Generation of Nitrenes from Alkanamidates and Alkanesulphonamidates

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N-Trimethylammoniododecanesulphonamidate and *N*-trimethylammoniododecanamidate have been degraded thermolytically and photolytically in nonaqueous solvents. Thermal decomposition of the sulphonamidate yielded a sulphonyl nitrene which was trapped by nucleophiles. The sulphonamidate was stable towards u.v. radiation. The alkanamidates decomposed thermally to give undecyl isocyanate by a concerted intramolecular process which did not involve the formation of a nitrene intermediate. Dodecanoyl nitrene, generated by photolysis of the alkanamidated in dimethyl sulphoxide, has been compared with similar nitrenes obtained photolytically from acyl azides. The electronic states of the nitrene intermediates are discussed.

By analogy with azides, sulphonamidates (I) and alkanamidates (II) are potential sources of sulphonyl and acyl nitrenes. Although both types of amidates have been known for some time,^{1, 2} little has been published on their properties.

$$\begin{array}{ll} \operatorname{RSO}_{2} \cdot \bar{N} \cdot \bar{N} \operatorname{Me}_{3} & \operatorname{RCO} \cdot \bar{N} \cdot \bar{N} \operatorname{Me}_{3} \\ (I) & (II) \\ a; R = p \text{-tolyl} & a; R = Ph \\ b; R = n \text{-}C_{12} \operatorname{H}_{25} & b; R = n \text{-}C_{11} \operatorname{H}_{23} \end{array}$$

N-Trimethylammoniotoluene-p-sulphonamidate¹ (Ia) was reduced by zinc and acetic acid to trimethylamine and toluene-p-sulphonamide; oxidation with hydrogen peroxide also gave the sulphonamide. Pyrolysis of *N*-trimethylammoniobenzamidate (IIa) was shown to give phenyl isocyanate³ whereas the related amidate (III) at elevated temperatures underwent⁴ a Stevens rearrangement. This reaction provides good evidence that the site of the negative charge in these compounds is the nitrogen atom. Nevertheless, the fact that the amidate (III) could be *O*-alkylated showed that the anion was stabilised in part by delocalisation through the carbonyl group.⁴



In the present work, the amidates (Ib) and (IIb) have been thermally and photolytically decomposed in nonaqueous solvents and attempts have been made to trap any reactive fragments which are formed by reaction with suitable substrates.

Thermolyses

N-Trimethylammoniododecanesulphonamidate (Ib).— Thermal decomposition of the sulphonamidate (Ib) in dimethyl sulphoxide at 170° was complete after 6 hr.

¹ S. Wawzonek and D. Meyer, J. Amer. Chem. Soc., 1954, 76, 2918.
 ² R. L. Hinman and M. C. Flores, J. Org. Chem., 1959, 24, 660.
 ³ M. S. Gibson and A. W. Murray, J. Chem. Soc., 1965, 880.

when no further trimethylamine was evolved. Two products only, dodecanesulphonamide (V) and the sulphoximine (VI) were formed, both of which can be accounted for by assuming that a sulphonyl nitrene (IV) is an intermediate in the reaction.

$$\begin{array}{ccc} C_{12}H_{25}SO_{2}\cdot\bar{N}\cdot\overset{+}{N}Me_{3} & & Me_{3}N + [C_{12}H_{25}SO_{2}\cdot N] \\ (Ib) & & (IV) \\ & & & \\ & \\ & & \\$$

The behaviour of sulphonyl azides has been shown to be analogous. Upon heating sulphonyl azides in pyridine ⁵ pyridiniosulphonamidates (VII) and sulphonamides were obtained, again by way of an intermediate nitrene.

$$RSO_2N_3 \rightarrow \boxed{RSO_2 \cdot N} \xrightarrow{\text{Pyridine}} RSO_2 \overline{N} - \overset{+}{N} \xrightarrow{(VII)} + RSO_2 \cdot NH_2$$

Sulphonyl nitrenes have also been generated by heating sulphonyl azides in dimethyl sulphoxide, the nitrenes being trapped by reaction with the solvent to give sulphoximines.⁶

The sulphonamidate (Ib), in decalin, decomposed at ca. 170° and in the presence of triphenylphosphine yielded the addition product $C_{12}H_{25}SO_2\cdot N=PPh_3$ (VIII) as well as dodecanesulphonamide. Even with less than one equivalent of triphenylphosphine and with a large excess of decalin, considerable amounts of compound (VIII) were still formed, thus providing evidence of the electrophilic nature of the nitrene intermediate. Furthermore, when a five-fold excess of triphenylphosphine was used, but still with a large excess of decalin, the formation of dodecanesulphonamide was completely suppressed and an increased yield of the triphenylphosphine imide (VIII) resulted.

