^5$ 25.0 °C	R k_1/k_H (25 °C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta F^{\ddagger} - \Delta F_0^{\ddagger}$
934-53-2	None	0.60	12.4	1.0	19.0	−12.6	0
13240-60-3	3-Methyl[a]	1.26	24.8	2.0	18.6	−11.8	−0.41
10477-70-0	3,5-Dimethyl[b]	2.44	47.3	3.9	18.6	−11.3	−0.81
42325-37-1	4-Phenyl	4.89	94.8	7.65	18.6	−9.9	−1.20
58502-71-9	3-Methyl-4-phenyl	3.17	61.7	4.98	18.6	−10.7	−0.95
58502-72-0	3,5-Dimethyl-4-phenyl	3.91	74.9	6.04	18.5	−10.6	−1.07
5650-08-8	4-Isopropyl	13.6	223	18.0	17.5	−11.8	−1.71
58502-73-1	3-Methyl-4-isopropyl	22.4	341[c]	27.5	17.0	−12.6	−1.96
58502-74-2	3,5-Dimethyl-4-isopropyl	34.5	507[c]	40.9	16.8	−12.6	−2.20
7175-64-6	4-Cyclopropyl	146.5	1905[c]	154	16.0	−12.6	−2.98
10477-69-7	3-Methyl-4-cyclopropyl	162.7	2100[c]	169	16.0	−12.6	−3.04
10477-71-1	3,5-Dimethyl-4-cyclopropyl	30.3	447[c]	36.0	16.9	−12.7	−2.12
40349-51-7	3,4-Dimethyl[c]	42.6	634	51.1	16.0	−14.8	−2.33
7243-79-0	4-Methyl[a]	20.6	322	26.0	17.3	−12.0	−1.92
19936-08-4	3-Isopropyl[a]	1.05	23.2	1.87	19.4	−10.2	−0.37
58502-75-3	3-Phenyl[d]		3.97	0.32	19.3	−13.9	0.67
19936-06-2	3-Cyclopropyl[e]	0.89	19.0	1.53	19.3	−10.9	−0.25

[a] Reference 17. [b] Unpublished research with T. Inukai. [c] Calculated from data at lower temperatures. [d] Reference 16. [e] Reference 53.

Table II. Rate Constants and Derived Data for the Solvolysis of *tert*-Cumyl Chlorides in 97.5% Aqueous Acetone

Substituents	k_1, $s^{-1} \times 10^5$ 0.0 °C	k_1, $s^{-1} \times 10^5$ 25.0 °C	R k_1/k_H (25 °C)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$	$\Delta F^{\ddagger} - \Delta F_0^{\ddagger}$
None	0.023[a]	0.46	1.0	18.8	−19.8	0
4-Isopropyl	0.46	7.15	15.5	17.2	−19.8	−1.63
3-Methyl-4-isopropyl	0.71	11.7	25.4	17.6	−17.6	−1.92
3,5-Dimethyl-4-isopropyl	1.26	18.8	40.9	16.9	−18.8	−2.20
4-Cyclopropyl	3.02	40.1	87.2	16.2	−19.8	−2.65
3-Methyl-4-cyclopropyl	3.41	44.5	96.7	16.1	−20.0	−2.71
3,5-Dimethyl-4-cyclopropyl	0.93	15.3	33.2	17.6	−17.1	−2.12

[a] Calculated from data at other temperatures.

Table III. Relative Rates of Solvolysis of Substituted *tert*-Cumyl Chlorides in 90% Aqueous Acetone at 25.0 °C

Substituted *tert*-cumyl chloride	k_{rel}	Effect of para substituent	% electronic contribution maintained
Hydrogen	1.0		
3-Methyl	2.0		
3,5-Dimethyl	3.9		
4-Phenyl	7.7	7.7	100
3-Methyl-4-phenyl	5.0	2.5	32.5
3,5-Dimethyl-4-phenyl	6.0	1.6	20.2
4-Isopropyl	18.0	18.0	100
3-Methyl-4-isopropyl	27.5	13.8	76.4
3,5-Dimethyl-4-isopropyl	40.9	10.5	58.3
4-Cyclopropyl	154	154	100
3-Methyl-4-cyclopropyl	169	84.5	54.9
3,5-Dimethyl-4-cyclopropyl	36.0	9.2	5.8
4-Methyl	26.0	26.0	100
3,4-Dimethyl	51.1	25.6	98.3
2-Fluorenyl	173	43.3	

comparison of predicted and observed rates in the series **4c–6c.** The isopropyl series **4b–6b** provides a steric and electronic approximation of the cyclopropyl series as well as providing information about the conformational requirements of the isopropyl substituent itself. The phenyl substituent, known to have conformational requirements from earlier studies of biphenyl compounds,[14,15] provides a reference against which the conformational requirements of the isopropyl and cyclopropyl substituents can be compared.

Results and Discussion

The appropriate kinetic data are summarized in Tables I–III. Because of the difficulty in following the rapid rates of some of the substituted *tert*-cumyl chlorides at 25 °C in 90% aqueous acetone by the titrimetric method used in previous rate studies of substituted *tert*-cumyl chlorides,[16,17] the rates of solvolysis of these compounds were calculated from data at other temperatures. As a check on the rates thus calculated, the rates of solvolysis of these compounds were also measured at 0 and 25 °C in 97.5% aqueous acetone. An excellent correlation between the two solvents was observed. With the exception of compounds **4c** and **5c**, both of which exhibited special rate enhancements, an approximately 30-fold decrease was observed in determining a given compound in 97.5% vs. 90% aqueous acetone. Earlier studies had shown that values of k_1/k_H do not change significantly in aqueous acetone of varying composition[18] and that entropy terms for a series of closely related compounds do not exhibit major variations.[19] An excellent parallel relationship of k_1/k_H between the two solvents of varied acetone content and agreement of entropy values within a given solvent system were observed.

