# Radical Adducts of *para*-Substituted 1,1-Diphenylethylenes: an Electron Spin Resonance Study

**Rino Leardini,* Antonio Tundo, and Giuseppe Zanardi**
*Istituto di Chimica Organica, Università, Viale Risorgimento 4, 40136 Bologna, Italy*
**Gian Franco Pedulli***
*Istituto di Chimica Organica, Università, Via Ospedale 72, 09100 Cagliari, Italy*

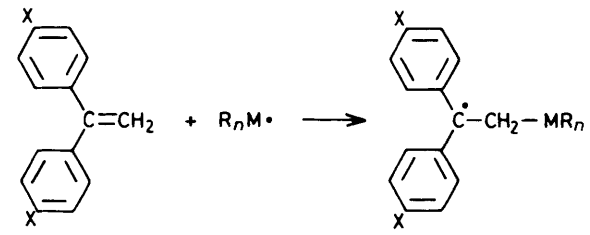
The e.s.r. spectral parameters of the paramagnetic adducts $(XC_6H_4)_2\dot{C}CH_2MR_n$, formed by reactions of transient $R_nM\cdot$ radicals centred at elements of Groups III—VI with *para*-substituted diphenylethylenes, are reported. Ring substitution with $OCD_3$, $SCD_3$, or $SO_2CD_3$ affects the hyperfine couplings at the phenyl and methylene protons to only a minor extent, except in the adducts of the benzoyloxyl radical. The present data are inconsistent with the interpretations which attribute the variations of the β-proton splittings in β-substituted ethyl radicals either to bond angle distortions or to the electronegativity of the $MR_n$ substituent.

The hyperfine splitting constant of β-protons in substituted ethyl radicals [$a(H_\beta)$] is usually considered to bear a $B\cos^2\theta$ relationship to the minimum-energy conformation, where θ is the torsion angle between the symmetry axis of the $2p_z$ orbital on $C_\alpha$ and the $C_\beta$–$H_\beta$ bond, and B is assumed to be a constant. However, in a number of ethyl radicals β-substituted with second- or higher-row substituents, which are believed to adopt the conformation with the substituent eclipsing the $2p_z$ orbital on $C_\alpha$, $a(H_\beta)$ deviates significantly from the value predicted by the above relation.[1] In particular, β-proton splittings larger or smaller than expected have been found with substituents such as $SiR_3$, $GeR_3$, $SnR_3$, or Cl, Br, SR, respectively. These deviations have been attributed either (i) to variations of the electron-releasing power of the $C_\beta$–$H_\beta$ bond towards the singly occupied orbital, due to the different electronegativity of the β-substituent, *i.e.* to the non-constancy of the B term;[2] or (ii) to distortions of the molecular skeleton causing the substituent to move towards the radical centre ('bridging' hypothesis) and the β-protons away from it with consequent decrease of $a(H_\beta)$ (or *vice versa*).[3]

If the interpretation based on the non-constancy of B is correct, a correlation should exist between $a(H_\beta)$ and the electronegativity of the β-substituent in structurally similar radicals adopting the same geometry. Since, however, in unhindered ethyl radicals bearing first-row β-substituents no preference for the eclipsed conformation is observed (in contrast with second- or higher-row substituents), it is not possible to separate the effects on $a(H_\beta)$ arising from the B or the $\cos^2\theta$ terms.

To overcome this difficulty we have studied a series of sterically hindered ethyl radicals in which the substituent is compelled to stay in the eclipsed position for steric reasons.[1] These are the β-substituted 1,1-diphenylethyl radicals, $Ph_2\dot{C}$–$CH_2MR_n$ (**1**), for which a preferred conformation very close to the eclipsed one can be inferred from the e.s.r. spectral parameters, independently of the nature of the $MR_n$ substituent.

