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# $^{13}$C N.M.R. STUDIES

## PART IV.[1] CARBON-13 N.M.R. SPECTRA OF SOME ALKYL PHENYL KETONES[2]

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## ABSTRACT

The 15.1 Mc/s $^{13}$C n.m.r. spectra of 21 substituted alkyl phenyl ketones, ArCOR, have been determined and the $^{13}$C chemical shifts measured. This group of compounds included examples of each of the ethyl, isopropyl, and *t*-butyl phenyl ketone series. Variations of the chemical shifts with structure are analyzed and compared with the results for substituted acetophenones. The study of steric inhibition of conjugation in these compounds by means of their $^{13}$C data is discussed in detail. The parameters for the acetyl carbons for a few methyl aryl ketones have been determined as well to examine the effect of orientation of this group on a polycyclic aromatic skeleton.

## INTRODUCTION

As an extension of our investigations of the carbon-13 nuclear magnetic resonance spectra of organic carbonyl groups (1, 2, 3), we have prepared a number of alkyl phenyl ketones and determined their $^{13}$C spectra at 15.085 Mc/s. Seven examples in each of the propiophenone, isobutyrophenone, and pivalophenone series have been included and, since our interest has centered primarily on the $^{13}$C shieldings in hindered systems, most of these compounds bear at least one ortho-substituent. As models for comparison with the results for these hindered systems, the parent ketone of each series and its para-methoxyl derivative were examined. Analyses of the spectra were carried out by the methods which have been described in detail in Part III of this series (3). The aromatic shieldings for the methoxyl derivatives permit an additional test of the additive relation of combined substituent effects on the chemical shifts of these nuclei (4).

The results for the hindered ketones show that variations of the $^{13}$C chemical shift parameters for the carbonyl carbon, the para-carbons, and the $\alpha$-carbon of the acyl group provide indications of the existence of steric interference to coplanarity of the acyl grouping. Application of the carbonyl shieldings to semiquantitative estimates of the angles of twist in these systems has been attempted, using an approach similar to that described for the analysis of the carbonyl data for the acetophenones. The limitations of the approach for these compounds place greater uncertainties on the calculated values, but the results are reasonable and appear to yield satisfactory estimates as a first approximation.

## EXPERIMENTAL

### *Nuclear Magnetic Resonance Spectra*

All spectra were determined at 15.085 Mc/s using the compounds described below containing $^{13}$C in natural abundance. Details of the experimental procedure have been presented (3).

### *Materials*

All of the compounds were prepared from readily available commercial products. Most of the ketones are well known and all were obtained by established procedures. In each case, infrared and proton spectra were determined to check their purity. The observed physical constants and the syntheses employed are collected

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[1] *Part III, ref. 3.*

[2] *These results were reported in part at the 46th Annual Conference of the Chemical Institute of Canada, Toronto, June 1963.*

[3] *Petroleum Research Fund Predoctoral Fellow, 1962–1964.*

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in Table I together with the reported constants. The analytical data are included for the new compounds: 2,3,4,5,6-pentamethylpropiophenone, 2,3,5,6-tetramethyl-, 2,3,4,5,6-pentamethyl-, and 2,4,6-triisopropylisobutyrophenone. The microanalyses were performed by Alfred Bernhardt and Associates, Mulheim, Germany. All melting points, determined on a Kofler hot stage, are uncorrected. The liquids were purified by distillation through a platinum-plated, spinning band column. The solvents used for spectral studies were Fisher "Spectro-Grade" reagents.

TABLE I

Physical data for the substituted alkyl phenyl ketones, $\phi$COR, prepared for this study