The desired *tert*-cumyl chlorides were synthesized by treating the substituted phenyldimethylcarbinol or the corresponding olefins dissolved in methylene chloride with hydrogen chloride at 0 °C using the automatic hydrochlorinator apparatus.[20] Inasmuch as the tertiary chlorides are unstable and difficult to purify, we were content to prepare pure sam-

ples of the tertiary alcohols or olefins, and to use the crude tertiary chlorides directly without further treatment. It has been demonstrated previously that this procedure has no measurable effect on the measured rate of solvolysis.[17]

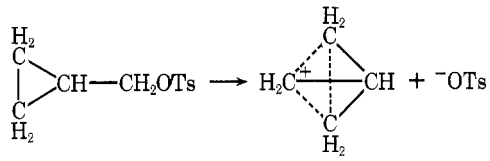
Perusal of the kinetic data for each of the meta- and para-substituted *tert*-cumyl chlorides indicated a rate enhancement for each of the substituents in the para position relative to 1. The para/meta relative rates in 90% aqueous acetone for each of the substituents are cyclopropyl, 101; phenyl, 23.4; isopropyl, 9.53. Thus the enhancement in rates cannot be due to inductive effects and must be due to special conjugative interactions which are possible in the para position, but not in the meta position.

Conformational Requirements of the Cyclopropyl Substituent. The *p*-cyclopropyl substituent produced the greatest enhancement in rate and exhibited the most pronounced effect of conformation upon electronic contribution to the electron-deficient center of any of the substituents studied in this investigation.

Considerable interest has surrounded the carbonium ion type reactions of cyclopropylcarbinyl derivatives. A vast body of literature exists which establishes the unusual ability of a cyclopropyl substituent to interact conjugatively with an adjacent electron-deficient center.[4,21] Cyclopropylcarbinyl cations are remarkably stable. Solvolyses leading to the formation of such ions exhibit dramatically enhanced rates. An example of this behavior is offered by the solvolysis of tertiary 2-R-2-propyl *p*-nitrobenzoates.[22] Thus major increases are exhibited from the 2-methyl derivative (1.0) to 2-phenyl (969) to cyclopropyl (503 000).

Many structures for the cyclopropylcarbinyl cation have been considered. Indeed, to account for the ease of interconversion of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives and the markedly enhanced solvolytic rates of cyclopropylcarbinyl derivatives, several different intermediate ions have been proposed in the literature. For example, tricyclobutonium,[23] unsymmetrical bicyclobutonium,[24] delocalized cyclobutyl[25] (symmetrical bicyclobutonium), bisected cyclopropylcarbinyl[4d] (symmetrical), and unsymmetrical homoallylic ions[26] have been advanced.

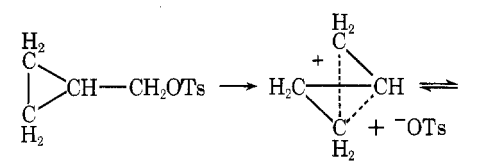
The fast rate of solvolysis of cyclopropylcarbinyl tosylate was originally attributed to the stabilization of the transition state leading to the formation of the presumably highly stabilized symmetrical tricyclobutonium ion (eq 2). This species



(2)

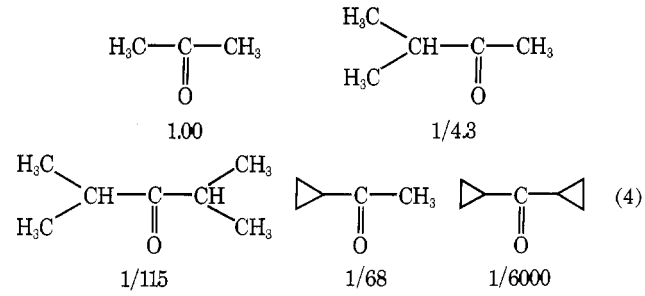
is σ bridged. Note that it contains three carbon atoms bonded to five different atoms.

Later it was observed that the reactions of tagged cyclopropylcarbinyl derivatives did not show the full equilibration of the tag required by the tricyclobutonium ion.[27] Consequently, it was proposed that the cyclopropylcarbinyl cation exists as a rapidly equilibrating set of three equivalent bicyclobutonium ions (eq 3). This is a σ-bridged species with one carbon atom bonded to five nearest neighbors.



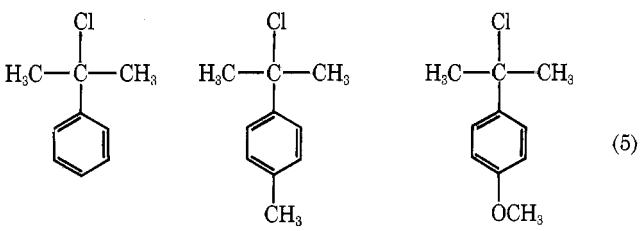
(3)

It was shown by Hart and Sandri that a number of secondary and tertiary derivatives containing cyclopropyl groups undergo solvolysis with similar rate enhancements but without rearrangements.[28] Consequently, the cyclopropyl group is capable of providing electron density to stabilize a carbonium ion without rearrangement of the structure occurring. Similarly, a study of the rates of reduction of ketones containing cyclopropyl groups established that these rates are quite low[29] (4). Consequently, the cyclopropyl group is capable of providing electron density to the carbonyl group in these ketones, as well as to the electron-deficient centers of carbonium ion.



(4)

The standard tool of the organic chemist in exploring electron deficiency in an organic system is to introduce substituents into the appropriate positions and ascertain the effect. For example, the proposed explanation for the stabilizing effect of the phenyl group in stabilizing the *tert*-cumyl cation postulates delocalization of the positive charge from the carbonium carbon to the ortho and para positions of the aromatic ring (1). Introduction of methyl and methoxy substituents into the para position of the *tert*-cumyl system should assist in satisfying this electron deficiency and result in an increase in the stability of the cation and an increase in the rate of solvolysis. This is observed[2d] (5).



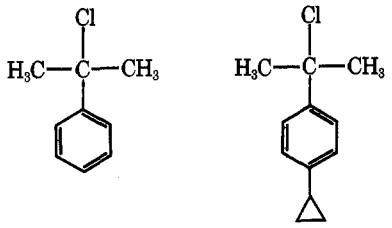
(5)

If the cyclopropyl group stabilizes a carbonium ion center to which it is attached, it should develop an electron deficiency in the ring.[4k] Indeed, the introduction of a methyl group or an ethoxy group into the ring results in large rate enhancements.[30] Moreover, these rates give a linear plot against the σ^+ constants.

Moreover, the authors made a detailed study of the effect of cumulative methyl groups.[30] They noted an unusually good additivity for each successive methyl substituent. The introduction of a 2- or 3-methyl substituent has almost the same effect [the factor for a trans 2- or 3-methyl (10–11) is slightly larger than the cis factor (7–10)] regardless as to whether or not there was already one such substituent. On the assumption that the ions have similar structures in the transition states leading to them, it was concluded that electron supply from the cyclopropyl ring must involve a symmetrical contribution and that their results are not consistent with the bicyclobutonium ion formulations.

