Electrocyclic Reactions. Part 12.[1] 1,5-Diphenyl-[2,3,4-²H₃]pentadienide Anion in the Caglioti Reaction

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A study, made by g.l.c.–mass spectrometry with appropriate deuterium labelling, of the Caglioti reaction applied to the toluene-*p*-sulphonohydrazide (6), has provided evidence supporting the mechanism, previously proposed, of the conversion of the 1,5-diphenylpentadienide anion, as (4), into 1,5-diphenyl-cyclopent-1-ene as (10).

An attempt has been made to confirm the mechanism of the conversion of the 1,5-diphenylpentadienide anion,[1] by way of a thermal symmetry-allowed disrotatory $[_\pi 2_s + _\pi S_s]$ cyclo-addition followed by a thermal symmetry-allowed supra-facial $[_\pi 4_s + _\sigma 2_s][1,4]$ sigmatropic shift and proton capture, into 1,5-diphenylcyclopent-1-ene by use of deuterium label-ling.

The Caglioti reaction[2] was applied using lithium aluminium deuteride: Ts–NH–N=C< ⟶ Ts–N̄–N=C< ⟶ N̄D–N=C< ⟶ N̄=N–CD< ⟶ N₂ + C̄D< to the toluene-*p*-sulphonohydrazide (6) of *trans,trans*-dibenzylidene-[²H₂]acetone (3), prepared from [²H₆]acetone (1) and benzalde-hyde (2).
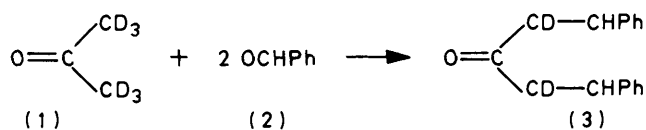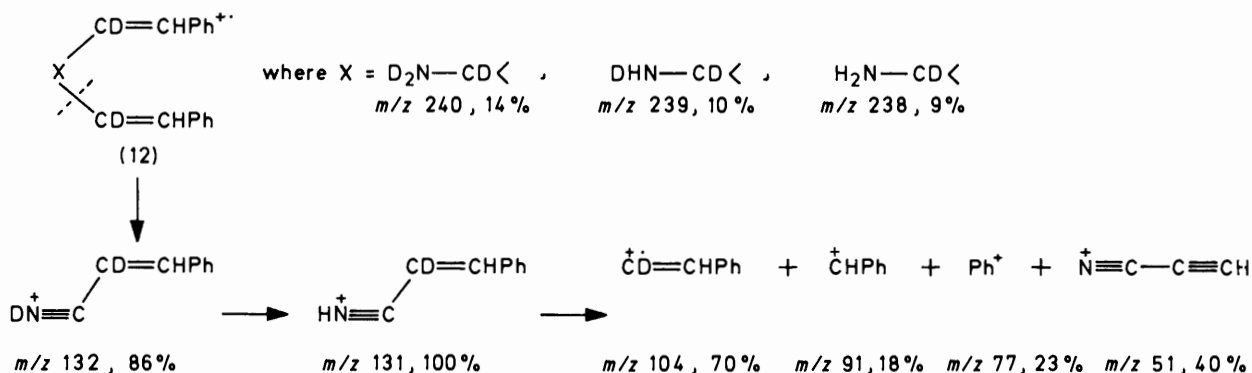

Treatment of the toluene-*p*-sulphonohydrazide (6) with lith-ium aluminium deuteride in THF at 65 °C gave *via* the sequence (5) ⟶ (4) ⟶ (8) ⟶ (9) and after quenching the reaction product with D₂O and saturated D₂O–ammonium chloride solution, a complex mixture of compounds including the heptadeuterioimine (7), 1,5-diphenyl[2,3,3,4-²H₄]cyclopent-1-ene (10), and 1,5-diphenyl[2,3,3,4-²H₄]cyclopent-5-ene (11).

The imine (7) is formed from the toluene-*p*-sulphonohydra-zide anion (6a) by fission of the N–N bond and reduction. The cyclopent-1-ene (10) and the isomeric doubly conjugated cyclopent-5-ene (11) are probably formed successively, or the latter is produced from the former compound during the acidic quenching of the reaction mixture. These three sub-stances were isolated by g.l.c.–mass spectrometry, and their structures are consistent with, and supported by, their fragmentation patterns.

