[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Steric Effect in α-Substituted Methyl Aryl Ketones

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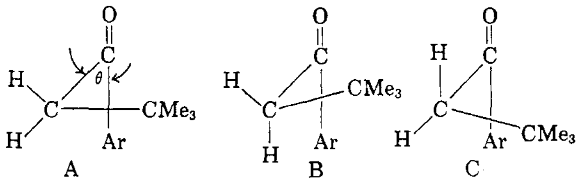
Received September 6, 1960

Study of the infrared carbonyl stretching frequencies exhibited by α-substituted methyl aryl ketones in carbon tetrachloride solution indicate that an important steric factor is operative in determining the character and position of the absorptions observed. Except for the neopentyl aryl ketones, where doublet carbonyl absorption is observed, the α-alkyl-substituted methyl aryl ketones provide carbonyl bands shifted to lower wave number. The conformational isomerism found with the polar substituted methyl aryl ketones is inhibited by the substitution of α-methyl groups. The probable preferred conformations for some of these ketones are proposed by consideration of steric and polar effects. The change to more polar solvent media appears to favor the bands associated with the conformation having the less polarized carbonyl group.

There have been numerous reported examples of doublet infrared carbonyl stretching absorption due to conformational isomerism.[1] In recent communications[2,3] we have reported the extension of this type of isomerism to α-methoxy-, α-piperidino- and α-morpholino-*p*-phenylacetophenones. A study of α-alkyl-substituted acetophenones and *p*-phenylacetophenones was undertaken in order to obtain reference ketones for further elucidation of the steric and polar effects associated with the various conformers. Measurements of the integrated carbonyl intensities of these α-alkyl substituted ketones now in progress may afford quantitative estimates of the steric effects involved.

The carbonyl stretching bands of the α-alkyl substituted ketones in carbon tetrachloride listed in Table I show a decrease in wave number with substitution, and band splitting is observed for the neopentyl ketones. The doublet carbonyl absorption, reported by House,[4] for neopentyl phenyl ketone (X) and ascribed to either conformational isomerism or Fermi resonance has been confirmed and found to also occur with neopentylbiphenylyl ketone (XI) (see Table I). The solid state spectra of the ketones XI, XII, XIII, and XVI (see Table I), which provide carbonyl band splitting in carbon tetrachloride solution, show a symmetrical carbonyl band similar in shape to that obtained for *p*-phenylacetophenone (II). It is therefore unlikely that the doublet carbonyl absorptions observed for this series of ketones is caused by Fermi resonance.[5]

It appears that various approaches to the assignment of conformers associated with doublet carbonyl absorption can be applied depending on the predominance of either steric or polar effects. For bulky nonpolar substituents like the neopentyl grouping favored conformers exist because of the steric exclusion of other possible structures and the positions of the bands are strongly influenced by variation in the carbonyl angles, θ, of the conformers (see structures A, B, and C). For neopentyl phenyl ketone (X) and neopentyl *p*-biphenylyl ketone (XI), where models would suggest the exclusion of the *cis* and *trans* conformers, the *gauche* forms A, B, and C provide a minimum of steric crowding and offer a tentative rationalization of the carbonyl absorptions observed. The high band has been assigned to the staggered *gauche* form A, the least crowded conformer. *gauche* Forms B and/or C would be expected to have an increased carbonyl angle, θ, caused by steric interaction involving the hydrogen atoms of the benzene ring which would account for the low band. In *gauche* form B the interaction would be caused by the hydrogens of the methylene group while in *gauche* form C the steric effect would involve hydrogen atoms of the methyl groups (angle distortion takes place in preference to rotation of the aryl group out of plane with the carbonyl grouping). An increase in the angle θ increases the *s*-character of the C to C bonding orbitals and the *p*-character of the C to O bond of the carbonyl group, resulting in a decrease in the carbonyl stretching frequency.[6]



X. Ar, C_6H_5 XI. Ar, $C_6H_4-C_6H_5$-*p*

gauche Conformations

The remaining nonpolar substituted ketones III IV, V, VI, VII, VIII, and IX provide a single carbonyl band and a shift to smaller wave numbers which we suggest is again associated with the increase in the carbonyl angle θ. Measurement of the

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(1) R. N. Jones and E. Spinner, *Can. J. Chem.*, **36**, 1020 (1958). This reference includes a literature review and a discussion of band assignments.

