Selectivity in the Electrophilic Addition of Carbenes and Nitrenes to Aliphatic Sulphides and to 4-t-Butylthian

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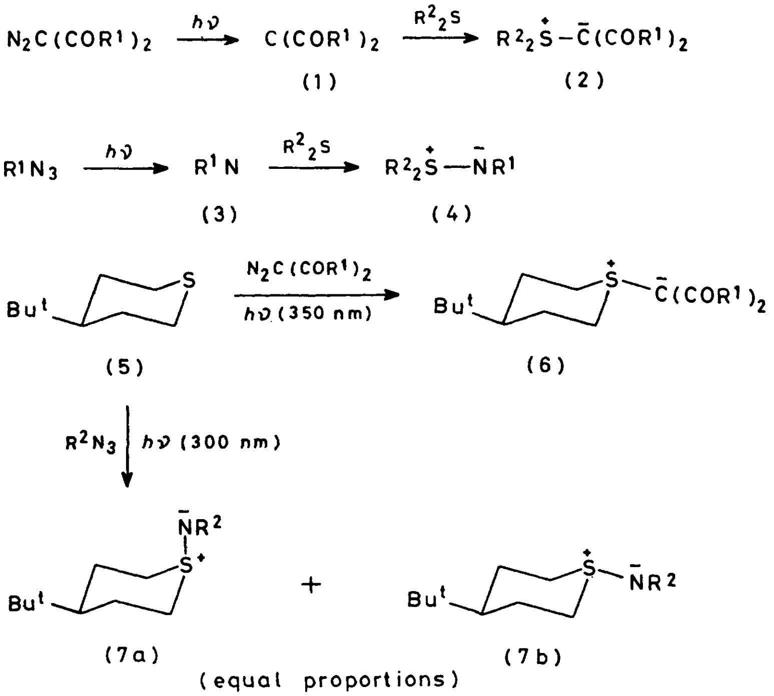
Photogenerated bisalkoxycarbonyl- and diacetyl-carbenes add exclusively equatorially to 4-t-butylthian and exhibit selectivity in competitive additions to mixtures of dimethyl and di-isopropyl sulphides. By contrast ethoxycarbonyl- and *p*-tolylsulphonyl-nitrene give equal proportions of axial and equatorial adducts with the thian, and show no selectivity in competitive reactions with dialkyl sulphides. The results in most or all cases appear to be determined by kinetic control.

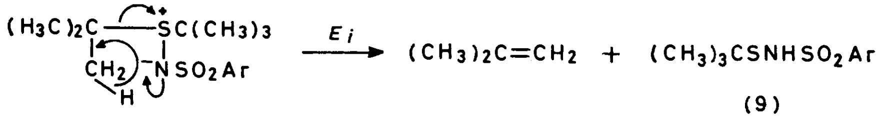
In a quest for suitable photogenerated electrophiles which might be employed for freezing the conformational equilibria in *N*-alkylpiperidines (*eq*-N-alk $\rightleftharpoons$ *ax*-N-alk) we examined the possible utility of carbenes and nitrenes (or equivalent reactive species) carrying electron-withdrawing substituents.[1] We also decided to use sulphides initially, rather than amines, to assess the selectivities of the electrophiles chosen, and specifically to explore with these very active reagents the steric course of additions to 4-t-butylthian (5) and the relative reactivities of simple dialkyl sulphides. The results described in this paper show that the nitrenes covered in our assessment are very much less selective than are the carbenes.



Ando and his co-workers have shown[2,3] that bisalkoxycarbonyl- or diacetyl-carbenes (1; $R^1 = OCH_3$, OC_2H_5, or CH_3) generated by photolysis of the corresponding diazo-compounds add to alkyl or aryl sulphides to yield the sulphonium ylides (2; $R^1 = OCH_3$, OC_2H_5, or CH_3; R^2 = alkyl or aryl). Analogous additions were also carried out with cyclic (polymethylene) sulphides. From triplet sensitisation and related studies it appeared that the singlet state of the carbenes was involved in these reactions, as indeed would be expected on theoretical grounds. Some additions were also effected when the diazo-precursors were decomposed thermally in presence of the sulphides and a copper or copper(II) catalyst; such thermal reactions are usually regarded[4] as proceeding *via* intermediate ' carbenoids ' rather than free carbenes. In analogous photochemical work, nitrenes (3; $R^1 = CO_2CH_3$ or *p*-$CH_3C_6H_4SO_2$) derived from alkyl azidoformates[5] or toluene-*p*-sulphonyl azide[6] were shown to add to dialkyl sulphides to yield sulphimides (sulphimines; iminosulphuranes; 4; $R^1 =$ CO_2CH_3 or *p*-$CH_3C_6H_4SO_2$; R^2 = alkyl).