Since the values of $a(H_\beta)$ were found to show no correlation with the electronegativity of the $MR_n$ group (taking into account both first- and second-row substituents), the first interpretation (i) of non-constancy of $a(H_\beta)$ for a given conformation could be dismissed. Several features were also inconsistent with the distortion hypothesis, although no definitive evidence against it could be obtained. According to this interpretation the smaller-than-expected β-proton coupling observed with chlorine and thio substituents is explained on the basis of partial bridging. This is usually justified in terms of




(**1**) X = H
(**2**) X = $OCD_3$
(**3**) X = $SCD_3$
(**4**) X = $SO_2CD_3$

resonance theory by noting that the greater the importance of the polar structure (B) the more the fragment $R_2C$–$CH_2$ will resemble a planar alkene cation, with consequent deviation of the bond angles from those predicted from $sp^3$ hybridization at $C_\beta$.[4] Bond angle deformation should then depend not only on

$$\underset{(A)}{R_2\dot{C}\text{–}CH_2X} \longleftrightarrow \underset{(B)}{R_2C^{\pm\cdot}CH_2\,X^-}$$

the nature of the substituent X, but also on the ionization potential of the radical, since the contribution of structure (B), and therefore the extent of bridging, should be inversely related to the ionization potential of $R_2\dot{C}$–$CH_2X$. To elucidate further the latter point we have examined the 1,1-diphenylethyl radicals (**2**)—(**4**) obtained by addition of transient $R_nM\cdot$ radicals to alkenes containing *para*-substituents able to produce either a decrease in the ionization potential of the resulting radical ($OCD_3$ or $SCD_3$) or an increase ($SO_2CD_3$).

## Results and Discussion

The radical adducts were generated in deoxygenated solutions of benzene by treating photolytically produced $R_nM\cdot$ radicals with the appropriate alkene. Toluene or dichloromethane was used as solvent; t-butylbenzene was unsuitable because of low solubility. The methods employed for generating the majority of the transient $R_nM\cdot$ radicals are described in a previous paper.[1] In the present study the range of attacking radicals has been extended to $Ph_2P\cdot$, $Ph_2PO$, $CF_3S\cdot$, and $BD_3^{-\cdot}$; $Ph_2P\cdot$ and $CF_3S\cdot$ were obtained by photolytic cleavage of the P–P bond of

**Table.** Room temperature hyperfine splitting constants [in G (1 G = $10^{-4}$ T)] and *g* factors for the radical adducts (1)—(4) in benzene