(2) N. H. Cromwell, R. E. Bambury, and J. L. Adelfang, *J. Am. Chem. Soc.*, **82**, 4241 (1960).

(3) N. H. Cromwell, F. H. Schumacher, and J. L. Adelfang, *J. Am. Chem. Soc.*, **83**, 974 (1961).

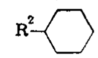
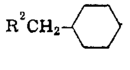
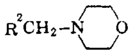
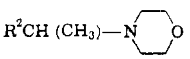
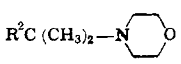
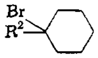
(4) H. O. House and E. J. Grubbs, *J. Am. Chem. Soc.*, **81**, 4733 (1959).

(5) P. Yates and L. L. Williams, *J. Am. Chem. Soc.*, **80**, 5896 (1958).

(6) P. D. Bartlett and M. Stiles, *J. Am. Chem. Soc.*, **77**, 2806 (1955).

TABLE I

INFRARED ABSORPTION SPECTRA OF ARYL ALKYL KETONES

Ketone ($R^1 = \overset{\overset{O}{\|}}{C}C_6H_5$, $R^2 = \overset{\overset{O}{\|}}{C}C_6H_4C_6H_5$-*p*)	No.	Carbonyl Stretching Bands (cm.$^{-1}$/% abs.) in Carbon Tetrachloride[a]
R^1CH_3	I	1691
R^2CH_3	II[b]	1690 (1682)[h]
$R^2C_2H_5$	III[c]	1687
$R^2CH_2C_2H_5$	IV[b]	1687
$R^2CH(CH_3)_2$	V[b]	1687
	VI[d]	1682
$R^2CH_2CH(CH_3)_2$	VII[b]	1681
	VIII	1685
$R^1C(CH_3)_3$	IX[e]	1680
$R^1CH_2C(CH_3)_3$	X[f]	1681/88, 1693/85
$R^2CH_2C(CH_3)_3$	XI	1680/55, 1687–1692/43 (1680)
$R^2CH_2OCH_3$	XII[g]	1686/84.5, 1707/85.5 (1695)
	XIII[h]	1684/70, 1700/62 (1690)
	XIV	1688
	XV[i]	1679
R^2CH_2Br	XVI	1686/85, 1708/47 (1687)
$R^2CH(CH_3)Br$	XVII[j]	1691
$R^2C(CH_3)_2Br$	XVIII[k]	1680
	XIX[d]	1674

[a] Infrared spectra were determined with a Perkin-Elmer instrument Model 21 using dilute solutions (~1%) and employing sodium chloride optics and matched cells. Each determination was calibrated with the water vapor maximum at 1700 cm.$^{-1}$ and duplicate determinations differed by ±1 cm.$^{-1}$ [b] L. M. Long and H. R. Henze, *J. Am. Chem. Soc.*, **63**, 1939 (1941). [c] S. Machlis and K. C. Blanchard, *J. Am. Chem. Soc.*, **57**, 176 (1935). [d] N. H. Cromwell and P. H. Hess, *J. Am. Chem. Soc.*, **82**, 136 (1960). [e] D. E. Pearson, *J. Am. Chem. Soc.*, **72**, 4169 (1950). [f] E. Berliner and F. Berliner, *J. Am. Chem. Soc.*, **72**, 222 (1950). [g] See Ref. 3. [h] See Ref. 2. [i] P. H. Hess, Ph. D. Thesis, University of Nebraska, 1960. [j] W. R. Bamford, T. S. Stevens, and J. W. Wright, *J. Chem. Soc.*, 4334 (1952). [k] B. R. Carpenter and E. E. Turner, *J. Chem. Soc.*, 869 (1934).

ultraviolet absorption spectra of the aceto-, propio-, *n*-butyro-, *iso*butyro-, and pivalophenones reported by Hedden and Brown[7] provides further evidence for the operation of steric crowding in this series. Alkyl substitution causes a decrease in the intensity of the benzoyl absorption observed at 240 mμ.

