(15) K. M. Johnston, G. H. Williams, and H. J. W. Williams, *J. Chem. Soc. B*, 1117 (1966).
(16) G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Chem. Soc. B*, 401 (1970).
(17) (a) S. Terabe and R. Konaka, *J. Amer. Chem. Soc.*, **91**, 5655 (1969); (b) O. E. Edwards, D. H. Paskovich, and A. H. Reddoch, *Can. J. Chem.*, **51**, 978 (1973).
(18) S. Terabe and R. Konaka, *J. Chem. Soc., Perkin Trans. 2*, 2163 (1972).
(19) We thank Dr. Wayne C. Danen for carrying out these experiments.
(20) Private communications from Dr. Danen and Dr. E. G. Janzen.
(21) We thank Dr. Konaka for the gift of a sample of **24**.
(22) L. F. Audrieth, J. R. Weisiger, and H. E. Carter, *J. Org. Chem.*, **6**, 417 (1941).
(23) S. F. Nelsen and D. H. Heath, *J. Amer. Chem. Soc.*, **91**, 6452 (1969).
(24) M. F. Capelli, A. Garzia, E. Kraushaar-Baldauf, and W. Semeria, *Ann. Chim. (Rome)*, **47**, 1225 (1957).
(25) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1964, p 332.
(26) Reference 25, p 329.
(27) B. A. Geller and L. S. Samosvat, *Zh. Obshch. Khim.*, **31**, 1681 (1961); *Chem. Abstr.*, **55**, 22194*h* (1961).
(28) F. R. Storrie and S. H. Tucker, *J. Chem. Soc.*, 2255 (1931).
(29) G. T. Morgan and J. G. Mitchell, *J. Chem. Soc.*, 3283 (1931).
(30) P. Ziersch, *Ber.*, **42**, 3797 (1909).
(31) T. S. Stevens and S. H. Tucker, *J. Chem. Soc.*, **123**, 2143 (1923).
(32) N. P. Buu-Hoi and R. Royer, *J. Org. Chem.*, **15**, 123 (1950).
(33) W. Lüttke, *Z. Elektrochem.*, **61**, 313 (1957).
(34) J. Burgers, W. van Hartingsveldt, J. van Keulen, P. E. Verkade, H. Visser, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **75**, 1327 (1956).
(35) J. E. Baldwin, A. K. Qureshi, and B. Sklarz, *J. Chem. Soc. C*, 1076 (1969).
(36) H. G. Aurich, *Ber.*, **101**, 1761 (1968).
(37) We thank Professor A. J. Bard and Miss Ann Lomax for many of the simulations and assisting J.-D. C. in simulation of some spectra.

The Reaction of Methanesulfonyl Nitrene with Benzene. Attempts to Generate Sulfonyl Nitrenes from Sources Other than the Azides

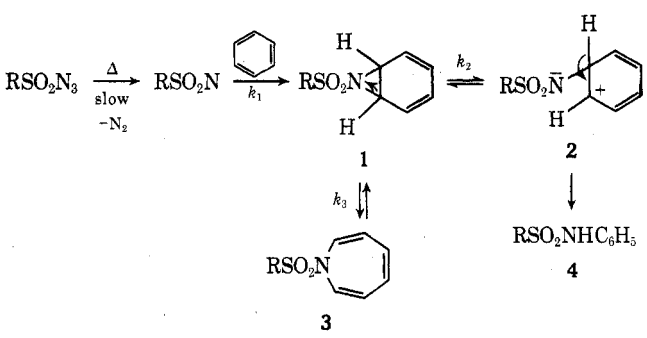
R. A. Abramovitch,* T. D. Bailey, T. Takaya, and V. Uma

Departments of Chemistry, University of Saskatchewan, Saskatchewan, Canada, and The University of Alabama, University, Alabama 35486

Received September 10, 1973

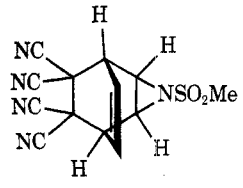
The reaction of methanesulfonyl nitrenes with benzene and other aromatic compounds has been studied in detail. The results have been rationalized in terms of the addition of the singlet nitrene to the aromatic molecule to give a benzaziridine intermediate which, under kinetic control conditions, gives the *N*-mesylazepine and, under conditions of thermodynamic control, gives the *N*-mesylanilines. While the azepines could not be detected in the thermolysis at 120° they could be trapped with tetracyanoethylene. At lower temperatures the *N*-mesylazepine itself could be isolated. Numerous attempts have been made at generating singlet sulfonyl nitrenes under mild conditions either by photolysis of sulfonyl azides or from nonazide precursors. No encouraging results were obtained.

Thermal decomposition of sulfonyl azides in aromatic solvents occurs slowly at 120°. The decomposition is unimolecular,[1] leading to a singlet nitrene.[2] This is followed by an addition to the aromatic nucleus to give a benzaziridine intermediate (**1**), with ring opening of the latter to form the observed *N*-sulfonamides[2] being a relatively fast, thermodynamically controlled process. The unsubstituted primary sulfonamides, products of hydrogen abstraction by the nitrene, are also formed in these reactions. In contrast to the reactions with ethyl azidoformate[3] and with cyanogen azide,[4] no sulfonylazepine (**3**) could be detected, even by thin layer chromatography which was shown, in control experiments, to permit detection of *ca.* 0.1% of **3**.

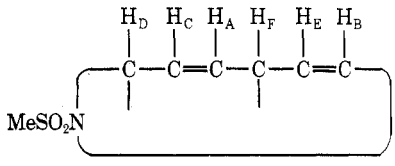


In an attempt to trap the benzaziridine **1**, the reaction between methanesulfonyl azide and benzene was repeated at 120° in the presence of tetracyanoethylene (TCNE).[5,6] A crystalline 1:1 adduct, $C_{13}H_9N_5O_2S$, was obtained (29.4%) and was formed at the expense of **4**, whose yield dropped from 54 to 6%. Methanesulfonamide (19%, up from 14%) was also obtained. The nmr spectrum of the adduct indicated clearly that it was not the symmetrical product **5** that would have resulted from a $[\pi 2_s + \pi 4_s]$ addition of TCNE to **1**. Indeed, spin-decoupling experiments confirmed that it had the partial structure **6**, and hence that it was the 1,4 adduct (**7**) of TCNE and *N*-methanesulfonylazepine (**3**). Thus, H_A gave rise to an octet (J_{AC} = 8.6, J_{AF} = 7.3, J_{AD} = 1.0 Hz) at δ 7.01, H_B gave rise to another octet (J_{BE} = 8.6, J_{BD} = 1.5, J_{BF} = 0.5 Hz) at δ 6.67, H_C gave rise to an octet (J_{CD} = 7.0, J_{AC} = 8.6, J_{CF} = 1.0 Hz) at δ 6.6, and H_D also gave rise to an octet (J_{CD} = 7.0, J_{AD} = 1.0, J_{BD} = 1.5 Hz) at δ 5.68, while H_E gave a triplet (J_{EF} = J_{BE} = 8.6 Hz) at δ 5.28, H_F gave a complex multiplet (J_{AF} = 7.3, J_{EF} = 8.6, J_{CF} = 1.0, J_{BF} = 0.5 Hz) at δ 3.91, and H_{Me} gave rise to a singlet at δ 3.32. These assignments are similar to those made by Kende and his coworkers[7] for the corresponding adduct between TCNE and *N*-ethoxycarbonylazepine. The structure of the adduct was confirmed by synthesizing an authentic sample from *N*-mesylazepine (kindly supplied by Dr. L. A. Paquette) and TCNE; the product was identical with that trapped in the azide thermolysis.

