An Electron Spin Resonance Investigation of β-Substituted 1,1-Diphenylethyl Radicals

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A large number of β-substituted 1,1-diphenylethyl derivatives $Ph_2\dot{C}CH_2MR_n$ have been generated by addition of $\cdot MR_n$ radicals to 1,1-diphenylethylene. The magnitude of the β-proton hyperfine splitting constants together with the observation of linewidth alternation effects on the CH_2 triplet, indicate that the preferred conformation of these radicals is close even though not coincident with that placing the MR_n group in an eclipsed position with respect to the $2p_z$ orbital on C_α. The slight departure of these adducts from an eclipsed geometry has been interpreted as due to the presence on C_α of the two phenyl rings which are somewhat twisted with respect to each other thus producing an asymmetric potential around the radical centre. Although all the 1,1-diphenylethyl derivatives which have been investigated adopt the same conformation, the β-proton splitting cover the range from 6 to 11 G. The two common interpretations invoked to explain the effect of β-substituents on this splitting are discussed.

The conformational preference of β-substituted ethyl radicals has been largely studied by e.s.r. spectroscopy. Simple ethyls of general structure $\dot{C}H_2CH_2MR_n$, have been found to adopt the conformation (I), in which the β-substituent MR_n eclipses the $2p_z$ orbital on C_α, when M is an atom from rows 2—4 of the Periodic Table,[1-8] or the staggered conformation (II) when M is from row 1.[9,10] Preference for the eclipsed conformation (I) is also exhibited by first row elements when the protons on the α-carbon are replaced by bulky groups, as for instance in the β-substituted 1,1-dimethyl- [10] and 1,1-di-t-butyl-ethyls.[11]

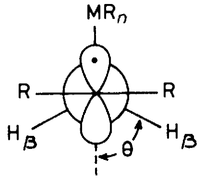
The minimum energy conformation of these radicals can be established from the isotropic hyperfine splitting at the β-protons, a_{H_β}, by means of the relation (1) [12] where θ is the

$$a_{H_\beta} = A + B\langle\cos^2\theta\rangle \qquad (1)$$

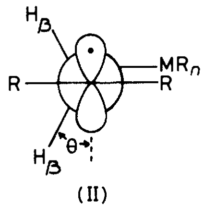
dihedral angle between the symmetry axis of the $2p_z$ orbital on C_α and the C_β–H_β bond. In equation (1) A is usually neglected [13] and B is assumed to be twice the hyperfine splitting at the methyl protons in the related $R_2\dot{C}CH_3$ radical, since for a freely rotating methyl group $\langle\cos^2\theta\rangle$ is 0.5. According to equation (1) the β-proton splittings should be $B/4$ in conformation (I) and $3B/4$ in conformation (II). However, only occasionally a_{H_β} has been found to correspond to one of these two values. Usually the measured splittings are intermediate between one of them and the $B/2$ value expected for free rotation of the CH_2MR_n group because of torsional oscillations around the minimum energy conformation.

Generally, a_{H_β} exhibits also a temperature dependence [positive or negative when the preferred conformation is (I) or (II), respectively], since temperature variations induce a change in the populations of the torsional levels determining the ensemble average $\langle\cos^2\theta.\rangle$

Interestingly there are a few β-substituted alkyl radicals adopting the eclipsed conformation (I) where the β-proton splitting is lower than $B/4$. Examples include ethyls bearing Br,[14] Cl,[2,11,15,16] and SR [1,17,18] β-substituents. A second remarkable class of radicals is represented by alkyls where the leading atom of the MR_n β-substituent is a Group IVB metal (Si, Ge, or Sn).[1,11,19] In these radicals a_{H_β} is invariably larger than $B/4$ even though the absence of temperature dependence of this splitting indicates that the MR_n group is fairly rigidly held in conformation (I).[11]



(I)



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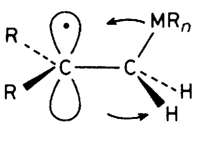
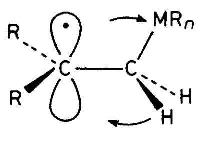


(III)



(IV)

The abnormally low values of a_{H_β} found with bromine, chlorine, or thio-substituents have been interpreted in terms of geometry deformations about the β-carbon due to an attractive interaction between these electronegative groups and the $2p_z$ orbital on the α-carbon.[1,16,20] This causes the substituent to move towards the radical centre and the β-protons away from it, as exemplified in structure (III), with the result of decreasing the overlap between the C–H bonds and the singly occupied orbital and, therefore, the value of a_{H_β}. This effect is commonly referred as asymmetric bridging.