| Radical | $MR_n$ | *a*(Ph) (*o*-, *m*-, *p*-H) | $a(H_\beta)$ | $a(MR_n)$ | *g* |
|---|---|---|---|---|---|
| (1) | $BD_3^-$ | 2.97, 1.21, 3.30 | 9.85 | 12.10($^{11}$B) | 2.0027 |
| | $PPh_2$ | 3.06, 1.24, 3.37 | 10.11 | 32.40($^{31}$P) | 2.0028 |
| | $P(O)Ph_2$ | 3.02, 1.25, 3.33 | 10.00 | 55.40($^{31}$P) | 2.0028 |
| | $SCF_3$ | 3.10, 1.26, 3.41 | 8.13 | 2.75(3F) | 2.0029 |
| (2) | Bu$^t$ | 3.08, 1.12 | 9.11 | | 2.0027 |
| | Ph | 3.16, 1.17 | 8.86 | | 2.0027 |
| | $CF_3$ | 3.14, 1.22 | 8.80 | 0.66(3F) | 2.0028 |
| | OC(O)Ph | 3.12, 1.14 | 7.62 | | 2.0028 |
| | $SiPh_3$ | 3.01, 1.14 | 10.84 | | 2.0027 |
| | $GePh_3$ | 3.00, 1.13 | 10.16 | | 2.0027 |
| | $SnPh_3$ | 2.94, 1.08 | 9.86 | | 2.0017 |
| | $P(O)(OEt)_2$ | 3.05, 1.16 | 9.74 | 66.11($^{31}$P) | 2.0028 |
| | SMe | 3.02, 1.12 | 7.56 | 0.41(3H) | 2.0031 |
| | SPh | 3.00, 1.10 | 7.62 | | 2.0031 |
| | $SCF_3$ | 2.94, 1.09 | 7.79 | 2.94(3F) | 2.0032 |
| (3) | $BD_3^-$ | 2.89, 1.20 | 9.31 | 11.42($^{11}$B) | 2.0028 |
| | $CH_3$ | 3.06, 1.26 | 8.44 | | 2.0028 |
| | Bu$^t$ | 2.96, 1.25 | 8.84 | | 2.0028 |
| | Ph | 3.02, 1.27 | 8.52 | | 2.0028 |
| | C(O)Ph | 3.05, 1.27 | 8.71 | | 2.0028 |
| | $CF_3$ | 3.13, 1.26 | 8.43 | 0.63(3F) | 2.0028 |
| | $CCl_3$ | 3.00, 1.24 | 7.86 | | 2.0033 |
| | OEt | 3.06, 1.26 | 9.02 | | 2.0028 |
| | OC(O)Ph | 3.05, 1.25 | 7.47 | | 2.0028 |
| | $SiPh_3$ | 2.97, 1.22 | 10.51 | | 2.0028 |
| | $GePh_3$ | 2.94, 1.21 | 9.87 | | 2.0027 |
| | $SnPh_3$ | 2.86, 1.17 | 9.60 | | 2.0018 |
| | $PPh_2$ | 3.02, 1.27 | 9.62 | 29.72($^{31}$P) | 2.0030 |
| | $P(O)(OEt)_2$ | 3.06, 1.28 | 9.32 | 62.70($^{31}$P) | 2.0031 |
| | SEt | 3.01, 1.24 | 7.28 | 0.55(2H) | 2.0032 |
| | SPh | 3.04, 1.25 | 7.41 | | 2.0032 |
| | $SCF_3$ | 3.08, 1.26 | 7.51 | 2.62(3F) | 2.0030 |
| (4) | $CH_3$ | 3.02, 1.28 | 8.96 | | 2.0028 |
| | Bu$^t$ | 2.95, 1.31 | 9.35 | | 2.0028 |
| | Ph | 3.07, 1.32 | 9.26 | | 2.0028 |
| | $CF_3$[a] | 3.13, 1.26 | 8.86 | 0.62(3F) | 2.0027 |
| | $CCl_3$ | 3.01, 1.26 | 8.37 | | 2.0033 |
| | OEt | 3.04, 1.28 | 9.07 | | 2.0028 |
| | $SiPh_3$ | 2.91, 1.18 | 11.16 | | 2.0027 |
| | $GePh_3$ | 2.87, 1.17 | 10.50 | | 2.0027 |
| | $SnPh_3$ | 2.74, 1.11 | 10.11 | | 2.0021 |
| | $PPh_2$ | 2.92, 1.25 | 9.78 | 28.40($^{31}$P) | 2.0030 |
| | $P(O)(OEt)_2$ | 3.04, 1.27 | 9.79 | 63.95($^{31}$P) | 2.0029 |
| | SMe | 2.98, 1.23 | 7.68 | 0.56(3H) | 2.0031 |
| | SPh | 3.00, 1.26 | 7.46 | | 2.0031 |
| | $SCF_3$ | 2.98, 1.21 | 8.40 | 2.41(3F) | 2.0030 |

[a] In $CH_2Cl_2$.

tetraphenyldiphosphine ($Ph_4P_2$) and of the S–S bond of bis(trifluoromethyl) disulphide. Diphenylphosphinoyl ($Ph_2\dot{P}O$) and the trideuterioborane radical anion ($BD_3^{-\bullet}$) were produced by hydrogen or deuterium abstraction with t-butoxyl from diphenylphosphine oxide and from tetra-n-butylammonium [$^2H_4$]borohydride prepared by literature procedures.[5]

Radical addition to the methylthio- and methylsulphonyl-substituted alkenes was observed in almost every case, and a limited number of radical adducts could be detected with the methoxy-substituted diphenylethylene (see Table). Disappointingly, in no case could we obtain chlorine adducts of the three investigated olefins. With the methylthio derivative a deep blue-green colour developed when gaseous HCl was added to the benzene solution containing $(Bu^tO)_2$; but no e.s.r. signal was observed even under irradiation. Attempts to generate the same radical by hydrogen abstraction with Bu$^t$O· from (4-$CD_3SC_6H_4)_2CH$–$CH_2Cl$ were also unsuccessful.