We explored the electronic contributions of the cyclopropyl substituent in the para position of the *tert*-cumyl system.[31] We also came to the conclusion that the electronic contributions from the cyclopropyl substituent cannot involve σ bridging through space.

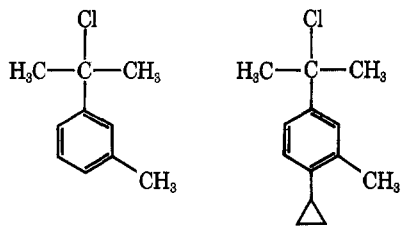
A *p*-isopropyl group increases the rate of solvolysis of *tert*-cumyl chloride in 90% aqueous acetone at 25 °C by a factor of 18. On the other hand, a *p*-cyclopropyl group is much more effective—it increases the rate by a factor of 154 (6). A



(6)

rel rate 1.0 154

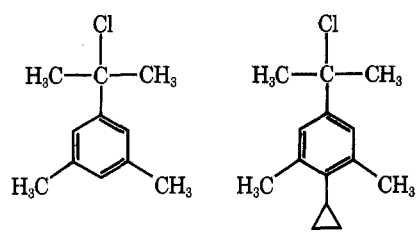
single *o*-methyl substituent, as in 3-methyl-4-cyclopropyl-*tert*-cumyl chloride, increases the relative rate to 169. Correcting for the contribution of the *m*-methyl substituent, a factor of 2, reveals only a modest decrease in the effect of the cyclopropyl group accompanying the introduction of the single methyl substituent (7). On the other hand, the observed rel-



(7)

rel rate 1.0 84.5

ative rate for 3,5-dimethyl-4-cyclopropyl-*tert*-cumyl chloride is 36. Correcting this for the contribution of two *m*-methyl substituents, a factor of 4, reveals a sharp drop in the contribution of the cyclopropyl substituent to the rate, to a factor of only 9 (8). Thus, with two *o*-methyl substituents, the con-



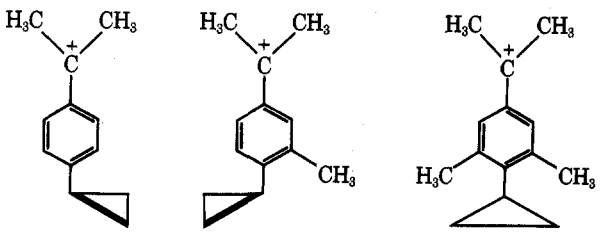
(8)

rel rate 1.0 9.0

tribution of the *p*-cyclopropyl substituent to the rate drops from its original high value of 154 down to a low value of 9, even lower than the effect of a simple alkyl substituent, such as 18 for isopropyl.

Parallel k_R/k_H values for the cyclopropyl substituted compounds were observed in both 90 and 97.5% aqueous acetone.

There is increasing evidence that the maximum interaction between a cyclopropane group and an adjacent electron-deficient center is achieved with the bisected conformation.[4,21a,b,30,32-34] Such a bisected arrangement for the cyclopropyl substituent in the *tert*-cumyl system readily accounts for the pronounced effect of the conformation of the cyclopropyl group on the relative rates. This is apparent from the examination of the structures **4'c–6'c**. The bisected arrange-



4'c **5'c** **6'c**

ment of the cyclopropyl group, shown in **4'c**, would not be seriously affected by the introduction of a single methyl group, as shown in **5'c**. However, two methyl substituents effectively block this conformation **5'c**, greatly reducing the electronic contributions from the cyclopropyl substituents.[4k]

Indeed, from a study of the reactivity of geometrically constrained cyclopropylcarbinyl systems as a function of angle, the reactivity (ranging over 11 powers of ten) of cyclopropylcarbinyl cations was shown to be a continuous function of the geometry between the vacant p orbital and the cyclopropyl ring.[35] The authors further noted that the cyclopropylcarbinyl cation with 60° geometry, approximately the geometry of a bicyclobutonium ion, is considerably less stable than the ion with 30 or 0° (i.e., bisected) geometries.[35] Moreover, solvolyses of optically active cyclopropylmethylcarbinyl derivatives do not yield optically active products.[36] A σ-bridged intermediate would have been expected to retain asymmetry.

Clearly, the enhanced rate of solvolysis of cyclopropylcarbinyl derivatives is not the result of σ bridging through space of the carbonium ion center with one or both of the more distant carbon atoms of the ring.

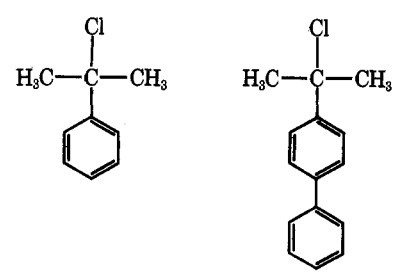
Although beyond the scope of the present publication, it should be pointed out that a σ-bridged structure has been proposed for the primary cyclopropylcarbinyl cation under stable ion conditions.[4a] This conclusion was based on a discrepancy between the observed ^{13}C shift and that calculated for a set of equilibrating classical cations. However, recent test of another NMR criterion proposed for such a σ-bridged cation, a high $J_{^{13}C-H}$ coupling constant for the methine hydrogen, has given negative results.[41] Consequently, the original conclusion[4a] must be considered questionable.[41]

Conformational Requirements of the Phenyl Substituent. Resonance between the developing p orbital of a cationic center and the π system of an aryl ring plays an important part in facilitating solvolysis of benzyl systems.[2c-e,3,37] For an aryl group to exhibit its maximum electronic contribution via resonance, it must assume a coplanar arrangement with the electron-deficient center.

The conformational requirements of a phenyl group are examined in the *p*-phenyl-*tert*-cumyl system.

Biphenyl exists in the gas phase in a noncoplanar conformation with an angle of approximately 45° between the plane of the two rings.[38,39] The electronic spectrum of biphenyl indicated an interplanar angle of 20° in solution and 40–43° in the vapor state.[40] The molecule presumably assumes this twisted conformation to minimize the steric interactions of the four ortho hydrogens. However, the relief of these steric interactions should also reduce the resonance contributions of a *p*-phenyl substituent in the solvolysis of *p*-phenyl-*tert*-cumyl chloride.

A *p*-phenyl group increases the rate by a factor of 7.65 (9).