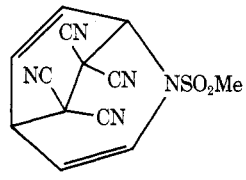
Similar adducts were obtained from the decomposition of methanesulfonyl azide in toluene and in chlorobenzene. In these cases, it is clear that a number of monosubstituted azepines can arise and that each one, in turn, may give one or more Diels–Alder products with TCNE. The nmr of the adduct from the toluene reaction suggests that it consists of a single isomer, namely **8**. It was very similar to that of **7**. Thus H_A gives rise to a quartet (J_{AB} = 8.6, J_{AE}



5

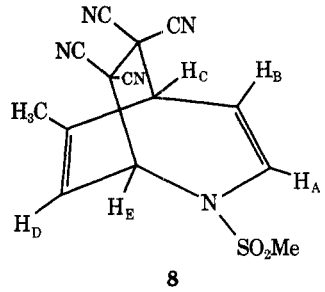


6

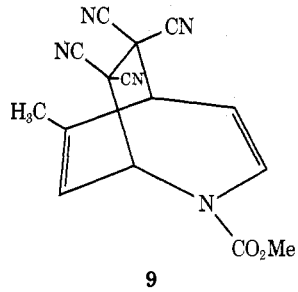


7

= 1.5 Hz) at δ 6.77, H_B gives rise to a triplet ($J_{AB} = J_{BC}$ = 8.6 Hz) at δ 5.34, H_D gives rise to two broad quartets centered at δ 6.42 (J_{DE} = 7.5, J_{CD} = 1.3, J_D = 1.5 Hz), H_E to a quartet at δ 5.68 (J_{DE} = 7.5, J_{AE} = 1.5 at δ 3.94 Hz), and H_C to a quartet (J_{BC} = 8.6, J_{CD} = 1.3 Hz) at δ 3.94. These assignments are similar to those made by Baldwin and Smith[8] for the adduct **9**.

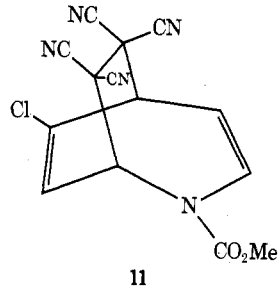


8

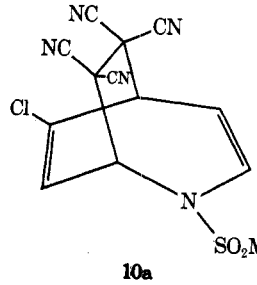


9

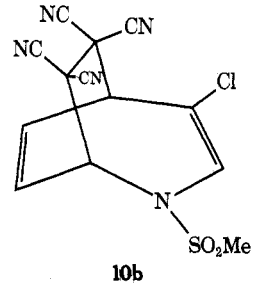
On the other hand, the TCNE adduct from the reaction in chlorobenzene could be a mixture of two isomers, as indicated by the two complex sets of signals centered around δ 7.3 and 6.7. Mixtures of isomers were also obtained from *x*-bromo-*N*-carbomethoxyazepine by Paul, Baldwin, and Smith.[9] The remaining three sets of protons, on the other hand, centered at δ 5.95, 5.45, and 4.38, showed identical splitting patterns with the corresponding ones in **8**, and are very similar to those reported for the adduct **11**.[8] Either or both of structures **10a** and **10b** would be acceptable according to the nmr spectral data.



11



10a



10b

Thus, while no azepine can be isolated from the reactions at 120°, its intermediacy can be detected by the trapping experiments. These results suggest that an equilibrium exists between 3 ⇌ 1 ⇌ 2 and that at 120° it lies mainly on the side of **2**, which rearranges irreversibly to **4**. This is best illustrated by means of a potential energy diagram (Figure 1) (in which **2** is represented as an intermediate; it is conceivable that the conversion 1 → 4 occurs in a concerted manner). To explain the results one would have to assume that the sigmatropic ring opening of **1** to **3** would be a kinetically controlled step ($k_3 > k_2$) but that **2** (and thence **4**) would be the product of thermodynamic control. At 120°, **3** would be formed first ($\Delta E_{1\to3} < \Delta E_{1\to2}$) but would possess enough energy not only to revert to **1** but to be converted to **4** *via* **2** irreversibly, so that insufficient stationary concentrations of **3** would be present to be detectable by tlc. If, on the other hand, a trapping agent were present, the small amounts of **3** would be trapped to a large extent before it could revert to **1**, and the adduct of **8** would accumulate at the expense of **4**. If such is the case, then by providing just sufficient energy to go from **1** to **3**, but not enough to convert **1** to **2**, it should be possible to isolate **3**, the proposed product of kinetic control.

Unfortunately, photolysis of aliphatic and aromatic sulfonyl azides in nonprotic, nonpolar solvents such as benzene or cyclohexane, or in a polar solvent such as pyridine, produces insoluble, high-melting materials that have not been characterized.[10-12] (The only sulfonyl azide known to photolyze smoothly under these conditions is ferrocenylsulfonyl azide.[13]) When, however, the photolysis of methanesulfonyl azide was carried out in benzene at 25° such that the walls of the photolysis vessel were not coated with "polymer," a very small amount of *N*-mesylazepine (**3**) was isolated. The main product was a yellow, amorphous solid which exhibited NH, SO_2, and azide bands in the infrared and which could not be characterized. No *N*-mesylaniline was detected.

As indicated above, the unassisted thermolysis of sulfonyl azides takes place slowly at 120°. When the thermolysis of $MeSO_2N_3$ in benzene was carried out at 80° for 100 hr mainly unchanged azide was recovered, but *N*-mesylazepine (**3**, 0.34%) and methanesulfonamide (<0.1%) were isolated by tlc. No *N*-mesylaniline was detected. As the reaction temperature was raised to 90°, the yield of **3** increased to 3.7% and that of methanesulfonamide to 0.5%, and some *N*-mesylaniline (**4**, 1.2%) was now formed. At 100°, the yield of **3** dropped to 0.9%, while that of **4** went up to 13.6%. These observations are entirely consistent with the hypothetical situation depicted in Figure 1. When **3** was heated at 120° in benzene it was converted to **4**, though some **3** still remained. It is possible that since no **3** is observed at 120° under the reaction conditions the isomerization of 3 → 4 is catalyzed by the slightly acidic sulfonamide, as suggested by Breslow.[1] Alternatively, it could be that the concentration of **3** at 120° is so small at any time that it would isomerize completely under the reaction conditions unless it were trapped. The azepine could not be detected by gas chromatography, since it was shown that it isomerized quantitatively to the mesylaniline **4** under the glc conditions. We conclude, therefore, that azepine formation is the kinetically controlled process while the aromatic substitution product is that of thermodynamic control in the attack of an aromatic nucleus by a singlet sulfonyl nitrene.