N-Trimethylammoniododecanamidate (IIb).— Upon heating the dodecanamidate (IIb) in dimethyl sulphoxide to 170° it decomposed smoothly to give di-nundecylurea (X) as the only product (shown by t.l.c.).

⁶ L. Horner and A. Christmann, Chem. Ber., 1963, 96, 388.

⁴ S. Wawzonek and E. Yeaker, J. Amer. Chem. Soc., 1960, **82**, 5718.

⁵ (a) J. N. Ashley, G. L. Buchanan, and A. P. T. Easson, J. Chem. Soc., 1947, 60; (b) G. L. Buchanan and R. M. Levine, J. Chem. Soc., 1950, 2248.

This must be formed from undecyl isocyanate (IX) by interaction with moisture during the course of the reaction. Similarly, the urea (X) was the only product when the thermolysis was performed in decalin containing an excess of triphenylphosphine. Thus, there is no evidence for the formation of an intermediate nitrene and a concerted mechanism is postulated for this reaction.

$$\begin{array}{ccc} C_{11}H_{23} & \overbrace{C=N}^{T} & \overbrace{N}^{T}Me & \longrightarrow & Me_{3}N + C_{11}H_{23} \cdot N:C:O \\ & \swarrow & \swarrow & H_{2}O & (IX) \\ & & & & & \\ (IIb) & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & & & & \\ & & & & &$$

Because of the known difficulty in obtaining anhydrous trimethylammoniododecanamidate, no attempt was made to run these experiments under strictly anhydrous conditions.

The thermal rearrangement of acyl azides to isocyanates (Curtius rearrangement) has usually been formulated 7,8 as proceeding through an intermediate nitrene, $RCON_3 \longrightarrow [RCON] \longrightarrow RN:C:O.$ However, as with the alkanamidates, a nitrene has never been trapped from such reactions and isocyanates are the sole products. In some cases, direct comparison of the photolytic and thermolytic decompositions of acyl azides has revealed a different reaction course 9, 10 and nitrenes have been trapped from photolytic processes where the corresponding thermal reaction has given only an isocyanate. It is probable that a discrete nitrene is not involved in the thermal rearrangement (a view which has also been expressed by Lwowski et al.⁹) and the most likely mechanism is a concerted process in which the loss of nitrogen and migration of alkyl group occur simultaneously.

$$\begin{array}{c} & & \\ R - C - N = N \\ & \\ 0 \\ & \\ 0 \\ \end{array} \xrightarrow{} N = N \\ & \\ N_2 + RN:C:O \\ \\ & \\ 0 \\ \end{array}$$

Photolyses

N-Trimethylammoniododecanesulphonamidate (Ib).---The sulphonamidate (Ib) was stable to irradiation in dimethyl sulphoxide, and also in dimethylsulphoxidebenzene; irradiation at 80° also failed to effect decomposition. These results reflect the increased stability of sulphonamidates over sulphonyl azides. The latter compounds are decomposed ⁶ by irradiation in dimethyl sulphoxide or dimethyl sulphide, solvents which trap the nitrene intermediates to form sulphoximines and sulphidimines respectively. In our own experiments we have observed that dodecanesulphonyl azide, when photolysed in dimethyl sulphoxide gave not only the

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corresponding sulphoximine but also a small amount of dodecanesulphonamide.

