Adducts of Group IVB Radicals with Sulphur-containing Diaryl Ketones

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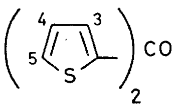
The hyperfine splitting constants for the paramagnetic adducts of $\cdot MR_3$ radicals (M = Si, Ge, or Sn) with some dithienyl and bisthienothienyl ketones, benzophenone, and fluorenone are reported and compared with those for the corresponding diarylhydroxymethyl radicals. From the results, and with the aid of INDO calculations, it has been found that in the former derivatives the O–M bond eclipses the $2p_z$ orbital of the carbonyl atom, at variance with the hydrogen adducts, which exhibit practically planar conformations. Barriers to rotation of the OH group in benzophenone and fluorenone derivatives have been determined from the temperature dependence of the a_H^{OH} splitting and are 5.1 and 6.5 kcal mol^{-1}, respectively.

ORGANOMETALLIC radicals of general formula $\cdot MR_3$ (M = Si, Ge, or Sn) are known to add easily to carbon–oxygen [1] or nitrogen–oxygen [2] double bonds, thus giving paramagnetic adducts which are reasonably stable and can be studied by e.s.r. spectroscopy. In both cases addition occurs at the oxygen atom because of the strength of the metal–oxygen bond.

In this paper we report an e.s.r. investigation on the radical adducts resulting from the reaction of diaryl ketones containing thiophen or condensed thiophen rings with $\cdot MR_3$ and hydrogen radicals. The compounds examined are (I)—(XIV).

The conformational preference and the electronic properties of the entering groups are discussed on the basis of the hyperfine splitting constants at the aromatic nuclei and at the metal atoms, which in several cases could be measured. INDO Calculations have also been carried out on the silyl and hydrogen adducts in order to rationalize the experimental results.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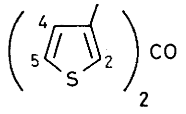
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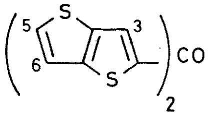
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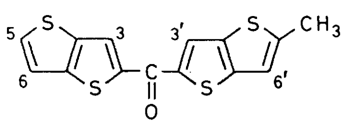
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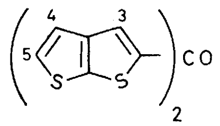
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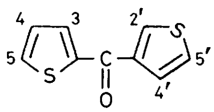
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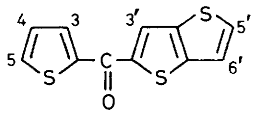
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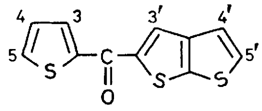
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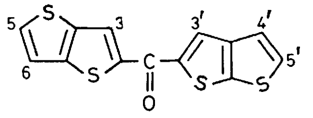
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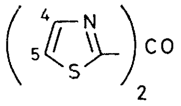
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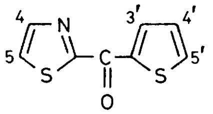
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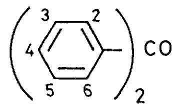
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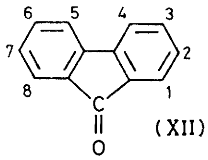
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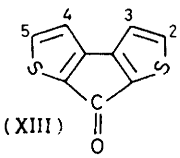
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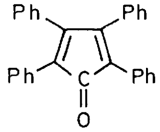

(XIV)

EXPERIMENTAL

Diaryl ketones not commercially available were prepared by methods described in the literature.[3] Triphenylsilane, triphenylgermanium hydride, triphenyltin hydride, hexa-n-butylditin, and hexamethylditin were purchased from Alpha Chemicals and used without further purification.

The radical adducts were generated by u.v. irradiation of a melt of the carbonyl derivative and the appropriate organometallic compound (silane, germanium hydride, or ditin compound). The mechanism of formation of the radical species has been already described by Hudson *et al.*[4]

The formation of the germanium and tin adducts was also found to take place by heating the reactant melt in the dark. In this case the initial step of the chain reaction is presumably thermal homolytic cleavage of the Ge–H or Sn–H (Sn–Sn) bonds.

Diarylhydroxymethyl radicals were produced by photolysing solutions of the parent ketone in 1 : 1 propan-2-ol–hexamethylphosphoramide (HMPA) or in pure HMPA.[5]

Photolyses were performed with a high pressure mercury lamp (1 kW) focused on the sample tube inside the e.s.r. cavity. The temperature was controlled by means of standard accessories and measured with a copper–constantan thermocouple.