| Parent compound (R) | Substituent(s) | Method of preparation | Physical constants<br>Observed<br>b.p./mm (m.p.) | <br>Observed<br>$n_D$ ($t$°) | <br>Reported<br>b.p./mm (m.p.) | <br>Reported<br>$n_D$ ($t$°) | Ref. |
|---|---|---|---|---|---|---|---|
| $C_2H_5$ | Nil | A1 | 61/0.4 | 1.5260 (23) | 85/7.5 | 1.5274 (20) | 5 |
| | 4-$CH_3O$ | A1 | 108–110/2 | 1.5450 (25) | 143–144/12 | 1.5484 (20) | 6 |
| | 2-$CH_3$ | B | 102/18 | 1.5250 (20) | 127/38 | 1.5250 (20) | 7 |
| | 2,4,6-$(CH_3)_3$ | A1 | 120/6 | 1.5112 (21) | 125/13 | — | 8 |
| | 2,3,5,6-$(CH_3)_4$ | A1 | (78–79) | — | (79) | — | |
| | 2,3,4,5,6-$(CH_3)_5$* | A1 | (84–85) | — | | | 9 |
| | 2,4,6-$(i\text{-}C_3H_7)_3$ | A1 | 145–146/11<br>(80–81) | — | 123–126/3<br>(81–83) | — | 10 |
| $i$-$C_3H_7$ | Nil | A2 | 73–75/1.2 | 1.5170 (25) | 115/29 | 1.5180 (20) | 5 |
| | 4-$CH_3O$ | A2 | 112–114/2.1 | 1.5355 (25) | 149–150/14 | 1.5390 (16.6) | 6 |
| | 2-$CH_3$ | B | 103–104/15 | 1.5135 (19.5) | 230/758 | — | 11 |
| | 2,4,6-$(CH_3)_3$ | A2 | 117/8 | 1.5085 (25) | 142–143/19 | — | 12 |
| | 2,3,5,6-$(CH_3)_4$† | A2 | (40–41) | — | | | |
| | 2,3,4,5,6-$(CH_3)_5$‡ | A2 | (42–43) | — | | | |
| | 2,4,6-$(i\text{-}C_3H_7)_3$§ | A2 | 106–107/0.9<br>(47–49) | — | | | |
| $t$-$C_4H_9$ | Nil | C | 97–98/16 | 1.5080 (20) | 98/11.5 | 1.5102 (20) | 5 |
| | 4-$CH_3O$ | A3 | 116–118/2 | 1.5260 (26) | 138–140/8 | — | 13 |
| | 2-$CH_3$ | C | 75/1.4 | 1.5057 (25) | 110/110 | — | 14 |
| | 2,4,6-$(CH_3)_3$ | A3 | 129–130/11 | 1.5092 (20) | 120–122/8 | 1.5150 (25) | 15 |
| | 2,3,4,6-$(CH_3)_4$ | A3 | 92–93/0.4 | 1.5192 (24) | 117–119/2 | 1.5170 (25) | 15 |
| | 2-$CH_3$-4-$CH_3O$ | A3 | 100/0.8 | | 126–128/4 | — | 15 |
| | 2-$CH_3$-5-$CH_3O$ | A3 | (51–52) | | (50–51) | — | 15 |

*Found: C, 81.94; H, 9.88. Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.87.
†Found: C, 82.04; H, 9.87. Calcd. for $C_{14}H_{20}O$: C, 82.30; H, 9.87.
‡Found: C, 82.38; H, 10.00. Calcd. for $C_{16}H_{22}O$: C, 82.38; H, 10.09.
§Found: C, 83.10; H, 10.99. Calcd. for $C_{19}H_{30}O$: C, 83.15; H, 11.02.
Methods used: (A1) acetylation via Friedel–Crafts reaction with $CH_3COCl$, ArH → $ArCOCH_3$ (10);
(A2) Friedel–Crafts acylation with $(CH_3)_2CHCOCl$, ArH → $ArCOCH(CH_3)_2$ (12);
(A3) Friedel–Crafts acylation with $(CH_3)_3CCOCl$, ArH → $ArCOC(CH_3)_3$ (15);
(B) Grignard reaction of RMgI (R = Me or Et) on the appropriate nitrile, ArCN → $ArCOCH_3$ (7);
(C) Grignard reaction of $(CH_3)_3CMgBr$ with the aldehyde, followed by $CrO_3$/HOAc oxidation, ArCHO → ArCH(OH)$CH_3$ → $ArCOCH_3$ (16).

## DISCUSSION

The results for the three closely related series of alkyl phenyl ketones are considered together to facilitate discussion and to emphasize the common features. The observed chemical shifts for each type of carbon nucleus are discussed under separate subheadings to allow ready intercomparison of the data from each series. The shieldings of the carbons of the acetyl group in a few polycyclic aryl methyl ketones are presented in a separate section. In the final section, the application of these $^{13}$C spectral results to the estimation of the extent of steric inhibition of conjugation of the acyl grouping is considered in detail.

The majority of the data have been obtained using the neat liquids or solutions of the ketones in carbon disulfide. In the latter cases, however, the maximum concentrations attainable were not sufficient to permit satisfactory measurements for all band positions and consequently certain data do not appear in the tables. Measurements for some of

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these bands were possible in chloroform solution and these figures are indicated in the tables. On the basis of our previous results (1, 3), it seemed unlikely that chloroform causes appreciable changes in the shielding of any but the carbonyl carbons, but, to confirm this point, a few examples were studied in both carbon disulfide and chloroform solutions.

TABLE II

$^{13}C$ chemical shifts for some substituted propiophenones (in p.p.m. from $CS_2$)

| | R—C=O | | | Aromatic nuclei* | | | | |
|---|---|---|---|---|---|---|---|---|
| Substituent(s) | C=O | —$CH_2$— | —$CH_3$ | C-1 | C-2,6 | C-3,5 | C-4 | Others |
| Nil | −5.6 | 162.2 | 185.8 | 56.5 | 65.6 | 65.6 | 61.7 | — |
| 4-$CH_3O$ | −4.7 | 162.3 | 185.4 | 63.3<br>(64.6) | 63.4<br>(64.7) | 79.9<br>(80.3) | 30.2<br>(31.5) | 138.1 |
| 2-$CH_3$ | −9.7 | 159.3 | 185.1 | 56.0 | 56.0 (C-2)<br>61.9 (C-6) | 61.9(C-3)<br>67.5(C-5) | 64.5 | 172.1 |
| 2,4,6-$(CH_3)_3$ | −15.0 | 156.2 | 185.3 | 53.7 | 61.5 | 65.3 | 56.2 | 173.6<br>175.4 |
| 2,3,5,6-$(CH_3)_4$† | −16.7 | (154.4)‡ | | 49.2 | 64.9 | 58.7 | 61.9 | 173.4<br>(176.7)‡ |
| 2,3,4,5,6-$(CH_3)_5$† | −16.9 | (154.7)‡ | | 51.1 | 65.3 | 59.2 | 59.2 | 175.1 |
| 2,4,6-($i$-$C_3H_7$)$_3$† | −16.3 | (153.1)‡ | | 53.8 | 49.0 | 71.3 | 43.6 | 160.0<br>168.4<br>176.8 |

*Data in parentheses are the calculated values assuming additivity of substituent effects.
†Saturated solution in $CS_2$, but owing to low concentration some data obtained in $CHCl_3$.‡
‡Data for saturated $CHCl_3$ solutions.