N-Trimethylammoniododecanamidate (IIb).— N-Trimethylammoniododecanamidate (IIb) was decomposed only very slowly by u.v. radiation. After prolonged (48 hr.) irradiation in dimethylsulphoxide much starting material remained and the only isolable product was dodecanamide (XII). This product is indicative of the formation of an intermediate nitrene (XI) which reacts by abstraction of hydrogen from the solvent. The nitrene appears to have no marked electrophilic character judging by its inability to form a sulphoximine with dimethyl sulphoxide.

$$\begin{array}{c} C_{11}H_{23}CO \cdot \bar{N} \cdot \bar{N}Me_{3} \longrightarrow \begin{bmatrix} C_{11}H_{23}CON \end{bmatrix} \\ (IIb) & (XI) \\ & \xrightarrow{Me_{2}SO} C_{11}H_{23}CO \cdot NH_{2} \\ & (XII) \end{array}$$

Nitrenes have often been trapped as amides during the photolysis of acyl azides.¹¹ However, the formation of a primary amide (XII) only, on photolysis of the dodecanamidate was somewhat surprising since Horner and Christmann⁶ found that photolysis of benzazide in dimethyl sulphoxide gave a small amount of the Curtius rearrangement product and also a sulphoximine (XIII) but no benzamide. We confirmed these results and also noted that benzanilide was formed in a yield comparable to that of the sulphoximine.

$$\frac{h\nu}{Me_2SO} \rightarrow PhCO \cdot N=S(O)Me_2 + PhCO \cdot NHPh$$
(XIII)

Horner et al.,¹² in much earlier work observed that photolysis of benzazide in an inert solvent followed by addition of aniline to the photolysate afforded a mixture of benzanilide and diphenylurea. Anselme 13 confirmed this result using benzonitrile as solvent and also examined the photolysate before addition of aniline; in this case dibenzamide, PhCO·NH·COPh was isolated. It was suggested 13 therefore that these reactions involved formation of benzovl nitrene which dimerised to an azo-compound. Reaction of the latter with added aniline or with further benzoyl nitrene explained the formation of benzanilide and dibenzamide. In the present work, no aniline was added to the photolysate and no dibenzamide was formed in the reaction; a different mechanism must therefore be operative.

When dodecanoyl azide was photolysed in dimethyl sulphoxide a more complex mixture of products was obtained. Here, apparently the same nitrene (XI) as that obtained from trimethylammoniododecanamidate

⁷ C. K. Ingold, ' Structure and Mechanism in Organic Chemis-

<sup>try, G. Bell, London, 1953, pp. 497-500.
Sidgwick's Organic Chemistry of Nitrogen,' Oxford University Press, Oxford, 1966, p. 500.
W. Lwowski and G. T. Tisue, J. Amer. Chem. Soc., 1965, 87, (202)</sup>

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¹⁰ J. W. ApSimon and O. E. Edwards, Canad. J. Chem., 1952, 40, 896. ¹¹ R. A. Abramovitch and B. A. Davis, *Chem. Rev.*, 1964, 64,

^{171.} 12 L. Horner, E. Spietschka, and A. Gross, Annalen, 1951, 573,

^{17.}

¹³ J.-P. Anselme, Chem. and Ind., 1966, 1794.

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was formed, but it underwent different reactions. A sulphoximine (XIV) and the Curtius rearrangement products (XV) and (X) were isolated * but no dodecanamide (XII) was found. Two minor products of the reaction were identified as the carbamoyl azide (XVI) and N-undecyldodecanamide (XVII).

$$\begin{array}{ccc} C_{11}H_{23} \cdot \text{CON}_3 & \xrightarrow{h\nu} & \begin{cases} C_{11}H_{23} \cdot \text{CO} \cdot \text{N} = \text{S}(\text{O})\text{Me}_2 & (\text{XIV}) \\ C_{11}H_{23} \cdot \text{N} : \text{CO} & (\text{XV}) \\ C_{11}H_{23} \cdot \text{N} : \text{CO} \cdot \text{NI} \end{bmatrix} \longrightarrow & \begin{cases} C_{11}H_{23} \cdot \text{N} : \text{CO} \cdot \text{N} = \text{S}(\text{O})\text{Me}_2 & (\text{XIV}) \\ C_{11}H_{23} \cdot \text{N} : \text{CO} \cdot \text{NI} + \text{S}(\text{O}) & (\text{XV}) \\ C_{11}H_{23} \cdot \text{N} : \text{CO} \cdot \text{NI} + \text{S}(\text{O}) & (\text{XVI}) \\ C_{11}H_{23} \cdot \text{N} : \text{CO} \cdot \text{CO} \cdot \text{I} & (\text{XVI}) \\ C_{11}H_{23} \cdot \text{N} : \text{CO} \cdot \text{CO} \cdot \text{I} + \text{I}_{23} & (\text{XVII}) \end{cases} \end{array}$$