The photolysis of dibenzoyl peroxide at room temperature in the presence of the alkene resulted in the trapping of PhC(O)O· when X was $CD_3O$ or $CD_3S$; for X = $CD_3SO_2$ only the phenyl adduct was formed. It seems therefore that in the latter case decarboxylation of benzoyloxyl is faster than addition to the double bond. The radical anion $BD_3^{-\bullet}$ was trapped only by 1,1-diphenylethylene and its *para*-methylthio derivative. The radical adducts from 1,1-diphenylethylenes *para*-substituted with methoxy, methylthio, and methylsulphonyl groups showed e.s.r. spectra not easily interpretable: the basic spectrum was further split by the septet arising from the coupling of the unpaired electron with the methyl protons. These couplings were measured for the triphenylsilyl adducts as 0.32, 0.42,

and 0.57 G for $CH_3O$, $CH_3S$, and $CH_3SO_2$, respectively. To reduce the complexity of the spectra, deuterium was substituted for hydrogen in the methyl groups. In the case of the deuteriated derivatives the hyperfine structure from $CD_3$ was not resolved, although its contribution to the linewidth was not negligible ($\Delta H_{pp}$ *ca.* 0.30 for $OCD_3$, 0.35 for $SCD_3$, and 0.41 G for $SO_2CD_3$). Because of the large intrinsic linewidth, the selective broadening of the central line of the $CH_2$ triplet was much less pronounced than in the radical adducts of 1,1-diphenylethylene.[1]

The measured spectral parameters for the various adducts are reported in the Table. In the adduct of $BD_3^{-\bullet}$ with 1,1-diphenylethylene the β-proton splitting of 9.85 G is very close to the average value found in the previous work for first-row $MR_n$ substituents [$a(H_\beta) = 9.35 \pm 0.45$], despite the very low electronegativity ($\chi$) of the borane group, which can be calculated as 1.10 by Huheey's rules.[6] Furthermore, in the case of the $SCF_3$ ($\chi = 3.39$) adduct of (1), $a(H_\beta)$ (8.13 G) is larger than for the related adducts of the less electronegative thio derivatives SMe, SEt, and SPh (7.65, 7.57 and 7.80 G, respectively). Thus, the interpretation in terms of the electronegativity of the $MR_n$ substituent as the major source of the variations of $a(H_\beta)$ is further contradicted by these additional data.

The other data in the Table show that ring substitution affects to a minor extent the hyperfine couplings of the unsubstituted hydrogens. The *ortho*, *meta*, and methylene proton splittings are generally slightly lower for the methoxy (**2**) and methylthio (**3**) derivatives than for (**1**), reflecting partial delocalization of the unpaired electron on oxygen or sulphur, respectively. In the methylsulphonyl adduct (**4**) the changes of the hyperfine splittings are on average negligible.

As mentioned in the introduction, in radical adducts containing electronegative β-substituents, bond angle deformation due to partial bridging should depend on the ionization potential of the radical. Although data for the present systems are not available, we would expect that the relative variations in (**1**)—(**4**) are not negligible. A comparison can be made with benzyl radicals where the ionization potential decreases from 7.76 to 6.82 eV on *para*-methoxy-substitution and increases to 8.36 eV on *para*-substitution with an electron-withdrawing substituent (*e.g.* CN).[7]

It is therefore conceivable that polar structures such as $[Ar_2C^{\pm\bullet}CH_2MR_n^-]$, if they are of any significance, should be more important for the electron-rich methoxy and methylthio derivatives (**2**) and (**3**) than for the ring-unsubstituted and methylsulphonyl-substituted 1,1-diphenylethyl radicals (**1**) and (**4**). On this basis, a decrease in the β-proton splitting should be expected for radicals (**2**) and (**3**) when $MR_n$ is a 'bridging' substituent. Thus, plots of $a(H_\beta)$ for adducts (**2**) and (**3**) as a function of the same splittings measured for the corresponding radicals from 1,1-diphenylethylene would be expected to give a straight line for the adducts containing $MR_n$ substituents which do not give rise to any specific intramolecular interaction. 'Bridging' substituents should give points below that line to an extent proportional to the amount of bond angle distortion.

These plots (see Figure) show that the β-proton splittings for the *para*-substituted and unsubstituted radicals are well correlated, with the exception, in both cases, of the benzoyloxy adduct. In particular, thio radicals which have been considered by some authors[3] as bridging substituents do not show any significant deviation from the straight line. In a similar plot for the methylsulphonyl derivatives (**4**) [Figure (c)] the data are, again, reasonably well correlated.