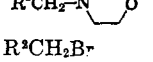
For polar substituents providing for only small steric contributions (α-methoxy-*p*-phenylacetophenone (XII)) the proposed orientations[3] occur in preference to other conformers that cannot be excluded on steric grounds. In these instances the existence of two conformers can only be rationalized by space-polar (*i.e.*, dipole-dipole and three-ring electrostatic) factors while the position of the bands is influenced by a combination of inductive and space-polar effects. The increased stability of *cis* conformers has been ascribed to dipole-dipole interactions[1] and we have proposed a weak pseudo three-ring electrostatic interaction for the *gauche* conformers.[2,3]

The inductive effect for electron withdrawing groups should raise the carbonyl frequency and would be essentially constant in the various conformers. The space-polar and steric effects would vary considerably. The α-haloacetophenones studied by Jones[1] show an inductive order for the iodo, bromo, and chloro derivatives in both carbon tetrachloride and chloroform solutions. The molecular absorption coefficients of these ketones indicate a shift to the *gauche* conformer as the size of the substituent increases. We have observed that the combination of steric and space-polar effects operative in the α,α-dialkyl-α-amino or α-halo ketones XV, XVIII, and XIX increases greatly the stability of the *gauche* conformer relative to the *cis* conformer and these ketones provide an unsymmetrical low frequency carbonyl band. It is not possible at this time to assign preferred conformers for the monoalkyl ketones XIV and XVII. These ketones give single symmetrical carbonyl bands with no significant shift in wave number compared to the reference ketone III.

The aryl ketones exhibiting conformational isomerism were also measured in chloroform and acetonitrile solution (see Table II). In general these more polar solvents afford less resolution of the multiple absorptions and the band envelope shift to lower wave number is of the same magnitude observed for *p*-phenylacetophenone. As has been found previously, the change to more polar solvent appears to favor the band associated with

TABLE II

INFRARED SPECTRA OF KETONES IN POLARIZING SOLVENTS

Ketone $R^1 = COC_6H_5$, $R^2 = COC_6H_4C_6H_5$-*p*	No.	Carbonyl Stretching Bands (cm.$^{-1}$/% abs.) Chloroform[a]	Acetonitrile
R^2CH_3	II	1681	1682
$R^1CH_2C(CH_3)_3$	X	1685/88sh,[b] 1674/93	
$R^2CH_2C(CH_3)_3$	XI	1685/65sh, 1674/89	1672
$R^2CH_2OCH_3$	XII	1697	1697
	XIII	1690/75, 1680/69sh	1691/72sh, 1681/74
R^2CH_2Br	XVI	1703/45sh, 1681/72	1700/53sh, 1681/69

[a] The chloroform was passed through a column of silicic acid and alumina just prior to use. [b] sh = shoulder.

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(7) G. D. Hedden and W. G. Brown, *J. Am. Chem. Soc.*, **75**, 3744 (1953).

the conformation having the less polarized carbonyl group.[2,8]

EXPERIMENTAL

α-Cyclohexyl-p-phenylacetophenone (VIII). Over a period of 20 min. at room temperature 2.2 g. (0.017 mole) of aluminum chloride was added with stirring to a mixture of 2.2 g. (0.014 mole) of cyclohexylacetyl chloride[8] and 2.2 g. (0.014 mole) of biphenyl dissolved in 10 ml. of methylene chloride. After standing for 1 hr. at room temperature the reaction mixture was poured into ice cold dilute hydrochloric acid and extracted with ether. After the ether layer was washed with water, dried over anhydrous sodium sulfate and concentrated, the crude ketone dissolved in benzene was passed through an alumina column. Concentration of the eluates followed by crystallization from methanol provided 1.1 g. (28%) of *α-cyclohexyl-p-phenylacetophenone*, m.p. 97–99°. Crystallization from methanol and then from ethyl acetate followed by sublimation under reduced pressure produced an analytical sample, m.p. 101.5–102.5°.