INDO Calculations were carried out on the hydrogen and silyl radical adducts of benzophenone (XI) and fluor-

TABLE 1

Hyperfine splitting constants (G) for the radical adducts from symmetrical ketones

Compd.	MR_3	a_1	a_2	a_3	a_4	a_5	a_6	a_N	a_M	a_R	t/°C
(I)	$SiPh_3$			5.18	1.08	4.34					90
	$GePh_3$			5.09	1.08	4.24					80
	$SnPh_3$			5.03	1.03	4.10			86.7, 91.0		50
	$SnMe_3$			5.04	1.10	4.15			75.8, 79.5	0.055	60
	H *			5.25	1.10	4.45			4.50		25
(II)	$SiPh_3$		5.31		1.28	0.70					170
	$GePh_3$		5.32		1.26	0.70					150
	$SnBu^t_3$		5.34		1.23	0.69					170
(IIIa)	$SiPh_3$			5.34		2.64	0.70				145
	$GePh_3$			5.28		2.59	0.69				145
	$SnBu^t_3$			5.25		2.57	0.69				60
	H *			5.50		2.68	0.71		4.80		25
(IV)	$SiPh_3$			5.74	<0.05	0.47			5.80		100
	$GePh_3$			5.69	<0.05	0.46			4.20		100
	$SnMe_3$			5.70	<0.05	0.47			76.0, 79.5	0.075	80
	H *			5.96	<0.05	0.49			5.10		25
(IX)	$SiPh_3$				0.43	3.80		2.78			110
	$GePh_3$				0.45	3.61		2.76			110
	$SnMe_3$				0.50	3.16		2.81			25
					0.42	3.16		2.50			
(XI)	$SiPh_3$		3.20	1.25	3.55	1.25	3.20				130
	$GePh_3$		3.16	1.22	3.55	1.22	3.16				130
	$SnMe_3$		3.10	1.20	3.50	1.20	3.10		87.2, 91.2		100
	H *		3.16	1.22	3.58	1.22	3.16		3.25		40
(XII)	$SiPh_3$	3.53	0.80	3.81	0.80						240
	$GePh_3$	3.40	0.80	3.72	0.80						210
	$SnMe_3$	3.20	0.75	3.57	0.75				71.0, 74.2		100
	H *	2.89	0.55	3.50	0.81				0.60		25
(XIII)	$SiPh_3$		3.65	0.42							250
	$GePh_3$		3.58	0.44							150
	$SnBu^t_3$		3.42	0.53							80
	H *		3.45	0.51					0.51		100
(XIV)	$GePh_3$								4.17		100
	$SnPh_3$								61.2		25
	$SnBu^t_3$								46.9		25
	$SnBu^t_3$ †								44.12		25

* In propan-2-ol–HMPA (1:1 v/v). † In C_6H_6.

TABLE 2

Hyperfine splitting constants (G) for the radical adducts from asymmetrical ketones

Compd.	MR_3	a_3	a_4	a_5	a_6	a_N	$a_{2'}$	$a_{3'}$	$a_{4'}$	$a_{5'}$	$a_{6'}$	a_M	t/°C
(IIIb)	$SiPh_3$	5.38		2.63	0.69			5.38		2.85 *	0.69		180
	$GePh_3$	5.30		2.60	0.68			5.30		2.80 *	0.68		100
	$SnBu^t_3$	5.20		2.58	0.68			5.20		2.58 *	0.68	60.2, 63.0	140
	H †	5.50		2.70	0.70			5.50		2.80 *	0.70	4.35	25
(V)	$SiPh_3$	6.00	1.28	5.14			4.25		1.09	0.59			100
	$GePh_3$	5.95	1.25	5.12			4.30		1.09	0.59			100
	$SnMe_3$	5.80	1.22	5.00			4.40		1.12	0.59		87.0	100
(VI)	$SiPh_3$	4.56	0.96	3.71				5.87		2.89	0.77		100
	$GePh_3$	4.59	0.95	3.80				5.80		2.90	0.78		100
	$SnMe_3$	4.65	0.95	3.75				5.65		2.80	0.85	72.6, 76.0	80
	H †	4.80	0.98	3.69				6.20		2.91	0.76	4.40	25
(VII)	$SiPh_3$	5.04	1.06	4.20				5.94	<0.05	0.49			100
	$GePh_3$	4.90	1.03	4.10				5.80	<0.05	0.48			100
	$SnMe_3$	4.94	1.07	4.12				5.82	<0.05	0.48		77.9, 81.5	80
	H †	5.14	1.09	4.30				6.04	<0.05	0.50		4.74	25
(VIII)	$SiPh_3$	5.65		2.83	0.74			5.15	<0.05	0.41			100
	$GePh_3$	5.66		2.85	0.75			5.25	<0.05	0.44			100
	$SnMe_3$	5.60		2.72	0.68			5.40	<0.05	0.48			80
	H †	5.87		2.85	0.78			5.52	<0.05	0.46		4.80	25
(X)	$SiPh_3$		0.50	3.72		2.83		5.20	0.98	4.48			110
	$GePh_3$		0.55	3.71		2.90		5.08	0.98	4.35			110
	$SnMe_3$		0.56	3.50		3.23		4.20	0.85	3.60			25

