Tetrahedron Vol. 39, No. 16, pp. 2715 to 2718, 1983
Printed in Great Britain.

0040-4020/83 $3.00 + .00

RADICAL INTERMEDIATES IN THE ADDITION REACTION OF SECOND ROW RADICALS TO STILBENE AND 2-BUTENE

AN ESR STUDY

RINO LEARDINI, ANTONIO TUNDO and GUISEPPE ZANARDI
Istituto di Chimica Organica dell'Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

and

GIAN FRANCO PEDULLI †*
Istituto del CNR dei Composti del Carbonio contenenti Eteroatomi, Ozzano Emilia, Bologna, Italy

(*Received in UK* 16 *August* 1982)

Abstract—The adducts of stilbene with triphenylsilyl, triphenylgermyl, diethoxyphosphonyl and phenylthiyl radicals, and of 2-butene with triethylsilyl and ethylthiyl radicals have been generated and their ESR spectra recorded. The resulting radical adducts show the same ESR spectrum starting either from the *cis* or the *trans* isomer of the title compounds. The existence of only one isomeric radical is consistent with the lack of stereospecificity in the elimination reaction of phenylthiyl radicals from 2-phenylthiobutyl.

The magnitude of the β-proton hyperfine splittings is indicative for a geometry where the entering group eclipses the $2p_z$ orbital on the radical carbon centre in the adducts with 2-butene. In the adducts with stilbene, on the other hand, the experimental data suggest a certain departure from a perfectly eclipsed conformation. Since the extent of this deviation decreases in the order $SiPh_3 > GePh_3 > P(O)(OEt)_2 > SPh$, sterical crowding seems to be responsible for this behaviour.

The addition of free radicals to olefins is a well known process largely exploited in synthetic chemistry. A great deal of spectroscopic studies on the paramagnetic intermediates formed during such reactions has also been reported. These investigations have been concerned with the structure, stereochemistry[1] and the rate of decay[2] of these labile species, thus providing very useful information for a better understanding of the mechanism of many homolytic reactions. However, the larger majority of these studies refers to radical intermediates obtained from simple alkyl substituted olefins, which from the spectroscopic point of view have the advantage of being highly soluble in many organic solvents and of giving rise to relatively simple ESR spectra, while aryl substituted olefins have been used only occasionally.

Since we are currently investigating the addition reactions of many radicals centred at elements of Groups IV to VII with diarylethylenes, we wish to report here the results of an ESR study on the intermediates formed during the reaction of second row radicals to *cis*- and *trans*-stilbene. In a previous paper the similar adducts obtained from 1, 1-diphenylethylene have been described.[3]

For purpose of comparison also the radicals resulting from the addition of triethylsilyl and ethylthiyl to *cis*- and *trans*-2-butene have been investigated.

EXPERIMENTAL

Cis- and *trans*-stilbene and *cis*- and *trans*-2-butene were commercially available products used without further purification.

Threo-2-Phenylthio-1, 2-diphenyl-1-bromoethane was obtained following the procedure given by Shevlin *et al.*[4] for the preparation of *threo*-2-bromo-3-phenylthiobutane. Diphenyl disulfide (3g) was dissolved in CH_2Cl_2 (40 ml). After cooling at −20°C, Br_2 (2.16 g) in CH_2Cl_2 (11 ml) was added to the stirred soln over a period of 15 min. Then *trans*-stilbene (8.06 g) in CH_2Cl_2 (20 ml) was added and the soln was stirred for 2 hr at −15°. After removal of CH_2Cl_2 the solid residue was crystallized twice from benzene: yield 60%, m.p. 115–118° (with decon).

The adducts from stilbenes were generated (Eqn 1) in degassed soln of t-butylbenzene and those from butenes in n-pentane. The $\cdot MR'_n$ radicals giving the addition reaction were produced by hydrogen abstraction with t-BuO·.

$$R\dot{C}H{=}CHR + \cdot MR'_n \longrightarrow R\dot{C}H{-}CHRMR'_n \qquad (1)$$

radicals generated photolytically from di-t-butyl peroxide with a high pressure (1 KW) mercury lamp (Eqn 2) for $MR'_n = SiEt_3$, $SiPh_3$ and $GePh_3$,

$$HMR'_n + \text{t-BuO}\cdot \longrightarrow \cdot MR'_n + \text{t-BuOH} \qquad (2)$$

by photolytic cleavage of the M–M bond of disulfides (eqn 3) for $MR'_n = SEt, SPh$ and by displacement of the diethoxyphosphonyl radical from tetraethylphyrophosphite[5] with t-BuO· (Eqn 4).