The imine (7) (M^+, 244) showed a group of peaks at m/z 244—241, of which that at m/z 243 was the most intense, suggesting that the DN=C< group undergoes proton ex-change during quenching to give the HN=C< group:
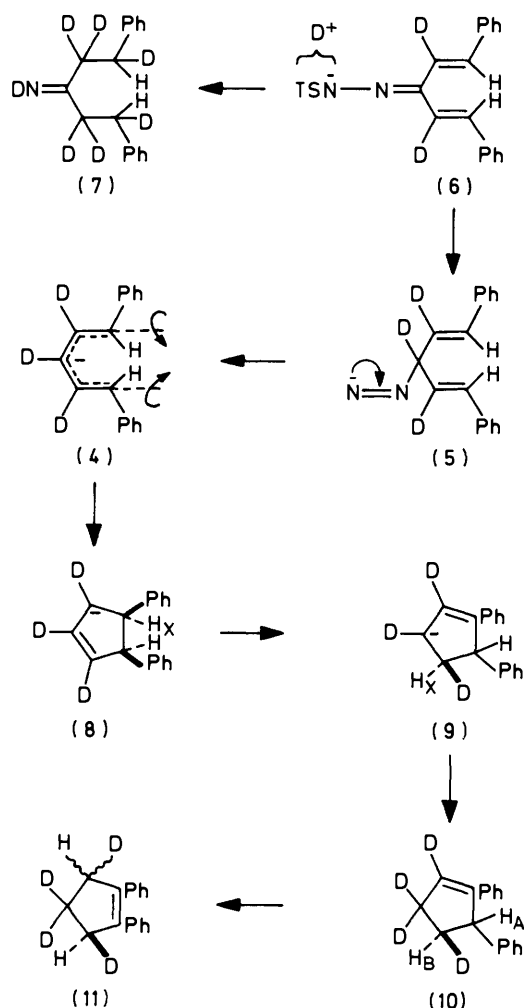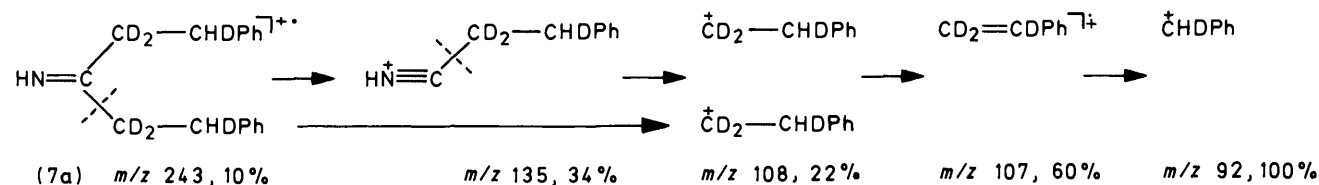
A set of partially reduced precursors of the imine (7) appeared in another g.l.c. fraction; a group of peaks at m/z 240, 239, 238 seem to correspond to 1,4-dienes (12), possibly formed by proton acquisition or proton exchange during quenching:
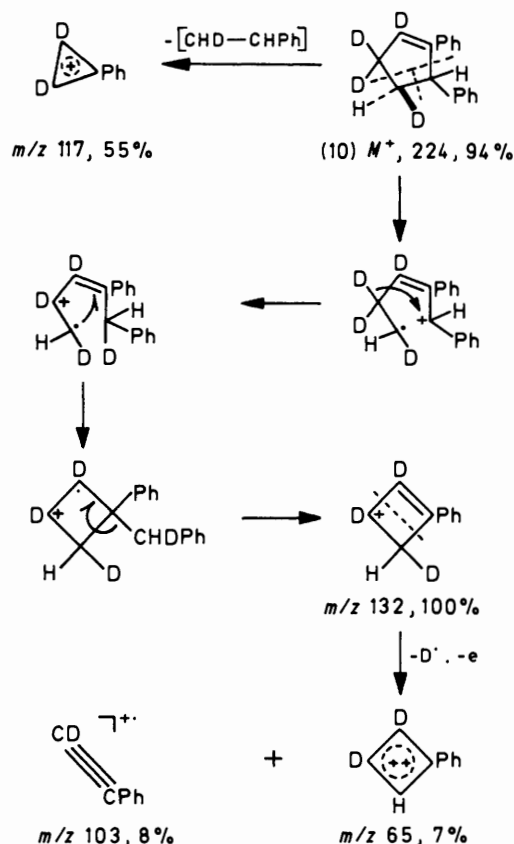
3 min 56 s and (11) t_R 4 min 19 s] sufficient for n.m.r. spectroscopy, which would have required *ca.* 10^3 runs. Attempts to enrich the cyclic products by treatment of the crude reaction mixture with non-polar solvents to precipitate polar material,