(9)

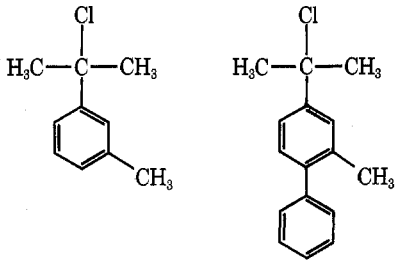
rel rate 1.00 7.65

Indeed, this is much lower than the rate increase of 43 for a *p*-phenyl group when corrected for the noncoplanarity.[14]

Since the interplanar angle of the rings in biphenyl is 20° in solution, this would account for the observed behavior of a phenyl group being a poorer source of electron density than an alkyl group in the *tert*-cumyl system. The $-I$ effect of the phenyl group would continue to be operative in the para po-

sition while the +*R* effect would be diminished owing to the deviation from coplanarity of the rings.

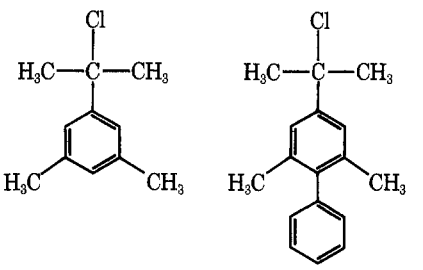
The introduction of an *o*-methyl group into biphenyl is reported to increase the interplanar angle in solution of *o*-methylbiphenyl to about 60°.[40] Hence there is less orbital overlap between the phenyl rings than in biphenyl. Indeed, this is exemplified in the decrease in the effect of a *p*-phenyl group by the introduction of a methyl group ortho to the *p*-phenyl group (10).



(10)

rel rate 1.00 2.49

The substitution of a second methyl group ortho to the *p*-phenyl substituent produces an additional loss of the electronic contribution of the phenyl substituent (11). Thus there must be substantial deviation from coplanarity of the rings.



(11)

rel rate 1.00 1.55

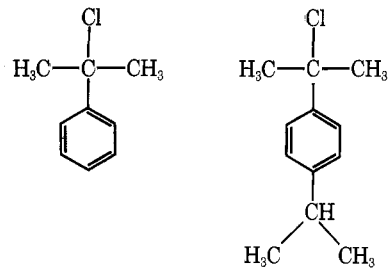
Thus the observed conformational requirements on the electronic contributions of the phenyl group are consistent with other reports. For example, a rate decrease resulting from steric inhibition to resonance was demonstrated by the introduction of ortho substituents into the *tert*-cumyl system.[42] In the solvolysis of 1-naphthyl-2-propyl chloride, the peri hydrogen is reported to interfere sterically with the preferred coplanar arrangement.[43]

Moreover, in a study of the solvolysis of highly crowded aryldialkylcarbinyl *p*-nitrobenzoates, it was shown that as the molecule becomes more crowded around the cationic center, the cation is less able to assume the planar conformation.[44] Hence the aryl group will be twisted out of coplanarity. This results in a marked decrease in reactivity.

Conformational Requirements of the Isopropyl Substituent. In a number of reactions of alkylated benzene derivatives an electron release from the alkyl groups in the order of methyl > ethyl > isopropyl > *tert*-butyl is observed (the Baker–Nathan order),[45] a sequence opposite to that of the usual inductive effect order, methyl < ethyl < isopropyl < *tert*-butyl. The Baker–Nathan order has been attributed to hyperconjugation[5a,46–49] in which carbon–hydrogen hyperconjugation is more effective than carbon–carbon hyperconjugation.

The conformational requirements of an isopropyl group were examined in the para position of the *tert*-cumyl system. The isopropyl substituent exhibited the smallest effect of conformation on electronic contribution to an electron-deficient center of any of the three substituents studied.

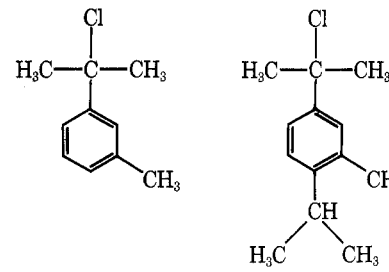
A *p*-isopropyl substituent in *tert*-cumyl chloride increases the rate by a factor of 18.0 (12).



(12)

rel rate 1.0 18.0

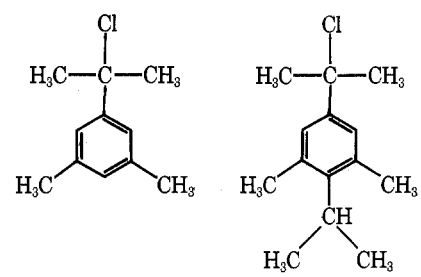
With a methyl group ortho to the isopropyl group, the stabilizing influence of the *p*-isopropyl on the rate decreases to 13.8 (13).



(13)

rel rate 1.0 13.8

Two methyl groups ortho to the isopropyl group resulted in a further decrease in the electronic contributions of the *p*-isopropyl. Thus the effect of the *p*-isopropyl substituent on the rate is only 10.5 (14). Parallel k_R/k_H values for the



(14)

rel rate 1.0 10.5

isopropyl substituted compounds were observed in both 90 and 97.5% aqueous acetone.

These results are suggestive of an example of steric inhibition of hyperconjugation. Possible steric interactions which are absent in 4-isopropyl-*tert*-cumyl chloride become more important in 3-methyl-4-isopropyl-*tert*-cumyl chloride and especially prominent in 3,5-dimethyl-4-isopropyl-*tert*-cumyl chloride. These increasing steric interactions would place the isopropyl group in a conformation in which the more important carbon–hydrogen hyperconjugation would be less likely. Hence, there is a decrease in the effectiveness of the *p*-isopropyl in stabilizing the transition state during ionization.

In a study of the relationship between hyperconjugation and conformation analogous to this investigation, the ethanolysis of 4-alkyldiphenylmethyl (4-alkylbenzhydryl) chlorides, where the alkyl group was methyl, ethyl, *n*-propyl, isobutyl, and neopentyl, exhibited rates decreasing in the order cited.[50] Thus the rate diminishes progressively as the nonbonding interaction of the side chain and the aromatic ring hinder carbon–hydrogen hyperconjugation. They also studied the corresponding 3,5-dimethyl-4-alkyldiphenylmethyl chlorides where the alkyl group was methyl, ethyl, and *n*-propyl. Here the investigators concluded that the hyperconjugative effect of a primary alkyl group is not affected by torsional rotation of the group about the bond between it and the benzene ring.[50]

It might be suggested that in the *p*-isopropyl-*tert*-cumyl system the results could also be explained by the increasing

steric hindrance to solvation of the para position as methyl groups are substituted in the 3 and 5 positions.[51] However, the observed rate of 3,4-dimethyl-*tert*-cumyl chloride coincides with the rate predicted by the additivity principle. Thus, the full electronic contribution of the 4-methyl substituent is maintained in contrast to the diminished electronic contribution of the 4-isopropyl substituent.