On the other hand no particular attention has been paid to the remarkably large values of the β-proton coupling in alkyls containing Group IVB substituents. However, there is at least one paper where larger than expected a_{H_β} splitting observed in trialkylsilyl adducts of 1,1-di-t-butylethylene are explained in terms of structural distortions of the radical due to steric crowding as indicated in (IV).[19]

As an alternative to explanations based on the deformation of the molecular skeleton, it has also been suggested that variations of a_{H_β} may be caused by the different electronegativities of the β-substituents simply by increasing or decreasing the electron-releasing power of the C_β–H_β bonds toward the singly occupied orbital.[4,21] In practice this means that the assumption, implicit in equation (1), that a unique value of B will describe the conformational dependence of a_{H_β} in any radical is not strictly correct. Computational support to the latter interpretation has been recently given for the case of alkyls containing silyl and thiyl substituents.[18]

A further complication is that these radicals may be non-planar at the radical carbon centre, especially when they bear alkyl substituents at C_α (see for instance the t-butyl radical).[22] In consequence, the presence of a more or less electronegative substituent on C_β may also induce a change in the degree of pyramidalization of the radical site and therefore in the magnitude of a_{H_β}.

We report here the e.s.r. spectral parameters of a large number of 1,1-diphenylethyls obtained by addition of $\cdot MR_n$ radicals to $Ph_2C=CH_2$. Since all these adducts adopt a conformation very close to the eclipsed (I) because of the crowding around the α-carbon, they are suitable probes to test the two interpretations discussed above. An advantage of these radicals is that they are likely to be more planar at the radical centre than 1,1-dialkylethyls, as the result of the extended delocalization of the unpaired electron in the two phenyl rings.

Experimental

1,1-Diphenylethylene was a commercial product which was distilled at reduced pressure prior to use. Ethyl t-butyl peroxide [23] and diacetyl peroxide [24] were prepared according to established methods. 1,1-Diphenyl-2-chloro- and 1,1-diphenyl-2-bromo-ethane were obtained by reaction of $Ph_2CHCH_2OSO_2C_6H_4CH_3$ [25] with LiCl or LiBr in hexamethylphosphoramide (HMPA) following the procedure given by Mosher *et al.* for the preparation of neopentyl chloride and neopentyl bromide.[26]

1,1-*Diphenyl*-2-*chloroethane*. A solution of the tosylate (3.52 g) and LiCl (0.34 g) in HMPA (13 ml) and water (10 drops) was heated at 90 °C for 8 h. The mixture was poured into cold water and extracted with chloroform. The organic phase was dried, the solvent removed, and the residue was eluted with light petroleum–diethyl ether (95 : 5). The product was obtained as an oil (1.2 g) which was vacuum distilled, b.p. 126—128 °C at 2 mmHg (lit.,[27] 112 °C at 0.05 mmHg).

1,1-*Diphenyl*-2-*bromoethane*. Using the same procedure described above for the chloro-derivative, the title compound (0.6 g) was obtained from the tosylate (3.52 g) and LiBr (0.82 g) in HMPA (10 ml), m.p. 61—63 °C (lit.,[28] 63 °C).

Other materials were commercially available and used without further purification.

The radical adducts were generated in degassed solutions of t-butylbenzene by reaction of $Ph_2C=CH_2$ (*ca.* 10%) with $\cdot MR_n$ radicals produced photochemically or thermally. Methylcyclohexane or n-pentane were used occasionally as solvents. The radical concentration was found to depend on temperature, stronger e.s.r. signals being generally obtained at higher temperature (*ca.* 370 K).

The $\cdot MR_n$ radicals were generated by the following methods. (i) Hydrogen abstraction from the appropriate precursor with t-butoxyl radicals [reactions (2) and (3)]. This method was

$$(Bu^tO)_2 \xrightarrow{h\nu} 2Bu^tO\cdot \quad (2)$$

$$Bu^tO\cdot + HMR_n \longrightarrow Bu^tOH + \cdot MR_n \quad (3)$$

used for $\cdot MR_n$ = $\cdot SiPh_3$, $\cdot GePh_3$, $\cdot SnPh_3$, $\cdot CCl_3$, $\cdot CHCl_2$, 1-adamantyl, $\cdot Cl$, $\cdot COMe$, $\cdot COPh$, $\cdot COC_6F_5$; all gave adducts with $Ph_2C=CH_2$.