Thus, although dodecanovl nitrene (XI) may be generated by the photolysis of either the dodecanamidate (IIb) or dodecanoyl azide in dimethyl sulphoxide the subsequent behaviour of the nitrene is different in each case. This difference may be explained by assuming different electronic states for the nitrenes.

Nitrenes can exhibit the properties either of triplet diradicals, R-N. (ground state), or of singlet electrophilic reagents, R-N (excited state), and an estimate of which of these forms is liberated is difficult to make with certainty on the basis of the nature of the final products alone. The e.s.r. spectra of several nitrenes generated photolytically at 77° k have been attributed to the triplet ground state.¹⁴

In the present work the dodecanovl nitrene (XI), generated photolytically from the amidate (IIb), was not an electrophile and its only reaction was to abstract two atoms of hydrogen from the solvent. This species must be regarded as the triplet nitrene, since it has radical, but no electrophilic character. The same nitrene (XI), generated by photolysis of dodecanoyl azide, showed typical electrophilic character in its reaction with dimethyl sulphoxide and significantly did not abstract hydrogen to form a primary amide. This behaviour is ascribed to that of a singlet species and on the basis of these comparisons it is possible to define the types of products obtained from triplet and singlet acyl nitrenes. Triplet acyl nitrenes do not react with nucleophiles but abstract two atoms of hydrogen from the solvent to give primary amides. Singlet acyl nitrenes do not abstract hydrogen in radical processes and will combine with any suitable nucleophile which is present.

Irrespective of its method of preparation, the sulphonyl nitrene (IV) reacted with added nucleophiles and also abstracted hydrogen from solvent molecules. Possibly, the singlet nitrene is liberated initially but a competing process of singlet-to-triplet decay occurs, and therefore both electronic forms contribute to the final product mixture. Some support for this is provided by recent work on the generation of ethoxycarbonylnitrene by an α -elimination process.¹⁵ It was found that singlet ethoxycarbonylnitrene was initially

formed and this species added stereospecifically to olefins, but some decay to the triplet state occurred also, and the latter added to olefins in a non-stereospecific manner.

EXPERIMENTAL

Spectra.-I.r. spectra were recorded with a Perkin-Elmer 'Infracord' spectrophotometer as Nujol mulls, and ¹H n.m.r. spectra were recorded in deuteriochloroform using a Varian HA-60 spectrometer with tetramethylsilane as internal reference.

Chromatography.-Silica gel and aluminium oxide (Hopkin and Williams) were used for column chromatography and silica gel (Merck, grade G) was used for t.l.c. Chromatograms were developed with iodine or a dilute solution of dichlorofluorescein in ethanol. V.p.c. was performed at 150° on an Argon chromatograph (Pve) using a stationary phase of Apiezon L.

Irradiations.-A Hanovia 1-1. Photochemical reactor with low-pressure mercury source was used.

Materials.—All m.p.'s are uncorrected. Light petroleum refers to the fraction, b.p. 60-80°. The amidates (Ib) and (IIb) were prepared as previously described.¹⁶

Thermolysis of N-Trimethylammoniododecanesulphonamidate (Ib).-(a) In dimethylsulphoxide. Dimethyl sulphoxide (15 ml.) was heated to 170° (oil-bath temperature) in a stream of nitrogen and, during 10 min., a solution of N-trimethylammoniododecanesulphonamidate (1.04 g.) in dimethyl sulphoxide (8 ml.) was added. After 6 hr. at this temperature evolution of trimethylamine had ceased. Solvent was removed under reduced pressure and the residue was shown (t.l.c.) to contain two components but no starting material. Chromatography on silica gel (100 g.) afforded (elution with 1:1 benzene-ether) dodecanesulphonamide (344 mg.), m.p. and mixed m.p. 88°. Prolonged elution with the same solvent or more rapidly with ether-ethyl acetate (19:1) and gave the sulphoximine (VI) (720 mg.), m.p. 83.5-84.5° (from ether-light petroleum) (Found: C, 51.7; H, 9.6. C₁₄H₃₁NO₃S requires C, 51.7; H, 9.5%), v_{max} 1060 cm.⁻¹ (SO); n.m.r.: τ 9.12 (C–Me), 8.71 (9H₂), 8.12 (broad, 1 H₂), 6.80 (triplet, -CH₂·SO₂), 6.60 (SOMe₂).