$$R'_nM{-}MR'_n \xrightarrow{h\nu} 2\,\dot{M}R'_n \qquad (3)$$

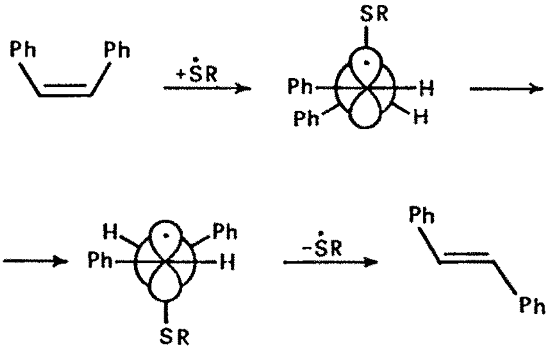
$$\begin{aligned}&\text{t-BuO}\cdot + (EtO)_2POP(OEt)_2\\ &\quad\rightarrow O = \dot{P}(OEt)_2 + \text{t-BuOP}(OEt)_2\end{aligned} \qquad (4)$$

With stilbenes the silyl and germyl adducts could be observed from 253 to 390 K, while a sufficiently intense ESR spectrum of the phosphonyl adduct could be obtained only at 390 K.

---

†On leave from Istituto Chimico dell'Università, Cagliari.

Addition of thiyl radicals to *trans*-stilbene did not give rise to any appreciable concentration of the adduct; with *cis*-stilbene, which is highly soluble in t-butylbenzene, photolysis in the presence of disulfides produced in a few seconds a ppt which resulted to be *trans*-stilbene. This indicates that addition of thiyl radicals to the olefinic double bond occurs easily. However, because of the reversibility of the addition reaction, the lifetime of the radical adduct is too short to produce a stationary concentration large enough to allow its detection by ESR. On the other hand, the radical has a lifetime sufficiently long to isomerize to the more stable conformer having the two phenyl rings in an almost *trans* position. The latter then eliminates the thiyl radical giving *trans*-stilbene (Scheme 1).



Scheme 1.

To increase the stationary concentration of the 2-phenylthio-1,2-diphenylethyl, this radical was generated from *threo*-2-phenylthio-1,2-diphenyl-1-bromoethane by Br abstraction with triphenylgermyl radicals. Using this procedure and operating at 253 K, an ESR spectrum sufficiently intense to be recorded could be obtained, although the ESR signals did not last for more than 2–4 min.

With butenes the adducts with silyl and thiyl radicals could be observed in the temp range 180–250 K; no evidence for the presence of other species such as the allylic radical $MeCH=CH-\dot{C}H_2$ was obtained.

In all the cases the same ESR spectrum for the radical adduct was observed starting either from the *cis* or the *trans* isomer.

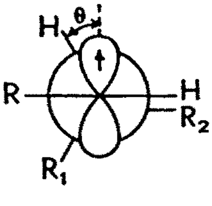
RESULTS AND DISCUSSION

The conformational preference of the adducts from stilbene and 2-butene can be established from the isotropic hyperfine splitting at the β-protons, a_{H_β}, by means of the well known relation (5).[6]

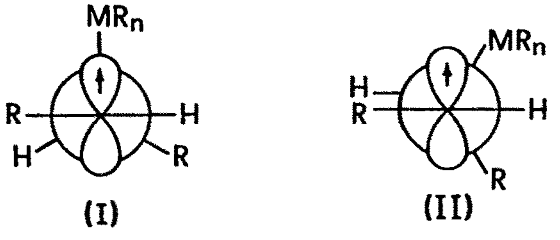
$$a_{H_\beta} = \mathbf{A} + \mathbf{B}\langle\cos^2\theta\rangle. \qquad (5)$$

Here, θ is the dihedral angle between the symmetry axis of the $2p_z$ orbital on C_α and the C_β–H_β bond (Scheme 2), **A** is usually neglected and **B** is assumed to be twice the hyperfine splitting of the Me protons in the related $R\dot{C}H-Me_3$ radical where, for symmetry reasons, $\langle\cos^2\theta\rangle = 0.5$.

Since for i-propyl $(Me_2\dot{C}H)a_H^{Me} = 24.74$ G[7] and for 1-phenylethyl $(Ph\dot{C}HMe)a_H^{Me} = 17.9$ G,[8] **B** can be taken as 49.48 G and 35.8 G for the radical adducts from 2-butene and stilbene, respectively. Since it is known that radicals of general formula $H_2(R_2)\dot{C}-CH_2MR_n$ tend to adopt the conformation where the β-substituent MR_n is eclipsed with the $2p_z$ orbital on Cα if M is a second or higher row element,[9–12] we can consider in the present case only the two limiting conformations shown in Scheme 3.