Anal. Calcd. for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.39; H, 8.37.

Neopentyl p-biphenylyl ketone (X). Reaction of *t*-butylacetyl chloride[9] with biphenyl was carried out in the manner described for the ketone VIII providing, after chromatography and crystallization from methanol, a 29% yield of *neopentyl p-biphenylyl ketone*. An analytical sample, m.p. 88–89°, was prepared by recrystallization from methanol followed by sublimation under reduced pressure.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.18; H, 8.01.

α-Morpholino-p-phenylpropiophenone (XIV). A mixture of 0.30 g. (0.00104 mole) of α-bromo-*p*-phenylpropiophenone[10] and 0.7 ml. of morpholine dissolved in 10 ml. of ether was allowed to stand at room temperature for 0.5 hr. The reaction mixture was washed with water and extracted with dilute hydrochloric acid. The acid extracts were washed with ether and neutralized with sodium carbonate. The crude amine was dissolved in ether, washed with water, and dried over anhyd. sodium sulfate. Crystallization from pentane-ether provided 0.15 g. (49%) of *α-morpholino-p-phenylpropiophenone*, m.p. 90–91.5°.

Anal. Calcd. for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74. Found: C, 77.65; H, 7.29; N, 4.83.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation, G. 10,034.

LINCOLN, NEB.

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(8) E. Hope and W. H. Perkin, *J. Chem. Soc.*, 1360 (1909).

(9) A. H. Homeyer, F. C. Whitmore, and V. H. Wallingford, *J. Am. Chem. Soc.*, **55**, 4209 (1933).

(10) See Ref. j, Table I.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Reaction of the Triphenylmethyl Radical with the Isomeric Xylenes

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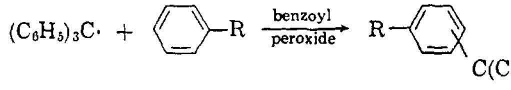
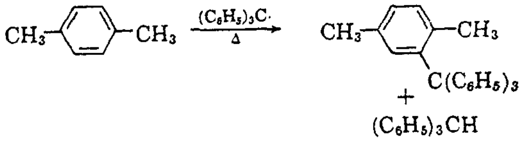
Received August 1, 1960

It has been found that the triphenylmethyl radical attacks the *side chain* of all *three* of the isomeric xylenes. These findings are quite contrary to an early report [*Ann.*, 401, 233 (1913)] which claims: (1) that only *o*- and *p*-xylene react with triphenylmethyl radicals and (2) that the products are tetraphenylmethane derivatives resulting from a *ring* attack by the radical.

Recently we disclosed that the triphenylmethyl radical, in the presence of benzoyl peroxide, attacked various aromatic substrates in a seemingly statistical fashion to form substituted tetraphenylmethanes.[1] In general, the solvent substrates we chose for this earlier study (*e.g.* chlorobenzene, benzotrifluoride, etc.) were such as to preclude any attack by the triphenylmethyl group on the side chain.



Of particular interest to us, was an early report by Wieland and Müller,[2] that, when the triphenylmethyl radical was refluxed with either *o*- or *p*-xylene, ring substitution occurred, resulting in the formation of a xylyltriphenylmethane. The structure of neither xylene product was rigorously established; the tetraphenylmethane formulations were based solely on elemental analyses, molecular weights, and a yellow coloration which each compound produced with dichromate. Particularly puzzling was the report[2] that *m*-xylene failed to react like the *ortho* and *para* isomers. From the orange-yellow oil which was formed in the *m*-xylene reaction, only *p*-benzhydryltetraphenylmethane could be isolated. Since this material had been shown previously to result from an irreversible dimerization of triphenylmethyl radicals,[3] it was concluded that the *m*-xylene had not entered into the reaction.



(1)

In order to resolve this anomalous situation, wherein only two of the three xylene isomers

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(1) R. A. Benkeser and W. Schroeder, *J. Am. Chem. Soc.*, **80**, 3314 (1958).

(2) H. Wieland and C. Müller, *Ann.*, **401**, 233 (1913).

(3) F. Ullmann and W. Borsum, *Ber.*, **35**, 2877 (1902).