(b) In decalin containing triphenylphosphine. A solution of triphenylphosphine (2.6 g., 0.01 mole) in decalin (80 ml.) was heated, under nitrogen, to 165° and a solution of the sulphonamidate (3.05 g., 0.01 mole) in decalin (20 ml.) and chloroform (30 ml.) was added. Chloroform was distilled off and the solution was maintained at 180° until trimethylamine evolution had ceased (8 hr.). The solution was concentrated under reduced pressure and t.l.c. showed that only components with the same $R_{\rm F}$ values as dodecanesulphonamide and the triphenylphosphine imide (VIII) were present. Chromatography on alkaline alumina (250 g.) resolved the mixture and elution with benzene-ether (9:1) gave the imide (VIII) (1.32 g.) m.p. $67.5-68.5^{\circ}$ (from light petroleum) (Found: C, 70.8; H, 8.0. C30H40NO2PS requires C, 70.7; H, 7.9%); n.m.r. spectrum: τ 9.13 (C-Me), 8.87 (9H₂), 8.27 (broad, 1H₂), 7.20 (triplet, ·CH₂SO₂) and $2 \cdot 53 - 2 \cdot 20$ (aromatic multiplet, 15H).

^{*} Note added in proof: W. Lwowski et al. (J. Amer. Chem. Soc., 1967, **89**, 6308) have shown that under photolytic condi-tions, isocyanate formation from acyl azides occurs by a concerted process occurring simultaneously with nitrene formation. GG

¹⁴ G. Smolinsky, E. Wasserman, and W. A. Yager, J. Amer. C. omonissy, E. wasserman, and W. A. Yager, J. Amer. Chem. Soc., 1962, 84, 3220. ¹⁵ J. S. McConaghy and W. Lwowski, J. Amer. Chem. Soc., 1967, 89, 2357.

¹⁶ R. W. H. Berry and P. Brocklehurst, J. Chem. Soc., 1964, 2264

In two further experiments, the sulphonamidate (0.92 g. 0.003 mole) was treated as before in decalin (40 ml.) containing triphenylphosphine[(a) 0.0015 mole] and [(b) 0.015 mole]. After chromatography on neutral alumina the products obtained were, in experiment (a), dodecane-sulphonamide (0.36 g.) and the imide (VIII) (0.25 g.), and (b), the imide (VIII) (0.84 g.) with no dodecane-sulphon-amide.

Thermolysis of N-Trimethylammoniododecanamidate (IIb). —(a) In dimethyl sulphoxide. Dimethyl sulphoxide (15 ml.) was heated, under nitrogen, to 150° and a solution of the dodecanamidate (2·0 g.) in dimethyl sulphoxide (10 ml.) was added. After 4 hr. at 150—170° trimethylamine evolution had ceased. Evaporation of the solvent under reduced pressure left a crystalline residue which was triturated with ether to give NN'-di-n-undecylurea (0·6 g.) m.p. 108° (benzene) (lit.,¹⁷ m.p. 105°) (Found: C, 74·9; H, 12·9. Calc. for C₂₃H₄₈N₂O: C, 75·0; H, 13·0%), v_{max}. 1630 (CO), 3400 (NH), and 1590 cm.⁻¹ (amide II); n.m.r. spectrum: τ 9·14 (C-Me), 8·70 (CH₂), 6·90 (CH₂-NH), and 4·54 (NH). The residues from the work up were examined by t.l.c. and column chromatographed on silica gel Further quantities of diundecylurea were obtained but no other compound was detected.