(ii) Photolytic cleavage (4) of the M–M bond of peroxides, disulphides, and diselenides. Adducts were observed for

$$R_nMMR'_n \xrightarrow{h\nu} R_nM\cdot + R'_nM\cdot \quad (4)$$

$\cdot MR_n$ = $\cdot SMe$, $\cdot SEt$, $\cdot SPh$, $\cdot OEt$, and $\cdot OCOPh$, while no radicals were detected in the temperature range 270—390 K for $\cdot MR_n$ = $Bu^tO\cdot$ and $PhSe\cdot$. The O–O cleavage (5) of diacetyl peroxide was immediately followed by decarboxylation [29] and we could observe only the adduct of 1,1-diphenylethylene with methyl radicals.

$$MeC(O)OOC(O)Me \xrightarrow{h\nu} 2MeC(O)O\cdot \longrightarrow 2CO_2 + 2Me\cdot \quad (5)$$

(iii) Photolysis of di-t-butyl peroxide (DTBP) in the presence of organometallic compounds. Through reaction (6) we could obtain the Ph· radical from triphenylarsine [30] and triphenylborine,[11] and $Bu^n\cdot$ and $Me_2N\cdot$ radicals from tri-n-butylphosphine and tris(dimethylamino)phosphine [31] respectively, all giving adducts with $Ph_2C=CH_2$. The olefin adduct was also observed with the $Bu^t\cdot$ radical obtained from triphenylphosphine or triethyl phosphite [reaction (7)],[32] while no addition of the intermediates phosphoranyl was detected. On the other hand, the diethoxyphosphonyl radical obtained from tetramethyl pyrophosphite [33] gave an adduct with $Ph_2C=CH_2$ [reaction (8)].

$$Bu^tO\cdot + X(MR_n)_3 \longrightarrow Bu^tO\dot{X}(MR_n)_3 \longrightarrow Bu^tOX(MR_n)_2 + \cdot MR_n \quad (6)$$

$$Bu^tO\cdot + PR_3 \longrightarrow Bu^tO\dot{P}R_3 \longrightarrow O{=}PR_3 + Bu^t\cdot \quad (7)$$

$$Bu^tO\cdot + (EtO)_2POP(OEt)_2 \longrightarrow O{=}\dot{P}(OEt)_2 + Bu^tOP(OEt)_2 \quad (8)$$

(iv) Iodine or bromine abstraction with $Bu^n_3Sn\cdot$ radicals [reactions (9) and (10)]. This method was applied to generate $\cdot CF_3$ and $Ph\dot{C}O$ radicals from CF_3I and PhCOBr respectively.[11] The olefin adduct with trifluoromethyl gave strong e.s.r. signals even at room temperature.

$$(Bu^n_3Sn)_2 \xrightarrow{h\nu} 2\ Bu^n_3Sn\cdot \quad (9)$$

$$Bu^n_3Sn\cdot + XMR_n \longrightarrow \cdot MR_n + Bu^n_3SnX \quad (10)$$

(v) Photolytic or thermal decomposition (11) of $R_nMN{=}NM'R_n'$.

$$R_nMN{=}NM'R'_n \longrightarrow N_2 + R_nM\cdot + R_n'M'\cdot \quad (11)$$

Room temperature photolysis of solution of $Ph_2C=CH_2$ and azobisisobutyronitrile resulted in the appearance of the e.s.r. spectrum of the $\cdot CMe_2CN$ radical. Above 330—340 K this spectrum was replaced by that one from the adduct with 1,1-diphenylethylene.

Decomposition of PhNHN=NPh gave only the adduct with Ph· and no evidence for the addition of the aniline radical $Ph\dot{N}H$ was obtained. When photolysing solutions containing Ph(Me)NN=NN(Me)Ph we could observe weak signals due to the phenyl methyl nitroxide $PhN(\dot{O})Me$, but no adduct with $Ph_2C=CH_2$.

Also other attempts to generate adducts with aminyl radicals, other than $Me_2N\cdot$, were unsucessful. Photolysis of $Ph_2C=CH_2$ and Ph_2NH in the presence of di-t-butyl peroxide (DTBP) yields the e.s.r. spectrum of diphenyl nitroxide, while without DTBP a strong and well resolved spectrum of diphenylaminyl $Ph_2N\cdot$ (a_N 8.76, a_o 3.62, a_m 1.50, a_p 4.25 G, g 2.0032) was observed.[34] The generation of aminyl radicals by photochemical reaction of secondary amines with olefins in non-polar solvents has been already observed and interpreted in terms of the formation of an intermediate exciplex followed by hydrogen transfer.[35]

Room temperature hyperfine splitting constants (G = 10^{-4}T) and g factors for the radical adducts $Ph_2\dot{C}CH_2MR_n$ of 1,1-diphenylethylene