In conclusion, it may be inferred that partial bridging is unimportant for the substituents investigated in the present work, with the possible exception of the benzoyloxy group, and that the origin of the large differences in the β-proton splittings observed in structurally similar β-substituted ethyl radicals remains a problem still to be solved. A single case of experimental e.s.r. evidence in favour of an asymmetric structure in which partial bridging occurs has been recently reported by Symons *et al.* for β-bromoethyl radicals.[8]

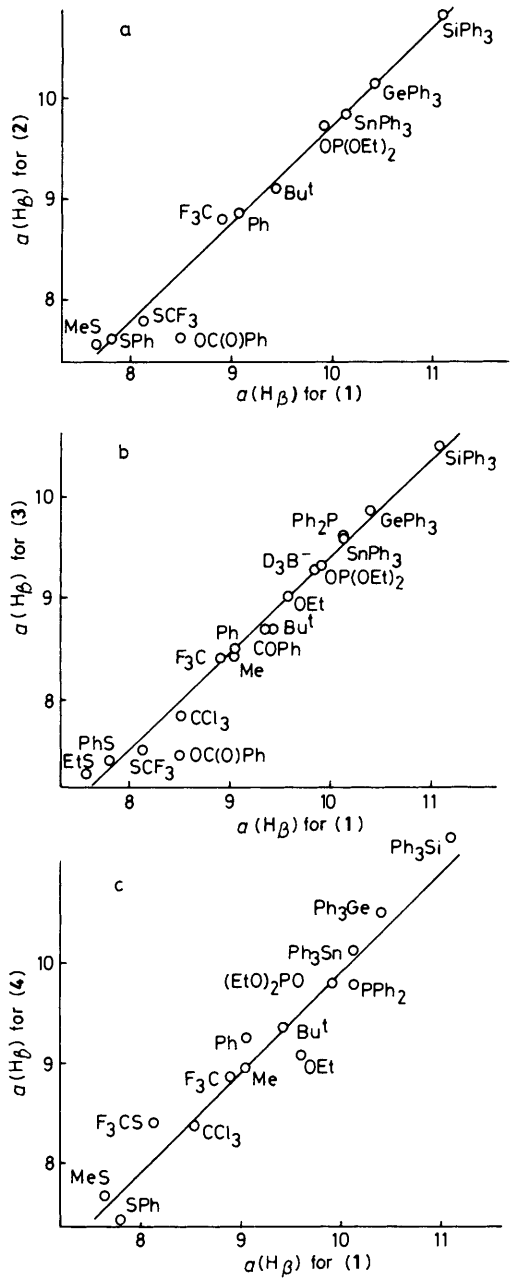



**Figure.** Experimental hyperfine splitting constants (G) at the β-protons for the radical adducts (**2**), (**3**), and (**4**) against the same splittings measured for (**1**)

## Experimental

1,1-Bis-(*p*-[$^2H_3$]methoxyphenyl)ethene, 1,1-bis-(*p*-[$^2H_3$]methylthiophenyl)ethene, 1,1-bis-(*p*-[$^2H_3$]methylsulphonylphenyl)-ethene, and 2,2-bis-(*p*-[$^2H_3$]methylthiophenyl)ethyl chloride were prepared as described later. 1-Bromo-4-[$^2H_3$]methoxybenzene and 1-bromo-4-[$^2H_3$]methylthiobenzene were prepared from *p*-bromophenol and *p*-bromobenzenethiol, respectively, with [$^2H_6$]dimethyl sulphate according to standard methods.

The $^1H$ n.m.r. spectra were recorded with a Varian EM 360L instrument ($Me_4Si$ as internal standard); mass spectra were obtained with a JEOL JMS-D100 spectrometer at an ionization energy of 70 eV.