Experimental Section

All products yielded physical constants in agreement with literature values and/or microanalytical data within the accepted limits as well as NMR spectra in agreement with the indicated structures. All spectra were run at 60 MHz and chemical shifts are expressed as δ values relative to internal tetramethylsilane. Homogeneity of the products was established by gas chromatographic examination.

The precursors to the 4-substituted *tert*-cumyl chlorides, *p*-isopropylphenyldimethylcarbinol,[17] 4-diphenyldimethylcarbinol,[52] and *p*-cyclopropyl-α-methylstyrene[53] were prepared by previously reported methods.

Preparation of Precursors to the Methyl-Substituted 4-Phenyl-*tert*-cumyl Chlorides. 3-Methyl-4-phenyl-α-methylstyrene. 3-Methyl-4-phenylbromobenzene[54] [bp 120–122 °C (1.5 mm), n^{20}D 1.6209] was converted into a Grignard reagent and allowed to react with acetone, and distillation of the crude product gave a 46.3% yield of the olefin, bp 120–122 °C (1.5 mm), n^{20}D 1.5994. The ^{1}H NMR spectrum showed peaks at δ 2.22 (s, 3 H, 3-methyl), 2.10 (m, 3 H, α-methyl), 4.97 and 5.28 (m, 2 H, olefinic protons), and 7.05–7.30 (m, 3 H, aromatic).

Anal. Calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.16; H, 7.99.

Gomberg Reaction between 5-Isopropyl-*m*-xylene and Aniline. Following procedures suggested by Hey[55] and Gomberg and Pernert[54] for analogous compounds, aniline was diazotized and allowed to react with 5-isopropyl-*m*-xylene to give an 18.4% yield of a 64/36 mixture of **3,5-dimethyl-4-phenylisopropylbenzene** and **3,5-dimethyl-2-phenylisopropylbenzene,** respectively. The 64/36 mixture was fractionated through a Todd column with a rating of 60 plates, operating at a 15:1 reflux ratio to give fractions enriched in the higher boiling 3,5-dimethyl-4-phenylisopropylbenzene and the fractions were separated using preparative vapor phase chromatography (F & M Model 770 automatic preparative gas chromatograph, Carbowax 20M on Chromosorb W, 200–250 °C, temperature programmed, 7.5 °C/min). One fraction from the Todd column fractionation, bp 140 °C (6 mm), analyzed pure by VPC analysis (Perkin-Elmer 226 instrument, 150-ft Apiezon L capillary column, 150 °C) for 3,5-dimethyl-4-phenylisopropylbenzene, n^{20}D 1.5600. The ^{1}H NMR spectrum showed peaks at δ 2.80 (septet, 1 H, methine proton), 1.25 (d, 6 H, isopropyl CH_3's), 1.96 (s, 3- and 5-methyl groups), 6.76 (s, 2 H, 2- and 6-protons), and 6.9–7.32 (m, 5 H, 4-phenyl protons).

Anal. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.82; H, 9.05.

A VPC purified sample of 3,5-dimethyl-2-phenylisopropylbenzene gave n^{20}D 1.5604. The ^{1}H NMR spectrum showed peaks at δ 2.63 (septet, 1 H, methine proton), 1.07 (d, 6 H, isopropyl CH_3's), 1.88 (s, 3 H, 3-methyl), 2.28 (s, 3 H, 5-methyl), 6.74 (d, 1 H, 6-proton), 6.84 (d, 1 H, 4-proton), and 6.88–7.32 (m, 5 H, 2-phenyl protons).

3,5-Dimethyl-4-phenylacetophenone. The oxidation was carried out according to eq 15

$$3\text{Ar—}i\text{-}C_3H_7 + 10CrO_3 + 30HOAc \xrightarrow{Ac_2O} 3\text{Ar—}COCH_3 + 3CO_2 + 21H_2O + 10Cr(OAc)_3 \quad (15)$$

found to be general for the selective oxidation of an exposed isopropyl group. In a 100-ml round-bottom flask equipped with a drying tube were placed 3,5-dimethyl-4-phenylisopropylbenzene (6.0 g, 0.0268 mol), acetic acid (16.1 g, 0.268 mol, 15.3 ml), and acetic anhydride (15.3 ml). Chromium trioxide was added portionwise in small amounts so that at no time did the temperature exceed 30–35 °C. A temperature rise accompanied each addition and after the addition was complete, an additional 16 ml of glacial acetic acid was added, and the solution stirred overnight. The mixture was then poured on ice and most of the acetic acid was neutralized, although care was taken to not reach the point where chromium salts would precipitate. Ether was added, the aqueous layer thoroughly extracted, and the combined ether extracts thoroughly washed with 10% sodium hydroxide to remove all acetic acid and then washed with water and dried over sodium sulfate/magnesium sulfate. Removal of solvent yielded 3.04 g (0.0136 mol) of the crude ketone corresponding to a 50.7% yield. A sample purified by preparative VPC (Aerograph instrument, Dow Corning Silicone 550 on Chromosorb W, 200 °C) gave the pure ketone, mp 73.5–74.5 °C, 2,4-DNP 249–250 °C. The ^{1}H NMR spectrum showed peaks at δ 2.04 (s, 6 H, 3- and 5-methyls), 2.48 (s, 3 H, acetyl methyl), 6.87–7.40 (m, 5 H, 4-phenyl protons), and 7.50 (s, 2 H, 2- and 6-aromatic protons).

Anal. Calcd for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.89; H. 7.18.

3,5-Dimethyl-4-phenyl-*tert*-cumyl Alcohol. 3,5-Dimethyl-4-phenylacetophenone was heated with methylmagnesium iodide to give an 81.8% yield of the carbinol, mp 120–121 °C (from 60–65 °C petroleum ether). The ^{1}H NMR spectrum showed peaks at δ 1.60 (s, 6 H, dimethylcarbinyl protons), 2.02 (s, 6 H, 3- and 5-methyls), and 6.95–7.39 (m, 7 H, aromatic).