MR_n	$a_H^{Ph}(o,m,p)$	a_{H_β}	$da_{H\beta}/dT$ (mG K^{-1})	a^{other}	g
CH_3	3.11, 1.26, 3.38	9.04	5		2.0028
Bu^n [a]	3.10, 1.26, 3.36	9.58	*b*	$a(\gamma\text{-}CH_2)$ 0.60 $a(\delta\text{-}CH_2)$ 0.15	2.0028
Bu^t	3.08, 1.27, 3.35	9.41	1.5	$a(\delta\text{-}CH_3)$ 0.14	2.0028
1-Adamantyl	3.10, 1.28, 3.37	9.44	1		2.0028
Ph	3.10, 1.27, 3.39	9.05	5.5	a(2H) 0.16	2.0028
$CHCl_2$ [a]	3.09, 1.27, 3.37	9.49	*b*		2.0028
CMe_2CN [c]	3.06, 1.25, 3.32	9.05	*b*	$a(\delta\text{-}CH_3)$ 0.14	2.0028
CCl_3	3.07, 1.26, 3.35	8.50	1		2.0033
CF_3	3.16, 1.28, 3.44	8.90	2	a(3F) 0.62	2.0028
C(O)Me [c]	3.14, 1.28, 3.42	9.67	*b*	a(3H) 0.13	2.0028
C(O)Ph	3.11, 1.26, 3.38	9.34	6		2.0029
$C(O)C_6F_5$ [a]	3.03, 1.24, 3.31	9.54	*b*		2.0028
NMe_2 [a]	3.08, 1.26, 3.36	9.56	5	a(N) 4.32	2.0028
OEt	3.12, 1.27, 3.40	9.58	2	$a(CH_2)$ 0.31 $a(CH_3)$ 0.22	2.0028
OC(O)Ph [c]	3.11, 1.28, 3.41	8.50	5		2.0027
$SiPh_3$	3.00, 1.22, 3.28	11.08	1		2.0028
$GePh_3$	2.97, 1.21, 3.26	10.39	*b*		2.0027
$SnPh_4$	2.92, 1.18, 3.18	10.12	*b*		2.0017
$P(O)(OEt)_2$ [d]	3.11, 1.28, 3.39	9.91	1	a(P) 66.40	2.0028
SMe	3.06, 1.27, 3.35	7.65	*b*	$a(CH_3)$ 0.43	2.0031
SEt	3.04, 1.26, 3.32	7.57	4	$a(CH_2)$ 0.50 $a(CH_3)$ 0.20	2.0031
SPh	3.04, 1.26, 3.33	7.80	2		2.0031
Cl [a]	2.98, 1.25, 3.25	6.00	*b*	$a(^{35}Cl)$ 10.88	2.0032

[a] T 370 K. [b] Not determined. [c] T 340 K. [d] da_P/dT – 7 mG K^{-1}.

Reaction of $Bu^tO\cdot$ radicals with di-isopropylamine in the presence of $Ph_2C{=}CH_2$, gave the adduct [a_o 3.07, a_m 1.28, a_p 3.34, a_{H_β} 9.41, a_H(6H) 0.15 G, g 2.0028] between the olefin and the carbon-centred radical $Me_2\dot{C}NHCHMe_2$. The latter (a_H^{Me} 17.7, $a_N = a_H^{NH}$ = 2.4 G) could be observed in a separate experiment in the absence of $Ph_2C{=}CH_2$. No e.s.r. evidence for the aminyl or the aminyl adduct was obtained.

The 1,1-diphenyl-2-chloroethyl radical was also produced by hydrogen abstraction from Ph_2CHCH_2Cl with DTBP, thus obtaining a slightly better spectrum than by addition of $\cdot Cl$ to $Ph_2C{=}CH_2$. A similar attempt to generate the $Ph_2\dot{C}CH_2Br$ radical from Ph_2CHCH_2Br was unsuccesful, this being a further example of the impracticability of detecting β-bromoalkyl radicals in the liquid phase by e.s.r.[14]

Results and Discussion

The e.s.r. spectral parameters of the radical adducts of 1,1-diphenylethylene are reported in the Table. An examination of these data shows that the ring proton couplings are practically independent of the nature of the MR_n β-substituent, values slightly less than the average being observed only for MR_n = $GePh_3$, $SnPh_3$, and Cl. This indicates that delocalization of the unpaired electron on the β-substituent is essentially the same in all the adducts. Also, the g-factors in the majority of cases are constant (g 2.0028 ± 0.0001), exceptions being found when MR_n is $SnPh_3$ (2.0017), SR (2.0031), Cl (2.0032), and CCl_3 (2.0033). The β-proton splittings on the other hand embrace a much larger range (6—11 G), and their temperature dependence is virtually negligible for substituents such as $SiPh_3$, $P(O)(OEt)_2$, Bu^t, 1-adamantyl, CCl_3 while it is of the order of 5—6 mG K^{-1} for CH_3,Ph,NMe_2, C(O)Ph, and OC(O)Ph.