In our work, irradiation through Pyrex at 350 nm of solutions of the appropriate diazo-precursors in excess of 4-t-butylthian (5) gave the sulphonium ylides (6; $R^1 =$ OCH_3, OC_2H_5 or CH_3). No evidence of more than one stereoisomeric form in each case was obtained by n.m.r. spectroscopic examination of the ylide or of its protonated derivative (sulphonium salt), and a similar result was obtained when diacetyldiazomethane was thermally decomposed in the presence of 4-t-butylthian and a copper sulphate catalyst. The *S*-equatorial configurations (6) are assigned by analogy with the steric course of ternerisation of thians [7] where the kinetic preferences for equatorial attack by alkylating agents are quite marked [7.3 : 1 for reaction of (5) with methyl iodide] although evidently less extreme than in our work. The greater selectivity shown by the very much more active reagents contrasts with the widely held if naive and theoretically unjustified view that faster reactions are in general expected to be less selective.

The strong preference for equatorial addition of carbenes to 4-t-butylthian is evidently of steric origin, and a similarly based discrimination in competitive additions to dialkyl sulphides might be predicted. We found that when bismethoxycarbonylcarbene was photochemically generated in the presence of a large excess of an equimolar mixture of dimethyl and di-isopropyl sulphides the molar product ratio of ylides was 5.3 : 1, attack on dimethyl sulphide being favoured.



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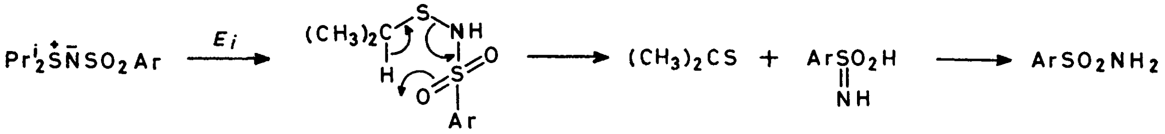

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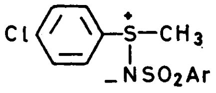

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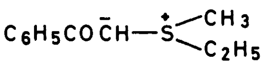

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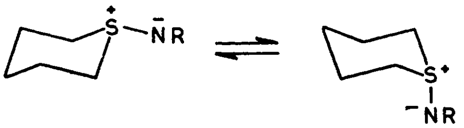

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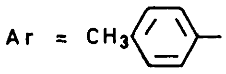


Similar experiments on additions of nitrenes gave strongly contrasting results. Irradiation of ethyl azidoformate at 300 nm in the presence of excess of 4-t-butylthian (5) gave the diastereoisomeric sulphimides (7; $R^2 = CO_2C_2H_5$) in equal proportions as determined by n.m.r. spectroscopy, and a similar result was obtained with toluene-*p*-sulphonyl azide [giving products (7; $R^2 = p\text{-}CH_3C_6H_4SO_2$)]. Likewise, on competitive additions to dimethyl and di-isopropyl sulphides, no discrimination was noted for either ethoxycarbonyl- or *p*-tolylsulphonyl-nitrene. An attempt to determine the relative ease of addition of photogenerated *p*-tolylsulphonylnitrene to dimethyl and di-t-butyl sulphides in an appropriate competitive experiment was complicated by the ready decomposition of the di-t-butylsulphimide (8) at or near room temperature to the analogous sulphenamide (9) by elimination of butene, but the sulphenamide and the dimethylsulphimide were found to be produced in approximately equimolar proportions (the latter slightly predominating) from an equimolar mixture of reactant sulphides. The E_i mechanism for the conversion of the sulphimide (8) into the product (9) is of course conventional [8,9] and the instability of (8) is doubtless caused by steric interactions of the bulky t-butyl groups. In an ensuing examination of the thermal stabilities of some related sulphimides and sulphenamides, *SS*-dimethyl-*N*-*p*-tolylsulphonylsulphimide was found to be stable up to 130°, but the analogous di-isopropylsulphimide decomposed at this temperature, apparently *via* sulphenamide (10), to toluene-*p*-sulphonamide. The mechanism illustrated for the second step in this sequence accords with the anhydrous conditions employed (excluding hydrolysis [9]), the stability of the t-butyl analogue (9) under similar conditions (reasonably excluding a radical mechanism initiated by S–N fission [10]) and the identification of evolved thioacetone as dinitrophenylhydrazone.