Anal. Calcd for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 85.18; H. 8.12.

Preparation of Precursors to the Methyl-Substituted 4-Isopropyl-*tert*-cumyl Chlorides. 2-Chloromethyl-1,4-diisopropylbenzene. The procedure suggested for the chloromethylation of an analogous compound was used.[56] Chloromethylation of 1,4-diisopropylbenzene[57] using stannic chloride and chloromethyl methyl ether gave a 79.8% yield of the desired compound, bp 124 °C (5 mm), n^{20}D 1.5175. The ^{1}H NMR spectrum showed peaks at δ 1.23 (d, 6 H, 4-isopropyl methyls), 1.25 (d, 6 H, 1-isopropyl methyls), 2.83 (septet, 1 H, methine proton of 4-isopropyl group), 3.25 (septet, 1 H, methine proton of 1-isopropyl group), 4.52 (s, 2 H, 2-chloromethyl protons), and 6.98–7.12 (m, 3 H, aromatic).

Anal. Calcd for $C_{13}H_{19}Cl$: C, 74.09; H, 9.09; Cl, 16.82. Found: C, 74.27; H, 9.04; Cl, 16.53.

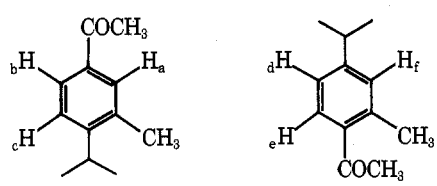
2-Methyl-1,4-diisopropylbenzene. Reduction of 2-chloromethyl-1,4-diisopropylbenzene using lithium aluminum hydride and lithium hydride[58] in tetrahydrofuran gave a 95.5% yield of the hydrocarbon, bp 71 °C (1.2 mm), n^{20}D 1.4977. The ^{1}H NMR spectrum showed peaks at δ 1.19 (d, 12 H, 1,4-diisopropyl methyls), 2.76 (septet, 1 H, methine proton of 1-isopropyl), 3.03 (septet, 1 H, methine proton of 4-isopropyl), 2.25 (s, 3 H, 2-methyl), and 6.74–6.98 (m, 3 H, aromatic).

Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.73. Found: C, 88.66; H, 11.67.

3-Methyl-4-isopropylacetophenone. 2-Methyl-1,4-diisopropylbenzene was oxidized by the chromium trioxide procedure described for 3,5-dimethyl-4-phenylacetophonone to give a 40.1% yield of the ketone, bp 84 °C (0.3 mm), n^{20}D 1.5249 [lit.[59] bp 254–256 °C (740 mm), n^{20}D 1.5320]. Gas chromatographic analysis (Perkin-Elmer 154 instrument, Dow Corning Silicone 550 on Chromosorb W, 155 °C) indicated the product to be homogeneous.

Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.75; H, 9.07.

The choice was between two possible ketonic products:



7 8

Structure 7 predicts that two protons will be shifted downfield due to the deshielding effect of the aceto group and one proton would appear upfield. (Both H_a, broad doublet due to meta coupling with H_b, and H_b, AB pattern with meta coupling, would appear downfield while H_c, AB pattern, would appear upfield). Structure 8 predicts the opposite: two protons appearing upfield and one proton appearing downfield (H_d, AB pattern with meta coupling, and H_f, broad doublet due to meta coupling with H_d, both appearing upfield, while H_e, AB pattern, would appear downfield). The spectrum observed is exactly that predicted for 3-methyl-4-isopropylacetophenone (7): H_a, broad doublet due to meta coupling with H_b, δ 7.57; H_b, AB pattern with meta coupling, δ 7.63; and H_c, AB pattern, δ 7.15 (cf. structure 7).

3-Methyl-4-isopropyl-α-methylstyrene. 3-Methyl-4-isopropylacetophenone was treated with methylmagnesium iodide to give a 94.9% yield of the crude carbinol which upon purification by preparative VPC (Aerograph instrument, Dow Corning Silicone 550 on Chromosorb W, 200 °C) gave the dehydration product, the olefin, n^{20}D 1.5322. The ^{1}H NMR spectrum showed peaks at δ 1.22 (d, 6 H, 4-isopropyl methyls), 2.29 (s, 3 H, 3-methyl), 3.08 (septet, 1 H, methine proton of isopropyl), 2.07 (m, 3 H, α-methyl group), 4.91 [m, 1 H, olefinic (cis to α-methyl)], 5.20 [m, 1 H, olefinic (trans to α-methyl)], and 7.09 (s, 3 H, aromatic).

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.50; H, 10.13.

Alkylation of 5-Isopropyl-*m*-xylene. In a 2-l. three-necked flask fitted with a stirrer and thermometer were placed reagent grade 5-isopropyl-*m*-xylene (250 g, 1.69 mol) and isopropyl alcohol (96 g, 1.60

mol). The solution was cooled to 0 °C. Previously cooled (~0 °C) 80% aqueous sulfuric acid (567 ml) was added at a rate such that the temperature did not exceed 20 °C during the addition. After the addition was complete, the reaction mixture was stirred for 3 days at room temperature. VPC analysis of an aliquot (Perkin-Elmer 154, Carbowax 20M on Chromosorb W, 90 °C) indicated approximately 50% conversion of the starting material. The layers were separated, and the organic layer washed with dilute base and then water and dried over sodium sulfate/magnesium sulfate. Removal of the unreacted 5-isopropyl-*m*-xylene, bp 89 °C (19 mm), using a Todd column left 130 g of isopropyl alkylates. VPC analysis (Perkin-Elmer 226, 150-ft, Carbowax 20M capillary column, 90 °C) indicated two major isomers which constituted 98% of the isopropyl alkylates. Utilizing the F & M 770 automatic preparative gas chromatograph (Carbowax 20M on Chromosorb P, 100–190 °C, temperature programmed at 7.5 °C/min) the isomers were separated to give **2,6-dimethyl-1,4-diisopropylbenzene** (55%), n^{20}D 1.5070, and **3,5-dimethyl-1,2-diisopropylbenzene** (45%), n^{20}D 1.5064. The ^{1}H NMR spectrum of 2,6-dimethyl-1,4-diisopropylbenzene showed peaks at δ 2.35 (s, 6 H, 2,6-dimethyls), 2.77 (septet, 1 H, methine proton of 4-isopropyl), 3.42 (septet, 1 H, methine proton of 1-isopropyl), 1.22 (d, 6 H, methyls of 4-isopropyl), 1.35 (d, 6 H, methyls of 1-isopropyl), and 6.78 (s, 2 H, aromatic). The ^{1}H NMR spectrum of 3,5-dimethyl-1,2-diisopropylbenzene showed peaks at δ 2.28 (s, 3 H, 3-methyl), 2.20 (s, 3 H, 5-methyl), 1.22 (d, 6 H, methyls of 1-isopropyl), 1.37 (d, 6 H, methyls of 2-isopropyl), 6.60 (s, 1 H, 4-proton), and 6.75 (s, 1 H, 6-proton). The septet peaks of the methine protons of the 1- and 2-isopropyl groups could not be readily assigned owing to extensive overlapping.