The cyclopent-1-ene (10) (M^+, 224) showed a base peak at m/z 132 ($M - $ CHDPh), a fragment which cannot directly be derived from the cation-radical corresponding to the molecule (10), and implies the occurrence of a skeletal rearrangement. An interpretation involving a cyclobutenium cation is given in Scheme 1; in view of the aromaticity of the cyclobutenium dication with four π-orbitals (E. Hückel's rule: the number of π-electrons $= n + 2$—here $n = 0$ [3]), the observation of a dication [4] peak at m/z 65 supports the proposed intermediate phenyl[$^2H_3$]cyclobutenium cation. It is to be noted that no peak at m/z 178, corresponding to PhC≡CPh, was observed (*vide infra*). There was however a prominent peak at m/z 117, regarded as corresponding to the aromatic phenyl[$^2H_2$]-cyclopropenium cation ($2n + 2$ π-electrons—here $n = 0$), which was not present in the fragmentation pattern of the isomeric cyclopent-5-ene (11) (see Scheme 3).

A Referee has suggested that a possible pathway from the cation-radical corresponding to the molecule (10) to the phenyl[$^2H_2$]cyclopropenium cation m/z 117 should be given (Scheme 2). This pathway is supported by observation of a peak at m/z 119 for the phenyl[$^2H_3$]propenium cation-radical PhC$_3$D$_3$$^{+\cdot}$. There appears to be some scrambling of deuterium and hydrogen since peaks at m/z 118 for the cation-radical PhC$_3$HD$_2$$^{+\cdot}$ and at m/z 116 for the phenyl[$^2H_1$]cyclopropenium cation PhC$_3$HD$^+$ are observed, and it will be seen that two routes can lead to the peak at m/z 117 for the phenyl[$^2H_2$]-cyclopropenium cation PhC$_3$D$_2$$^+$. A peak at m/z 115 was not seen.

The cyclopent-5-ene (11) (M^+, 224) gave a peak at m/z 178 corresponding to diphenylacetylene and, like its isomer (10), showed a base peak at m/z 132 accompanied however by a very prominent peak at m/z 131; production of these two peaks is consistent with the dual possibility of elimination of hydrogen or of deuterium. The observation of two peaks at m/z 65 and m/z 64.5, corresponding to the formation of two cyclobutenium dications, furnishes strong support for the proposed intermediate phenyl[$^2H_3$]cyclobutenium and phenyl-[$^2H_2$]cyclobutenium cations. As is to be expected, there was no peak at m/z 117 (*vide supra*). The mass spectrum of (11) is given in Scheme 3; peaks for $\overset{+}{C}D_2$Ph, m/z 93, 60% and for $\overset{+}{C}$HDPh, m/z 92, 30% are not shown.

These fragmentation patterns afford convincing evidence for structures (10) and (11), and support the mechanism, previously proposed [1] for their production. Regrettably, preparative g.l.c., using a new capilliary system of extremely high resolving power, failed to give amounts of the cyclopentenes [(10) t_R

Scheme 1.

and to remove basic nitrogenous material by extraction with dilute acetic acid, failed.