Scheme 2.



Scheme 3.

The electronic interactions stabilizing the eclipsing of M and the singly occupied molecular orbital (SOMO) are maximized in conformation (I), however steric repulsion between R and MR_n may somehow destabilize this geometry. Conformation (II) represents a compromise between minimum crowding and best overlap between the C_β–M bond and the SOMO.

By using eqn (5) and the **B** values given above, a_{H_β} is calculated to be 12.4 and 9.0 G in the 2-butene and stilbene adducts respectively if conformation (I) is adopted (θ = 60°), while a negligibly small β-proton splitting is predicted if (II) is the preferred geometry. In principle, eqn (5) might allow a precise determination of the angle θ to be made, however this will be meaningless for the following reasons. First, $\langle\cos^2\theta\rangle$ represents an ensemble average over the thermally populated torsional levels of the $CHRMR'_n$ group[6] and therefore the β-proton splittings at the temperatures of experiment are expected to be larger than the limiting values calculated for conformations (I) and (II). An accurate determination of θ should include a complete torsional analysis. In the second place, the assumption that a unique value of **B** will describe the angular dependence of a_{H_β}, whichever is the MR_n substituent, is incorrect, mainly for second and higher row M elements. Actually, β-proton splittings larger than those predicted by eqn (5) are usually found with IV and V Group elements, and smaller with VI and VII Group elements. The two common interpretations of this behaviour have been widely discussed by the present authors in a recent paper.[3]

Nevertheless, eqn (5) is still very valuable since it may provide us with a reliable estimate of the conformational preference of a given radical, if all the factors affecting the magnitude of a_{H_β} are taken into account.

On this basis we may now start to discuss the geometry of the radicals generated from stilbene and 2-butene whose hyperfine splitting constants are reported in Tables 1 and 2. The β-proton splittings of 14.98 G for the triethylsilyl and of 11.81 G for the ethylthiyl adduct of 2-butene compare favourably with the 12.4 G value expected for conformation (I) and therefore are indicative for the latter geometry. Moreover, the observed splittings are very close to those measured in the two related radicals

Table 1. Hyperfine splitting constants (Gauss) and g-factors of the radical adducts $Ph\dot{C}HCH(Ph)MR_n$ from stilbene measured in *t*-tubylbenzene

MR_n	a_o	a_m	a_p	$a_{H\alpha}$	$a_{H\beta}$	a_{other}	g	T/K
$SiPh_3$	4.73	1.62	5.76	15.29	5.99[a]	--	--	253
$GePh_3$	4.72	1.63	5.64	15.12	6.42[b]	--	2.0026	253
$P(O)(OEt)_2$	5.00	1.70	6.00	16.10	6.75	46.12(^{31}P)	--	373
SPh	4.70	1.61	5.67	15.04	6.62	--	--	253

[a] $da_{H\beta}/dT = + 2\ mGK^{-1}$. [b] $da_{H\beta}/dT = +3.8\ mgK^{-1}$

Table 2. ESR spectral parameters of the radical adducts $Me\dot{C}HCH(Me)MR_n$ from 2-butene measured in *n*-pentane

MR_n	a_{Me}	$a_{H\alpha}$	$a_{H\beta}$	$da_{H\beta}/dT$	g	T/K
$SiEt_3$	23.98	20.67	14.98	--	2.0027	178
SEt	23.86	20.97	11.81	+ 11.5	2.0030	180

$Me_2\dot{C}CH_2SiEt_3$ (15.35 G) and $Me_2\dot{C}CH_2SMe$ (11.20 G)[9] which are known to exist in the eclipsed conformation.

With the adducts from stilbene, on the other hand, the measured a_{H_β} couplings are always lower than the 9 G value predicted for conformation (I). It seems therefore that in the latter radicals steric crowding prevents perfect eclipsing of the C_β–M bond and the $2p_z$ orbital on C_α. The minimum energy geometry should then be somewhere in between conformations (I) and (II). It is difficult to quantify the extent of deviation of the MR_n group from the eclipsed geometry (I), since the **B** value of Eq. (5) is not constant on changing the chemical nature of the β-substituent, as it has been pointed out before. However a rough estimate of this deviation may be obtained by comparing the β-couplings with those measured in the related 1, 1-diphenylethyls $Ph_2\dot{C}CH_2MR_n$. These have been found to exist in the eclipsed conformation and to have a_{H_β} values of 11.08, 10.39, 9.91 and 7.80 G in the order for the triphenylsilyl, triphenylgermyl, diethoxyphosphonyl and phenylthiyl adducts.[3]