The question arises whether the product ratios we have observed on addition of the carbenes and nitrenes to sulphides are determined by kinetic or thermodynamic control. In the competitive experiments with mixtures of aliphatic sulphides a process of ' transylidation ' could in principle lead towards equilibration of products, by photochemical detachment of the carbene or nitrene residue from one sulphide (under the conditions of the experiment) and subsequent thermal attachment of this residue to the competitive sulphide. However, such a process is extremely unlikely at 350 nm where the sulphonium ylides made in our work are virtually transparent. Transylidation at 254 nm between sulphimide and sulphide has been demonstrated in one literature example,[11] but we operated in a longer wavelength band (around 300 nm) in preparation of sulphimides, and deliberately held our yields to *ca.* 15% in order to screen the products as formed with excess of azide. We also showed in trial experiments with *N-p*-tolylsulphonylsulphimides at 300 nm, in which there was no azide screening, that no transylidation occurred. We believe therefore that our results with aliphatic sulphides reflect kinetic control, and are determined simply by the fact that the nitrenes, having only one group covalently attached to the reaction centre (nitrogen) are less subject to differential steric influences than are the carbenes with two such covalent groups. It is of interest that in other competitive reactions, where kinetic control may depend less on simple steric effects, nitrenes are more selective than carbenes.[12]

Additions of nitrenes and carbenes to 4-t-butylthian could in principle be thermodynamically controlled not only by transylidation but also by stereochemical inversion at sulphur. Inversion at sulphur in our sulphonium ylides and in some sulphimides [13] is too slow for barrier-height measurement by n.m.r., but selected optically active examples studied indicate quite high inversion barriers for sulphimides,[14] for example, 29 kcal mol^{-1} for (11), and one [15] of 24 kcal mol^{-1} (half-life 40 min at 50° in CCl_4) for the sulphonium ylide (12). If the higher barrier quoted is typical for sulphimides our results for nitrene addition to the thian are likely to be kinetically controlled, notwithstanding the similarity of the product ratios to the conformational equilibrium constants,[13] also near unity, for the system (13; $R = H$, p-$CH_3C_6H_4SO_2$, or $C_6H_5SO_2$): the kinetic and thermodynamic preferences in the nitrene additions may be quite similar. Despite the somewhat uncomfortably low inversion barrier quoted for the sulphonium ylide (12), we feel that our carbene additions to 4-t-butylthian are also probably kinetically controlled, as the high product ratios observed contrast strongly with equilibrium ratios for diastereoisomeric thianium salts.[7] The *eq*-S-methyl cation derived from (5), for example, is preferred over the *ax*-S-methyl isomer by only 1.4 : 1.

EXPERIMENTAL

^{1}H N.m.r. spectra were taken on Varian Associates HA 100 or Perkin-Elmer R12A spectrometers, and mass spectra on A.E.I. MS9 or MS12 instruments. Chromatographic separations were carried out on columns except where otherwise specified, using either alumina (CAMAG, M.F.C., neutral, Hopkin and Williams) or silica gel (M.F.C., Hopkin and Williams). T.l.c. was on silica gel (Reeve-Angel Scientific). Light petroleum was the fraction of b.p. 40—60°.

Reactants.—Dimethyl and di-t-butyl sulphides were commercial samples. The following were prepared by literature procedures: di-isopropyl sulphide, b.p. 118° (lit.,[16] 119°); thian, b.p. 138—140° (lit.,[17] 141°) (Found: C, 58.85; H,9.75. Calc. for $C_5H_{10}S$: C, 58.75; H, 9.85%); 4-t-butylthian, b.p. 78—79° at 9 mmHg (lit.,[18] 47—48° at 1 mmHg); dimethyl diazomalonate, b.p. 63—64° at 0.7 mmHg (lit.,[19] b.p. 63° at 1 mmHg); diethyl diazomalonate, b.p. 71—72° at 0.9 mmHg (lit.,[20] 84—85° at 1 mmHg) (Found: C, 45.4; H, 5.1; N, 15.25. Calc. for $C_7H_{10}N_2O_4$: C, 45.15; H, 5.4; N, 15.05%); diacetyldiazomethane, b.p. 57—59° at 0.15 mmHg (lit.,[21] 57° at 0.1 mmHg) (Found: C, 47.25; H, 4.8; N, 22.1. Calc. for $C_5H_6N_2O_2$: C, 47.6; H, 4.8; N, 22.2%); ethyl azidoformate, b.p. 46—47° at 41 mmHg) (lit.,[22] 40° at 31 mmHg); toluene-*p*-sulphonyl azide, m.p. 21° (lit.,[23] 22°). In all cases the n.m.r. and i.r. spectroscopic properties of the products accorded with expectation.

