Laboratory, Poona, India, and to Dr. S. N. Mehra of the Camphor and Allied Products, Bareilly, India, for generous gifts of (+)-longifolene and (+)-3-carene. We thank the National Institutes of Health for support of this research program, afforded by Grant GM 10937-22.

Registry No. 3, 96705-75-8; 4, 4017-88-3; Lgf_2BH, 96705-76-9; Lgf_3B, 96705-77-0; Car_2BH, 96705-78-1; Car_3B, 96705-79-2; (+)-longifolene, 475-20-7; (+)-3-carene, 498-15-7.

1,3-Dipolar Cycloadditions of 3,5-Dichloro-2,4,6-trimethylbenzonitrile Oxide to (Phenylsulfonyl)allenes

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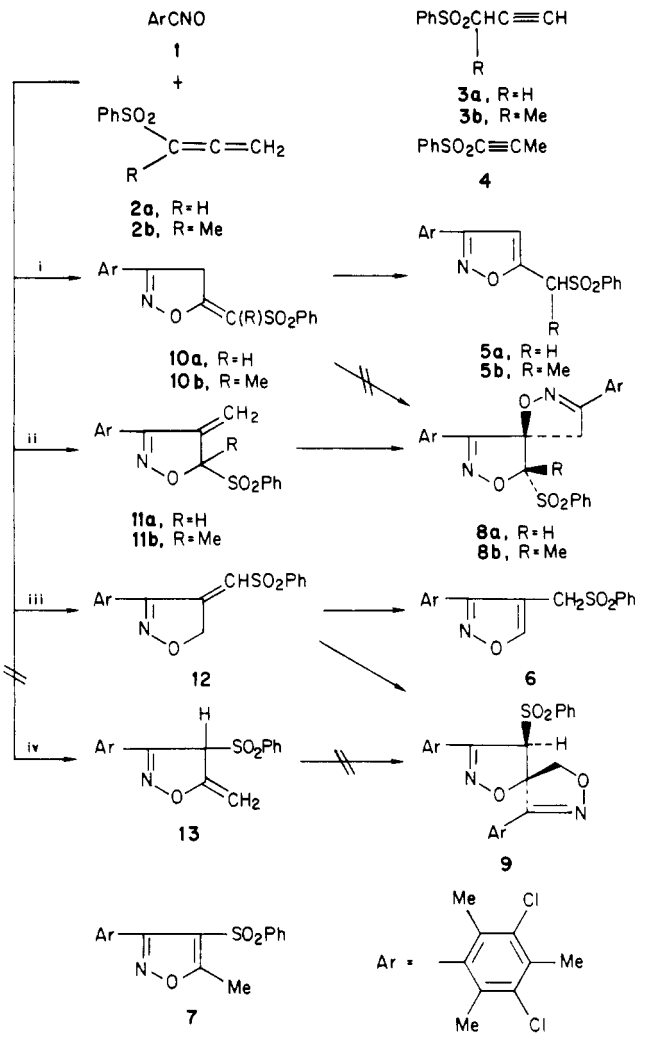
1,3-Dipolar cycloadditions to allenes present a number of synthetic and mechanistic possiblities.[2-10] In previous papers, we have described the reaction of 3,5-dichloro-2,4,6-trimethylbenzonitrile oxide (1) with 1,1-diphenylallene, phenoxyallene, and 1-methyl-1-phenoxyallene. These substrates give exclusively cycloadducts due to bond formation between the carbon of the 1,3-dipole and the central carbon of the allenic function. To gain information about the generality and the origin of this pattern of behavior, we have now studied the reaction of the same nitrile oxide with strongly polarized, electron-deficient allenes such as the phenylsulfonyl-substituted substrates **2a,b**.

The reactions of nitrile oxide 1 with allenes **2a,b** were carried out in boiling carbon tetrachloride using equimolar amounts of the reactants. The time necessary to complete disappearance of starting **1**, as shown by periodic TLC and IR analyses, was 9 and 21 h, respectively. In the case of allene **2a**, the chromatographic treatment of the complex product mixture gave, apart from recovered **2a** (28%) and side products due to isomerization or dimerization of **1**, the monoadducts **5a** (23%), **6** (21%), and **7** (2.5%) and the diadducts **8a** (4%) and **9** (1.8%).[11] Compounds **5a** and **7** were obtained as the only products by treating **1** with the alkyne derivatives **3a** and **4**, respectively. The reaction of **1** with **2b** resulted in a less complex mixture than that arising from **2a**. The monoadduct **5b** (55%) and the diadduct **8b** (11%) were obtained. Minor quantities of unchanged allene and of unidentified side products were also present. Compound **5b** was found to be the exclusive product of the reaction between **1** and **3b**.