1,1-*Bis*-(p-[$^2H_3$]*methoxyphenyl*)*ethene*.—To an ethereal Grignard solution from 1-bromo-4-[$^2H_3$]methoxybenzene (5.70 g, 30 mmol) and magnesium (0.73 g, 30 mmol), ethyl acetate (1.32 g, 15 mmol) was added dropwise. The mixture was kept at room temperature for 1 h, then carefully hydrolysed with 10% hydrochloric acid; the organic layer was separated and dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was crystallized from light petroleum–benzene (1:1, v/v) to give the title compound (3.25 g, 88%), m.p. 141—142 °C (mixed m.p. with the corresponding protic compound[9] shows no depression); $\delta_H(CDCl_3)$ 5.20 (2 H, s, C=$CH_2$) and 6.65—7.35 (8 H, 2AA'BB', ArH); *m/z* 246 (100%, $M^+$), 228(18), 212(21), and 165(11).

1,1-*Bis*-(p-[$^2H_3$]*methylthiophenyl*)*ethene*.—The procedure described for the methoxy derivative, with 1-bromo-4-[$^2H_3$]methylthiobenzene (6.15 g, 30 mmol), afforded the title compound, which was crystallized from petroleum (3.55 g, 85%), m.p. 129—130 °C (mixed m.p. with the corresponding protic compound[9] shows no depression); $\delta_H(CDCl_3)$ 5.30 (2 H, s, C=$CH_2$) and 7.15 (8 H, s, ArH); *m/z* 278 (100%, $M^+$), 260(8), 228(17), 178(35), and 165(14).

1,1-*Bis*-(p-*methylsulphonylphenyl*)*ethene*.—According to the procedure described by Carpino,[10] to a solution of 1,1-bis-(*p*-methylthiophenyl)ethene (1.95 g, 7.2 mmol) in dichloromethane (60 ml), 85% *m*-chloroperbenzoic acid (6 g, 30 mmol) was added over 6—7 min at room temperature with stirring. After 30 min the mixture was shaken in a separatory funnel with a 5% sodium hydrogen carbonate solution; the organic layer was separated and dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue, by crystallization from ethanol, afforded the *title compound* (1.45 g, 55%), m.p. 172—174 °C; $\delta_H(CDCl_3)$ 3.05 (6 H, s, $2CH_3SO_2$), 5.65 (2 H, s, C=$CH_2$), and 7.30—8.05 (8 H, 2AA'BB', ArH); *m/z* 336 (100%, $M^+$), 273(15), 257(31), 178(67), and 165(26) (Found: C, 57.2; H, 4.8; S, 18.95. $C_{16}H_{16}O_4S_2$ requires C, 57.1; H, 4.8; S, 19.1%).

1,1-*Bis*-(p-[$^2H_3$]*methylsulphonylphenyl*)*ethene*.—From 1,1-bis-(*p*-[$^2H_3$]methylthiophenyl)ethene (2 g, 7.2 mmol), the procedure described above afforded the title compound (1.5 g, 60%), m.p. 172—174 °C (mixed m.p. with the protic derivative not depressed).

2,2-*Bis*-(p-*methylthiophenyl*)*ethanol*.—The procedure of Lane[11] was followed. To a solution of 1,1-bis-(*p*-methylthiophenyl)ethene (3.1 g, 11.4 mmol) in dry tetrahydrofuran (20 ml), borane–dimethyl sulphide complex (2M; 2.2 ml, 4.4 mmol) was added dropwise at 0—5 °C under nitrogen with stirring. After the addition of the hydride (1 h), the cooling bath was removed and the solution was stirred for 3 h at 20—25 °C. Ethanol (4 ml) was then added, followed by aqueous 3M-sodium hydroxide (1.35 ml). After cooling to 0—5 °C again, 30% hydrogen peroxide (1.5 ml) was added dropwise at such a rate that the reaction mixture warmed to 25—35 °C. Immediately after the peroxide addition, the solution was refluxed for 1 h then poured into ice–water (50 ml) and extracted several times with diethyl ether. The organic phase was washed with water and dried ($Na_2SO_4$). The solution was filtered and the solvent removed under reduced pressure. The solid residue was crystallized from benzene to give the title *carbinol* (2.5 g, 75%), m.p. 77—78 °C; $\delta_H$ ($CDCl_3$) 1.80 (1 H, brs, OH), 2.35 (6 H, s, $2CH_3S$), 3.90 (3 H, brs, CH–$CH_2$), and 7.05 (8 H, brs, ArH); *m/z* 290 (25%, $M^+$), 259(100), 244(8), 197(10), and 165(22) (Found: C, 66.05; H, 6.3; S, 22.1. $C_{16}H_{18}OS_2$ requires C, 66.2; H, 6.2; S, 22.1%).

