Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

NOTE

THE METHYL PROTON CHEMICAL SHIFTS IN SUBSTITUTED TRIMETHYLPHENYLSILANES

J. F. R. JAGGARD* AND A. PIDCOCK
The Chemical Laboratory, University of Sussex, Brighton, BN1 9QJ (Great Britain)

(Received October 8th, 1968)

The compounds *o*-, *m*-, and *p*-$XC_6H_4SiMe_3$ have single sharp resonances in the ^1H NMR spectra corresponding to the proton of the $SiMe_3$ groups. The chemical shifts of these resonances vary with the nature and orientation of the substituent on the aromatic ring and Sakurai and Ohtsuru[1] have recently reported a linear correlation (correlation coefficient $r=0.936$) between these shifts and the appropriate Hammett

TABLE 1

CHEMICAL SHIFTS δ[a] OF TRIMETHYLSILYL PROTONS OF *o*-, *m*-, AND *p*-$XC_6H_4SiMe_3$ COMPOUNDS IN CARBON TETRACHLORIDE

o-$XC_6H_4SiMe_3$		*m*-$XC_6H_4SiMe_3$		*p*-$XC_6H_4SiMe_3$	
X	$\delta(SiMe_3)$	X	$\delta(SiMe_3)$[b]	X	$\delta(SiMe_3)$[b]
MeCO	0.30	Me_2N	1.25[c](1)	Me_2N	3.25[c](10)
Me_3SiCH_2	−1.88	Me	1.06[c](2)	MeO	1.81[c](11)
NO_2	−2.70	$(Me_3Si)_3C$	0.70	Me	1.605[c](12)
Me	−3.29	Me_2NCH_2	0.45	Et	1.32[c](13)
PhCO	−4.50	MeO	0.37[c](3)	tert-Bu	1.27[c](14)
HOOC	−5.95	tert-Bu	0.10[c](4)	MeS	1.15
Cl	−6.51	Me_3Si	−0.50[c](5)	Me_3SiCH_2	0.86[c](15)
I	−9.10	Br	−0.85[c](6)	iso-Pr	0.66[c](16)
		Cl	−0.915[c](7)	F	0.52[c](17)
		PhCO	−2.80	Me_3Si	0.47[c](18)
		CF_3	−3.26[c](8)	Me_2As	0.45
		NO_2	−5.06[c](9)	Cl	0.30[c](19)
				Br	0.00[c](20)
				Me_2NCH_2	−0.05
				MeCO	−1.65[c](21)
				HOOC	−2.74
				PhCO	−3.05[c](22)
				NO_2	−3.79[c](23)

[a] Shift in Hz from $C_6H_5SiMe_3$; a positive value of δ implies a sample resonance at higher field strength than the reference. [b] Numbers between parentheses correspond to the numbers in Fig. 1 [c] Data used in correlation with Hammett constants.

---

* Present address: ICI Ltd., Plastics Division, Bessemer Road, Welwyn Garden City, Heats (Great Britain).

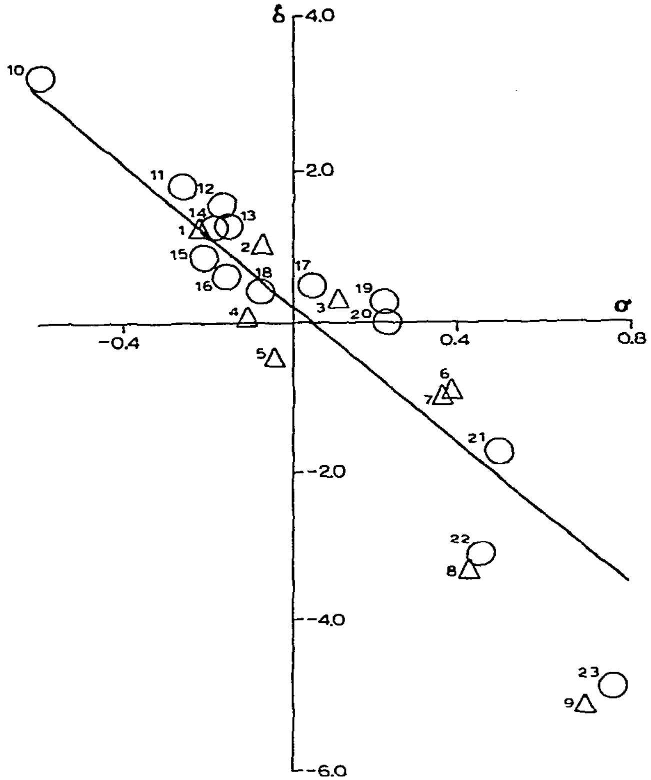

Fig. 1. Correlation of trimethylsilyl proton chemical shifts with Hammett σ-constants. Numbers correspond to numbered compounds in Table 1; △ *m*-compound, ○ *p*-compound.

σ-constants of the substituents X for a total of six *m*- and *p*-substituted arylsilanes.

Our similar results[2] for some 39 compounds are given in Table 1. For those compounds for which Hammett σ-constants are available[3,4] (24 compounds) least squares analysis shows that the data fit the equation:

$$\delta = -(4.95 \pm 0.35) \cdot \sigma + (0.25 \pm 0.12)$$

with a correlation coefficient $r = 0.89$. The value of $\rho = -4.95$ Hz/σ is consistent with the value $-(5.86 \pm 0.94)$ obtained previously[1].

Comparison with other similar correlations[5] in benzene systems shows that the shifts of the protons of the $SiMe_3$ group are rather less sensitive to changes in σ than are protons in other groups in which there are two atoms between the proton and the aromatic ring, such as SMe.

EXPERIMENTAL

The preparation of most of the compounds used have already been published. The remaining compounds will be described later[6].

The spectra of the liquid compounds were measured as 5% by volume (*ca.*

0.22 *M*) solutions and the solids as 0.22 *M* solutions, both in carbon tetrachloride containing ~2% by volume of tetramethylsilane.

Shifts to tetramethylsilane were determined with a Perkin–Elmer R10 or a Varian A60 Spectrometer operating at 60MHz, with an error of not more than 0.3 Hz.

ACKNOWLEDGEMENTS

A research scholarship from I.C.I. Nobel Division (to J.F.R.J.) is gratefully acknowledged.

REFERENCES

1 Hideki Sakurai and Masako Ohtsuru, *J. Organometal. Chem.*, 13 (1968) 81.
2 J. F. R. Jaggard, D. Phil. Thesis, University of Sussex, 1965.
3 D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 23 (1958) 420.
4 H. H. Jaffe, *Chem. Rev.*, 53 (1953) 191.
5 S. H. Marcus, W. F. Reynolds and S. I. Miller, *J. Org. Chem.*, 31 (1966) 1872.
6 C. Eaborn and J. F. R. Jaggard, to be published.