TABLE III

$^{13}C$ chemical shifts for some substituted isobutyrophenones (in p.p.m. from $CS_2$)

| | R—C=O | | | Aromatic nuclei* | | | | |
|---|---|---|---|---|---|---|---|---|
| Substituent(s) | C=O | —CH— | —$CH_3$ | C-1 | C-2,6 | C-3,5 | C-4 | Others |
| Nil | −10.3 | 157.9 | 174.4 | 56.7 | 64.6 | 64.6 | 60.1 | — |
| 4-$CH_3O$ | −8.5 | 158.2 | 173.7 | 64.3<br>(64.8) | 62.9<br>(63.7) | 79.6<br>(79.3) | 30.1<br>(29.9) | 138.1 |
| 2-$CH_3$ | −13.9 | 155.2 | 174.6 | 56.1 | 56.1(C-2)<br>61.8(C-6) | 61.8(C-3)<br>67.0(C-5) | 65.1 | 172.6 |
| 2,4,6-$(CH_3)_3$ | −18.2 | 151.4 | 174.9 | 53.4 | 60.2 | 64.7 | 55.7 | 173.2 |
| 2,3,5,6-$(CH_3)_4$† | −19.8 | 148.0 | (175.0)‡ | 49.4 | 63.1 | 57.6 | 60.1 | 172.4 |
| 2,3,4,5,6-$(CH_3)_5$† | −20.1 | 149.0 | (174.5)‡ | 52.3 | 64.4 | 59.8 | 59.8 | 174.5 |
| 2,4,6-($i$-$C_3H_7$)$_3$† | −19.5 | 149.9 | (175.7)‡ | 54.7 | 48.2 | 71.4 | 43.5 | 175.7 |

*Data in parentheses are the calculated values assuming additivity of substituent effects.
†Saturated solution in $CS_2$ but owing to low concentration methyl shifts obtained in $CHCl_3$.‡
‡Data for saturated $CHCl_3$ solutions.

### *Alkyl Phenyl Ketones*

#### *(a) Aromatic Carbons*

The chemical shifts of the aromatic carbon nuclei in the propiophenone, isobutyrophenone, and pivalophenone series are given in Tables II, III, and IV, respectively. The analyses and assignments in the aromatic regions of these spectra were accomplished by the methods which were described in detail in the preceding part of this series (3). The data for the parent ketone for each of these series show that the substituent effects of the three acyl groups are similar and not greatly different from those caused by an acetyl group. To compare the effects of various carbonyl-containing groups on the aromatic shieldings, the relevant data are listed in Table V in which the substituent

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TABLE IV

$^{13}$C chemical shifts for some substituted pivalophenones (in p.p.m. from $CS_2$)

| | R—C=O | | | Aromatic nuclei* | | | | |
|---|---|---|---|---|---|---|---|---|
| Substituent(s) | C=O | —C— | $CH_3$ | C-1 | C-2,6 | C-3,5 | C-4 | Others |
| Nil | −14.4 | 149.0 | 164.6 | 54.7 | 65.2 | 65.2 | 62.4 | — |
| 4-$OCH_3$ | −11.0 | 149.7 | 164.8 | 63.6<br>(62.8) | 62.5<br>(64.3) | 80.1<br>(79.9) | 31.5<br>(32.2) | 138.2 |
| 2-$CH_3$ | −19.2 | 148.6 | 166.0 | 52.3 | 59.1(C-2)<br>65.3(C-6) | 65.3(C-3)<br>68.2(C-5) | 62.8 | 174.3 |
| 2-$CH_3$-5-$CH_3O$† | −19.2 | 148.2 | 164.6 | 62.6 | 60.4(C-2)<br>81.3(C-6) | 65.1(C-3)<br>39.3(C-5) | 81.3 | 136.7 |
| 2-$CH_3$-4-$CH_3O$† | −18.8 | 148.4 | 165.1 | 52.7 | 60.7(C-2)<br>66.0(C-6) | 76.4(C-3)<br>80.6(C-5) | 37.3 | 137.8 |
| 2,4,6-$(CH_3)_3$ | −23.0 | 149.2 | 165.0 | 53.9 | 61.8 | 64.9 | 56.7 | 173.2 |
| 2,3,4,6-$(CH_3)_4$ | −22.9 | 149.2 | 165.7 | 35.0 | 64.3(C-3)<br>59.2(C-6) | 62.2<br>64.7(C-5) | 62.2 | 178.6 |

*Data in parentheses are the calculated values assuming additivity of substituent effects.
†Saturated solution in $CS_2$.