These observations made it desirable to develop an alternative source of singlet sulfonyl nitrenes, preferably one in which the reactive intermediate could be generated at ambient, or only slightly higher, temperatures. One such abortive attempt to do so by the photolysis of *N*-sulfonyliminopyridinium ylides has already been reported.[14] Below are outlined a number of other attempts to achieve this goal. It was hoped that, if such a suitable source of singlet

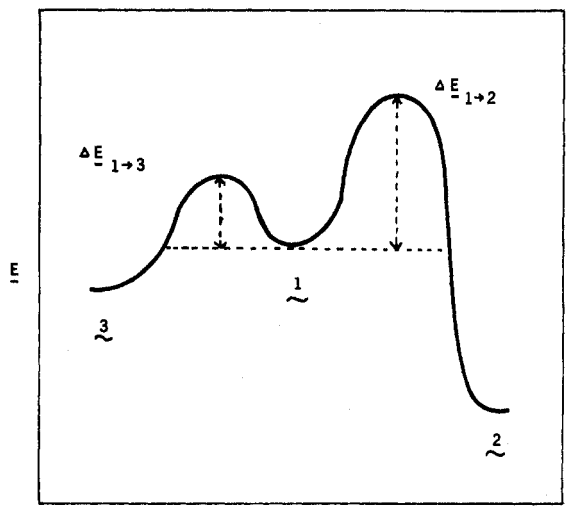


Figure 1. Hypothetical potential energy diagram for the reaction of $MeSO_2N_3$ with benzene.

sulfonyl nitrenes would be available, it would then be possible to obtain at will either the azepine or the aniline, depending upon the source of nitrene used. It would also permit the study of the reaction of such nitrenes with olefins without the accompanying complications of concerted attack by the olefin on the azide and elimination of nitrogen, or of triazoline formation.[15]

Breslow and Sloan[16] reported that the reaction of dichloramine-T with zinc dust in cyclohexane gave the insertion product *N*-cyclohexyl-*p*-toluenesulfonamide in high yield, and suggested that a free sulfonyl nitrene was formed as an intermediate. We had already shown[11] (see Experimental Section) that when *N,N*-dichloromethanesulfonamide (**12**) was heated in benzene at 120° only methanesulfonamide was formed (82%) and biphenyl was detected by glc but not determined quantitatively. No azepine or *N*-mesylaniline was observed. Similar results were obtained on photolysis of **12** in benzene. Thermolysis of **12** in toluene also gave methanesulfonamide and some bibenzyl.

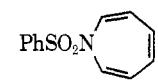
$$\underset{\mathbf{12}}{CH_3SO_2NCl_2} + C_6H_6 \xrightarrow[\text{or } h\nu \text{ or } \Delta/Zn]{\Delta} CH_3SO_2NH_2 + PhPh$$

Dichloramine-T behaved similarly. In view of Breslow's work, these thermolyses were repeated in the presence of zinc powder, but the results were the same. It does not appear likely, therefore, that the reactions of these *N,N*-dichlorosulfomamides in aromatic solvents involve the intermediacy of a free nitrene, whether or not zinc is present. (Similarly, no intramolecular cyclization of *N,N*-dichlorobiphenyl-2-sulfonamide could be effected.[17])

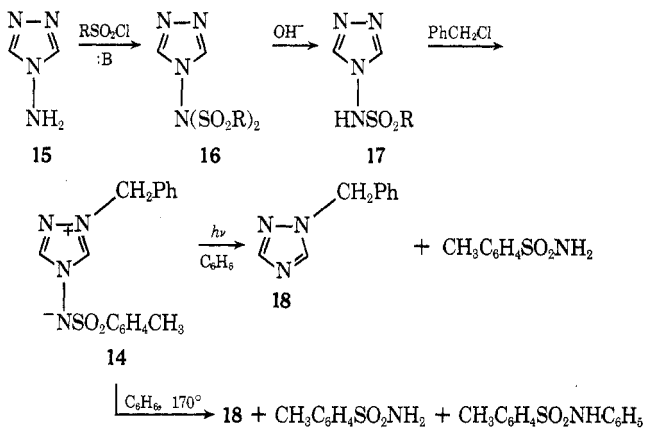
Lead tetracetate oxidation of carboxylic acid amides leads to isocyanates and it was suggested that an acyl nitrene may be involved.[18] It seems more likely that a concerted oxidation–migration is taking place.[19] In any event, the primary sulfonamides, *e.g.*, methanesulfonamides, proved to be completely resistant to oxidation by LTA, both in benzene alone and in benzene containing acetic acid. With lead tetra(trifluoroacetate), oxidation of the benzene occurred but the sulfonamide was unaffected.[17]

The decomposition of the triethylammonium salt of *N*-*p*-nitrobenzenesulfonoxybenzenesulfonamide (**13**) in protic solvents (MeOH, EtOH, $PhNH_2$) gives products derived from a Lossen-type rearrangement.[12] The rearrangement was thought not to involve a free nitrene, since, when the decomposition was carried out in toluene–methylene chloride or in benzene, no sulfonanilides were obtained. We repeated the decomposition in benzene under various conditions in the hope of detecting some *N*-benzenesulfonylazepine (**14**) but none could be detected or trapped, nor was any benzenesulfonanilide observed. Only very small amounts of benzenesulfonamide were isolated, in addition to tars. It appears, therefore, that free singlet sulfonyl nitrenes are not generated in this reaction.

$$PhSO_2NH_2 + \text{tars} \longleftarrow \underset{\mathbf{13}}{[PhSO_2\bar{N}\text{-}OSO_2C_6H_4NO_2]\ Et_3\overset{+}{N}H} \not\rightarrow$$



Photolyses of 4-imino-1,2,4-triazolium ylides have been claimed to give nitrenes.[20] The decomposition of 1-benzyl-4-*p*-toluenesulfonimido-1,2,4-triazolium ylide (**14**) in benzene and in mesitylene was therefore studied. As was found by Becker and Timple,[20a] monosulfonylation of 4-amino-1,2,4-triazole (**15**) is difficult to achieve, the *N,N*-disulfonyl derivative (**16**) being formed with extreme ease. Hydrolysis of **16** to **17** occurred with base. Mono-N-tosylation could be effected but was invariably accompanied by ditosylation. Photolysis of **14** in benzene containing acetonitrile or methylene chloride to improve the solubility of **14** and using either 2537-Å or 3000-Å radiation gave only 1-benzyl-1,2,4-triazole (**18**) and a small amount of *p*-toluenesulfonamide. No sulfonanilide or azepine was observed, suggesting that if a free sulfonyl nitrene is formed to a minor extent in these reactions it must be the triplet species. On the other hand, while **14** is stable at 150°, its thermolysis in benzene at 170° did lead to a small amount (2.5%) of *N*-*p*-toluenesulfonanilide (**19**), so that it appears that a singlet sulfonyl nitrene is formed to a certain extent under those conditions. This approach, however, is clearly less advantageous than that using the sulfonyl azides, except that it might eventually be used to study the behavior of singlet sulfonyl nitrenes with olefins not complicated by the possibility of dipolar additions of the azides to the double bonds before, or concerted with, N–N bond cleavage.