Scheme I



Structural assignments for the products rely upon analytical data, spectral properties, and chemical evidence. The formulas **5a,b** and **6** were readily established on the basis of the chemical shifts of the isoxazolic protons. The fully substituted isoxazole **7** was prepared independently by treatment of **1** with (phenylsulfonyl)acetone in the presence of sodium hydroxide; the proposed regiochemical course of this reaction is highly probable in light of the well-known behavior of nitrile oxides toward active methylene compounds.[12]

The diadduct structures come from the following evidence. Both ^1H and ^{13}C chemical shifts as well as the geminal coupling constants are consistent with the endocyclic methylene group being adjacent to carbon in **8a,b** and to oxygen in **9**. On the other hand, the methine sp^3 carbon resonates at δ 73.1 in **9**, while it is much more deshielded in **8a** (δ 96.1). Moreover, the chemical shifts of the spiro carbons of the three diadducts are practically coincident, in harmony with the assigned structures which present similar chemical environments at the spiro center. It is to be noticed that each diadduct was obtained as one diastereoisomer; the marked NMR nonequivalence of the geminal protons may reflect a spatial influence of the sulfonyl moiety, thus indicating a cis relationship between the endocyclic methylene group and the $PhSO_2$ substitu-

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ent. Compound **9** represents a rare example of a 5-unsubstituted 4,5′-spirobi(2-isoxazoline).

The isomeric isoxazoles **5a** and **6** could in principle derive from the preliminary isomerization of **2a** to **3a** and subsequent 1,3-dipolar cycloaddition to the triple bond. However, we reject this hypothesis because the reaction of **1** with **3a** proceeds more slowly and gives exclusively **5a**. Thus, the primary cycloadducts **10a** and **12** are thought to be the real precursors of the isolated isoxazoles **5a** and **6**, their facile prototropic rearrangement being justified by the pronounced acidity of the migrating hydrogen (see Scheme I). By analogy, it is reasonable to posit that the formation of **5b** goes through the intermediacy of **10b**. On the contrary, despite the lack of clear-cut evidence, the most plausible pathway leading to the minor adduct **7** involves the initial isomerization of **2a** to **4** followed by 1,3-dipolar cycloaddition to the internal triple bond. This view is consistent with the fact that **2a** readily undergoes thermal isomerization to **4**, whose reaction with **1** affords **7** as the sole product.

As to the mechanism of formation of the diadducts, the question arises as to which of the conceivable primary cycloadducts **10–13** are actually involved in the reaction (see Scheme I). The species **11** and **13** would seem acceptable intermediates on the basis of the known reactivity of *exo*-methylene five-membered heterocycles as dipolarophiles. However, it is clear from the literature that the oxygen of nitrile oxides typically bonds to the endocyclic ethylenic carbon of *exo*-methylene-2-isoxazolines.[3a,9,13] Since there are no atypical electronic or steric factors here, the intermediacy of **13** in the formation of **9** seems unlikely. In this context, critical evidence was acquired on reacting **1** and **2a** in the molar ratio 2.5:1. Under these conditions, the allene was reacted completely, and the products were **5a** (36%), **6** (22%), **8a** (15%), and **9** (14%). This finding shows that (i) excess of nitrile oxide favors the formation of the diadducts mainly at the expense of the monoadduct **6** and (ii) the yield of the diadduct **9** increases to a greater extent than that of **8a**. Such a trend is consistent with the set of parallel–consecutive reactions depicted in the scheme, according to which compounds **6** and **9** derive from the common intermediate **12**.

In conclusion, the nitrile oxide **1** adds to both double bonds of the allenes **2a,b**, with a marked preference for the β,γ-one. This is at variance with the low selectivity previously observed in the reactions of **1** with 1,1-diphenylallene and phenoxyallenes.[3] Moreover, while the sp-hybridized carbon of the latter substrates attacks exclusively the carbon of the nitrile oxide, the reversed direction of attack is also operative in the case of **2a,b**. This result can be rationalized in terms of FMO theory. Cycloaddition of nitrile oxides to carbon–carbon multiple bonds is usually controlled by the LUMO(dipole)–HOMO(dipolarophile) interaction, unless electron-withdrawing substituents lower the orbital energies of the dipolarophile, thus enhancing the importance of the HOMO(dipole)–LUMO(dipolarophile) interaction.[14] Assuming that the latter interaction is significant in the present case and that the β-carbon of the allenes **2a,b** has the larger LUMO coefficient, the change in orientation on going from the previously investigated allenes to **2a,b** becomes explicable. The superimposition of steric effects could possibly account for the observed differences between **2a** and **2b**; pathway iii, which puts the substituents of the allenic moiety close to the bulky aryl group, is lacking in the case of the 1,1-disubstituted allene **2b**.