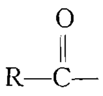
effects are given relative to benzene. The figures for the formyl group are from Spiesecke and Schneider (17). The effects of the acyl groups at the ortho- and meta-positions are slightly less than those of the formyl and the differences between the effects for the various  $R\!-\!\overset{O}{\overset{\|}{C}}\!-$ groups are within experimental error. For these acyl groups, appreciable differences are found, however, at the C-1 and C-4 nuclei, but there is no apparent trend for these changes at either position. No explanation can be offered to account for the small, but distinct, variations.

TABLE V

$^{13}$C chemical shifts of the aromatic nuclei in some monosubstituted benzenes (in p.p.m. relative to $C_6H_6$)

| | Chemical shifts | | | |
|---|---|---|---|---|
| Substituent | C-1 | C-2,6 (ortho) | C-3,5 (meta) | C-4 (para) |
| —CHO* | −9.0 | −1.2 | −1.2 | −6.0 |
| —$COCH_3$† | −9.0 | −0.4 | −0.4 | −4.0 |
| —$COCH_2CH_3$ | −8.5 | +0.6 | +0.6 | −3.3 |
| —$COCH(CH_3)_2$ | −8.3 | −0.4 | −0.4 | −4.9 |
| —$COC(CH_3)_3$ | −10.3 | +0.2 | +0.2 | −2.6 |

*Reference 17.
†Averaged values of data reported in refs. 1 and 17.

The para-methoxyl derivative of each parent ketone was examined to test for additivity of substituent effects, since an additive relation has been found to hold to a good approximation for several meta- and para-substituted aromatic compounds (3, 4, 18, 19). The methoxyl group was chosen since the effect of this grouping differs considerably at the various aromatic nuclei and thus provides a more definitive test. The agreement between the observed and calculated chemical shifts for the ring carbons was found to be within 1.3 p.p.m. with one exception, the 2- and 6-positions (which are equivalent) in 4-methoxypivalophenone. These differences are comparable to those found for acetophenones (3). We have assumed that these results confirm our peak assignments.

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The remaining compounds were examined primarily to study the variations of the chemical shifts of nuclei in the substituent groups of other hindered systems to compare with our previous results and to test conclusions drawn therefrom. The shieldings of the aromatic carbon nuclei of these compounds are listed in the tables (II, III, and IV) but little comment can be offered at this time. As before, ortho-positioning of substituent groupings on the ring produces marked deviations of the observed shifts from the values calculated by assuming an additive relation. Remarkable differences are also observed for those cases in which an aromatic methyl group is flanked on both sides by substituents. The acyl derivatives of durene and pentamethylbenzene exhibit this behavior as does 2,3,4,6-tetramethylpivalophenone. For each of these examples, one of the methyl-substituted aromatic nuclei absorbs in the range, 63.1–65.3 p.p.m., indicating that the usual deshielding effect of ca. 9 p.p.m. due to methyl substitution is largely overcome by some other factor. As before (3), we have assigned this signal to the aromatic carbon(s) bearing the most crowded methyl group(s) which for the durene derivatives are the C-2 and C-6 nuclei. The other methyl-substituted aromatic nuclei in these derivatives are also abnormally shielded but to a lesser degree. Evidence suggesting that this shielding effect is due, at least in part, to the acyl group comes from the observation that only *two* aromatic carbons absorb near 65 p.p.m. in the pentamethyl derivatives. Thus, this effect would not appear to arise merely from a simple crowding of the methyl substituents and consequently the highest field signal in the aromatic region has been assigned to the C-2 and C-6 nuclei in these compounds. By the same reasoning, the signal at 64.3 p.p.m. in the spectrum of 2,3,4,6-tetramethylpivalophenone has been assigned to carbon-2. Similar effects have been noted for the polymethylated acetophenones (3). Further indication that the acyl group is largely responsible for this up-field shift is given by the shieldings for the aromatic nuclei of hexamethylbenzene at 60.4 p.p.m. (20) and pentamethylbenzene in which the substituted ring carbons appear at 60.8 p.p.m. (21). Clearly both show a shift to higher field relative to less highly substituted compounds, but the relative change is considerably less than that observed for the ketones.

The chemical shifts for the C-4 aromatic nuclei in the ortho-substituted derivatives exhibit variations similar to those found for the acetophenone series (3) in that substitution at the ortho-position(s) tends to reduce the deshielding effect of the acyl group at the para-position. A comparison of the observed C-4 shifts for propiophenone or isobutyrophenone and the corresponding 2-methyl derivative illustrates the trend without allowing for the small effect of the methyl group at C-4. The observed changes are consistent with previous observations in the acetophenone series, even the exceptions are similar (i.e. the 2,3,4,5,6-pentamethylated derivatives) and these have been discussed (3). We attribute the increased shielding at the para-carbon to steric inhibition of conjugation in the ortho-substituted compounds relative to compounds lacking ortho-substituents.

Apart from the observations and interpretations noted above, present knowledge of aromatic shieldings in general does not permit a fuller evaluation of our results.