Conformational Behaviour.—The preferred conformation of the $Ph_2\dot{C}CH_2MR_n$ adducts can be established from a_{H_β} and equation (1) if B is known. Since in the $Ph_2\dot{C}CH_3$ radical a methyl proton splitting of 15.6 G has been reported,[36] B can be taken for this class of radicals as 31.2 G. Therefore a lower limit of 7.8 G for a_{H_β} is predicted in the eclipsed conformation (I) where θ is 60° for both the CH_2 protons. A β-proton coupling of 23.4 G can instead be calculated for the staggered conformation (II). The experimental values of 6—11 G are thus indicative that all the β-substituted 1,1-diphenylethyls we have generated adopt a conformation very close to the eclipsed (I). Actually, some deviation of the angle φ between the C_β–M bond and the symmetry axis of the $2p_z$ orbital on C_α from 0°, as expected for perfect eclipsing, can be inferred from the linewidth of the central multiplet corresponding to $m(CH_2) = 0$ which in many cases is broader than the low- and high-field multiplets with $m(CH_2) = \pm 1$. In Figure 1, which shows as an example the e.s.r. spectrum of the phosphonyl adduct of $Ph_2C{=}CH_2$, this linewidth alternation effect is clearly observable at room temperature while it disappears at 370 K. The broadening of the central multiplet is more pronounced at low temperature and with bulky substituents, thus when M is a Group IVB element its width increases in the order $SnPh_3 < GePh_3 < SiPh_3 < Bu^t$. Strong broadening is also apparent at room temperature in the spectra of the 1-adamantyl, $\cdot C(Me)_2CN$, and $\cdot CCl_3$ adducts, while with the $\cdot CH_3$, $\cdot CF_3$, and $\cdot$SMe adducts deviation from the expected 1 : 2 : 1 intensity ratio of the three CH_2 multiplets starts to be observed at lower temperatures. This effect is due to an in-phase modulation of the a_{H_β} splittings which are non-equivalent in the minimum energy conformation.

The departure of these radicals from an eclipsed geometry is presumably related to the presence on C_α of the two phenyl rings which are somewhat twisted with respect to each other as in benzophenone ketyl.[37] As a consequence the MR_n group will experience an asymmetric potential and will be compelled to be bent toward the phenyl exhibiting reduced steric hindrance. The conversion of one enantiomer into the