The structures of other products formed in the Caglioti reaction of (6) with lithium aluminium deuteride, separated by g.l.c., as suggested by their mass spectral fragmentation patterns, are less secure. Capture of a deuteron by the open-chain anion (4) appears to have yielded the acyclic [$^2H_4$]-compound (13), further reduced (although lithium aluminium deuteride does not normally reduce carbon–carbon double bonds) to the [$^2H_6$]-compound (14).

Apparently related to the [$^2H_6$]-compound (14) is a [$^2H_7$]-

m/z 224, 94% ≡ "(10)" m/z 224, 94%

$-[CHD-CHPh]$ $-[CHD-CHPh]$

other
canonical
structures

scrambling $PhC_3D_3^{+\cdot}$, m/z 119, 7% scrambling

$PhC_3HD_2^{+\cdot}$, m/z 118, 39% $PhC_3H_2D^{+\cdot}$, m/z 117, 55%

$-D^\cdot, -e$ $-H^\cdot, -e$ $-D^\cdot, -e$ $-H^\cdot, -e$

PhC_3HD^+, m/z 116, 10% $PhC_3D_2^+$, m/z 117, 55% PhC_3HD^+, m/z 116, 10%

Scheme 2.

m/z 178, 10% (11) M^+, 224, 51%

m/z 103, 10% m/z 65, 3% m/z 132, 100%

$-D^\cdot, -e$

m/z 102, 4% m/z 64.5, 5% m/z 131, 77%

$-D^\cdot, -e$

Scheme 3.

$$(4) \longrightarrow PhCH{=}CD{-}CD_2{-}CD{=}CHPh \longrightarrow PhCHD{\dotplus}CD_2{-}CD_2{\stackrel{\frown}{-}}CD{=}CHPh^{\rceil+\cdot}$$

$$(13) \hspace{4cm} (14)\ m/z\ 228,14\%$$

$$PhCHD^+ \quad + \quad PhCHD{-}CD_2{-}CD{=}CD^{+\cdot} \quad + \quad CHDPh^+$$

$$m/z\ 92,100\% \hspace{1.5cm} m/z\ 136,88\% \hspace{2cm} m/z\ 92,100\%$$

compound (15) seemingly formed by addition of D–H (or inversely H–D), which suggests the presence of some incompletely deuteriated species $LiAlD_mH_n$ ($m = <4$, $n = >0$) in the lithium aluminium deuteride used in the Caglioti reaction:
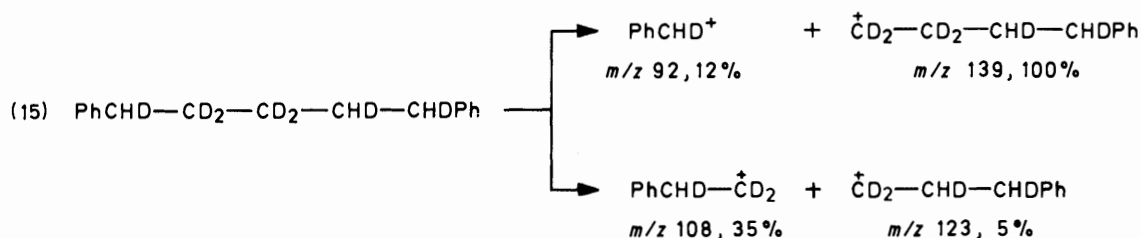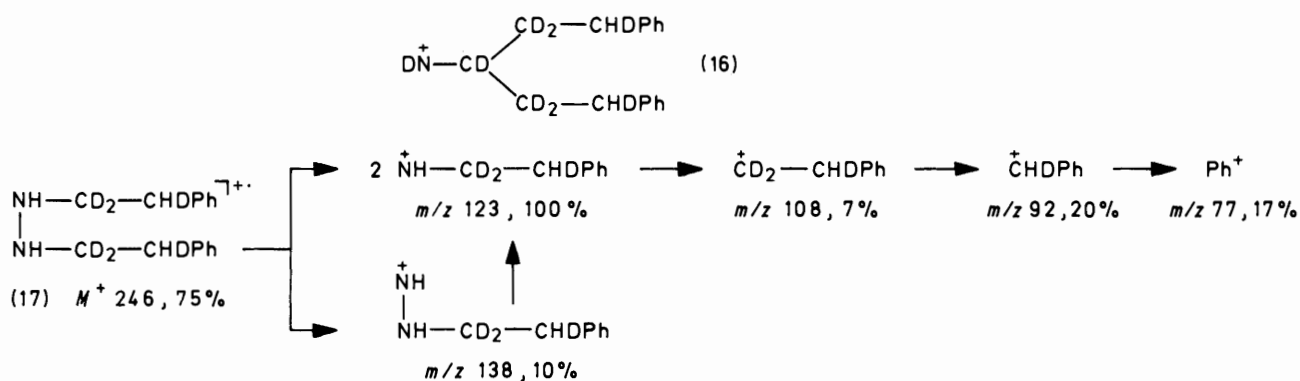
focalisation, 103.5 V; multiplier voltage, 1.8 kV; polarisation dynode, -3.46 kV; ion energy -5.5 V; extractor energy $+5.5$ V; source temperature 190 °C; electrometer gain 10^6 V/A; sensitivity 0.3 V. Mass matching was performed using a

