o-Methyl Proton Chemical Shifts in Sterically-much-hindered Aromatic Ketones

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(Received February 16, 1966)

Proton chemical shifts of α-hydrogen atom in the aromatic side chain have theoretically been explained by the ring current model. Furthermore, it is known experimentally that *o*-carboxy, *o*-carbonyl, and *o*-nitro substituents cause a paramagnetic shift (i. e., a shift to a lower τ-value) of about 0.2—0.3 p. p. m. to the α-hydrogen atom of the methyl group on the aromatic ring.¹⁾ The present author has found that *o*-methyl protons of sterically-much-hindered ketones, alkyl-substituted benzophenone derivatives and alkyl-substituted pivalophenone derivatives show, rather, a shift to a higher τ-value of about 0.2—0.3 p. p. m. The results are shown in Table I. NMR spectra for all compounds were obtained in a carbon tetrachloride solution using tetramethylsilane as the inner reference. Carbon tetrachloride solutions with concentrations from five to ten percent were used for all the measurements because there was no appreciable difference in chemical shifts within this concentration for these compounds. The values of the chemical shifts were corrected by the side-band method. A 60 Mc. 3H-60 spectrometer, manufactured by the Japan Electron Optics Laboratory, was used in these measurements.

Synthetic method and their physical constants of the compounds from No. 22 to No. 27 have been reported in this Bulletin.²⁾

As one can easily see in Table I, methyl protons of the 2, 6-position and of the 2, 6, 2′, 6′-position of alkylated benzophenone derivatives (No. 14—No. 21) appear at a considerably higher field side than do methyl protons of sterically-less-hindered benzophenone derivatives (No. 7—No. 13). In methylated pivalophenone derivatives, again, methyl protons of the 2-position and of the 2, 6-position appear at a higher field side. Because the paramagnetic shielding effect of the *o*-carboxy, *o*-carbonyl, and *o*-nitro groups on the methyl group will be most effective if the benzene ring and these substituents have coplanarity, the observed effects (i. e., the shift to a higher field side) in sterically-much-hindered ketones might be due to the loss of coplanarity among two benzene rings, the carbonyl group, and methyl groups.* Methyl-proton chemical shifts of 2, 6, 2′-trimethylbenzophenone (No. 15) are likely to be typical and to show these circumstances most clearly: 2, 6-CH_3, $\delta(10-\tau)$: 2.04, 2′-CH_3, δ : 2.64. That is to say, 2, 6-CH_3 protons appear at a higher field side than do 2-CH_3 of 2-methylbenzophenone, and 2′-CH_3 appears at a far lower field side than that. Considering the molecular model, the two benzene rings in 2, 6, 2′-trimethylbenzophenone are exactly perpendicular to each other at the most strain-free average molecular state, and the 2′-methyl group may take the position which is affected most effectively by the magnetic deshielding effect of the carbonyl group (see Fig. 1). On the other hand, 2- and 6-methyl groups must be under the influence of the magnetic shielding effect of the carbonyl group because the plane of the carbonyl double bond and the plane of the disubstituted benzene ring are perpendicular; then the signal moves upfield. Although two benzene rings in 2, 6, 2′, 6′-tetramethylbenzophenone are also able to be perpendicular to each other with a slight sterical repulsion of a methyl group (i. e., 6′-CH_3 on ring B) and a benzene ring (i. e., ring A), this state could not be the most strain-free molecular state. Two benzene rings and the carbonyl group should take a twisted position to each other in the more strain-free state, and then the four methyl groups may be non-equivalent in this state. Two of the four methyl groups can be near the other benzene ring, and the other two methyl groups near the

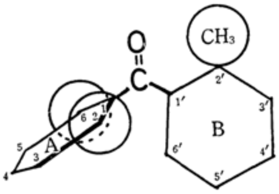

Fig. 1. Configuration of 2, 6, 2′-trimethylbenzophenone.

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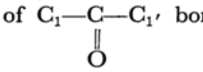
1) J. C. P. Schwarz, "Physical Method in Organic Chemistry," Oliver and Boyd, London (1964), p, 175.

2) H. Suzuki, H. Wada, K. Maruyama and R. Goto, This Bulletin, **39**, 1201 (1966).