* Three protons. † In propan-2-ol–HMPA (1 : 1 v/v).

enone (XII), by employing a program parametrized for second-row elements according to Benson and Hudson.[6]

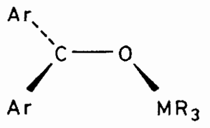
RESULTS AND DISCUSSION

The hyperfine splitting constants of the organometallic and hydrogen adducts of the diaryl ketones

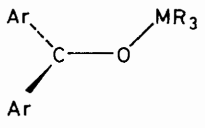
(I)—(XIV) are reported in Tables 1 and 2. For most derivatives, it has been possible to measure the coupling constants with the two isotopes, ^{117}Sn (7.67%, I $\frac{1}{2}$) and ^{119}Sn (8.68%, I $\frac{1}{2}$), of the tin atom. As an example, Figure 1 shows the e.s.r. spectrum of the radical from bis-2-thieno[2,3,*b*]thienyl ketone (IV). Due to the large values of the tin splittings (79.5 and 76.0 G) the satellite lines are shifted to lower field with respect to the main spectrum as predicted by second-order perturbation theory. In the adducts of (IV) the ^{29}Si (4.70%, I $\frac{1}{2}$) and ^{73}Ge (7.61%, I 9/2) splittings could be measured as 5.80 and 4.40 G, respectively. Attempts to detect tin satellites in the adducts of the ketones (IX) and (X) containing the thiazolyl ring were unsuccessful, despite the good quality of the e.s.r. spectra. This is an indication that for these derivatives the coupling at the Sn atom is very close to zero at variance with the adducts of the other ketones for which $60 < a_{\mathrm{Sn}} < 90$ G.

FIGURE 1 E.s.r. spectrum of the trimethyltin radical adduct with bis-2-thieno[2,3-*b*]thienyl ketone (IV). The satellite lines due to ^{117}Sn (■) and ^{119}Sn (●) have been recorded with higher amplification

Conformations of the Adducts.—For the radical adducts of diaryl ketones two limiting conformations may be envisaged, one with the R_3M group on the plane containing the sp^2 hybrids centred on the methyl carbon (A), and the other in which the O–M bond essentially eclipses the $2p_z$ orbital of the central carbon atom (B).



(A)



(B)

Like all β-couplings the metal splitting is expected to be large and positive in the orthogonal conformation (B) and small and negative in the planar form (A).

Inspection of molecular models suggests that the bulky organometallic groups adopt conformation (B) because of steric repulsion with the aromatic rings. In the case of the organotin derivatives, experimental evidence for this is provided by (i) the measured values of the Sn hyperfine splittings which are much larger than for the adducts of *cis*-α-diketones (3—8 G) [1c] where the metal atom is probably held close to the molecular plane by interaction with the carbonyl oxygen atoms and (ii) the similarity of the a_{Sn} couplings with that found for the analogous adduct of tetraphenylcyclopentadienone (XIV), in which the serious crowding about the carbonyl oxygen makes it unlikely for the organometallic group to adopt any position other than over the cyclopentadienone ring. No attempt to interpret the proton hyperfine structure of this radical was made; however, its stability together with the small overall splitting and the presence of metal satellites leave little doubt that the species being observed is really the product of addition of $\cdot MR_3$ to the C=O group of (XIV).