Photolytic Additions.—Reactions were carried out in a Rayonet photochemical reactor equipped with eight lamps of the appropriate wavelength (300 or 350 nm), the solutions being contained in stoppered Pyrex tubes (quartz for some of the nitrene additions: no differences in outcome were observed) with quartz outer jackets, cooling water (10—15°) being passed through the interannular space. The solutions were flushed with nitrogen or argon before photolysis (while cooling to −40° when working with the more volatile reactants) with slow continued passage of the gas during the photolysis. Progress of the reaction was monitored by spectroscopic examination of portions. Thermal blanks were carried out in all cases.

The diazo compound, ethyl azidoformate, or toluene-*p*-sulphonyl azide (0.2—0.5 ml) was dissolved in a substantial excess of sulphide (1—3 ml) and photolysed at 350 nm for 24 h (diazo compounds: isolated yields of sulphonium ylides 30—55%) or at 300 nm for 2 h (ethyl azidoformate or toluene-*p*-sulphonyl azide: isolated yields of sulphimides *ca.* 15%). In working up the sulphonium ylide preparations, excess of sulphide, if volatile, was removed by distillation, and the residue was then triturated with cold light petroleum and purified by recrystallisation; otherwise, with higher boiling sulphides, the reaction mixtures were chromatographed on alumina, the sulphonium ylides being eluted in chloroform. In preparations of *N*-ethoxycarbonylsulphimides (from ethyl azidoformate) the mixtures were concentrated to small volume under reduced pressure, and the residues were chromatographed on silica gel, the sulphimides being eluted with ether–methanol. In the preparation of *N-p*-tolylsulphonylsulphimides (from toluene-*p*-sulphonyl azide) the crude reaction mixtures were separated into undecomposed reactants, soluble in cold light petroleum, and crude sulphimides (insoluble); the latter were then purified by chromatography on alumina, being eluted with chloroform. In experiments where mixtures of two sulphonium ylides or sulphimides were (or might have been) produced, product ratios were determined by n.m.r. examination of total crude reaction mixtures (or residues after removal of excess of easily volatile sulphides) as well as of isolated products.

(i) *Sulphonium Ylides.*—The following were prepared: dimethylsulphonium bismethoxycarbonylmethylide (2; $R^1 = R^2 = CH_3$), m.p. 169—171° (lit.,[3] 169—170°); di-isopropylsulphonium bismethoxycarbonylmethylide [2; $R^1 = CH_3$, $R^2 = CH(CH_3)_2$], m.p. 120—121° (lit.,[3] 121—122°); *thianium diacetylmethylide* (14), m.p. 161—161.5°