### (b) Acyl Groups

*(i) Carbonyl carbons.*—The easily recognized singlet peaks due to the carbonyl carbon nuclei are the lowest field bands in all of these spectra and the observed resonance positions (Tables II, III, and IV) clearly show that methyl substitution on the $\alpha$-carbon of the acyl group tends to deshield the carbonyl carbon. These bands appear at $-3.2$, $-5.6$, $-10.3$, and $-14.4$ p.p.m. for the acetyl, propionyl, isobutyryl, and pivaloyl groups, respectively. These changes are in *qualitative* agreement with those found for

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the comparable series of alkyl methyl ketones (1) as well as the differences in chemical shift of the unsaturated carbon in the system $=\!\mathrm{C{-}R}$, where R = ethyl, isopropyl, *t*-butyl for both aromatic (3) and aliphatic (22) hydrocarbons. In the latter case, the assignments for the appropriate olefinic carbon nuclei have not been made by the original authors, but, by analogy with their other results the most probable assignment supports the above claim. There are significant *quantitative* differences, however, between these effects and those found for methyl substitution in the aliphatic and aromatic ketones. In the present series, successive substitution on the α-carbon tends to deshield the carbonyl nucleus by ca. 4 p.p.m. per methyl group whereas, in the aliphatic ketones the carbonyl carbon shift difference between the isopropyl methyl and *t*-butyl methyl ketones is only 0.8 p.p.m. Further discussion of this point is presented in the final section.

In each series, there are distinct variations in the carbonyl shieldings with substitution on the aromatic ring. In contrast to the results for the acetophenone series, the para-methoxyl group shifts the carbonyl resonance to higher field relative to its position for the parent ketone. These differences of 0.9, 1.8, and 3.4 p.p.m. for the propiophenone, isobutyrophenone, and pivalophenone derivatives, respectively, appear to increase with increasing size of the acyl group suggesting that the origin of the effect is probably steric. The results of the study of the acetophenone series established that the polar nature of substituent groups was of minor effect on the carbonyl shieldings in planar systems while some evidence for a shielding effect operative in hindered systems was obtained for certain electron-releasing groups in the para-position. The present results, therefore, seem consistent with the latter condition.

The remaining examples in each of the three series bear one or two ortho-substituents and a comparison of the changes in carbonyl chemical shift with substitution shows that similar variations are found for each series. For example, introduction of an ortho-methyl group produces an average change of $-4.2 \pm 0.6$ p.p.m. for each carbonyl carbon shift relative to that observed for the parent ketone, while a second ortho-methyl substituent gives an additional average change of $-4.5 \pm 0.7$ p.p.m. The observed changes for these and other substitutions are collected in Table VI. The average effects are given in the last column of Table VI, and, although the deviations are slightly larger than experimental error, the effects are closely similar. A more important observation is probably the fact that the order throughout each series is the same. This order follows that expected on the grounds of increasing steric interference of the substituents with the acyl groups thus hindering the carbonyl group from attaining coplanarity with the aromatic ring.

*(ii) Alkyl carbons.*—The observed chemical shifts of the alkyl carbon nuclei of the three acyl groups of the parent ketones (Tables II, III, and IV) may be compared to the shifts observed for ethyl, isopropyl, and *t*-butyl groups directly bonded to aromatic

TABLE VI

Substituent effects on the carbonyl shieldings of some alkyl phenyl ketones, $\mathrm{RCOC_6H_{(5-n)}R_n'}$
(in p.p.m. relative to shift of parent compound)

| | R group | | | |
|---|---|---|---|---|
| Substituent(s) (R′) | Et | *i*-Pr | *t*-Bu | Average effects |
| 2-$CH_3$ | −4.1 | −3.6 | −4.8 | −4.2±0.6 |
| 2,4,6-$(CH_3)_3$ | −9.4 | −7.9 | −8.6 | −8.6±0.7 |
| 2,3,5,6-$(CH_3)_4$ | −11.1 | −9.5 | — | −10.3±0.8 |
| 2,3,4,5,6-$(CH_3)_5$ | −11.3 | −9.8 | — | −10.5±0.7 |
| 2,4,6-$(i\text{-}C_3H_7)_3$ | −10.7 | −9.2 | — | −9.9±0.7 |

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TABLE VII

$^{13}C$ chemical shifts of alkyl carbons in some substituted benzenes (p.p.m. from $CS_2$)

| | Chemical shifts | | | | | |
|---|---|---|---|---|---|---|
| | α-Carbon | | | β-Carbon | | |
| Alkyl group | $C_6H_5$- | $C_6H_5CO$- | Δδ* | $C_6H_5$- | $C_6H_5CO$- | Δδ* |
| $CH_3$- | 171.8 | 167.9 | −3.9 | — | — | |
| $CH_3CH_2$- | 164.8 | 162.2 | −2.6 | 177.7 | 185.5 | +7.8 |
| $(CH_3)_2CH$- | 159.8 | 157.9 | −1.9 | 169.5 | 174.4 | +4.9 |
| $(CH_3)_3C$- | 158.1 | 149.0 | −9.1 | 162.1 | 164.6 | +2.5 |

*Difference between shifts for ketone and hydrocarbon.