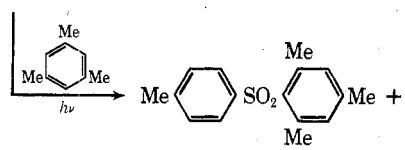


Some isocyanates undergo photolysis to the desired nitrenes and CO, *e.g.*, the photolyses of styryl isocyanate,[21] 2-biphenylyl isocyanate,[22] and methyl isocyanate.[23] We have examined the photolysis (2537 Å) of *p*-toluenesulfonyl isocyanate (**20**) in benzene and have indeed observed the formation of very small amounts (1.1%) of **19** together with mainly unchanged starting material. No attempt was made to see how much of the *p*-toluenesulfonamide isolated was formed by hydrogen abstraction by the nitrene and how much resulted from the hydrolysis of undecomposed

isocyanate (the latter was definitely present in the reaction mixture after irradiation for 30 hr). No azepine was detected in this reaction. On the other hand, no sulfonanilide derivative was detected on photolysis of **20** in mesitylene. Instead, 2,4,4′,6-tetramethyldiphenyl sulfone (**21**) was formed, together with the primary sulfonamide (probably mostly hydrolysis of isocyanate on work-up) and *N,N*-di-*p*-toluenesulfonylurea (by the addition of sulfonamide to unreacted isocyanate). Similar results were obtained on thermolysis of **20** in mesitylene at 185°, except that a trace of *N*-*p*-toluenesulfonylaminomesitylene could be detected by gas chromatography in this case.

$$CH_3C_6H_4SO_2N{=}C{=}O \xrightarrow[C_6H_6]{2537\ \text{Å}} \mathbf{19} + CH_3C_6H_4SO_2NH_2$$

20



21

$$CH_3C_6H_4SO_2NH_2 + (CH_3C_6H_4SO_2NH)_2CO$$

Finally, in another search for a good leaving group, the decomposition of sulfonimidophenyliodonium ylides in benzene was investigated. Thermolysis of methanesulfonimidophenyliodonium ylide (**22**, R = Me) in benzene at 130° gave iodobenzene (83.5%), methanesulfonamide (52.5%), and *N*-mesylaniline (1.1%). At 100°, similar results were obtained and no *N*-mesylazepine could be detected. With **22** (R = *p*-$CH_3C_6H_4$), no anilide could be

$$\underset{\mathbf{22}}{RSO_2\bar{N}\text{-}\overset{+}{I}Ph} \xrightarrow[C_6H_6]{\Delta} PhI + RSO_2NH_2 + RSO_2NHPh$$

isolated and only $TsNH_2$ was formed together with PhI. It would seem, therefore, that only a small amount of singlet sulfonyl nitrene is produced under these conditions. The predominance of triplet-derived product might be explained by assuming that the singlet nitrene initially formed undergoes rapid intersystem crossing catalyzed by the leaving iodine substituent present at its birthplace.

Experimental Section

All melting points are uncorrected. Nmr spectra were recorded on a 100 MHz instrument.

Decomposition of Methanesulfonyl Azide in Benzene Containing TCNE. Methanesulfonyl azide (0.434 g, 3.58 mmol) and freshly recrystallized tetracyanoethylene (1.28 g, 10.0 mmol) in benzene (14.0 g, 0.179 mol) was heated in an oil bath at 120° (sealed bomb tube) for 60 hr. The reaction mixture was filtered and washed with hot benzene (25 ml). The filtrate was concentrated to *ca.* 12 ml and then cooled in the refrigerator overnight, when the adduct separated (0.328 g, 29.4%) and was recrystallized from acetonitrile: mp 200° dec; ir (KBr) 3030 (w), 2940 (w), 1635 (m), 1375 (m), 1360 (m), 1340 (s), 1275 (m), 1170 (s), 1030 (m), 960 (m), 890 (s), 765 (s), 735 (m), and 680 cm^{-1} (m). This was identical with the adduct obtained from TCNE and authentic *N*-mesylazepine[24] (kindly supplied by Dr. L. A. Paquette).

Anal. Calcd for $C_{13}H_9N_5O_2S$: C, 52.16; H, 3.03; N, 23.40. Found: C, 52.00; H, 2.99; N, 23.13.

The mother liquors were concentrated using a long fractionating column to remove solvent. The concentrate was analyzed quantitatively by gas chromatography using a 6 ft × 0.25 in. column packed with precipitated asphalt (25%) on Chromosorb W (60–80 mesh) at 220°. Coumarin was used as the internal standard. The results of three runs (mean) were as follows: TCNE adduct, 30.4 ± 0.5%; methanesulfonamide, 19.3 ± 1.5%; *N*-mesylaniline, 6.0 ± 0.5%; overall yield based on azide, 55.7 ± 2.5%. Doubling the amount of TCNE used relative to azide had no effect on the product ratio.

When *N*-mesylaniline (0.186 g) and TCNE (0.148 g) were dissolved in benzene (15 ml) and heated to 120° for 40 hr, no TCNE adduct was formed and the mesylaniline was recovered.

Decomposition of Methanesulfonyl Azide in Toluene Containing TCNE. Methanesulfonyl azide (0.3 g, 2.5 mmol) was decomposed in toluene (15 ml) in the presence of TCNE (0.3–0.8 g, 2.5–6 mmol) at 120° for 48 hr. The hot mixture was filtered and allowed to stand overnight. The adduct(s) was filtered and recrystallized from acetone–methanol to give crystals: mp 202–203° dec (yield 12–17%); ir (KBr) 3000 (vw), 2940 (w), 2920 (w), 1635 (m), 1370 (m), 1340 (s), 1270 (m), 1150 (s), 1030 (s), 975 (m), 885 (m), 770 (s), and 670 cm^{-1} (w).

Anal. Calcd for $C_{14}H_{11}N_5O_2S$: C, 53.69; H, 3.54; N, 22.36. Found: C, 53.61; H, 3.62; N, 22.58.