For 2,6-dimethyl-1,4-diisopropylbenzene:

Anal. Calcd for $C_{14}H_{22}$: C, 88.35; H, 11.65. Found: C, 88.39; H, 11.89.

3,5-Dimethyl-4-isopropylacetophenone. 2,6-Dimethyl-1,4-diisopropylbenzene was oxidized to the crude ketone in 56.1% yield by the procedure described for 3,5-dimethyl-4-phenylacetophenone. Purification by preparative VPC (Aerograph instrument, Dow Corning Silicone 550 on Chromosorb W, 180 °C) gave the pure ketone, n^{20}D 1.5350, 2,4-dinitrophenylhydrazone, mp 238–238.5 °C. The ^{1}H NMR spectrum showed peaks at δ 1.31 (d, 6 H, methyls of 4-isopropyl), 3.41 (septet, 1 H, methine proton of 4-isopropyl), 2.38 (s, broad, 9 H, 3,5-dimethyls and acetyl methyl), and 7.32 (s, 2 H, aromatic).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.53. Found: C, 82.06; H, 9.46.

3,5-Dimethyl-4-isopropyl-α-methylstyrene. 3,5-Dimethyl-4-isopropylacetophenone was treated with methylmagnesium iodide to give an 87.1% yield of the crude carbinol which on purification by preparative VPC (Aerograph instrument, Dow Corning Silicone 550 on Chromosorb W, 180 °C) gave the dehydration product, the olefin, n^{20}D 1.5365. The ^{1}H NMR spectrum showed peaks at δ 1.30 (d, 6 H, methyls of 4-isopropyl), 3.35 (septet, 1 H, methine proton of 4-isopropyl), 2.33 (s, 6 H, 3,5-dimethyls), 2.06 (m, 3 H, α-methyl), 4.87 (m, 1 H, olefinic proton cis of α-methyl), 5.16 (m, 1 H, olefinic proton trans to α-methyl), and 6.86 (s, 2 H, aromatic).

Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 88.99; H, 10.73.

Preparation of Precursors to the Methyl-Substituted 4-Cyclopropyl-*tert*-cumyl Chlorides. 3-Methyl-4-cyclopropylacetophenone. Aluminum chloride catalyzed acetylation of *o*-methylphenylcyclopropane[60] in anhydrous chloroform at −45 °C gave a 66.6% yield of ketone, bp 112 °C (1 mm), n^{20}D 1.5610, 2,4-dinitrophenylhydrazone, mp 215 °C. VPC analysis (succinate polyester of butanediol, 150-ft capillary, 160 °C) indicated a single product. The ^{1}H NMR spectrum showed an AB pattern at δ 6.92, an AB pattern at δ 7.70 with meta coupling, and a broad doublet at δ 7.78 superimposed upon the δ 7.70 AB pattern.

Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 83.05; H, 8.29.

3-Methyl-4-cyclopropyl-α-methylstyrene. 3-Methyl-4-cyclopropylacetophenone was treated with methylmagnesium iodide to give a 95% yield of the crude carbinol which on purification by preparative VPC (Aerograph instrument, Dow Corning Silicone 550 on Chromosorb W, 180 °C) gave a 52.2% isolated yield of the olefin, n^{22}D 1.5554. The ^{1}H NMR spectrum showed peaks at δ 2.05 (m, 3 H, α-methyl), 2.37 (s, 3 H, 3-methyl), 7.14 (d, 1 H, 2-proton), 7.08 (d, 1 H, 6-proton), 4.93 and 5.24 (m, 2 H, olefinic), 1.54–1.93 (m, 4 H, methylene protons of cyclopropyl), and 0.5–1.0 (m, 1 H, methine proton of cyclopropyl).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.51; 90.48; H, 9.38; 9.46.

2,6-Dimethylphenylcyclopropane. 2,6-Dimethylstyrene was treated with excess methylene iodide and zinc–copper couple following the LeGoff modification of the Simmons–Smith procedure,[61] except that all of the olefin was added initially to the reaction vessel followed by slow addition of methylene iodide. The product was obtained in 63% yield, bp 54 °C (1 mm), n^{21}D 1.5257. The ^{1}H NMR spectrum showed peaks at δ 2.31 (s, 6 H, 2,6-dimethyls), 6.86 (s, broad, 3 H, aromatic), and 0.20–0.50 and 0.63–0.98 (m, 4 H, methylene protons of cyclopropyl).

Acetylation of 2,6-Dimethylphenylcyclopropane. Aluminum chloride catalyzed acetylation of 2,6-dimethylphenylcyclopropane in anhydrous chloroform at −35 °C gave an 89.9% yield of a mixture separable by preparative VPC (Aerograph instrument, Dow Corning Silicone 550 on Chromosorb W, 180 °C) which consisted of 85% of **2,4-dimethyl-3-cyclopropylacetophenone,** n^{20}D 1.5498, 2,4-dinitrophenylhydrazone, mp 210–211 °C, and 15% of **3,5-dimethyl-4-cyclopropylacetophenone,** n^{20}D 1.5511, 2,4-dinitrophenylhydrazone, mp 234–235 °C. The ^{1}H NMR spectrum of 3,5-dimethyl-4-cyclopropylacetophenone showed peaks at δ 7.43 (s, 2 H, aromatic), 2.41 (s, 9 H, 3,5-dimethyls and acetyl methyl), and 0.38–0.69 and 0.72–1.21 (m, 4 H, cyclopropyl methylene protons).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.99; H, 8.54.

The ^{1}H NMR spectrum of 2,4-dimethyl-3-cyclopropylacetophenone showed peaks at δ 6.87 (AB pattern, 1 H, 5-proton), 7.27 (AB pattern, 1 H, 6-proton), 2.47 (s, 3 H), 2.39 (s, 6 H), and 0.80–1.19 and 0.34–0.59 (m, 4 H).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.97; H, 8.49.