(from ether–light petroleum) (Found: C, 59.9; H, 8.05%; $M^{+\cdot}$, 200.0872. $C_{10}H_{16}O_2S$ requires C, 60.0; H, 8.05%; $M^{+\cdot}$, 200.0871); τ($CDCl_3$) 5.35 (2 H, m, one pair of ring protons adjacent to S^+), 7.20 (2 H, m, second pair of ring protons adjacent to S^+), and 7.63 [6 H, s, $(COCH_3)_2$]; trans-4-*t-butylthianium bismethoxycarbonylmethylide* (6; $R^1 = OCH_3$), m.p. 183—185° (from light petroleum) (Found: C, 58.15; H, 8.2; S, 11.0%; $M^{+\cdot}$, 288.1385. $C_{14}H_{24}O_4S$ requires C, 58.3; H, 8.4; S, 11.1%; $M^{+\cdot}$, 288.1395); τ($CDCl_3$) 6.30 (6 H, s, CO_2CH_3) and 9.12 [9 H, s, $C(CH_3)_3$]: evidence for only one isomer was seen in n.m.r. spectra also taken in $CDCl_3$–HCl (sulphonium salt), C_6D_6, $C_6D_5NO_2$, and $CCl_2{=}CCl_2$; trans-4-*t-butylthianium bisethoxycarbonylmethylide* (6; $R^1 = OC_2H_5$), m.p. 78—79° (from light petroleum) (Found: C, 60.2; H, 8.6%; $M^{+\cdot}$ 316.1714. $C_{16}H_{28}O_4S$ requires C, 60.7; H, 8.9%; $M^{+\cdot}$, 316.1708); τ($CDCl_3$) 5.83 (4 H, q, $OC\mathit{H}_2CH_3$), 8.70 (6 H, t, $OCH_2C\mathit{H}_3$), and 9.12 [9 H, s, $C(CH_3)_3$]: evidence for only one isomer was seen also in $CDCl_3$–HCl, C_6D_6, $C_6D_5NO_2$, and $CCl_2{=}CCl_2$; trans-4-*t-butylthianium diacetylmethylide* (6; $R^1 = CH_3$), m.p. 153—155° (from light petroleum) (Found: $M^{+\cdot}$, 256.1502. $C_{14}H_{24}O_2S$ requires $M^{+\cdot}$, 256.1497); τ($CDCl_3$) 7.68 [6 H, s, $(COCH_3)_2$], 9.12 [9 H, s, $C(CH_3)_3$]: again only one isomer was seen in n.m.r. spectra taken in $CDCl_3$–HCl, C_6D_6, $C_6D_5NO_2$, and $CCl_2{=}CCl_2$. With a 20 molar excess of an equimolar mixture of dimethyl and di-isopropyl sulphides, dimethyl diazomalonate yielded a 5.3 : 1 mixture of the analogous sulphonium ylides, the mixture being analysed by comparison of the $\overset{+}{S}(CH_3)_2$ peak; τ($CDCl_3$) 7.12, with the lower of two peaks from the pairs of diastereotopic methyl groups, τ($CDCl_3$) 8.52 and 8.70 (each 6 H, d), corresponding to $\overset{+}{S}[CH(C\mathit{H}_3)_2]_2$. These peaks were well separated from others in the n.m.r. spectrum of the reaction mixture.

(ii) *Sulphimides derived from Ethoxycarbonylnitrene from Ethyl Azidoformate.*—Compounds of this type prepared by other workers [5] were yellow oils, readily decomposing on vacuum distillation and difficult to purify. We prepared the following: *SS*-dimethyl-*N*-ethoxycarbonylsulphimide [5b] (4; $R^1 = CO_2C_2H_5$; $R^2 = CH_3$), pale yellow oil (Found: $M^{+\cdot}$, 149.0508. Calc. for $C_5H_{11}NO_2S$: $M^{+\cdot}$, 149.0510); τ($CDCl_3$) 5.92 (2 H, q, $OC\mathit{H}_2CH_3$), 7.29 [6 H, s, $\overset{+}{S}(CH_3)_2$], and 8.75 (3 H, t, $OCH_2C\mathit{H}_3$); SS-*di-isopropyl*-N-*ethoxycarbonylsulphimide* [4; $R^1 = CO_2C_2H_5$; $R^2 = CH(CH_3)_2$], pale yellow oil (Found: $M^{+\cdot}$, 205.1136. $C_9H_{19}NO_2S$ requires $M^{+\cdot}$, 205.1136); τ($CDCl_3$) 5.89 (2 H, q, $OC\mathit{H}_2CH_3$), 6.89 [2 H, septet, $-\overset{+}{S}(CH\langle)_2$], 8.64 {12 H, d, $[CH(C\mathit{H}_3)_2]_2$; the diastereotopic methyls have in this case the same chemical shift}, and 8.71 (3 H, t, $OCH_2C\mathit{H}_3$); N-*ethoxycarbonylthian*-1-*imide* (13; $R = CO_2C_2H_5$) pale yellow oil, very slowly solidifying at 0° (Found: $M^{+\cdot}$ 189.0826. $C_8H_{15}NO_2S$ requires $M^{+\cdot}$, 189.0824); τ($CDCl_3$) 5.99 (2 H, q, $OC\mathit{H}_2CH_3$), 8.90 (3 H, t, $OCH_2C\mathit{H}_3$); N-*ethoxycarbonyl*-4-*t-butylthian*-1-*imides*, mixture of *cis*- and *trans*-forms in ratio (1.0 : 1 [(7a + 7b; $R^2 = CO_2C_2H_5$)], pale yellow oil slowly solidifying at room temperature and separating from ether as almost colourless needles, m.p. (decomp.) 100—140° (Found: C, 58.55; H, 9.65; N, 5.50; S, 13.05%; $M^{+\cdot}$, 245.1439. $C_{12}H_{23}NO_2S$ requires C, 58.75; H, 9.45; N, 5.7; S, 13.05%; $M^{+\cdot}$, 245.1439); τ($CDCl_3$) 5.92 (2 H, 2q, Δν between isomers, 1.5 Hz at 100 MHz, $OC\mathit{H}_2CH_3$), 8.76 (3 H, 2t, Δν between isomers 1.5 Hz, $OCH_2C\mathit{H}_3$), and 9.10 [9 H, s, $C(CH_3)_3$]. With a 20 molar excess of an equimolar mixture of dimethyl and di-isopropyl sulphides, a 1.0 : 1 mixture of the derived *N*-ethoxycarbonylsulphimides was obtained, the mixture being analysed by comparison of the signals $\overset{+}{S}(CH_3)_2$ and $\overset{+}{S}[C\mathit{H}(CH_3)_2]_2$ which were well clear of others in the n.m.r. spectrum ($CDCl_3$) of the mixture.