$$PhCHD^+ \quad + \quad \overset{+}{C}D_2{-}CD_2{-}CHD{-}CHDPh$$

$$m/z\ 92,12\% \hspace{2cm} m/z\ 139,100\%$$

$$(15)\quad PhCHD{-}CD_2{-}CD_2{-}CHD{-}CHDPh \longrightarrow$$

$$PhCHD{-}\overset{+}{C}D_2 \quad + \quad \overset{+}{C}D_2{-}CHD{-}CHDPh$$

$$m/z\ 108,35\% \hspace{2cm} m/z\ 123,5\%$$

One component of the reaction mixture with M^+ 246 remains an enigma; a possible molecular formula is $C_{17}H_{12}D_8N$ and a structural formula (16) can be drawn; but the mass spectral fragmentation pattern strongly suggests a symmetrical dimer (17) with C_{16} (not C_{17}!) and N_2, whose genesis is obscure.*

CEC 21-110B (Consolidated Electrodynamics Corp. double focussing mass spectrometer) machine operating at an emission potential of 70 eV, accelerating voltage 8 kV, ion source temperature 150—170 °C, and photoplate detection, with resolution of *ca.* 15×10^4. The ^1H n.m.r. spectrum was recorded on a Brucker HX-360 machine with

$$D\overset{+}{N}{-}CD\overset{\displaystyle CD_2{-}CHDPh}{\underset{\displaystyle CD_2{-}CHDPh}{\Big\langle}} \hspace{1cm} (16)$$

$$\begin{array}{l} NH{-}CD_2{-}CHDPh \\ | \\ NH{-}CD_2{-}CHDPh \end{array}^{\rceil+\cdot} \longrightarrow 2\ \overset{+}{N}H{-}CD_2{-}CHDPh \longrightarrow \overset{+}{C}D_2{-}CHDPh \longrightarrow \overset{+}{C}HDPh \longrightarrow Ph^+$$

$$(17)\ M^+\ 246,75\% \hspace{2cm} m/z\ 123,100\% \hspace{1cm} m/z\ 108,7\% \hspace{1cm} m/z\ 92,20\% \quad m/z\ 77,17\%$$

$$\begin{array}{l} \overset{+}{N}H \\ | \\ NH{-}CD_2{-}CHDPh \end{array}$$

$$m/z\ 138,10\%$$

In brief, the evidence adduced supports the mechanism previously proposed [1] for the Caglioti reaction applied to the toluene-*p*-sulphonohydrazide (6); the reaction appears to be more complicated than was previously thought.[5]

Experimental

M.p.s were taken on a Büchi hot-stage (Tottoli system) with an uncorrected thermometer. G.l.c. was carried out with a Fractovap instrument (Carlo Erba, Milan, Italy, type 4160) using a glass column (internal diam. 0.3 mm, length 15 m) packed with SE 30 (layer thickness 0.3 µm) in helium (flow rate 24 ml s^{-1}), programmed for the range 160—280 °C (rise 6 °C min^{-1}) with split-mode injection, and injection port at 300 °C. Mass spectra were measured on a Ribermag R 10-10C machine (a quadrupole apparatus with mass range 1—1 500)