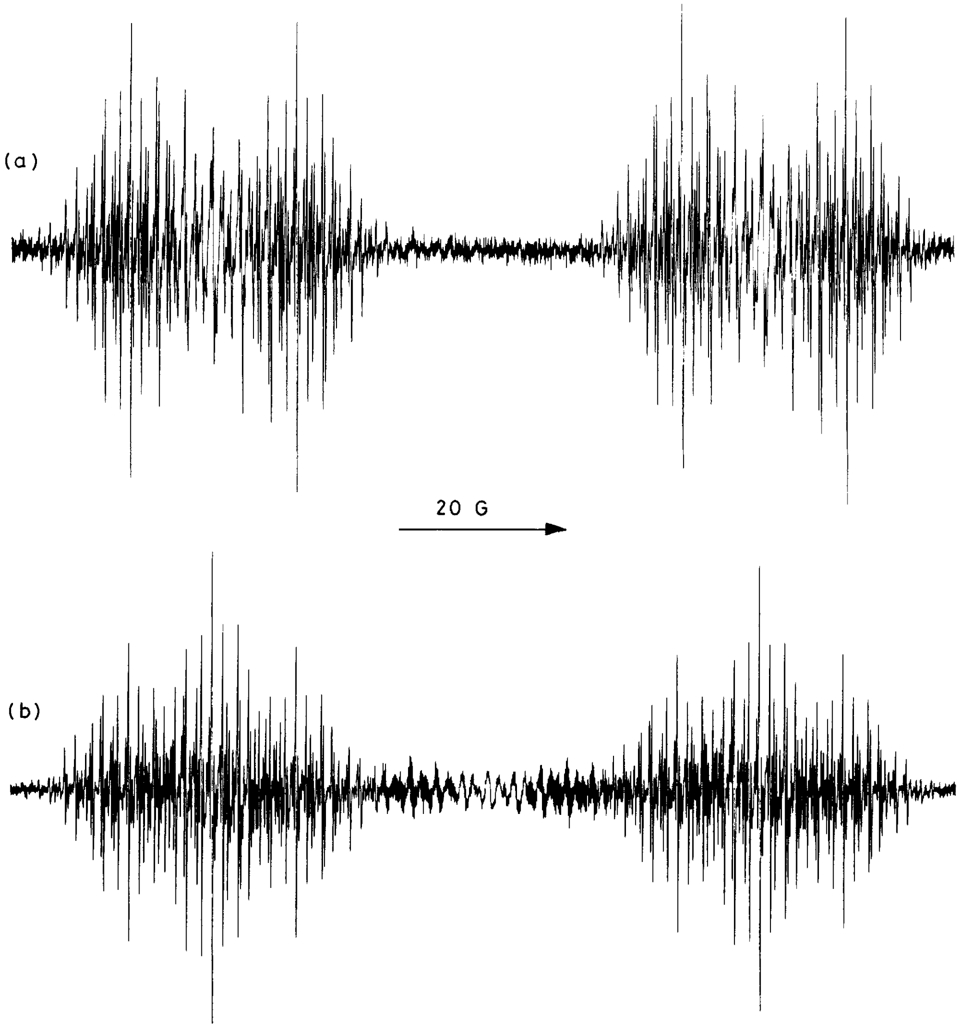


Figure 1. E.s.r. spectrum of the $Ph_2\dot{C}CH_2P(O)(OEt)_2$ radical recorded at room temperature (a) and at 373 K (b). In the central region of the latter one it can also be observed the spectrum of the adduct of $Ph_2C=CH_2$ with the $Bu^t\cdot$ radical

other through a partial rotation of the phenyl groups,[37] will force the β-substituent to interchange its position as shown in the Scheme.

If this is the case, we should expect the oscillation of MR_n to be governed by the movement of the two phenyl rings and thus to be characterized by an activation energy typical for the latter process. In principle the activation parameters for the two kind of motions might be determined from the temperature dependence of the line shape if the hyperfine splitting in the slow exchange region can be determined. However, none of the adducts was found to give e.s.r. spectra strong enough to be recorded below 220 K, a temperature which is not sufficiently low to freeze either dynamic process.

Nevertheless, an estimate of the activation energy for the oscillation of the MR_n group may be made without knowing the limiting values a_1 and a_2 of a_{H_β}, by comparing the heights of the central lines of the three multiplets corresponding to $m(CH_2) = \pm 1,0$.[38] The widths of these lines are given by equation (12)[39] where $T_{2,0}^{-1}$ is the contribution to the widths

$$T_2^{-1}(m) = T_{2,0}^{-1} + \frac{\gamma_e^2}{8}(m_1 - m_2)^2(a_1 - a_2)^2\tau \quad (12)$$

from other relaxation mechanisms and is assumed to be independent of $m(CH_2)$, m_1 and m_2 are the nuclear quantum numbers of the individual protons, and $\tau = 1/k$, the mean lifetime between jumps. From (12) equation (13) follows or

$$\tau = \left(\frac{T_2^{-1}(0)}{T_2^{-1}(\pm 1)} - 1\right)\frac{8T_{2,0}^{-1}}{\gamma_e^2(a_1 - a_2)^2} \quad (13)$$

by substituting to the widths the intensities I_m of the lines, (14). Thus, by assuming a temperature dependence for τ of the

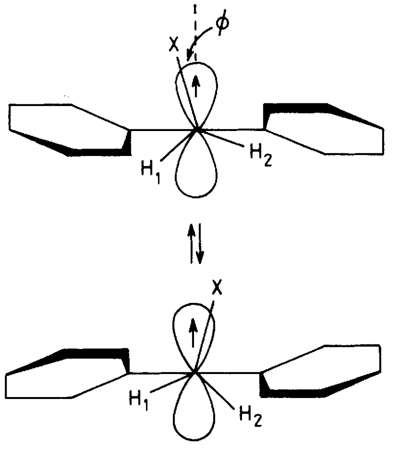
$$\tau = \left(\sqrt{\frac{2I_{\pm 1}}{I_0}} - 1\right)\frac{8T_{2,0}^{-1}}{\gamma_e^2(a_1 - a_2)^2} \quad (14)$$

form (15) a plot of log $[(2I_{\pm 1}/I_0)^{\frac{1}{2}} - 1]$ as a function of $1/T$ will

$$\tau = \tau_0 \exp(E_a/RT) \quad (15)$$

give a straight line with slope $E_a/2.303\ R$.[38]

The determination of the activation energy for the motion of the β-substituent in the triphenylsilyl and phosphonyl adducts of $Ph_2C=CH_2$, where overlapping of the low- and high-field multiplets with the central line is negligible, gives in both cases E_a 5.5 ± 0.5 kcal mol^{-1}. Although we do not know the corresponding activation energy for the internal rotation of the phenyl rings, presumably this one will not be too different



Scheme

from the value measured in the benzophenone ketyl, *i.e.* 6.35 ± 0.2 kcal mol^{-1}.[37] From the similarity of these two values it may be inferred that the oscillation of the MR_n group is actually governed by the twisting of the phenyls.