The mother liquors were concentrated by fractional distillation and analyzed by glc using an 8 ft × 1/16 in. column packed with Apiezon L (25%) on Chromosorb W (60–80 mesh) at 205° (coumarin internal standard). The yields of products were unaffected (except as indicated) by a 2.5-fold increase in the relative amount of TCNE over azide and were as follows: methanesulfonamide, 18.4 ± 0.6% (using a 1:1 azide:TCNE molar ratio), 25.0 ± 2.0% (using a 1:2.5 azide:TCNE molar ratio); *N*-mesyltoluidides, 40.8 ± 1.0% (ortho:meta:para ratio = 67.9:4.4:27.7); overall yield based on azide, 73–80%.

***x*-Chloro-*N*-mesylazepine–TCNE Adduct.** Methanesulfonyl azide (0.3 g) was decomposed in a 50 molar excess of chlorobenzene containing TCNE (0.6 g) at 120° for 48 hr. The reaction mixture was filtered while still hot and, on cooling, the adduct crystallized out: mp 207–209° (with decomposition beginning at 200°) (10%, from acetone–ethanol); ir (KBr) 3010 (w), 1650 (s), 1373 (m), 1348 (s), 1335 (m), 1280 (m), 1175 (m), 1162 (s), 1035 (m), 972 (m), 895 (m), 775 (m), 730 (m), and 680 cm^{-1} (m).

Anal. Calcd for $C_{13}H_8ClN_5O_2S$: C, 46.79; H, 2.42; N, 20.99. Found: C, 46.81; H, 2.46; N, 20.84.

Methanesulfonamidation of Benzene. At 80°. A. Methanesulfonyl azide (2.40 g) in dry benzene (30 ml) was heated at 80° for 100 hr in a sealed tube. The benzene was evaporated *in vacuo* and the residue was chromatographed on a column (4 × 30 cm) of neutral alumina (60–80 mesh). Elution with light petroleum (bp 30–60°) gave unreacted methanesulfonyl azide (1.75 g, 73%). Elution with light petroleum (bp 30–60°)–benzene (1:1 v/v) gave *N*-methanesulfonylazepine (4.1 mg, 0.34%): mp 89–92° (lit.[24] mp 91.5–92.5°); ir (KBr) 1640, 1340, and 1150 cm^{-1}; identical with an authentic sample.[24] Elution with ethyl acetate–methanol (95:5 v/v) gave methanesulfonamide (1.1 mg, <0.1%), identical with an authentic sample.

B. When the reaction was carried out at 80° for 120 hr, azide (66%), *N*-mesylazepine (0.49%), and *N*-mesylaniline (0.16%), mp 89.5–91.5° (identical with authentic sample), were obtained.

At 90°. When the thermolysis was carried out at 90° for 100 hr in degassed dry benzene a 4% yield of *N*-mesylazepine was obtained, together with 39% of recovered azide.

If the thermolysis was allowed to proceed for 120 hr at 90°, only 22.4% of azide was recovered and there were obtained *N*-mesylazepine (3.7%), methanesulfonamide (0.5%), and *N*-mesylaniline (1.2%).

At 100°. Decomposition of the azide in dry degassed benzene for 100 hr followed by chromatographic work-up gave unchanged azide (31%), *N*-mesylazepine (0.9%), methanesulfonamide (1.9%), and *N*-mesylaniline (13.6%).

Thermal Stability of *N*-Mesylazepine. A. *N*-Mesylazepine was heated in benzene at 120° for 12 hr. The solution was concentrated and examined by tlc on 0.25-mm thick silica gel G using $CHCl_3$–MeOH (95:5 v/v). Mainly unchanged *N*-mesylazepine (R_f 0.65) was observed, together with some *N*-mesylaniline (R_f 0.35).

B. The thermolysis was repeated at 120° for 48 hr. Four spots were detected by tlc, the main one being due to *N*-mesylaniline. A small amount of *N*-mesylazepine remained unchanged.

C. Pure *N*-mesylazepine, mp 93.5–94°, was injected onto a glc column consisting of 10% OV-17 on Gas-Chrom Q operated at 205° and the single compound observed was collected and shown by its infrared spectrum to be *N*-mesylaniline.

Photolysis of Methanesulfonyl Azide in Benzene. The azide (1.6 g) in benzene (150 ml) was photolyzed at 28° under nitrogen in a water-cooled quartz vessel using three medium-pressure mercury lamps (GE-H100-A4). The solution was stirred with a glass stirrer fitted with glass wool bristles which scraped the sides of the vessel and prevented their getting coated with polymer. After 24 hr, *N*-mesylazepine (<0.5%) was detected by tlc (R_f 0.65) and isolated. Two other products were detected as faint spots on tlc (R_f 0.15 and 0.20). No *N*-mesylaniline was detected in this reaction. The yellow mother solution was concentrated when a pale yellow amorphous solid (*ca.* 0.5 g) separated. It deepened in color at about 50°, turned a dark brown at 100–120°, and softened to a

gum at 150–160°: ir (KBr) 3280–3400 (m), 3020 (w), 2930 (w), 2130 (w) (N_3), 1630–1660 (br), 1310–1330 (s, SO_2), 1140–1160 (s, SO_2), 1035 (m), 960 (m), 760 (s), and 685 cm^{-1} (w). Addition of TCNE to the reaction mixture gave extremely impure *N*-mesylazepine–TCNE adduct contaminated with the above yellow material.

When the photolysis was repeated at 80° a brown solid (0.3 g) separated whose infrared spectrum was the same as that of the yellow solid above. The mother liquors were treated with TCNE to give, on standing at 0° overnight, the TCNE–*N*-mesylazepine adduct (0.75–1%), mp 195–198° dec, whose infrared spectrum was identical with that of the authentic sample. From the mother liquors, methanesulfonyl azide (0.6 g, 40%) was recovered.

Decomposition of *N,N*-Dichloromethanesulfonamide in Benzene. *N,N*-Dichloromethanesulfonamide[25] (0.36 g) was heated in benzene (15 ml) for 45 hr at 120° under pressure. Methanesulfonamide (0.18 g, 82%) separated from the cooled reaction mixture. The mother liquors were analyzed qualitatively by gas chromatography and methanesulfonamide and biphenyl were detected, but no methanesulfonylanilide.

Similar results were obtained when *N,N*-dichloromethanesulfonamide (0.8 g) was photolyzed in benzene (25 ml) in a quartz tube using a 140-W Hanovia lamp for 48 hr. Again, methanesulfonamide (80%) was isolated and biphenyl was detected but not *N*-methanesulfonylanilide.

N,N-Dichloromethanesulfonamide (2.26 g) in benzene (100 ml) was stirred and boiled under reflux with zinc powder (1.0 g) for 22 hr to give methanesulfonamide (1.132 g, 80%), mp 87–90°, and recovered dichloroamide (0.125 g, 5%). No anilide was detected.