Further, the very small dependence on temperature of the tin splitting indicates that the equilibrium position for torsion of the MR_3 group corresponds to a deep potential-energy minimum. For instance, the ^{119}Sn coupling is 91.2 G at 100 °C and 92.4 G at 180 °C for the adduct of benzophenone, and 73.7 G at 70 °C and 75.2 G at 160 °C for that from fluorenone. Although the sign of the temperature coefficient is opposite to that expected for structure (B), the small variations suggest that they may be better understood in terms of a larger amplitude for the bending vibration of the C–O–M bond angle rather than a different torsional averaging for the rotational motion of the organometallic group about the C–O bond.

The silicon and germanium splittings, which again may give useful information on the conformational preference of the corresponding adducts, could be determined only for the radicals from (IV) and (XIV) (only for Ge). A ^{29}Si splitting of 7.1 G has been reported previously for triphenylsiloxydiphenylmethyl radical[7] from (XI) but, to the best of our knowledge, this is the first report of a ^{73}Ge splitting for adducts of carbonyl derivatives.

The smaller couplings to germanium (4.2 G) and silicon (5.8 G) than for tin, observed in the radicals from (IV), are consistent with the different values of a_0 (isotropic hyperfine coupling for one electron in the appropriate s orbital of the atom), 1 207 G for ^{29}Si,[8a] 850 G for ^{73}Ge,[8b] and 15 400 G for the ^{119}Sn isotope.[8b]

Actually, if the measured isotropic splittings are divided by the corresponding a_0 values the fractions of unpaired spin on the relevant s orbital of the three metal atoms are found to be 4.8×10^{-3}, 4.9×10^{-3}, and 5.0×10^{-3} for Si, Ge, and Sn, respectively. The virtual identity of the $a : a_0$ ratios suggests that the hyperconjugative mechanism of spin transfer from the π-system to the metal atoms has the same efficiency in the three different adducts and therefore that the orthogonal conformation (B) is also favoured by the organosilyl and organogermyl groups.

Additional evidence for the proposed conformational preference is provided by the g factors of the H (2.003 95), SiPh$_3$ (2.003 77), GePh$_3$ (2.003 57), and SnPh$_3$ (2.003 08) adducts of (I), which decrease with increasing size of the metal atom. This trend parallels that found for β-substituted ethyl radicals and can be rationalized in terms of σ–π conjugation or p–d homoconjugation if (B) is the more stable conformation.[9] On the other hand, if the planar conformation (A) is favoured, we would expect negligible variation of the g factors within the same series of adducts since the bridging oxygen prevents possible conjugative interactions between the radical centre and the organometallic group, and therefore electron spin delocalization onto the latter. This has been found for planar adducts of α-diketones.[10]

An exception to this behaviour is shown by the tin adducts of the two ketones containing thiazolyl rings, (IX) and (X), in which coupling to the Sn atom is too small to be detected. It seems likely that in these radicals the tin atom is chelated by the carbonyl oxygen and one of the thiazole nitrogens, and therefore forced into conformation (A). This explanation is consistent with the observed magnetic non-equivalence of the two thiazole rings in the adduct of the symmetrical dithiazol-2-yl ketone (IX), and also with the marked decrease in the proton splittings of the thienyl ring in the organotin radical from (X), when compared with the corresponding silyl and germyl adducts. If one ring is held coplanar, or nearly so, with the C–O bond by chelation, it seems reasonable that the second ring will deviate significantly from planarity because of the greater steric hindrance, with consequent decrease of the spin density upon it. The non-equivalence of the two rings, shown by the tin adduct of (IX), has also been observed for the radical ion pairs of the same derivative, where the alkali counter-ion is again chelated by the carbonyl oxygen and one thiazole nitrogen atom with loss of molecular symmetry.[2b] The organosilyl and organogermyl adducts of (IX) and (X), where the couplings for the aromatic protons give no indication of penta-co-ordination by the metal, are likely to behave as the adducts of the other diaryl ketones. This is not surprising in view of the fact that tin is known to give penta-co-ordinated complexes more easily than the lighter atoms of group IVB.[11]