rings (3). In each case, the α-carbon is deshielded and the β-carbons (methyl) are shielded for the ketone relative to the values for the corresponding alkylbenzene. These figures are collected in Table VII for comparison. The largest difference for the α-carbon shielding is found for the *t*-butyl group and is much greater than any of the others. Indeed, this difference appears to break the trend (compare the figures in Table VII). The shielding effect at the β-methyl carbons decreases with increasing size of the alkyl group. Apart from this variation for the β-methyl carbon shifts, however, the shielding of these nuclei is relatively insensitive to the introduction of substituents in the aromatic ring. It appears that the methyl carbon shieldings are not sensitive to changes in the polarization of the carbonyl bond, at least in the first approximation. With the exception of the pivalophenone series, a similar behavior is not observed for the α-carbon shieldings. One would expect the α-carbon shift to reflect changes in the carbonyl polarization since this nucleus is directly bonded thereto. The fact that the α-carbon shieldings are decreased with increasing ortho-substitution is completely consistent with the existence of steric interference to coplanarity of the carbonyl group and the observed changes are strikingly similar to those observed for the acetyl methyl carbon in similarly substituted acetophenones (3). For example, the average change caused by the introduction of a 2-methyl group is $-3.2 \pm 0.5$ p.p.m. for the acetophenone, propiophenone, and isobutyrophenone systems, while substitution of a second ortho-methyl group (from the results for the 2,4,6-trimethyl derivatives) produces an average shift of $-6.25 \pm 0.25$ p.p.m. relative to the parent ketone in each of these three systems. It is reasonable to suggest that these changes arise from a common origin which is steric inhibition of conjugation of the carbonyl grouping.

### *Other Carbons*

The observed chemical shifts for the various types of carbon nuclei in the substituent alkyl groups are similar to those reported earlier in the acetophenone series. As before, an increased crowding of the methyl groups on an aromatic ring tends to shift the methyl carbon resonance toward higher field. It is important to note that in view of considerable overlapping of the bands for the various alkyl carbons in these spectra, their data are the least precise. The methoxyl carbons, however, absorb in a region of the spectrum which is uncluttered and their signals are easily measured. The shieldings of $138.1 \pm 0.1$ p.p.m. are unexceptional (3, 4).

### *Methyl Polycyclic Aryl Ketones*

The shieldings of the carbonyl carbon nuclei for a few methyl aryl ketones having polycyclic aryl groupings have been reported (3) and these data together with those for the methyl carbon nuclei are collected in Table VIII. The figures for acetophenone are

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TABLE VIII

$^{13}$C shieldings of the acetyl group of some methyl aryl ketones (in p.p.m. from $CS_2$)

| Aryl group | Chemical shifts | |
|---|---|---|
| | C=O | $CH_3$ |
| Phenyl | −3.2 | 167.9 |
| 2-Naphthyl | −3.0 | 167.0 |
| 1-Naphthyl | −6.7 | 164.0 |
| 3-Phenanthranyl* | −2.9 | 167.0 |
| 9-Phenanthranyl* | −7.5 | 163.0 |
| 9-Anthranyl* | −14.5 | 159.0 |

*Saturated solution in $CHCl_3$.

included for comparison. The variations in these results clearly indicate that there are steric interactions between the acetyl group and the aromatic ring system for those cases in which *peri*-hydrogens could interfere with the rotation of the acetyl group, namely, 1-naphthyl, 9-phenanthranyl, and 9-anthranyl. The latter case exhibits the most pronounced deshielding effect at both the carbonyl and methyl carbons presumably owing to the fact that two *peri*-hydrogen interactions may be involved. Although three of these examples were studied in chloroform solution only, the observed chemical shifts would not be expected to differ greatly from values for comparable concentrations in less polar media. An upper limit for the solvent effect on the resonance positions of these carbons would, in all probability, not exceed 2 p.p.m. on the basis of previous results (1, 3). The chemical shifts of certain nuclei in chloroform solution relative to those in carbon disulfide are listed in Table IX, and it is evident that the solvent effects are relatively small. Thus, there is clear evidence for steric inhibition of conjugation for these three cases. Owing to the complexity of the aromatic regions in these spectra, and, for the solids, the relatively low concentrations of the solutions obtainable, satisfactory analyses of the aromatic patterns were not possible and the chemical shift measurements are limited to the carbons of the acetyl grouping. In the case of 9-acetylanthracene, spin-decoupling experiments were carried out to locate and measure the position of the acetyl methyl signal.

### *Steric Inhibition of Conjugation*

A number of the variations in the chemical shift results for alkyl aryl ketones which provide evidence for the existence of steric inhibition of conjugation in several cases