(b) In decalin containing triphenylphosphine. A solution of trimethylammoniododecanamidate (1.25 g., 4.9 mmole) and triphenylphosphine (2.6 g., 10 mmole) in decalin (15 ml.) was heated under nitrogen at 170° until no more trimethylamine was evolved (5—6 hr.). Decalin was distilled off under reduced pressure and chromatography on silica gel gave di-n-undecylurea (m.p. 108°). No other product could be detected.

Photolysis of N-Trimethylammoniododecanamidate (IIb).— The dodecanamidate (1.5 g.) in dimethyl sulphoxide (25 ml.) was irradiated for 48 hr. with a source emitting at 180 and 254 mµ; no undecyl isocyanate could be detected by g.l.c. Dimethyl sulphoxide was distilled off at 50° under reduced pressure and the dark residue was found (by t.l.c.) to contain two components, one of which was indistinguishable from the starting material. Chromatography on silica gel (100 g.) gave a small amount of dark, intractable oil, and then dodecanamide (0.17 g. eluted with benzene-ether, 1:1) m.p. and mixed m.p. 97—99° (from light petroleum). The i.r. spectrum was identical with that of an authentic specimen. Starting material was obtained on elution with methanol-ether (1: 3).

Irradiation of N-Trimethylammoniododecanesulphon-

amidate (Ib).—The sulphonamidate (200 mg.) in dimethyl sulphoxide (20 ml.) was irradiated for 48 hr. No reaction occurred, and repetition of the experiment in dimethyl sulphoxide-benzene and in ethanol also gave negative results. No reaction was observed when the sulphonamidate was irradiated in dimethyl sulphoxide-benzene at 80° .

Photolysis of Benzoyl Azide.—Benzoyl azide ¹⁸ (1 g.) in dimethyl sulphoxide (25 ml.) was irradiated for 8 hr. The solution was diluted with water (25 ml.) and extracted with chloroform (2 \times 25 ml.). The extract was washed several times with water to remove dimethyl sulphoxide, dried (Na₂SO₄) and shaken with decolourising charcoal. Evaporation under reduced pressure left a residue (0.85 g.) which showed two major components on t.l.c. using

¹⁷ T. Curtius, J. prakt. Chem., 1914, [2], 89, 518.

¹⁸ E. W. Barrett and C. W. Porter, *J. Amer. Chem. Soc.*, 1941, **63**, 3434.

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benzene-ether solvent systems. Small amounts of other materials which ran as streaks were also present. Chromatography on silica gel (50 g.) gave two fractions which were (a) benzanilide (215 mg.) eluted with benzene-ether (4:1), m.p. and mixed m.p. 160° (from aqueous acetone), and (b) N-benzoyl-SS-dimethylsulphoximine (250 mg.), eluted with ether, m.p. 107-108° (from water) (lit.,6 m.p. 107—108°) (Found: \bar{C} , 55·1; H, 5·4. Calc. for $C_9H_{11}NO_2S$: C, 54.8; H, 5.6%), v_{max} , 1605 (CO), and 1030 cm.⁻¹ (SO). Photolysis of Dodecanoyl Azide.-The azide was prepared by shaking an ethereal solution of dodecanoyl chloride (8 g.) with aqueous sodium azide (4 g.) at room temperature for 2 hr. The ether layer was separated and dried (Na_2SO_4) . The i.r. spectrum of a sample showed absorption at 2128 (azide) and 1724 cm.⁻¹ (acyl azide carbonyl). There was no absorption at 1786 or 2250 cm.⁻¹ which could be attributed to acid chloride or isocyanate.

Dimethyl sulphoxide (25 ml.) was added to the azide solution and ether was removed by evaporation under reduced pressure at 18°. The resulting solution was photolysed for 8 hr. and the reaction products were isolated by chloroform extraction. The chloroform was evaporated and the residue was dissolved in hot benzene. On cooling the solution NN'-diundecylurea (1.1 g.), m.p. 101-103°, separated. The residue (4.8 g.) was chromatographed on silica gel (250 g.). Elution with benzene gave in order of retention (a) undecyl isocyanate (0.93 g.) and (b) undecylcarbamoyl azide (0.35 g.), m.p. and mixed m.p. 52° (from light petroleum); $v_{max.} 3320$ (NH), 2150 (N₃), 1680 (CO), and 1545 cm.⁻¹ (amide \overline{II}); the i.r. spectrum was identical with that of an authentic sample. Further elution with benzene-ether (4:1) afforded N-undecyldodecanamide (1.4 g.), (ethanol), m.p. and mixed m.p. 77–81°; v_{max} 3300 (NH), 1640 (CO), and 1560 cm.⁻¹ (amide II). Finally, elution with ether gave the sulphoximine (XIV) (0.41 g.) m.p. 78-79° (from light petroleum) (Found: C, 61.2; H, 10.4. $C_{14}H_{29}NO_2S$ requires C, 61.0; H, 10.5%), v_{max} 1625 cm.⁻¹ (SO), n.m.r. spectrum: τ 9.12 (C-Me), 8.73 (9H₂), 7.68 (·CH₂CO·), and 6.70 (Me₂SO·).