The results for the diarylhydroxymethyl radicals are, on the other hand, indicative of different conformational behaviour. The equilibrium position of the O–H bond may be inferred from the hydroxy proton splitting whose dependence on the torsional angle α about the C–O internuclear axis is given by [equation (1)], α being 0

$$a_{\mathrm{H}}^{\mathrm{OH}} = B_0 + B_2 \langle \sin^2\alpha \rangle \qquad (1)$$

and $\pi/2$ in the planar and orthogonal conformations, respectively. Since for hydroxymethyl radical B_0 and B_2 have been determined as -5.3 and 41.5 G,[12] we should expect values of $a_{\mathrm{H}}^{\mathrm{OH}}$ to be small and negative for $\alpha = 0$ and large and positive for $\alpha = \pi/2$. In the two radicals from the rigid ketones (XII) and (XIII) the hydroxy-proton splitting is <1 G and shows a negative temperature dependence ($\mathrm{d}|a_{\mathrm{H}}^{\mathrm{OH}}|/\mathrm{d}T < 0$) suggesting that its sign is negative. It seems therefore that in these two cases the more stable conformation is the planar one (A). In the hydrogen adducts of flexible ketones the $a_{\mathrm{H}}^{\mathrm{OH}}$ coupling is always positive ($\mathrm{d}|a_{\mathrm{H}}^{\mathrm{OH}}|/\mathrm{d}T > 0$) with values ranging between 3 and 5 G. This finding is still consistent with an energy minimum at $\alpha = 0°$ provided the barrier to hindered rotation about the C–O bond is lower than in the corresponding radicals from rigid ketones. Quantitative information on the height of these barriers may be obtained by fitting the experimental temperature dependence of $a_{\mathrm{H}}^{\mathrm{OH}}$ using well established quantum-mechanical procedures.[13] It is assumed that the observed splitting at a given temperature is the Boltzmann average of the expectation values of $a_{\mathrm{H}}^{\mathrm{OH}}$ for all the significantly populated rotational levels [equation (2)]. The expectation values and the energies

$$a_{\mathrm{H}}^{\mathrm{OH}}(T) = \sum_i \langle a_{\mathrm{H}}^{\mathrm{OH}}(\alpha) \rangle_i \times \exp(-E_i/kT)/\sum_i \exp(-E_i/kT) \qquad (2)$$

E_i of the single rotational states were calculated from the relevant torsional Hamiltionian in which a potential

$$V(\alpha) = V_0 + \tfrac{1}{2}V_2(1 + \cos 2\alpha) \qquad (3)$$

of the form (3) was introduced. By using the first 20 eigenfunctions of the symmetric rotor as a truncated basis set, the required values could be obtained by numerical diagonalization of the Hamiltonian matrix.

Computations were performed on the radicals from benzophenone (XI) and fluorenone (XII) which were chosen as model systems for flexible and rigid derivatives. The reduced moment of inertia was taken as 1.252×10^{-40} g cm^2 in both cases. The energy barriers were calculated by the following procedure: (i) fitting the experimental data of Figure 2 for a given energy barrier V_2, by using equation (1) thus determining the B_0 and B_2 coefficients; (ii) since B_0 was found to be always negative and virtually independent of the value of V_2, the height of the barrier was chosen as that giving B_2 a value coincident with the one calculated by the INDO method (*i.e.* 35.9 G for diphenylhydroxymethyl and 30.9 G for 9-hydroxyfluorenyl). Rotational energy barriers of 5.1 and 6.5 kcal mol^{-1} were found for the hydrogen adducts from (XI) and (XII), respectively. It is possible that in the other flexible diarylhydroxymethyl radicals which show larger hydroxy-proton splittings, the barriers to rotation are even lower than in the adduct of benzophenone.