* The experimental results of UV measurements made on an extensive series of methyl-substituted benzophenones by Rekker and Nauta indicate a loss of coplanarity between two benzene rings attributed to the steric effects of *o*- and *o*′-substituted methyl groups. R. F. Rekker and W. T. Nauta, *Rec. Trav. Chim.*, **73**, 969 (1954); **77**, 714 (1958); **80**, 747 (1961); **80**, 764 (1961).

Table I. Proton chemical shifts of methyl group of alkylated benzophenones and of alkylated pivalophenones at 23°C

No.	Compound	CH_3 Proton chemical shifts $\delta(10-\tau)$	Others
1	Toluene	2.32	
2	*o*-Xylene	2.23	
3	*o*-Nitrotoluene	2.45	
4	*o*-Carboxytoluene	2.62	
5	*m*-Carboxytoluene	2.37	
6	*p*-Carboxytoluene	2.37	
	Benzophenone derivatives		
7	2-Methyl-	2.23	
8	3-Methyl-	2.22	
9	4-Methyl-	2.21	
10	2, 2′-Dimethyl-	2.35	
11	2, 4′-Dimethyl-	2.21 (2-CH_3), 2.33 (4′-CH_3)	
12	2-Methyl-4′-*t*-butyl-	2.23	1.22 (*t*-Bu)
13	4, 4′-Dimethyl-	2.33	
14	2, 4, 6-Trimethyl-	1.98 (2, 6-CH_3), 2.23 (4-CH_3)	
15	2, 6, 2′-Trimethyl-	2.04 (2, 6-CH_3), 2.64 (2′-CH_3)	
16	2, 6-Dimethyl-4-*t*-butyl-	2.06	1.32 (*t*-Bu)
17	2, 6-Dimethyl-4-*t*-butyl-4′-nitro-	2.00	1.30 (*t*-Bu)
18	2, 6-Dimethyl-4-*t*-butyl-4′-chloro-	2.05	1.32 (*t*-Bu)
19	2, 6, 2′, 6′-Tetramethyl-	2.04	
20	2, 6, 2′, 6′-Tetramethyl-4, 4′-di-*t*-butyl-	2.06	1.26 (*t*-Bu)
21	2, 4, 6, 2′, 4′, 6′-Hexamethyl-	1.98 (2, 6, 2′, 6′-CH_3), 2.17 (4, 4′-CH_3)	
	Pivalophenone derivatives		
22	2, 4-Dimethyl-	2.07 (2-CH_3), 2.22 (4-CH_3)	1.14 (*t*-Bu)
23	2, 3, 4-Trimethyl-	1.99 (2-CH_3), 2.07 (3-CH_3), 2.18 (4-CH_3)	1.14 (*t*-Bu)
24	2, 4, 5-Trimethyl-	2.07 (2-CH_3), 2.15 (4, 5-CH_3)	1.14 (*t*-Bu)
25	2, 4, 6-Trimethyl-	2.06 (2, 6-CH_3), 2.18 (4-CH_3)	1.14 (*t*-Bu)
26	2, 3, 4, 5-Tetramethyl-	2.01 (2-CH_3), 2.14 (3, 5-CH_3), 2.21 (4-CH_3)	1.14 (*t*-Bu)
27	2, 3, 5, 6-Tetramethyl-	1.98 (2, 6-CH_3), 2.16 (3, 5-CH_3)	1.14 (*t*-Bu)

carbonyl. However, this state is interconvertible with a rotation of  $C_1\text{—}\underset{\underset{O}{\|}}{C}\text{—}C_{1'}$ bondings without any appreciable sterical repulsion through the molecular state in which two benzene rings are perpendicular to each other. Thus, four methyl groups are supposed to become equivalent to the average molecular state. Recently, Mislow and co-workers[3] have observed the methyl proton chemical shifts of *o*, *o*′-bridged biphenyl derivatives and found that the signal moved upfield with an increase in the angle of torsion between the two benzene rings; they ascribed this effect to the magnetic shielding effect of the other benzene ring on which the methyl was not attached. Therefore, a part of the shielding effect might also be ascribed to that of the benzene ring in 2, 6, 2′, 6′-tetramethylbenzophenone. Thus, four methyl groups may be supposed to be under the magnetic shielding effect of both the carbonyl group and the benzene ring, although it is not clear which is the more important of the said shielding effects.

A similar explanation may be applied to all the compounds examined here which show a shift to the upfield side of the methyl proton signal.

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[3] K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon and G. H. Wahl, Jr., *J. Am. Chem. Soc.*, **86**, 1710 (1964).