Equations (14) and (15) may also provide us with an estimate of the difference $a_1 - a_2$, and therefore of the angle φ (see Scheme), if log $1/\tau_0$ is assumed to be the same as log A for benzophenone ketyl, *i.e.* 13.1. The angle φ may be derived from a_1 and a_2 by rearranging equations (11)—(15). This gives

$$\frac{a_1}{a_2} = \frac{\cos^2(\theta + \varphi)}{\cos^2(\theta - \varphi)} \qquad (16)$$

φ 6.1 and 4.7° for $Ph_2\dot{C}CH_2P(O)(OEt)_2$ and $Ph_2\dot{C}CH_2SiPh_3$, respectively. Larger values are expected for more bulky substituents such as Bu^t, whose adduct shows selective line broadening even at 370 K; however in no case should φ exceed 15°.

Substituent Effect on the β*-Proton Splittings.*—In the preceding section it has been shown that the preferred conformation of all the $Ph_2\dot{C}CH_2MR_n$ adducts is close to the eclipsed (I), with some departure from it of the order of few degrees. The average value of a_{H_β} we are measuring is then given in terms of equation (1), by (17). For $\varphi < 10°$ this quantity does

$$a_{H_\beta} = \frac{B}{2}\left[\cos^2(\theta + \varphi) + \cos^2(\theta - \varphi)\right]$$
$$\cong B(\cos^2\theta - \varphi^2\cos 2\theta) \qquad (17)$$

not substantially differ from $B\cos^2\theta$. We may then ignore in the following discussion the small deviation of the MR_n group from a perfectly eclipsed conformation.

On this basis the β-proton splitting is predicted by equation (1) to be 7.8 G in the low temperature limit. Since we are working at relatively high temperatures, torsional oscillations are expected to somehow increase this value. Actually a_{H_β} lies in the range 9—9.6 G for the large majority of the first row MR_n substituents, the only noticeable exceptions being found with CCl_3 and OC(O)Ph (8.50 G). With second row substituents, on the other hand, the a_{H_β} values are remarkably different and decrease on going from left to right in the Periodic Table from 11.08 G for $SiPh_3$ and 6.00 G for Cl.

The scattering of these splittings indicates that equation (1), although extremely valuable in distinguishing between eclipsed and staggered conformations, it is to a certain extent inadequate fully to describe the conformational dependence of the β-proton coupling in these radical adducts, as it has been previously found in related β-substituted ethyls. The two proposed interpretations of this behaviour have been extensively discussed in the Introduction and can be summarized here as follows. (i) Equation (1) is assumed to be valid which ever is the β-substituent and departures of a_{H_β} from the expected values are due to a change of the $C_\alpha C_\beta H_\beta$ bond angle from sp^3 geometry. (ii) The validity of equation (1) is challenged in the sense that the B term should depend on the electronegativity of the β-substituent and perhaps a more complex form of a_{H_β} on the angle θ should be considered.[18]

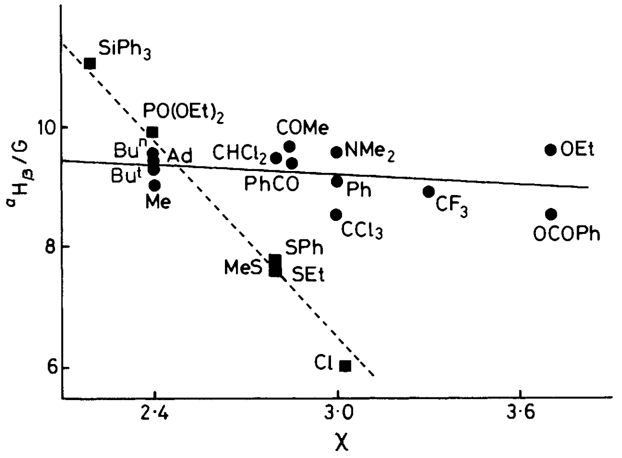


Figure 2. Room temperature hyperfine splitting constants at the β-protons in the $Ph_2\dot{C}CH_2MR$ radicals against the mutually consistent group electronegativities [40] of the MR_n substituents

As far as the latter interpretation is concerned an obvious test of it is to plot the a_{H_β} couplings as function of the electronegativity of the MR_n group to verify whether these two quantities are correlated. The choice of a suitable group electronegativity scale is not an easy one since many sets based on different assumptions are reported in the literature. We used the mutually consistent group electronegativities given by Wells,[40] and the related plot is shown in Figure 2. It is apparent that no correlation at all exists for first row substituents; actually a least square fitting of these data gives a correlation coefficient of only 0.35. With second row substituents on the other hand a correlation coefficient of 0.98 can be calculated. No better total correlation is obtained if different electronegativity scales, such as that calculated by Huheey,[41] are employed. Hence, from the absence of a common correlation for first and second row MR_n groups, it may be inferred that variations of the B term of equation (1) with electronegativity cannot be responsible for the observed changes of a_{H_β}, although the good correlation coefficient found with second-row substituents may have some interesting implications.