Experimental Section

Melting points were taken with a Büchi apparatus and are uncorrected. NMR spectra were recorded with Varian HA-100 (^{1}H) and XL-100 (^{13}C) instruments; chemical shifts are given in δ from internal standard Me_4Si and refer to deuteriochloroform solutions.

Compounds **1**,[15] **2a**,[16] **2b**,[17] **3a**,[16] **3b**,[17] and **4**[16] were prepared according to the literature methods.

Reaction of 1 with (Phenylsulfonyl)acetone. A solution of **1** (0.50 g) and (phenylsulfonyl)acetone (0.44 g) in ethanol (100 mL) was treated with 0.22 M ethanolic sodium hydroxide (1 mL) and refluxed for 30 min. The solvent was partly removed under reduced pressure, and the residue was taken up with ether, washed with water, and dried over Na_2SO_4. After evaporation of the solvent, the crude product was chromatographed on a silica gel column with benzene–ethyl acetate (9:1) as eluent to give 3-(3,5-dichloro-2,4,6-trimethylphenyl)-5-methyl-4-(phenylsulfonyl)isoxazole (**7**) (0.51 g, 57%): mp 179 °C (from hexane–benzene); ^{1}H NMR δ 1.73 (6 H, s), 2.61 (3 H, s), 2.95 (3 H, s), 7.3–7.7 (5 H, m). Anal. Calcd for $C_{19}H_{17}Cl_2NO_3S$: C, 55.61; H, 4.17; N, 3.41. Found: C, 55.43; H, 3.94; N, 3.53.

Reaction of 1 with Alkyne 4. A solution of **1** (1.0 g) and **4** (0.78 g) in carbon tetrachloride (43 mL) was refluxed for 24 h. The solvent was evaporated, and the residue was taken up with diisopropyl ether and filtered to afford isoxazole **7** (1.4 g, 78%) of purity better than 95% (NMR).

Reaction of 1 with Alkyne 3a. A solution of **1** (1.0 g) and **3a** (0.78 g) in carbon tetrachloride (43 mL) was refluxed for 20 h. The solvent was evaporated, and the residue was taken up with diisopropyl ether. Filtration gave 3-(3,5-dichloro-2,4,6-trimethylphenyl)-5-[(phenylsulfonyl)methyl]isoxazole (**5a**) (1.5 g, 84%): mp 150 °C (from chloroform); ^{1}H NMR δ 2.10 (6 H, s), 2.55 (3 H, s), 4.65 (2 H, s), 6.24 (1 H, s), 7.4–7.9 (5 H, m). Anal. Calcd for $C_{19}H_{17}Cl_2NO_3S$: C, 55.61; H, 4.17; N, 3.41. Found: C, 55.50; H, 4.14; N, 3.30.

Reaction of 1 with Allene 2a. A solution of **1** (5.0 g) and **2a** (4.2 g) in carbon tetrachloride (220 mL) was refluxed for 9 h. The solvent was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column (1 kg) with benzene as eluent. First fractions gave some solid material (0.30 g; ^{1}H NMR δ 2.0–2.8) followed by 3,3′-bis(3,5-dichloro-2,4,6-trimethylphenyl)-5-(phenylsulfonyl)-4,5′-spirobi(2-isoxazoline) (**8a**) (0.56 g, 4%): mp 246 °C (from hexane–benzene); ^{1}H NMR δ 1.87 (6 H, s), 2.37, 2.46, 2.48, 2.58 (12 H, 4 s), 3.17, 4.71 (2 H, AB type, J = 19.5 Hz), 5.59 (1 H, s), 7.5–7.8 (3 H, m), 8.0–8.2 (2 H, m); ^{13}C NMR δ 17.2–19.6, 40.1 (t), 96.1 (d), 99.6 (s), 123.7–137.1, 157.0 (s), 157.6 (s). Anal. Calcd for $C_{29}H_{26}Cl_4N_2O_4$: C, 54.38; H, 4.09; N, 4.38. Found: C, 54.71; H, 4.16; N, 4.22.