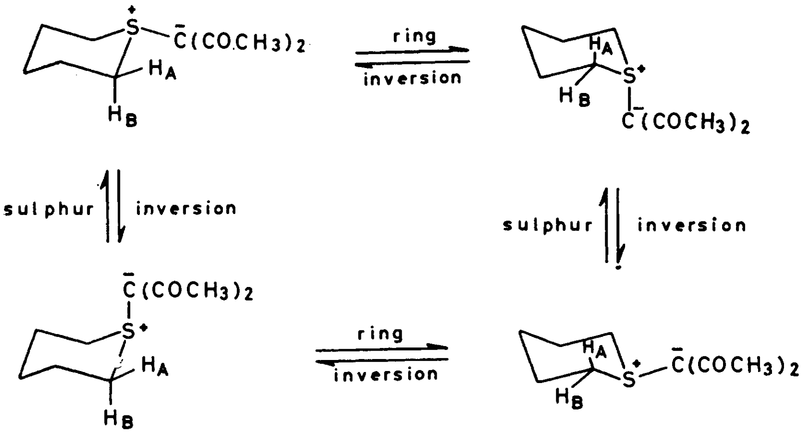
(iii) *Sulphimides derived from* p-*Tolylsulphonylnitrene from Toluene*-p-*sulphonyl Azide.*—We prepared the following: *SS*-dimethyl-*N*-*p*-tolylsulphonylsulphimide (4; $R^1 = p\text{-}CH_3C_6H_4SO_2$, $R^2 = CH_3$), m.p. 158.5—160° (lit.,[24] 157—157.5°), *SS*-di-isopropyl-*N*-*p*-tolylsulphonylsulphimide [4; $R^1 = p\text{-}CH_3C_6H_4SO_2$, $R^2 = CH(CH_3)_2$], m.p. 116—118° (lit.,[24] 117—118°), *N*-*p*-tolylsulphonylthian-1-imide (13; $R = p\text{-}CH_3C_6H_4SO_2$), m.p. 149—151° (lit.,[24] m.p. 148—149°), 4-t-butyl-*N*-*p*-tolylsulphonylthian-1-imides, mixture of *cis*- and *trans*-forms in ratio 1.0 : 1 [(7a + 7b; $R^2 = p\text{-}CH_3C_6H_4SO_2$)], m.p. 150—180° (from benzene) (Found: C, 59.4; H, 7.6; N, 4.3; S, 19.6%; $M^{+\cdot}$, 327.1334. Calc. for $C_{16}H_{25}NO_2S_2$: C, 58.7; H, 7.7; N, 4.3; S, 19.55%; $M^{+\cdot}$, 327.1327); τ($CDCl_3$) 2.23 and 2.80 (4 H, AB, *J* 8 Hz, Ar), 7.63 (3 H, s, CH_3), and 9.14 [9 H, 2s, Δν between isomers 2 Hz at 100 MHz, $C(CH_3)_3$]. Products, m.p. 150—151.5° and 187—188°, to which were assigned structures (7a and b), respectively, have previously [25] been prepared by thermal procedures; there was, however, some doubt expressed about the actual relationship between the two compounds described, and an attempt at photochemical preparation from the thian and the azide failed.[25]