(Nermag S.A., Paris, France) with the following characteristics: emission current, 0.13 mA; emission potential, 70 eV; Fourier transform in [^2H]chloroform with tetramethylsilane as internal reference.

trans,trans-*Dibenzylidene*[$^2H_2$]*acetone* (3).—Freshly distilled benzaldehyde (21.2 g, 0.2 mol) and [$^2H_6$]acetone (6.4 g, 0.1 mol; Fluka, 99.5 atom %D and $< 0.02\%$ $H_2O + D_2O$) were mixed and added to a stirred solution at 25 °C of sodium deuterio-oxide (20.5 g, 0.5 mol, prepared from sodium oxide, Merck 98%, and deuterium oxide, CIBA-GEIGY $> 99\%$ D_2O) in deuterium oxide (200 ml) and [$^2H_1$]ethanol (160 ml, Merck $> 99\%$ EtOD). After 12 h at 25 °C, the precipitate was filtered off, washed with distilled water until the washings were neutral, dried, and twice recrystallised from ethyl acetate to give yellow crystals of trans,trans-dibenzylidene-[$^2H_2$]acetone (11.4 g), m.p. 110 °C (Found: C, 86.8; H + D, 6.7; O, 6.9%; M^+, 236.1171. Calc. for $C_{17}H_{12}D_2O$: C, 86.4; H + D 6.8; O, 6.8%; M^+, 236.1170).

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* See Note added in proof on p. 2373.

trans,trans-Dibenzylidene[^{2}H$_2$]acetone Toluene-p-sulphono-hydrazide (6). trans,trans-Dibenzylidene[^{2}H$_2$]acetone (4.9 g, 0.21 mmol) in [^{2}H$_1$]ethanol (50 ml) was treated with toluene-p-sulphonohydrazide (m.p. 106—108 °C, 3.9 g, 0.21 mmol) dissolved in hot [^{2}H$_1$]ethanol [ca. 25 ml, containing 5 drops of deuterium chloride (Merck, 37% in D$_2$O, >99% deuteriated)]. Refluxing of the mixture gave after ca. 15 min a sudden precipitate; after cooling to 20 °C and storage overnight at −10 °C, the yellow crystals were filtered off, washed with water, and dried at 25 °C. Recrystallisation from ethanol gave yellow needles, m.p. 140—142 °C (4 g, 52.5%) (Found: C, 71.6; H + D, 6.0; N, 6.9; O, 8.1; S, 7.8%; M^+, 404.1522. Calc. for C$_{24}$H$_{20}$D$_2$N$_2$O$_2$S: C, 71.3; H + D, 6.0; N, 6.9; O, 7.9; S, 7.9%; M^+, 404.1527). Another product, m.p. 164—166 °C, was isolated but not further examined.

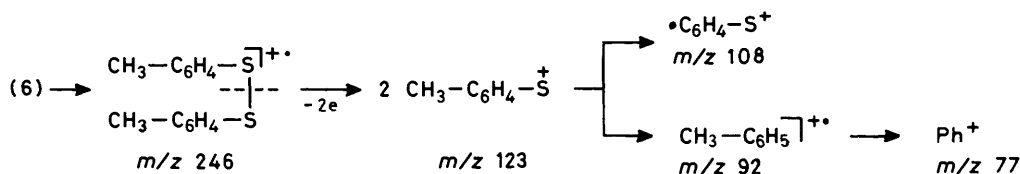*Reduction of the Toluene-p-sulphonohydrazide (6) with Lithium Aluminium Deuteride.*—Lithium aluminium deuteride (3 g) was added to tetrahydrofuran (50 ml, redistilled, peroxide free) in nitrogen at 0 °C; a solution of the [^{2}H$_2$]sulphonohydrazide (6) (2 g, 5 × 10^{-2} mol) in tetrahydrofuran was added slowly dropwise so that the exothermic reaction temperature was always <20 °C. The grey-green mixture was then refluxed in nitrogen at 65 °C for 24 h and became dark blue. After the mixture had been cooled to 0 °C in an ice-bath, deuterium oxide (20 ml) [dissolved in tetrahydrofuran (50 ml)

but the results of g.l.c.–mass spec. analysis were unchanged, showing a peak M^+ 224, for (10) and (11), in low yield.