3,5-Dimethyl-4-cyclopropyl-α-methylstyrene. 3,5-Dimethyl-4-cyclopropylacetophenone was treated with methylmagnesium iodide to give 95.6% yield of the crude carbinol which on purification by preparative VPC (Aerograph instrument, Dow Corning Silicone 550 on Chromosorb W, 180 °C) gave the dehydration product, the olefin, n^{22}D 1.5518. The ^{1}H NMR spectrum showed peaks at δ 2.08 (m, 3 H, α-methyl), 2.40 (s, 6 H, 3,5-dimethyls), 4.93 (m, 1 H, olefinic cis to α-methyl), 5.26 (m, 1 H, olefinic trans to α-methyl), 6.99 (s, 2 H, aromatic), and 0.37–1.18 (m, 4 H, cyclopropyl methylene protons).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.12; H, 9.58.

Preparation of *p*-Cyclopropyl-Substituted *tert*-Cumyl Chlorides. The chlorides were prepared from the corresponding α-methylstyrene according to the general procedure.[20] In all cases formation of the chloride occurred without opening of the cyclopropyl ring. No olefinic protons were observed in the NMR spectra of the chlorides.

Determination of the Products of Solvolysis of the *p*-Cyclopropyl-Substituted *tert*-Cumyl Chlorides. The solvolyses were conducted in 90% aqueous acetone. The acetone was removed by evaporation from the solution of the solvolyzed chloride, the aqueous layer extracted with ether, and the ether extract washed with aqueous sodium bicarbonate followed by washing with water and then dried over magnesium sulfate. The ether was removed to give the crude solvolysis products.

Each of the solvolysis mixtures was analyzed by two methods: VPC analysis and the correlation in the NMR spectra between observed peak areas and predicted peak areas if the solvolysis mixture consisted of only a single component. The only products observed were the non-ring-opened carbinols and olefins (identified both by VPC retention time and NMR spectrum of authentic samples). The only olefinic protons in the spectra of the solvolysis mixtures were those at the same location and with the same splitting patterns as those in the precursor *p*-cyclopropyl-substituted α-methylstyrenes. No other olefinic components were detected by either analytical method.

Solvolysis in 90% aqueous acetone yielded from 4-cyclopropyl-*tert*-cumyl chloride, 38% alcohol and 62% olefin; from 3-methyl-4-cyclopropyl-*tert*-cumyl chloride, 49% alcohol and 51% olefin; and from 3,5-dimethyl-4-cyclopropyl-*tert*-cumyl chloride, 75% alcohol and 25% olefin.

Registry No.—7, 58502-76-4; 3,5-dimethyl-4-cyclopropyl-α-methylstyrene, 58502-77-5; 2-fluorenyl-*tert*-cumyl chloride, 58502-78-6; *p*-isopropylphenyldimethylcarbinol, 3445-42-9; 4-diphenyldimethylcarbinol, 34352-74-4; *p*-cyclopropyl-α-methylstyrene, 19936-10-8; 3-methyl-4-phenyl-α-methylstyrene, 58502-79-7; 3-methyl-4-phenylbromobenzene, 5002-26-6; 5-isopropyl-*m*-xylene, 4706-90-5; aniline, 62-53-3; 3,5-dimethyl-4-phenylisopropylbenzene, 58502-80-0; 3,5-dimethyl-2-phenylisopropylbenzene, 58502-81-1; 3,5-dimethyl-4-phenylacetophenone, 58502-82-2; 3,5-dimethyl-4-phenyl-*tert*-cumyl alcohol, 58502-83-3; methyl iodide, 74-88-4; 2-chloromethyl-1,4-diisopropylbenzene, 58502-84-4; 1,4-diisopropylbenzene, 100-18-5; chloromethyl methyl ether, 107-30-2; 2-methyl-1,4-diisopropylbenzene, 58502-85-5; 3-methyl-4-isopropyl-α-methylstyrene, 58502-86-6; 2,6-dimethyl-1,4-diisopropylbenzene, 42412-93-1; 3,5-dimethyl-1,2-diisopropylbenzene, 58502-87-7; 3,5-dimethyl-4-isopropylacetophenone, 58502-88-8; 3,5-dimethyl-4-isopropylacetophenone 2,4-DNPH, 58502-89-9; 3,5-dimethyl-4-isopropyl-α-methylstyrene, 58502-90-2; *o*-methylphenylcyclopropane, 27546-46-9; 3-methyl-4-cyclopropylacetophenone, 58502-91-3; 3-methyl-4-cy-

clopropylacetophenone 2,4-DNPH, 58502-92-4; 3-methyl-4-cyclopropyl-α-methylstyrene, 58502-93-5; 2,6-dimethylphenylcyclopropane, 36825-29-3; 2,6-dimethylstyrene, 2039-90-9; 2,4-dimethyl-3-cyclopropylacetophenone, 58502-94-6; 2,4-dimethyl-3-cyclopropylacetophenone 2,4-DNPH, 58502-95-7; 3,5-dimethyl-4-cyclopropylacetophenone, 58502-96-8; 3,5-dimethyl-4-cyclopropylacetophenone 2,4-DNPH, 58502-97-9.

References and Notes

(1) National Science Foundation Fellow, 1961–1963, Research Assistant, 1963–1964, on grant (GP 3719) from the National Science Foundation. Gulf Research and Development Corp. Fellow, 1964–1965.
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Copyrolysis of *sym*-Tetramethoxydimethyldisilane and 2,5-Dimethylfuran

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The reaction of methoxymethylsilylene (generated by pyrolysis of *sym*-tetramethoxydimethyldisilane) with 2,5-dimethylfuran yields 2-methoxy-2,3,6-trimethyl-1-oxo-2-silacyclohexa-3,5-diene and 2-methoxy-2,4,7-trimethyl-1,3-dioxo-2-silacyclohepta-4,6-diene.

The synthesis of unsaturated organosilicon heterocycles whose spectral properties might permit elucidation of the extent and nature of the interaction between vacant 3d orbitals on silicon and an adjacent π electron system has attracted considerable interest.[1,2]

The 1-oxo-2-silacyclohexa-3,5-diene (I) system has been a goal of our efforts. Interaction of a lone pair of electrons on oxygen with an empty 3d orbital on silicon and with the diene system would yield a 6π electron system possessing a nodal plane. Such a system is antiaromatic by the Mobius concept.[3,4]