Thermolysis of *N,N*-Dichloromethanesulfonamide in Toluene. The dichloroamide (0.43 g) in toluene (15 ml) was heated at 120° for 40 hr under pressure to give methanesulfonamide (0.19 g, 78%). Glc analysis of the mother liquors indicated the presence of methanesulfonamide, bibenzyl, and two other minor components (probably dimethylbiphenyls), but no *N*-methanesulfonyltoluidides.

Reaction of Dichloramine-T with Benzene. Dichloramine-T (0.36 g) was heated in benzene (15 ml) at 120° for 20 hr under pressure. *p*-Toluenesulfonamide, mp 138° (ir identical with that of the authentic specimen), separated. Only unchanged dichloramine-T was present in the mother liquors; no *p*-toluenesulfonylanilide was detected by glc.

Similar results were observed when a solution of dichloramine-T (1.2 g) was irradiated with medium-pressure mercury lamps for 2 days.

Reaction of Dichloramine-T with Toluene. Dichloramine-T (0.56 g) was heated in toluene (15 ml) at 120° for 20 hr under pressure to give *p*-toluenesulfonamide (0.348 g, 87%). Glc analysis of the mother liquors indicated only the presence of *p*-toluenesulfonamide and bibenzyl.

Attempted Reaction of Methanesulfonamide in Benzene with Lead Tetraacetate. A solution of methanesulfonamide (1.90 g) in benzene (8.0 g) was treated with lead tetraacetate (8.86 g) in acetic acid (32 g) and the solution was stirred for 3 hr at 85–90°. Only unchanged methanesulfonamide (1.36 g, 72%) could be isolated.

Reaction of *N*-*p*-Nitrobenzenesulfonoxybenzenesulfonamide and Triethylamine with Benzene. The sulfonoxysulfonamide (3 g) was suspended in dry, degassed benzene (300 ml), treated with triethylamine (0.845 g), and stirred at room temperature for 24 hr. The suspension was evaporated to dryness *in vacuo* and the residue was extracted with ether, chloroform, and benzene. The residue (2.45 g, 99.2%) was triethylammonium *p*-nitrobenzenesulfonate, mp 121°, identical with an authentic sample. The extracts were each evaporated to dryness and the residues were chromatographed on silica gel columns and individual fractions analyzed by tlc. Only benzenesulfonamide (28 mg, 1%), mp 150°, could be resolved from the tarry oils formed. No benzensulfonanilide or *N*-benzenesulfonylazepine could be detected.

When the reaction was repeated at 0° for 96 hr, the solvent was evaporated, and the oily residue was treated with 10% hydrochloric acid, the *N*-*p*-nitrobenzenesulfonoxybenzenesulfonamide (0.344 g, 96%), mp 178–179° (lit.[3] mp 179°), was recovered.

The reaction was repeated at 25° for 96 hr but using pyridine (0.79 g) instead of triethylamine. Unchanged sulfonoxysulfonamide (2.91 g, 83%) was recovered, in addition to some benzenesulfonamide (0.01 g, 0.6%), mp 149–150°.

The original reaction was repeated but in the presence of tetracyanoethylene (1.28 g). The solution darkened immediately, but no identifiable adducts could be isolated.

The original reaction was repeated without tetracyanoethylene but at 80°. The triethylammonium salt, mp 120–121°, was again isolated (87.1%) together with benzenesulfonamide (1.9%). No other products could be identified.

4-Dibenzenesulfonamido-1,2,4-triazole. 4-Amino-1,2,4-triazole (0.84 g, 0.01 mol) was added to a 10% aqueous potassium hydroxide solution (20 ml). Benzenesulfonyl chloride (3.52 g, 0.02 mol) was added with stirring, and after 10 min the solution was acidified with HCl. The precipitated 4-dibenzenesulfonamido-1,2,4-triazole (3.59 g, 98.5%), had mp 178–179° (from ethanol) (lit.[20a] mp 187°); mass spectrum *m/e* (rel intensity) 364 (10, M^+), 299 (8.4), 223 (60), 171 (10.9), 159 (6.9), 1.57 (10.3), 141 (19), 125 (8.4), 94 (11), 77 (100).

Anal. Calcd for $C_{14}H_{12}N_4S_2O_4$: C, 46.14; H, 3.32. Found: C, 46.30; H, 3.41.

The same product was obtained, but in lower yield (45%), when the reaction was carried out in boiling pyridine.

4-Benzenesulfonamido-1,2,4-triazole. The dibenzensulfonyl derivative (0.364 g) was suspended in 10% aqueous KOH (50 ml) and the suspension was heated to 80° when the disulfonyl derivative dissolved. The solution was cooled and acidified to give 4-benzenesulfonamido-1,2,4-triazole (0.20 g, 89%), mp 181–182° (lit.[20a] mp 184°).

Anal. Calcd for $C_8H_8N_4O_2S$: C, 42.85; H, 3.59. Found: C, 43.09; H, 3.74.

4-*p*-Toluenesulfonamido-1,2,4-triazole. 4-Amino-1,2,4-triazole (1.68 g, 0.02 mol) in pyridine was treated with *p*-toluenesulfonyl chloride (3.80 g, 0.02 mol) portionwise. After 15 min at room temperature the solution was poured over ice. The solid which separated was filtered, washed with water, and recrystallized from ethanol to give 4-di-*p*-toluenesulfonamido-1,2,4-triazole (0.61 g, 15%): mp 186° (lit.[4] mp 186°); mass spectrum *m/e* (rel intensity) 237 (48), 171 (2.7), 155 (100), 139 (2), 108 (1), 107 (1), 106 (6), 92 (23), 91 (97), 89 (8), 77 (4), 69 (4), 65 (52), 63 (10), 51 (7), 50 (4), 39 (17).

The filtrate was acidified with 3 *N* HCl and the precipitate was filtered and recrystallized from ethanol to give the title compound (1.81 g, 26.2%), mp 220–221.5° (lit.[4] mp 222°), *m/e* 238 (12, M^+).

1-Benzyl-4-*p*-toluenesulfonimido-1,2,4-triazolium Ylide. 4-Tosylamido-1,2,4-triazole (0.238 g) was dissolved in benzyl chloride (10 ml), potassium carbonate (0.25 g) was added, and the mixture was heated at 110° for 15 min. The excess benzyl chloride was distilled off (66°, 12 mm) and the residue was chromatographed on a silica gel column (2.5 × 20 cm). Elution with benzene gave *p*-toluenesulfonamide (1.8 mg, 1%), mp 136–138°. Elution with $CHCl_3$–EtOH (9:1 v/v) gave 1-benzyl-4-*p*-toluenesulfonimido-1,2,4-triazolium ylide (29.5 mg, 9%): mp 171–173° (from Et_2O–EtOH); mass spectrum *m/e* (rel intensity) 328 (1, M^+); nmr ($CDCl_3$) δ 9.95 (s, 1 H, H_5), 7.80 (s, 1 H, H_3), 7.52 (d, 2 H, $J_{o,m}$ = 10 Hz, H_o in Tos), 7.30 (m, 5 H, Ph), 7.08 (d, 2 H, $J_{o,m}$ = 10 Hz, H_m in Tos), 5.42 (s, 2 H, CH_2), 2.38 (s, 3 H, CH_3).