Because of the impossibility of obtaining adequate amounts of the cyclopentenes (10) and (11) by g.l.c. for ^{1}H n.m.r. spectroscopy, a sample of the crude reaction product was examined and showed small resonances at the expected chemical shifts [1]; δ 4.22 (H$_A$), 2.44 (H$_B$) for the [^{2}H$_4$]cyclopentene (10); these δ values are the centres of signals, which may be doublets, but were insufficiently resolved to be described as such.

This work was commenced in 1979–1980 at Macquarie University, and was continued in the research laboratories of CIBA-GEIGY Ltd., Basle; we express our best thanks for this continuation to Dr. Ernst Vischer, Vice-President of CIBA-GEIGY, to Professor H. M. Widmer, and to Dr. W. J. Richter, and for the use of superb modern analytical equipment. One of us (C. W. S.) acknowledges the helpful comments of a Referee.

Note added in proof: Since the only analytical data are m/z values, it is possible that the corresponding ions, or molecular ions, contain not two atoms of nitrogen but two atoms of sulphur, and are derived by S—N bond fission of the toluene-p-sulphono moiety of (6); however, the peak at m/z 138 cannot now be accommodated unless the radical precursor of the ion m/z 123 captures a methyl group.

$$(6) \longrightarrow \begin{array}{c} CH_3{-}C_6H_4{-}S \\ {-}{-}|{-}{-} \\ CH_3{-}C_6H_4{-}S \end{array} \Big]^{+\cdot} \xrightarrow{-2e} 2\ CH_3{-}C_6H_4{-}\overset{+}{S}$$

m/z 246   m/z 123

•C$_6$H$_4$–S$^+$ m/z 108

CH$_3$–C$_6$H$_5$]$^{+\cdot}$ ⟶ Ph$^+$ m/z 92   m/z 77

to reduce the violent reaction with excess lithium aluminium deuteride, prevent local overheating, and avoid clump formation so as to permit rapid stirring] was added in an atmosphere of nitrogen at <20 °C. A saturated solution of ammonium chloride in deuterium oxide (100 ml) at ca. 0 °C was added, and after the mixture had been stirred for 0.5 h the organic layer was separated and the aqueous phase extracted with ether (5 × 200 ml). The organic layer and the ethereal extracts were combined, washed with water (5 × 200 ml), dried with sodium sulphate, and evaporated; the last traces of water were removed azeotropically with benzene. The product (1.28 g) was a yellow oil, which was used (a) directly, and (b) after an attempt to enrich cyclic products by extraction with hexane and to remove basic material by extraction with 2M-acetic acid, for g.l.c.–mass spec. analysis (see text).

In another similar experiment, quenching of the reaction mixture was performed using concentrated deuterium chloride solution (30 ml) in deuterium oxide (80 ml) at 0 °C,

References

1 Part 11, C. W. Shoppee and G. N. Henderson, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1028; there is a typing error in this paper on p. 1028, right column, line 5, where δ(H$_A$) should read 6.45 (not 5.45), whilst in line 6 the value 6.44 (given by Shoppee and Henderson, *J. Chem. Soc., Perkin Trans. 1*, 1975, 770, left column, line 7) is correct.

2 L. Caglioti and M. Magi, *Tetrahedron*, 1963, **19**, 1127; L. Caglioti, *ibid.*, 1967, **22**, 487.

3 A. Streitweisser, Jr., ' Molecular Orbital Theory for Organic Chemists,' John Wiley and Sons Inc., London, 1962, **10**, 256; P. J. Garrett, ' Aromaticity,' McGraw-Hill, London, 1971, 78.

4 H. H. Freedman and A. E. Young, *J. Am. Chem. Soc.*, 1964, **86**, 734; G. A. Olah, J. M. Bollinger, and A. M. White, *ibid.*, 1969, **91**, 3667.

5 M. Fischer, Z. Pelak, D. H. Williams, and C. Djerassi, *Chem. Ber.*, 1965, **98**, 3236.