TABLE IX

Solvent effects on certain $^{13}$C shieldings in alkyl phenyl ketones ($\delta_C{}^{CS_2} - \delta_C{}^{CHCl_3}$, in p.p.m.*)

| Parent compound | Substituents | Acyl group | | Aromatic carbons | | | |
|---|---|---|---|---|---|---|---|
| | | C=O | α-C | C-1 | C-2,6 | C-3,5 | C-4 |
| $\phi COCH_2CH_3$ | 2,3,5,6-$(CH_3)_4$ | −1.7 | † | −0.4 | −0.5 | −0.1 | −0.8 |
| | 2,3,4,5,6-$(CH_3)_5$ | −1.3 | † | −1.4 | −0.3 | −1.1 | −1.0 |
| | 2,4,6-$(i\text{-}C_3H_2)_3$ | −1.5 | † | −0.8 | −0.3 | −0.5 | −0.5 |
| $\phi COCH(CH_3)_2$ | 2,3,5,6-$(CH_3)_4$ | −0.8 | −2.0 | −1.3 | −1.4 | −1.4 | −2.2 |
| | 2,3,4,5,6-$(CH_3)_5$ | 0.0 | −1.4 | −1.1 | −0.9 | −0.7 | −1.6 |
| | 2,4,6-$(i\text{-}C_3H_7)_3$ | −1.7 | † | −0.5 | −0.6 | −0.2 | −0.1 |
| $\phi COC(CH_3)_3$ | 2-$CH_3$-4-$CH_3O$ | 0.9 | +0.1 | −0.2 | −0.3 | −0.7(C-3)<br>−1.2(C-5) | −0.2 |

*Chemical shift difference for saturated $CHCl_3$ solutions relative to saturated $CS_2$ solution.
†Concentration in $CS_2$ solution was too low to permit measurements.

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have been noted in the preceding sections. Our previous studies of the $^{13}C$ spectra of substituted acetophenones permitted the development of a semiquantitative approach to an estimation of the magnitude of the steric interference in terms of the angles of twist, $\theta$, between the planes of the carbonyl group and the aromatic ring. The present series affords an opportunity to investigate the use of this method for similar estimates in some closely related systems.

Of the four series of compounds included in this study, the polycyclic aryl methyl ketones are perhaps the least different from the acetophenones, if one is to judge on the basis of the observed chemical shifts of the acetyl carbon nuclei. These shieldings for the 2-naphthyl and 3-phenanthranyl systems are the same, within experimental error, as those found for acetophenone (Table VIII). The other examples exhibit deshielding effects which we attribute to steric interference with the *peri*-hydrogens. Assuming that the empirical expression (2, 3) relating $\theta$ with the carbonyl carbon shift is applicable, substitution of the observed values yields the following angles of twist for these hindered cases: 1-naphthyl, 25°; 9-phenanthranyl, 28°; 9-anthranyl, 49°. All of these values seem to be reasonable estimates although figures with which comparisons might be made are lacking. The effect of varying contributions due to ring currents in these aromatic skeletons have been neglected in these calculations but any differences arising from this effect are small relative to the overall changes observed for the hindered and planar cases. An estimate, using the calculated values for ring current contributions from Johnson and Bovey (23) and assuming independent contributions by each ring in the polycyclic system (24), of the additional ring current effect for the most extreme case, 9-acetylanthracene, relative to acetophenone is calculated to be $-1.02$ p.p.m. for the carbonyl carbon shielding. Clearly, the ring current contributions, as estimated by the generally accepted models, are of secondary importance, although the calculated angles of twist may be somewhat larger than the actual angles. Differences due to varying ring current contributions at the various acetyl methyl carbons will be even smaller than those at the carbonyl nuclei owing to their greater distance from the aromatic ring systems and the fact that these methyl groups are not in the plane of the aromatic skeleton.

A direct comparison of the carbonyl carbon shifts for acetophenone, propiophenone, isobutyrophenone, and pivalophenone clearly shows that the effect of methyl substitution on the $\alpha$-carbon is substantial, as pointed out above. Since the ethyl and isopropyl groups in propiophenone and isobutyrophenone, respectively, can adopt conformations which have the same non-bonded interactions as the methyl group in acetophenone, it is generally assumed that the carbonyl group is coplanar with the aromatic ring in each of these compounds (25, 26). The observed differences in the shieldings, therefore, must be primarily due to polar effects of methyl substitution. Attention has been drawn to the similarities of these changes with those observed for the corresponding methyl alkyl ketones and olefins, although no clear explanation for these changes can be offered. Assuming that these effects are entirely due to the alkyl substituents bonded to the carbonyl groups, the variations in carbonyl carbon shielding caused by alkyl substitution on the ring may be employed to calculate the angles of twist, $\theta$, for the hindered systems. For this purpose, the original expression must be modified to, $\cos^2\theta = (\delta_C^X + 20)/20$ where $\delta_C^X$ represents the difference in carbonyl shielding for the X-substituted compound relative to the corresponding parent ketone. The necessary data are given in the first two columns of Table VI. Using these figures, angles of twist have been calculated for the propiophenone and isobutyrophenone series and these are listed in Table X. As

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described in previous papers (2, 3), there is evidence that an ortho-methyl substituent tends to shield the carbonyl carbon nucleus by ca. 1 p.p.m. and, taking this effect into account, "corrected" estimates of $\theta$ have been calculated and included in Table X. A detailed discussion of the significance of these "corrections" has been presented (3) and need not be repeated. The estimates in this table seem reasonable although, again, other estimates for these systems are not available for comparison. Two interesting features are apparent from these results: (*a*) the hindrance of two ortho-isopropyl groups is apparently slightly greater than that caused by two ortho-methyls, and (*b*) there are indications of a buttressing effect by the additional methyl groups in durene and pentamethylbenzene derivatives relative to the acylmesitylenes. Both of these observations are in agreement with the results from the acetophenone study.