Subsequent fractions contained 3,3′-bis(3,5-dichloro-2,4,6-trimethylphenyl)-4-(phenylsulfonyl)-5,4′-spirobi(2-isoxazoline) (**9**) (0.26 g, 1.8%): mp 260 °C (from chloroform); ^{1}H NMR δ 0.84 (3 H, s), 2.31, 2.44, 2.51, 2.56 (15 H, 4 s), 4.83 (1 H, s), 5.05, 5.87 (2 H, AB type, J = 12 Hz), 7.0–7.5 (5 H, m); ^{13}C NMR δ 16.4–19.6, 73.1 (d), 74.0 (t), 100.0 (s), 125.2–137.2, 149.3 (s), 154.5 (s). Anal. Calcd for $C_{29}H_{26}Cl_4N_2O_4S$: C, 54.38; H, 4.09; N, 4.38. Found: C, 54.07; H, 3.98; N, 4.24.

Further elution gave isoxazole **7** (0.23 g, 2.5%), allene **2a** (1.2 g, 28%), and isoxazole **5a** (2.1 g, 23%). Subsequent fractions provided 3-(3,5-dichloro-2,4,6-trimethylphenyl)-4-[(phenylsulfonyl)methyl]isoxazole (**6**) (1.9 g, 21%): mp 136 °C (from chloroform); ^{1}H NMR δ 1.93 (6 H, s), 2.57 (3 H, s), 3.94 (2 H, s), 7.4–7.9 (5 H, m), 8.65 (1 H, s). Anal. Calcd for $C_{19}H_{17}Cl_2NO_3S$: C, 55.61; H, 4.17; N, 3.41. Found: C, 55.44; H, 4.10; N, 3.28.

Reaction of 1 with Alkyne 3b. A solution of **1** (1.0 g) and **3b** (0.84 g) in carbon tetrachloride (43 mL) was refluxed for 20 h. After removal of the solvent, the residue was taken up with diisopropyl ether and filtered to give 3-(3,5-dichloro-2,4,6-trimethylphenyl)-5-[(1-phenylsulfonyl)ethyl]isoxazole (**5b**) (1.7 g,

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92%): mp 168 °C (from cyclohexane–benzene); ^{1}H NMR δ 1.86 (3 H, d, J = 7 Hz), 2.12 (6 H, s), 2.56 (3 H, s), 4.63 (1 H, q, J = 7 Hz), 6.22 (1 H, s), 7.3–8.0 (5 H, m). Anal. Calcd for $C_{20}H_{19}Cl_2NO_3S$: C, 56.61; H, 4.52; N, 3.30. Found: C, 56.80; H, 4.41; N, 3.13.

Reaction of 1 with Allene 2b. A solution of 1 (5.0 g) and **2b** (4.3 g) in carbon tetrachloride (220 mL) was refluxed for 21 h. The solvent was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column (0.7 kg) with benzene as eluent. First fractions gave some solid material (0.4 g; ^{1}H NMR δ 2.0–2.8) followed by 3,3′-bis(3,5-dichloro-2,4,6-trimethylphenyl)-5-methyl-5-(phenylsulfonyl)-4,5′-spirobi(2-isoxazoline) (**8b**) (1.6 g, 11%): mp 240 °C (from hexane–benzene); ^{1}H NMR δ 1.84, 1.87 (9 H, 2 s), 2.44, 2.48, 2.52, 2.59 (12 H, 4 s), 3.32, 4.65 (2 H, AB type, J = 19.5 Hz), 7.5–7.8 (3 H, m), 8.0–8.2 (2 H, m); ^{13}C NMR δ 16.3–19.7, 41.8 (t), 100.0 (s), 101.1 (s), 124.4–136.7, 157.2 (s), 157.6 (s). Anal. Calcd for $C_{30}H_{28}Cl_4N_2O_4S$: C, 55.05; H, 4.24; N, 4.19. Found: C, 54.97; H, 4.32; N, 4.27. Further elution gave isoxazole **5b** (5.1 g, 55%).

Registry No. **1**, 13456-86-5; **2a**, 2525-42-0; **2b**, 13603-90-2; **3a**, 2525-40-8; **3b**, 13603-88-8; **4**, 2525-41-9; **5a**, 96965-01-4; **5b**, 96965-05-8; **6**, 96965-04-7; **7**, 96965-00-3; **8a**, 96965-02-5; **8b**, 96965-06-9; **9**, 96965-03-6; $PhSO_2CH_2COCH_3$, 5000-44-2.

The Photochemistry of 1-Phenyl-1,2-dihydronaphthalene. A Simple Preparation of *cis*-Dibenzobicyclo[3.3.0]octa-2,7-diene

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In a previous paper[1] we reported that 1-phenyl-1,2-dihydronaphthalene (1) irradiated with a broad-spectrum lamp in an apolar solvent yields in 4 h, apart from polymeric material, only one product, viz., *exo*-4-phenylbenzobicyclo[3.1.0]hex-2-ene (*exo*-**4**) (Scheme I).