Distortions at C_β, with the MR_n substituent moving closer to the $2p_z$ orbital on C_α when M is a Group VI or VII element and away from it when M belongs to Group IV or V, would explain the trend of the β-proton splittings in the adducts of $Ph_2C{=}CH_2$ with second row substituents. However, conclusive evidence for this interpretation is lacking. Moreover, asymmetrical bridging by chlorine has been dismissed in a recent *ab initio* calculation[42] performed on the 2-chloroethyl radical where the chloromethyl group has been found essentially tetrahedral. This result is at variance with that of a previous INDO calculation[20] predicting a $C_\alpha C_\beta Cl$ angle of only 90° in the same radical. It should be mentioned, however, that no explanation of the unusually low value of a_{H_β} was given in that paper.[42]

To this purpose it may also be worth comparing the three radicals $Me_2\dot{C}CH_2Cl$,[7] $Bu^t{}_2\dot{C}CH_2Cl$,[11] and $Ph_2\dot{C}CH_2Cl$ where the β-proton splittings are similar, *i.e.* 6.18, 6.88, and 6.00 G, respectively, while the ^{35}Cl coupling is much smaller in the diphenyl derivative (21.24, 22.45, and 10.88 G, respectively). If asymmetric bridging is accepted, a measure of it should be given by the ratio a_{Cl}/a_{H_β}, which is 3.44, 3.26, and 1.81 in the three radicals. This means that the amount of deformation at C_β ought to be considerably lower in the unsaturated 1,1-diphenyl-2-chloroethyl. Since bridging is usually associated with the importance of ionic structures such as $R_2C\overset{+\cdot}{-}CH_2\ X^-$,[43] its extent is expected to be the larger the lower is the ionization potential of the R_2C fragment. As the ionization potential of $Ph_2\dot{C}H$ (7.32 eV)[44] is slightly less than that of $Me_2\dot{C}H$ (7.5 eV)[45] the maximum extent of bridging should be experienced by the $Ph_2\dot{C}CH_2Cl$ radical. This is just opposite to what can be inferred by the measured hyperfine splitting constants.

In conclusion, it seems that neither interpretation can satisfactorily account for the experimental data and that more experimental and computational work is needed fully to clarify the behaviour of β-substituted ethyl derivatives.

Rate of Trapping.—It is known that photolysis of DTBP in t-butylbenzene leads to the neophyl radical $PhCMe_2\dot{C}H_2$ which then rearranges to 1-methyl-1-benzylethyl $\cdot CMe_2CH_2Ph$.[46,47] If the photolysis is carried out at *ca.* 370 K in the presence of 1,1-diphenylethylene, the radical formed by hydrogen abstraction from t-butylbenzene is trapped by the olefin to give an adduct whose e.s.r. spectrum can be interpreted in terms of the following hyperfine splitting constants: a_o 3.08, a_m 1.28, a_p 3.32, a_{H_β} 9.74 G. A further splitting of 0.15 G from an even number of protons (6 or 8) can also be resolved. Since the latter coupling is practically the same as those from the δ protons in the adducts of $Bu^t\cdot$ or $\cdot CMe_2CN$, the trapped radical can be recognized as the rearranged $\cdot CMe_2CH_2Ph$. Further, in the hypothetical adduct of neophyl a coupling of *ca.* 0.5 G from the two γ-protons, as in the $Ph_2\dot{C}CH_2Bu^n$ radical, ought to be expected.

Therefore, if considering that the neophyl rearrangement is a rather slow process ($k_{370\ K}{}^R$ $5.8 \times 10^3\ s^{-1}$)[48] the rate constant K^A for the addition of this carbon-centred radical to $Ph_2C=CH_2$ has to be relatively small for a radical reaction. A rough estimate of its higher limit can be obtained by using equation (18).[49] Although equation (18) is strictly valid only if

$$k^A = \frac{k^R[Ph_2\dot{C}CH_2CH_2CMe_2Ph]}{[Ph_2C=CH_2][Ph_2\dot{C}CH_2CMe_2CH_2Ph]} \qquad (18)$$

the spin trapping is not reversible and when the resulting adducts do not decay with time, the limit of the trapping rate determined as $k_{370\ K}{}^A < 400\ l\ mol^{-1}\ s^{-1}$ compares favourably with that estimated for the addition of the hex-5-enyl radical to di-t-butylethylene ($k_{298\ K}{}^A < 850\ l\ mol^{-1}\ s^{-1}$).[49]

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