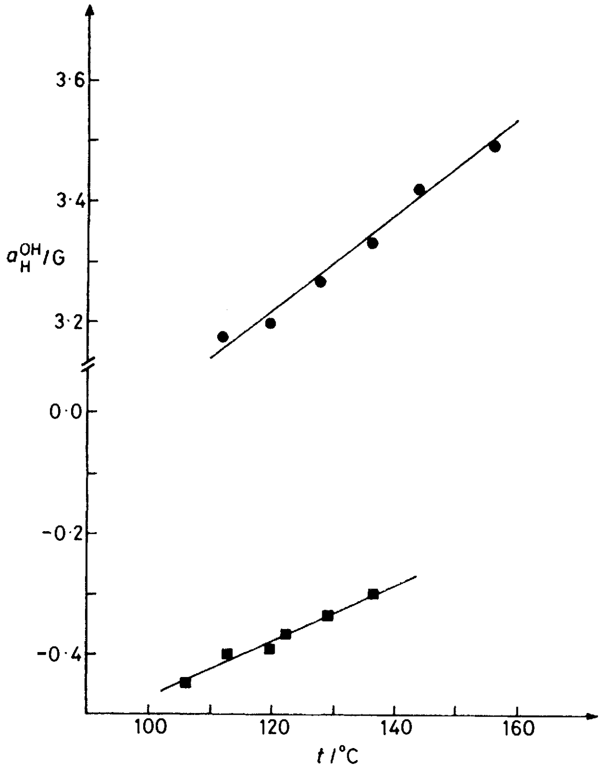


FIGURE 2 Temperature dependence of the $a_H{}^{OH}$ splitting in the diphenylhydroxymethyl (●) and 9-hydroxyfluorenyl (■) radicals in pure HMPA

The B_2 values given by our INDO calculations are somehow larger than those reported by previous workers. For instance, using the extensive work of Sullivan [14] on the rotational barriers of the hydroxy-group in cation radicals and adapting the equation used by this author to our expression (1) by employing the INDO-computed spin densities at the methyl carbon and at the oxygen atom, *i.e.* 0.439 4 and 0.089 5 and 0.362 6 and 0.087 1, respectively, for the radicals from (XI) and (XII), we found B_2 25.1 ± 4.8 and 21.2 ± 4.1, respectively. However it should be emphasized that the amount of electron transfer from the π system to the s orbital of the hydrogen atom strongly depends on the relative energies of the singly occupied MO and of the σ and σ^* orbitals of the O–H bond, and therefore we may expect variations in the magnitude of the B_0 and B_2 coefficients on going from electrically charged to neutral radicals. In any case the use of the latter values of B_2 does not lead to very large changes in the heights of the rotational barriers, which are computed to be 3.7 for the hydrogen adduct of benzophenone and 5.0 kcal mol^{-1} for that from fluorenone.

INDO Calculations.—To clarify the conformational behaviour of the hydrogen and silyl adducts of the investigated ketones we have performed INDO calculations on the hydroxyl radicals from benzophenone (XI) and fluorenone (XII). In the adduct from (XI) the geometrical parameters reported for the related radical anion [15] were employed, while with fluorenone all the C–C bonds were set equal to 1.40 Å. In both cases C–O and O–H bond distances of 1.394 and 0.96 Å, and a C–O–H bond angle of 115.2° were chosen. The potential energy curves for the rotation of the OH bond have been determined by repeating the calculations every 10° from α 0 to 90° keeping fixed the C–O–H bond angle, and were found to have a single minimum corresponding to the planar conformation with barriers of 4.48 and 5.21 kcal mol^{-1} for the radicals from (XI) and (XII), respectively. The computed curves were also found to be well fitted by a potential relationship of the form of equation (3). The INDO computations give a larger barrier to rotation for 9-hydroxyfluorenyl with respect to diphenylhydroxymethyl, in agreement with the results obtained by analysing the temperature dependence of the $a_H{}^{OH}$ splitting.

Since the stability of the planar conformation is presumably due to conjugation of the oxygen lone-pair with the π-system, the origin of the different barriers in the radicals from (XI) and (XII) may be found in the nature of the singly occupied MO which is antibonding between oxygen and the methyl carbon. In diphenylhydroxymethyl the twisting of the phenyl rings reduces their ability to delocalize the unpaired electron. This makes the SOMO coefficient at the carbonyl carbon (0.662 9) greater than in 9-hydroxyfluorenyl (0.602 2), thus leading to a smaller C–O bond order with consequent destabilization of conformation (A). If this explanation is correct, we expect the potential energy profile for the torsional motion of the O–H bond to be in general more flat in the adducts of flexible than of rigid ketones. The hydroxy-proton splittings should therefore be larger in the former radicals as found experimentally.

INDO Calculations have also been performed on the silyl adduct of benzophenone to check whether the ^{29}Si splitting computed for the orthogonal (B) conformation is comparable with the experimental value. Calculations have been made using an O–Si interatomic distance of 1.633 Å and a C–O–Si bond angle of 135° for conformation (A) and 120° for conformation (B).* The silicon splitting was computed by multiplying the spin density on the 3*s* orbital by a scaling factor of 1 234 G.[17] Values of a_{Si} of -1.97 and 7.03 G were determined for conformations (A) and (B), respectively. The good agreement between the latter value and the experimental splitting of 7.1 G gives further support to the assignment of the orthogonal conformation to the silyl adducts of diaryl ketones.