TABLE X

Estimated angles of twist, $\theta$, for some hindered alkyl phenyl ketones (given in degrees)

| | Alkyl group | | | |
|---|---|---|---|---|
| | $C_2H_5$ | | $i$-$C_3H_7$ | |
| Substituents | | Corrected | | Corrected |
| Nil | 0 | 0 | 0 | 0 |
| 2-$CH_3$ | 27 | 30 | 25 | 28 |
| 2,4,6-$(CH_3)_3$ | 43 | 49 | 39 | 45 |
| 2,3,5,6-$(CH_3)_4$ | 48 | 55 | 44 | 49 |
| 2,3,4,5,6-$(CH_3)_5$ | 49 | 55 | 44 | 50 |
| 2,4,6-$(i\text{-}C_3H_7)_3$ | 47 | 53 | 43 | 48 |

As noted in a previous section, the carbonyl shielding of pivalophenone is towards lower field by −4.1 p.p.m. relative to isobutyrophenone, while the difference in carbonyl carbon shifts for methyl isopropyl and methyl *t*-butyl ketones is only 0.8 p.p.m. and this difference is even less (0.2 p.p.m.) for diisopropyl and di-*t*-butyl ketones. This distinct difference for pivalophenone indicates that its carbonyl carbon is deshielded by an effect in addition to that of the *t*-butyl group. The most probable interpretation of this observation appears to be the presence of steric inhibition of conjugation due to interference between the aromatic protons and the $\beta$-methyls of the *t*-butyl grouping since it cannot assume a conformation having non-bonded interactions similar to those of methyl, ethyl, or isopropyl. If this is a valid explanation, the magnitude of the angle of twist for this system may be estimated using the empirical expression given above and the figure −3.6, for $\delta_C^X$, since this is the difference between the observed change in pivalophenone and the average of the two *t*-butyl aliphatic examples, all relative to the corresponding isopropyl derivatives. In this way, the angle of twist is found to be 25° which may be compared to the value of 34°, estimated from ultraviolet spectral data (25). Both of these estimates agree well with those found for ortho-methylacetophenone by the corresponding methods (3, 25). Although this analysis of the $^{13}C$ chemical shift data is crude, it is interesting that the estimated angle is not unreasonable for this system. For the substituted pivalophenones, the observed variations of the carbonyl shieldings are comparable to those for the related series and estimates of the extent of steric inhibition can be made in a similar fashion. In view of the uncertainties of the approach to the estimated value for the parent compound, however, the significance of such estimates is questionable. For the 2-methyl and 2,4,6-trimethyl derivatives, the

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calculated angles are found to be 40° and 51°, respectively, and the figures for the other derivatives correspond closely with these values, for the mono- and di-ortho-substituted examples, respectively. In any event, the differences in the carbonyl shieldings for the pivalophenone series are qualitatively consistent with the other findings.

Another feature of these spectra of the alkyl phenyl ketones, which was mentioned earlier but deserves further comment, is the effect of the para-methoxyl group on the carbonyl carbon shieldings. For each of the three series, a shift of the resonance position of the carbonyl carbon toward higher field is observed upon the introduction of this substituent and is most pronounced for pivalophenone (3.4 p.p.m.). This change provides supporting evidence of steric interference in pivalophenone itself since it may reasonably be attributed to an increased conjugation of the carbonyl group with the ring due to the strong electron-releasing tendency of the methoxyl group. In other words, it is suggested that the conjugative interaction of the methoxyl oxygen with the carbonyl group, acting through the aromatic ring, reduces the angle of twist in the substituted case relative to the parent ketone. Support for this conclusion is provided by the very much reduced effect of the methoxyl group on the carbonyl shielding in 2-methyl-4-methoxypivalophenone (relative to that for the 2-methyl derivative) for which it would appear that any conjugative interaction is not sufficient to overcome the more pronounced nonbonded interactions. The effect of the para-methoxyl substituent on the isobutyrophenone carbonyl shielding (1.8 p.p.m.) is appreciable and it follows, therefore, that there is some hindrance to coplanarity of the carbonyl group in the unsubstituted ketone. Some evidence for minor steric interference in secondary alkyl phenyl ketones has been noted from ultraviolet studies (25), but no appreciable hindrance to coplanarity would be expected since conformations similar to those for acetophenone may be adopted. In the event there is some interference, the estimated angles of twist collected in Table X for the isobutyrophenone series will be low by a few degrees. There is no compelling evidence to suggest that steric inhibition of conjugation occurs in propiophenone, since the observed effect of the para-methoxyl group, while directionally similar to the other series, is much smaller, 0.9 p.p.m., and is not outside the limits of experimental uncertainty. No evidence from other sources which would indicate deviations from coplanarity has been found.

In summary, the $^{13}$C spectral results for the present examples of alkyl phenyl ketones and methyl aryl ketones support the conclusions drawn from the previous results for the acetophenones and are in good agreement with expectations based on simple steric considerations. Although the proposed semiquantitative approach to estimates of the angles of twist in these systems may be subject to some error due to presently unrecognized effects, there is no question that the variations of the chemical shifts are qualitatively reasonable and provide a potentially useful method for investigating related systems.

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