Anal. Calcd for $C_{16}H_{16}N_4O_2S$: C, 58.52; H, 4.91. Found: C, 58.25, H, 4.93.

The reaction was repeated, leaving out the potassium carbonate, and heating the solution at 90° for 48 hr. Evaporation of the excess benzyl chloride and continuous extraction of the residue with ether followed by concentration of the ether and cooling to 0° gave the desired ylide (60%), mp 171–173°.

Thermolysis of 1-Benzyl-4-*p*-tolylsulfonimido-1,2,4-triazolium Ylide in Benzene. The ylide (0.576 g) was suspended in dry degassed benzene and heated in a sealed tube at 170° for 40 hr. Evaporation of the solvent *in vacuo* gave a tarry solid which was chromatographed on a silca gel column (5 × 30 cm). Elution with light petroleum–benzene (3:1 v/v) gave 1-benzyl-1,2,4-triazole (0.017 g, 20%), bp 91–97° (0.005 mm) [lit.[20b] bp 114–116° (0.06 mm)]. Further elution with the same solvent gave *N*-*p*-toluenesulfonylanilide (5.1 mg, 2.5%), mp 102–104°, identical with an authentic sample. Elution with benzene–ether (9:1 v/v) gave *p*-toluenesulfonamide (0.048 g, 20.3%), identical with an authentic sample. Finally, elution with benzene–ethyl acetate (6:1 v/v) gave unchanged ylide (0.096 g, 16.6%).

When the thermolysis was carried out at 150°, unchanged ylide (98%) was recovered.

Photolysis of 1-Benzyl-4-*p*-tolylsulfonamide-1,2,4-triazolium Ylide in Benzene. A solution of 1-benzyl-4-*p*-tolylsulfonamido-1,2,4-triazolium ylide (0.32 g) in benzene–acetonitrile (75 ml, 1:2 v/v) was irradiated (Pyrex filter) under dry, oxygen-free nitrogen using 3000-Å lamps (Rayonet reactor) for 24 hr. The solvent was evaporated under vacuum and the residue was chromatographed on a column of silica gel. Elution with light petroleum–chloroform (7:1 v/v) gave 1-benzyl-1,2,4-triazole (45 mg, 28%), bp 110° (0.1 mm). Elution with chloroform gave *p*-toluenesulfonamide (3.1 mg, 1.8%), mp 136–138°, while elution with chloroform–methanol gave unchanged ylide (0.115 g, 28%).

Similar results were obtained using 2537-Å radiation or using benzene–methylene chloride as the solvent.

Decomposition of 1-Benzyl-4-*p*-tolylsulfonimido-1,2,4-triazolium Ylide in Mesitylene. A. Photolysis. This was carried out as above but using 2537-Å lamps to give 1-benzyl-1,2,4-triazole (44.9%), *p*-toluenesulfonamide (16.3%), and *p*-tolyl *p*-toluenethiosulfonate (1%), mp 71–73°, identical with an authentic sample.[26]

B. Thermolysis. The ylide (0.45 g) was suspended in mesitylene (35 ml) and heated at 170° for 40 hr to give 1-benzyl-1,2,4-triazole (0.031 g, 17.4%), a mixture of *p*-tolyl *p*-toluenethiosulfonate (8.6 mg, 0.3%) and *p*-tolyl disulfide (3.1 mg, 0.8%),[27] mp 44–46°, separated by preparative tlc, and *p*-toluenesulfonamide (51 mg, 3.1%), in addition to unreacted ylide (90 mg, 19.1%).

Photolysis of *p*-Toluenesulfonyl Isocyanate in Benzene. The isocyanate (0.93 g) in dry degassed benzene under nitrogen was irradiated with three 100-W medium-pressure mercury lamps (Vycor filter) for 30 hr. The solution was concentrated *in vacuo* and any unreacted isocyanate was allowed to hydrolyze in contact with moist air. The products were separated by column chromatography on silica gel to give *p*-toluenesulfonamide (0.69 g, 85%) and *N*-*p*-toluenesulfonanilide (13 mg, 1.1%), mp 101–103°, identical with an authentic sample. No azepine was detected by tlc.

Decomposition of *p*-Toluenesulfonyl Isocyanate in Mesitylene. A. Thermolysis. A solution of the isocyanate (3.94 g) in dry, degassed mesitylene (50 ml) was heated in a sealed tube at 185° for 48 hr. The solvent was evaporated and the residue was chromatographed on a column of silica gel (4 × 25 cm). Elution with light petroleum–benzene (9:1 v/v) gave 2,4,4′,6-tetramethyldiphenyl sulfone (0.43 g, 8%), mp 108–109° (from pentane) (lit.[28] mp 119°), identical with a sample prepared from tosyl chloride, mesitylene, and aluminum chloride at 50°: ir (KBr) 1305 (s), 1150 cm^{-1} (s, SO_2); nmr ($CDCl_3$) δ 7.6 (d, 2 H, $J_{o,m}$ = 8 Hz, H_2, H_6), 7.2 (d, 2 H, $J_{o,m}$ = 8 Hz, H_3, H_5), 6.85 (s, 2 H, $H_{3',5'}$), 2.51 (s, 6 H, 2′,6′-Me_2), 2.38 (s, 3 H), 2.25 (s, 3 H); *m/e* 274 (20, M^+). Elution with ethyl acetate gave *N*,*N*′-di(*p*-toluenesulfonyl)urea (0.915 g, 12.4%), mp 157–159° (from EtOH) (lit.[29] mp 155–157°). Only a trace of *N*-*p*-toluenesulfonylaminomesitylene could be detected by gas–liquid chromatography of the crude reaction mixture.

B. Photolysis. The isocyanate (3.94 g) in dry mesitylene (50 ml) was irradiated under N_2 using 2537-Å lamps (Vycor filter) for 56 hr. The sides of the vessel became coated with a film and much unreacted isocyanate remained. Work-up as above gave the tetramethyldiphenyl sulfone (0.59 g, 10.6%), *p*-toluenesulfonamide (1.55 g, 46.5%), and di(*p*-toluenesulfonyl)urea (0.98 g, 13.5%). Similar results were obtained by using 3000-Å lamps.

Methanesulfonimidophenyliodonium Ylide. Methanesulfonamide (1.90 g, 0.02 mol) suspended in ether (20 ml) was treated with pyridine (25 ml), and to the now homogeneous solution was added iodoxybenzene diacetate (3.22 g, 0.01 mol) in portions over a period of 10 min. The mixture was stirred for 24 hr and the methanesulfonimidophenyliodonium ylide (1.26 g, 42.5%), mp 135° (detonation), which precipitated was filtered, washed with cold water, ether, and chloroform, and dried: ir (KBr) 3010 (w), 2890 (w), 1215 (s, SO_2), 1095 (s, SO_2), 965 (s, C–I), 920 (m), and 725 cm^{-1} (s); nmr (DMSO-d_6) δ 8.13 (m, 2 H, H_2, H_6), 7.60 (m, 3 H, H_3, H_4, H_5), 2.71 (s, 3 H, CH_3); *m/e* 284 (M^+).