From toluene-*p*-sulphonyl azide and a 20 molar excess of an equimolar mixture of dimethyl and di-isopropyl sulphides we obtained by the standard photochemical procedure described above mixed sulphimides in ratio 1.0 : 1 as determined from the n.m.r. spectrum by comparison of the peaks [τ($CDCl_3$)] at 7.33 [$\overset{+}{S}(CH_3)_2$] and 8.79 and 8.82 {diastereotopic methyls, each 6 H, d, *J* 7 Hz, $\overset{+}{S}[CH(C\mathit{H}_3)_2]_2$}. The position of the *S*-methyl peak seemed sensitive to (undetermined) conditions, varying up to ±0.05 p.p.m. from the value quoted with different preparations of the reaction mixture.

High-temperature N.m.r. Spectra.—Spectra of thianium diacetylmethylide (14) and of its 4-t-butyl derivative (6; $R^1 = CH_3$) in $C_6D_5NO_2$ showed similar patterns to those taken in $CDCl_3$, with no alteration of the type expected from configurational or conformational change associated with inversion at sulphur when the solutions were heated up to 150°. In particular, there was no exchange or progress towards exchange of the diastereotopic protons H_A and H_B in the thianium ylide (14) which in this solvent appeared as multiplets (both 2 H) centred on τ 5.5 and 7.25. Such exchange would require *both* ring inversion *and* inversion at sulphur, as illustrated [(14)].

Thermal Preparation of Sulphonium Ylides.—For comparison with the photochemically prepared compounds, two of the ylides, thianium diacetylmethylide (14) and its 4-t-butyl derivative (6; $R^1 = CH_3$) were also prepared by the copper(II) catalysis procedure. Diacetyldiazomethane (1 ml), the appropriate thian (2.5 ml), and anhydrous copper sulphate (50 mg) were heated together at 95° with vigorous stirring until all the diazo compound was decomposed (absence of i.r. band at 2 125 cm^{-1}); the process took 5 h for thian and 18 h for 4-t-butylthian. The reaction mixture was diluted with chloroform (50 ml) and filtered, the filtrate was distilled to remove the chloroform, and the residue was chromatographed on alumina. Unchanged thians were eluted with benzene and the ylides (70%) with chloroform. Their properties were identical with samples prepared as described above by the photochemical route; of particular note, only one stereoisomer was produced from 4-t-butylthian.

U.v. Spectroscopic Properties of Nitrene and Carbene Precursors and of Photochemical Products: Attempted Transylidations.—Aliphatic diazo-compounds used had $\lambda_{max.}$ (cyclohexane) 250 (ε 7 500) and 355 nm (23): derived sulphonium ylides had $\lambda_{max.}$ (methanol) 236 nm (ε 13 000); ε_{350} *ca.* 1. Ethyl azidoformate and derived sulphimides had no selective absorption in methanol above 220 nm; ε_{300} for both azido-ester and sulphimides was *ca.* 3, but the sulphimide samples were faintly yellow and (as noted above) difficult to purify; presumably the pure products are colourless. Toluene-*p*-sulphonyl azide had $\lambda_{max.}$ (methanol) 232 (ε 13 200) and 267 nm (ε 1 400); ε_{300} 45. Derived sulphimides had $\lambda_{max.}$ (methanol) 234 nm (ε 8 000—11 000); ε_{300} 9—16.



(14)

SS-Dimethyl-*N*-*p*-tolylsulphonylsulphimide (0.1 g) was suspended in di-isopropyl sulphide (2.7 g) and after deoxygenation the mixture was irradiated through Pyrex at 300 nm for 6 h at 20°, shaking frequently to maintain suspension of the insoluble sulphimide. The sulphide was then removed *in vacuo* and the residue examined by n.m.r. for incorporation of isopropyl residues, but no evidence for transylidation was obtained. A similar result was obtained with the sulphimide in di-t-butyl sulphide, and with *SS*-di-isopropyl-*N*-*p*-tolylsulphonylsulphimide in dimethyl sulphide.