In the paper mentioned[1] we gave arguments for the supposition that the actual product (*exo*-**4**) originates from the more stable, primary ring opening product cZc-**3**, formed from PE-**1**, via a [π^4a + π^2a] photocycloaddition of cZt-**3**. Furthermore, it was argued that the lifetime of cZc-**2** might be too short to give *endo*-**4** in an analogous way; cZc-**2** should undergo rapid photoisomerization to cZc-**3** or reversal to **1** or both of them.

In further studies devoted to possible photochemical additions of alcohols to unsaturated systems like **1** and **2**, we irradiated **1**, dissolved in methanol, in the presence or absence of an acid, using a ca. 254-nm light source to suppress the formation of *exo*-**4**. On irradiation for 20 h **1** had completely disappeared, and the reaction mixture contained a novel photoproduct, different from *exo*-**4**, which could be readily purified by crystallization. Formation of any photoaddition product could be excluded because the same product was formed even quantitatively when **1** was irradiated with 254-nm light in *hexane* for 24 h.

The mass spectrum (M^+ = 206) showed that the product had the same molecular formula as **1** ($C_{18}H_{14}$). The UV spectrum contained two maxima (272 and 265 nm) of nearly equal height, pointing to a benzene derivative

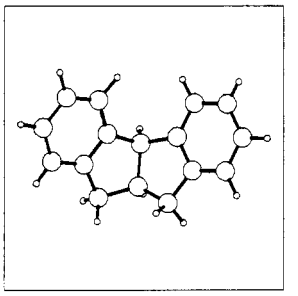
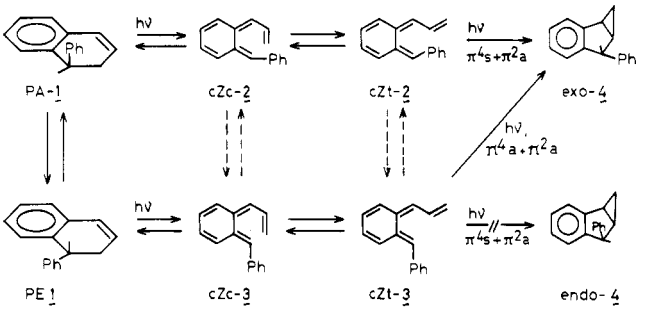
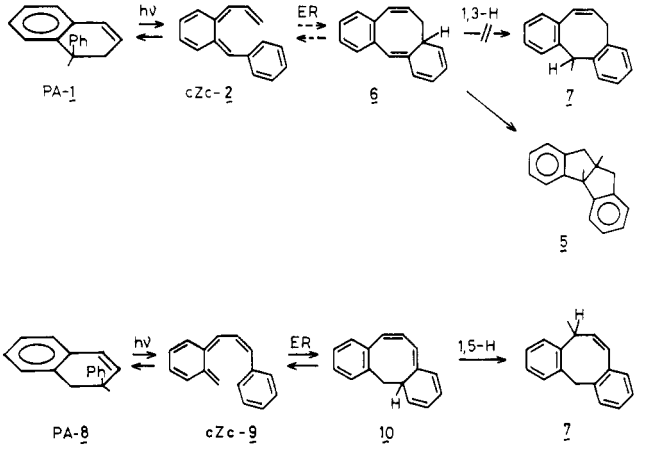


Figure 1. X-ray of **5**.

Scheme I



Scheme II



without extended conjugation. The NMR spectrum, containing two multiplets at δ 2.1–2.9 (2 H) and 3.1–3.6 (3 H), a broadened doublet (δ 4.64, 1 H), and a signal of eight aromatic protons (δ 7.0–7.3), added insufficient information to assign a definite structure. X-ray analysis[2] revealed, however, that the product was *cis*-dibenzobicyclo[3.3.0]octa-2,7-diene (**5**). The molecular configuration is given in Figure 1.

Irradiation of **1**, dissolved in CD_3OD, yielded **5** without any incorporation of deuterium. This excludes that **5** is formed via an ionic or radical process.

A mechanism is given in Scheme II. It implies that the product originates from a primary formed intermediate (cZc-**2**) belonging to the PA conformer of **1**. The electrocyclic reaction cZc-**2** → **6** is similar to the conversion cZc-**9** → **10** (see Scheme II), which was previously proposed[3] to explain the photochemical conversion of 2-phenyl-1,2-di-

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