Photolysis of Dodecanesulphonyl Azide.—The azide (1.55 g.) in dimethyl sulphoxide (30 ml.) was irradiated for 8 hr. The solution was diluted with chloroform, washed several times with water and dried (Na_2SO_4) . Examination by t.l.c. showed the presence of two compounds with the same $R_{\rm F}$ values as dodecanesulphonamide and the sulphoximine (VI). Chromatography of the crude product (1.4 g.) on silica gel (65 g.) as previously described gave the sulphonamide (0.13 g.) and the sulphoximine (VI) (0.42 g.), m.p. $82-83^{\circ}$ (from ether-light petroleum). Unchanged sulphonyl azide (0.53 g.) was also recovered from the reaction mixture.

SS-Dimethyl-N-dodecanesulphonylsulphoximine (VI).—Dimethylsulphoximine ¹⁹ (0.53 g.) was treated with dodecanesulphonyl bromide (1.78 g.) in pyridine (5 ml.) for 16 hr. at 20°. Water (2 drops) was added and after 1 hr. the solution was poured into water, and a crystalline product (1.4 g.) was isolated with chloroform. Three recrystallisations from ether-light petroleum gave the sulphoximine, m.p. 83° (not depressed on admixture with the previous sample).

N-Dodecanesulphonyl-PPP-triphenylphosphine Imide (VIII).—Sodium azide (2 g.) in water (15 ml.) was added dropwise at 0° to a solution of dodecanesulphonyl bromide ¹⁹ H. R. Bentley and J. K. Whitehead, J. Chem. Soc., 1950, 2081. (5 g.) in acetone (90 ml.) and the solution was stirred for 2 hr. Water was added, and extraction with chloroform gave the azide (v_{max} . 2120 cm.⁻¹). Without further purification, a portion of the azide (1·3 g.) in benzene (5 ml.) was treated with a solution of triphenylphosphine (1·2 g.) in benzene (10 ml.). The resulting solution was gently warmed until no more nitrogen was released (10 min.) and then was evaporated to dryness to give N-dodecane-sulphonyl-PPP-triphenylphosphine imide (1·5 g.) m.p. 67--68° (from light petroleum) (not depressed on admixture with the previous sample).

Undecylcarbamoyl Azide (XVI).—To a solution of undecyl isocyanate (1 g.) in chloroform (5 ml.) was added a solution of hydrazoic acid in chloroform (4% solution; $6\cdot3$ ml.). The solution was kept at 50° for 1 hr. and was then set aside overnight at 20°; finally it was heated at 50° for a further 1 hr. Solvent was removed under reduced pressure to give the *azide* (XVI) (0.7 g.) m.p. 53° (from light petroleum) (Found: C, 60.1; H, 10.05. C₁₂H₂₄N₄O requires C, 60.0; H, 10.0%), $\nu_{max.}$ 3320, 2150, 1680, and 1545 cm.⁻¹.

N-Undecyldodecanamide (XVII).—Undecylamine (0.85 g.) in pyridine (5 ml.) was treated with dodecanoyl chloride (1.09 g.). After 1 hr. the semisolid reaction mixture was poured into iced water and filtered to yield the *amide* (1.2 g.), m.p. 80—81° (from ethanol) (Found: C, 78.2; H, 13.1. $C_{23}H_{47}NO$ requires C, 78.2; H, 13.3%). The i.r. spectra of the two samples of amide (XVII) were identical.

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