Attempted Preparation of SS-*Di-t-butyl*-N-p-*tolylsulphonylsulphimide.*—Toluene-*p*-sulphonyl azide (0.4 g) in di-t-butyl sulphide (8 g) was deoxygenated and irradiated through Pyrex for 12 h at 300 nm by the standard procedure described above. The excess of sulphide was removed *in vacuo* at 35—45° and the residue was separated by t.l.c. (silica gel; $CHCl_3$) into recovered azide (0.16 g) and crude S-*t-butyl*-N-p-*tolylsulphonylsulphenamide* (9) of which the purest fraction (70 mg) had m.p. 73—76° (from light petroleum); $\tau(CDCl_3)$ 2.25 and 2.72 (4 H, AB, *J* 8 Hz, Ar), 4.21 (1 H, s, NH), 7.59 (3 H, s, ArC*H*$_3$), and 8.72 [9 H, s, $C(CH_3)_3$]. While the product was thermally stable for up to 2 h at 130° under anhydrous conditions, it was difficult to purify by further chromatography, apparently because of ease of hydrolysis to toluene-*p*-sulphonamide.

An attempt to prepare the sulphimide by an alternative (thermal) procedure [24] from di-t-butyl sulphide and chloramine T also failed, no definite product being isolated.

Competitive Reaction of p-*Tolylsulphonylnitrene with Dimethyl and Di-t-butyl Sulphides.*—A solution of toluene-*p*-sulphonyl azide in a 20 molar excess of an equimolar mixture of dimethyl and di-t-butyl sulphides was deoxygenated and irradiated through Pyrex for 6 h at 300 nm by the standard procedure described above. Excess of sulphides was removed *in vacuo* at 60° and the residue was analysed by n.m.r. spectroscopy: it consisted of *SS*-dimethyl-*N*-*p*-tolylsulphonylsulphimide (4; $R^1 = p\text{-}CH_3C_6H_4SO_2$, $R^2 = CH_3$), *S*-t-butyl-*N*-*p*-tolylsulphonylsulphenamide (9), and unchanged azide. The sulphimide : sulphenamide ratio was estimated at 1.2 : 1 by measurements of peaks [$\tau(CDCl_3)$] at 7.33 [$\overset{+}{S}(CH_3)_2$ in sulphimide] and 8.72 [$SC(CH_3)_3$ in sulphenamide]. As in the previous similar example, the position of the *S*-methyl peak in different preparations of reaction mixture varied by up to ±0.05 p.p.m. from the value stated.

Pyrolysis of SS-*Di-isopropyl*-N-p-*tolylsulphonylsulphimide.*—No reaction (n.m.r. observation) took place when the sulphimide [4; $R^1 = p\text{-}CH_3C_6H_4SO_2$, $R^2 = CH(CH_3)_2$] was heated for 5 h at 65°, but decomposition started slowly at 100°. On being heated in the range 100—130° the sulphimide gave a product with an n.m.r. spectrum in agreement with that expected for *S*-isopropyl-*N*-*p*-tolylsulphonylsulphenamide (10): $\tau(CDCl_3)$ 2.21 and 2.73 (4 H, AB, *J* 8 Hz, Ar), 4.07 (1 H, s, NH), 6.75 [1 H, septet, C*H*$(CH_3)_2$], 7.60 (3 H, s, ArC*H*$_3$), 8.85 [6 H, d, CH(C*H*$_3$)$_2$]. On further heating, this spectrum was replaced by that of toluene-*p*-sulphonamide: $\tau(CDCl_3)$ 2.20 and 2.72 (4 H, AB, *J* 8 Hz, Ar), 5.16 (2 H, s, NH_2), and 7.60 (3 H, s, $ArCH_3$). Heating at 130° for 1 h gave the greatest proportion of sulphenamide with respect to sulphimide and sulphonamide, and a crude specimen having the appropriate n.m.r. spectrum was isolated by t.l.c. (silica gel; $CHCl_3$; yield 33% from sulphimide). On being heated this product was rapidly converted into toluene-*p*-sulphonamide. In another experiment, when the sulphimide was decomposed by being heated to 140—150°, the evolved gases were passed through

Brady's reagent (a solution of 2,4-dinitrophenylhydrazine in alcoholic sulphuric acid). Hydrogen sulphide (smell; lead acetate paper blackened) was produced together with a yellow precipitate, which on recrystallisation from alcohol had m.p. 125—126°, undepressed on admixture with authentic acetone 2,4-dinitrophenylhydrazone. The pyrolysis mixture gave further evidence of formation of thioacetone by low resolution mass spectrometry, *m/e* 296 (tetramer) and 222 (trimer).

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