2,2-*Bis*-(p-[$^2H_3$]*methylthiophenyl*)*ethanol*.—From 1,1-bis-(*p*-[$^2H_3$]methylthiophenyl)ethene (3.2 g, 11.4 mmol), the procedure described for the protic carbinol furnished the title compound (2.8 g, 80%), m.p. 76—78 °C (mixed m.p. with the protic carbinol showed no depression).

2,2-*Bis*-(p-*methylthiophenyl*)*ethyl Tosylate*.—A solution of 2,2-bis-(*p*-methylthiophenyl)ethanol (1.6 g, 5.5 mmol), toluene-*p*-sulphonyl chloride (1.03 g, 5.5 mmol), and dry pyridine (0.45 g, 6.0 mmol) in dry benzene (25 ml) was refluxed for 5 h. After cooling, the mixture was poured into water and extracted twice with chloroform. The organic layer was washed with water and dried ($Na_2SO_4$). The solvent was removed under reduced pressure. Crystallization of the residue from benzene gave the *tosylate* as white crystals (2.15 g, 90%), m.p. 72—73 °C; $\delta_H$ ($CDCl_3$) 2.35 (9 H, s, $3CH_3$), 4.00—4.50 (3 H, m, CH–$CH_2$), and 6.80—7.65 (12 H, m, ArH); *m/z* 444 (3%, $M^+$), 272(100), 259(21), 172(34), and 91(41) (Found: C, 62.2; H, 5.5; S, 21.6. $C_{23}H_{24}O_3S_3$ requires C, 62.1; H, 5.4; S, 21.6%).

2,2-*Bis*-(p-[$^2H_3$]*methylthiophenyl*)*ethyl Tosylate*.—The reaction described for the protic tosylate, performed on 2,2-bis-(*p*-[$^2H_3$]methylthiophenyl)ethanol (1.7 g, 5.57 mmol), gave the title tosylate (2.25 g, 90%), m.p. 72—73 °C (mixed m.p. with protic tosylate not depressed).

2,2-*Bis*-(p-*methylthiophenyl*)*ethyl Chloride*.—As in the procedure of Mosher and his co-workers,[12] a solution of the corresponding ethyl tosylate (2.22 g, 5 mmol) and lithium chloride (0.17 g, 4 mmol) in hexamethylphosphoramide (5 ml), together with a little water (5 drops) was heated at 90 °C for 8 h. The solution was then poured into water and extracted with diethyl ether. The organic phase was washed with water, dried ($Na_2SO_4$), and evaporated under reduced pressure. The residue was chromatographed on a silica gel (Kieselgel 60, 70—230 mesh ASTM, Merck) column eluted with light petroleum–diethyl ether (98:2). The product was first obtained as a viscous oil, which crystallized on treatment with light petroleum. Recrystallization from light petroleum afforded the ethyl chloride as white crystals (1.0 g, 70%), m.p. 51—52 °C; $\delta_H$ ($CDCl_3$) 2.35 (6 H, s, $2CH_3$), 3.80—4.30 (3 H, m, CH–$CH_2$), and 7.05 (8 H, brs, ArH); *m/z* 310(17%, $M^+ + 2$), 308(40, $M^+$), 259(100), 244(10), and 165(19) (Found: C, 62.1; H, 5.6; Cl, 11.4; S, 20.7. $C_{16}H_{17}ClS_2$ requires C, 62.2; H, 5.55; Cl, 11.5; S, 20.8%).

2,2-*Bis*-(p-[$^2H_3$]*methylthiophenyl*)*ethyl Chloride*.—The procedure described for the protic chloride, with 2,2-bis-(*p*-[$^2H_3$]methylthiophenyl)ethyl tosylate (2.25 g, 5 mmol), afforded the title chloride (1.2 g, 75%), m.p. 51—52 °C (mixed m.p. with the protic chloride not depressed).

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