In the present radicals eclipsing of the MR_n group would require the observation of the same βproton splitting corrected for the change of spin density at the α-carbon. Since this change can be evaluated from the Me coupling in $Ph_2\dot{C}Me$ (15.6 G)[13] and $Ph\dot{C}HMe$ (17.9 G),[8] the correction factor is 1.15. Now we can use the ratio between the β-proton couplings calculated in this way and those observed in the adducts from stilbene, as a parameter related to the deviation of the MR_n substituent from conformation (I). Since this ratio is 0.47, 0.53, 0.59 and 0.75 for $MR_n = SiPh_3$, $GePh_3$, $OP(OEt)_2$ and SPh respectively, the amount of departure from eclipsing seems to increase with the bulk of the β-substituent, being the larger with the triphenylsilyl and the smaller with the phenylthio group.

Also the coupling at phosphorus in the adduct of stilbene with the phosphonyl radical, indicates the non-eclipsing of the latter group with the SOMO. Actually the a_P value (46.12 G) is considerably smaller than the same splitting measured in the corresponding adduct with 1, 1-diphenylethylene $Ph_2\dot{C}CH_2P(O)(0Et)_2$(66.40 G).[3] It may be tempting to try to extract precise values of the dihedral angle φ made by the C_β–P bond and the symmetry axis of the $2p_z$ orbital. If we do that by assuming an angular dependence of the ^{31}P coupling of the same form given by eqn (5) with $\mathbf{B} = 66.4 \times 1.15$ G, an angle φ of 39 degrees can be calculated. However, cross checking this value by using the β-proton splitting in the same radical within the assumption of sp^3 hybridization at the β-carbon, we can work out two possible solutions for φ, i.e. 7 and 53 degrees. The latter value seems rather unlikely, since it implies better eclipsing of the β-phenyl than of the phosphonyl group with the $2p_z$ orbital on C_α, against massive evidence that second row elements show a larger tendency to be eclipsed than first row elements.[1] The value of 7° on the other hand is far away from the 39° angle calculated from the phosphorous splitting. This is a further demonstration that a precise determination of the geometry of free radicals can not be made without taking explicitely into account the thermal population of the torsional energy levels of the $CHRMR'_n$ group.

In conclusion, it may be inferred from the experimental data that the adducts of second row radicals (including $Ph_3Ge\cdot$) with stilbene, because of steric reasons, exist in a conformation which is in between (I) and (II); presumably much closer to (II) with silyl substituents and to (I) with thio substituents. In the adducts with 2-butene, where sterical crowding is less important, the more stable geometry corresponds to the eclipsed conformation (I) as in related radicals bearing only one substituent at C_β.

Finally, it may be worth pointing out that the observation of the same ESR spectrum from the adducts of EtS with either *cis* or *trans*-2-butene is consistent with the lack of stereospecificity in the elimination reaction of phenylthiyl radicals from 2-phenylthiobutyl.[4] In fact, the existence of only one of the two isomeric radicals that can be formed, demonstrates that internal rotation about the central C–C bond is a faster process than elimination of the thiyl radical.

Acknowledgement—Financial support from C. N. R. (Rome) and Ministero P.I. is gratefully acknowledged.

REFERENCES

[1] J. K. Kochi, In *Advances in Free Radical Chemistry* (Edited by G. H. Williams), Vol. 5, p. 189. Elek Science, London (1975).

[2] K. U. Ingold, *Free Radicals* (Edited by J. K. Kochi) Vol. 1., p. 37. Wiley–Interscience, New York (1973).

[3] R. Leardini, A. Tundo, G. Zanardi and G. F. Pedulli, *J. Chem. Soc.* Perkin Trans. II, 285 (1983).

[4] T. E. Boothe, J. L. Greene Jr. and P. B. Shevlin, *J. Am. Chem. Soc.* **98**, 951 (1976).

[5] A. G. Davies, D. Griller and B. P. Roberts, *Ibid.* **94**, 1782 (1972).

[6] P. B. Ayscough, *Electron Spin Resonance in Chemistry.* Methuen, London (1967).

[7] P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.* **90**, 7155 (1968).

[8] A. J. Dobbs, B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc.* Perkin Trans. II, 786 (1972).

[9] P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.* **93**, 846 (1971).

[10] A. R. Lyons and M. C. R. Symons, *J. Chem. Soc.* Faraday Trans. II, **68**, 622 (1972).

[11] R. O. C. Norman and P. M. Storey, *Ibid.* B, 1009 (1971).

[12] J. Cooper, A. Hudson and R. A. Jackson, *Tetrahedron Letters* 831 (1973).

[13] .K. Schreiner and A. Berndt, *Ibid.* 4083 (1973).