Anal. Calcd for $C_7H_8INO_2S$: C, 28.29; H, 2.71. Found: C, 28.24; H, 2.75.

Thermolysis of Methanesulfonimidophenyliodonium Ylide in Benzene. The ylide (2.84 g) suspended in degassed benzene (20 ml) was heated at 130° for 12 hr. The solvent was evaporated under vacuum. Tlc analysis on silica gel showed the absence of *N*-mesylazepine and glc analysis indicated the absence of biphenyl. Column chromatography on silica gel (5 × 20 cm) gave iodobenzene (1.71 g, 83.5%), *N*-mesylaniline (0.021 g, 1.1%), mp 100–101°, and methanesulfonamide (0.491 g, 52.5%), mp 89–90°.

When the thermolysis was carried out at 100° the same products were formed: PhI (91%), $MeSO_2NHPh$ (1.0%), $MeSO_2NH_2$ (47.5%), and again no azepine could be detected.

Thermolysis of *p*-Toluenesulfonimidophenyliodonium Ylide in Benzene. The ylide (3.72 g) was thermolyzed in benzene (20 ml) at 130° for 12 hr to give iodobenzene (1.1 g, 82%), *p*-toluenesulfonamide (0.51 g, 31.3%), starting ylide (0.33 g, 8.5%), and much tar. No azepine or anilide could be detected. Similar results were obtained by carrying out the thermolysis at 100°.

Acknowledgments. We wish to thank the National Research Council of Canada for its support of the work carried out at Saskatchewan and for the award of a Studentship to V. U. (1966–1967), to the National Science Foundation for its support of the work carried out at Alabama, to Dr. L. A. Paquette for a sample of *N*-mesylazepine, and to Mr. M. Mazurek of the N. R. C., Prairie Regional Laboratory, for assistance with the spin-decoupling experiments.

Registry No. **3** (R = Me), 20646-53-1; **4** (R = Me), 1197-22-4; **7**, 20696-93-9; **8**, 49558-81-8; **10a**, 49558-82-9; **10b**, 49558-83-0; **12**, 17396-47-3; **13**, 24230-25-9; **14**, 49558-86-3; **15**, 584-13-4; **16** (R = Ph), 32539-53-0; **16** (R = *p*-$CH_3C_6H_4$), 32539-54-1; **17** (R = Ph), 49558-89-6; **17** (R = *p*-$CH_3C_6H_4$), 32585-76-5; **20**, 4083-64-1; **21**, 5184-64-5; **22** (R = Me), 49558-93-2; **22** (R = *p*-$CH_3C_6H_4$), 49558-94-3; methanesulfonyl azide, 1516-70-7; dichloramine-T, 473-34-7; methanesulfonamide, 3144-09-0.

References and Notes

(1) D. S. Breslow in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, p 245.
(2) R. A. Abramovitch, J. Roy, and V. Uma, *Can. J. Chem.*, **43**, 3407 (1965).
(3) W. Lwowski, T. J. Maricich, and T. W. Mattingly, Jr., *J. Amer. Chem. Soc.*, **85**, 1200 (1963); K. Hafner and C. König, *Angew. Chem., Int. Ed. Engl.*, **2**, 96 (1963).
(4) F. D. Marsh and M. E. Simmons, *J. Amer. Chem. Soc.*, **87**, 3529 (1965).
(5) For preliminary communication, see R. A. Abramovitch and V. Uma, *Chem. Commun.*, 797 (1968).
(6) Since the above preliminary communication was published, some surprise was expressed by Dr. L. A. Paquette at the high yield of adduct obtained here. This experiment was repeated by Mr. G. N. Knaus in our laboratories, who confirmed the obtention of yields of *ca.* 30% of **7** in this reaction.
(7) A. S. Kende, P. T. Izzo, and J. E. Lancaster, *J. Amer. Chem. Soc.*, **87**, 5044 (1965).
(8) J. E. Baldwin and R. A. Smith, *J. Amer. Chem. Soc.*, **87**, 4819 (1965).
(9) I. C. Paul, J. E. Baldwin, and R. A. Smith, *J. Amer. Chem. Soc.*, **88**, 3653 (1966).
(10) L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963).
(11) V. Uma, Ph.D. Thesis, University of Saskatchewan, 1967.
(12) W. Lwowski and E. Scheiffele, *J. Amer. Chem. Soc.*, **87**, 4359 (1965).
(13) R. A. Abramovitch, C. I. Azogu, and R. G. Sutherland, *Chem. Commun.*, 1439 (1969).
(14) R. A. Abramovitch and T. Takaya, *J. Org. Chem.*, **38**, 3311 (1973).
(15) R. A. Abramovitch in "Organic Reactive Intermediates," S. McManus, Ed., Academic Press, New York, N. Y., 1973, p 127.
(16) D. S. Breslow and M. F. Sloan, *Tetrahedron Lett.*, 5349 (1968).
(17) R. A. Abramovitch and T. Takaya, unpublished results, 1970.
(18) B. Acott, A. L. J. Beckwith, A. Hassalani, and J. W. Redmond, *Tetrahedron Lett.*, 4093 (1965); B. Acott and A. L. J. Beckwith, *Chem. Commun.*, 161 (1965).
(19) W. Lwowski in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, p 185.
(20) (a) H. G. O. Becker and H. J. Timple, *J. Prakt. Chem.*, **312**, 1112 (1970); (b) H. G. O. Becker, D. Beyer, and H. J. Timple, *Z. Chem.*, **10**, 264 (1970); (c) G. V. Boyd and A. J. H. Summers, *J. Chem. Soc. B*, 1648 (1971).
(21) J. H. Boyer, W. E. Kreuger, and G. J. Mikol, *J. Amer. Chem. Soc.*, **89**, 5504 (1967); J. H. Boyer and G. J. Mikol, *J. Heterocycl. Chem.*, **9**, 1325 (1972).
(22) J. S. Swenton, *Tetrahedron Lett.*, 2855 (1967).
(23) D. A. Bamford and C. H. Bamford, *J. Chem. Soc.*, 30 (1941).
(24) L. A. Paquette, D. E. Kuhla, J. H. Barrett, and R. J. Haluska, *J. Org. Chem.*, **34**, 2866 (1969).
(25) A. G. Newcombe, *Can. J. Chem.*, **33**, 1250 (1955).
(26) P. Harrison, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 2079 (1926).
(27) H. Beckurts and R. Otto, *Ber.*, **11**, 2061 (1878).
(28) H. Meyer, *Justus Liebigs Ann. Chem.*, **433**, 327 (1923).
(29) L. Field and F. Grunwald, *J. Amer. Chem. Soc.*, **75**, 934 (1953).