Electronic Distributions.—The hyperfine splitting constant of the aromatic ring protons may give useful information on the relative electron donor or acceptor character of the various groups. As far as the effect of the aromatic nuclei is concerned an increase in the proton splittings of a given ring when going from a symmetrical to an asymmetrical ketone is indicative of a greater ability to delocalize the unpaired electron with respect to the second ring. An examination of Tables 1 and 2 shows that the electron-withdrawing power decreases in the order 2-thieno[3,2-*b*]thienyl > 2-thieno[2,3-*b*]thienyl ⩾ 2-thienyl > 3-thienyl. This trend, which parallels that found for the radical anions of the same ketones,[3] is also reflected by the tin hyperfine splittings whose values increase in the same sequence, thus indicating that the spin density at the carbonyl group is greater the smaller the electron-accepting ability of the aromatic rings.

Previous studies have shown that organometallic substituents behave as acceptors for the unpaired electron, their electron-withdrawing power decreasing upon increasing the size of the metal atom. The effect exerted on the hyperfine splitting constants is large when the entering group is directly bonded to the π-system, as in the adducts of substituted pyridines.[18]

In the present case the differences between the ring couplings in the various organometallic derivatives are much smaller than in the above mentioned radicals, even if the trend is still in agreement with a reduction of the electron-accepting character of the MR_3 groups on descending the periodic table. The effect is probably less important since only hyperconjugative interactions operate in the present situation. A comparison with the corresponding hydroxymethyl radicals is worthless because of the different conformational preference of the latter adducts.

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* A larger value of the C–O–Si bond angle had to be used for the planar conformation to reduce destabilization due to steric hindrance. On the other hand C–O–Si is known to be 'soft' bond angle as can be inferred from values reported [16] which range from 120 to 140°.[16]

REFERENCES

[1] (*a*) A. Hudson and R. A. Jackson, *Chem. Comm.*, 1969, 1323; (*b*) A. J. Bowles, A. Hudson, and R. A. Jackson, *J. Chem. Soc.* (*B*), 1971, 1947; (*c*) A. Alberti and A. Hudson, *Chem. Phys. Letters*, 1977, **48**, 331.

[2] (*a*) C. M. Camaggi, G. F. Pedulli, P. Placucci, and M. Tiecco, *J.C.S. Perkin II*, 1974, 1226; (*b*) G. F. Pedulli, P. Zanirato, A. Alberti, and M. Tiecco, *ibid.*, 1975, 293.

[3] G. F. Pedulli, M. Tiecco, A. Alberti, and G. Martelli, *J.C.S. Perkin II*, 1973, 1816, and references therein.

[4] J. Cooper, A. Hudson, and R. A. Jackson, *J.C.S. Perkin II*, 1973, 1933.

[5] R. S. Davidson and P. Wilson, *J. Chem. Soc.* (*B*), 1970, 71.

[6] H. G. Benson and A. Hudson, *Theor. Chim. Acta*, 1971, **23**, 259.

[7] A. R. McIntosh and J. K. S. Wan, *Mol. Phys.*, 1971, **22**, 183.

[8] (*a*) J. R. Morton, *Chem. Rev.*, 1964, **64**, 453; (*b*) R. V. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, 1973, **85**, 2459.

[9] T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 648.

[10] A. Alberti, A. Hudson, and G. F. Pedulli, to be published.

[11] B. Schroeder, W. P. Neumann, and H. Hillgärtner, *Chem. Ber.*, 1974, **107**, 3494.

[12] P. J. Krusic, P. Meakin, and J. P. Jesson, *J. Phys. Chem.*, 1971, **75**, 3438.

[13] P. B. Ayscough, M. C. Brice, and E. D. McCluny, *Mol. Phys.*, 1971, **20**, 41.

[14] P. D. Sullivan, *J. Phys. Chem.*, 1971, **75**, 2195.

[15] F. Bernardi, M. Guerra, and G. F. Pedulli, *J. Phys. Chem.*, 1974, **78**, 2144.

[16] M. J. Bennet, W. A. G. Graham, R. A. Smith, and R. P. Steward, jun., *J. Amer. Chem. Soc.*, 1973, **95**, 1684.

[17] I. Biddles and A. Hudson, *Mol. Phys.*, 1973, **25**, 707.

[18] A. Alberti and G. F. Pedulli, *Tetrahedron Letters*, 1978, 3283.