the participation of the triplet EtOCON in the insertion reaction.[13]

In conclusion, the above results indicate in both cases the formation of a dichloromethane–singlet ethoxycarbonylnitrene complex and the probable involvement of triplet EtOCON in the insertion reaction in the benzylic C–H bonds.

Experimental Section

GC analyses were performed on a Perkin-Elmer F 11 gas chromatograph equipped with a column of 2% OV 17 (2 m × 2 mm). Absolute yields have been evaluated by comparison of the peaks of the reaction mixture with those of standard solutions. Infrared spectra (in CCl_4) were obtained on a Perkin-Elmer 257 Infracord instrument. Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R32 90 MHz spectrometer, using Me_4Si as an internal standard and CCl_4 as solvent. GC–MS were obtained on an AEI-MS 12 spectrometer at an ionization potential of 70 eV, coupled to a Varian 1400 gas chromatograph using a column of 2% OV 17 (2 m × 2 mm).

Ethyl azidoformate was prepared from ethyl chloroformate and sodium azide.[14] Adamantane was obtained from EGA. **3** and **4** were prepared according to a reported procedure.[8] **3:** IR 3440 (NH) and 1725 cm^{-1} (CO); NMR δ 1.2 (t), 1.6–2.2 (m), 4.0 (q), 4.2 (broad). **4:** IR 3450 (NH) and 1720 cm^{-1} (CO); NMR δ 1.2 (t), 1.6–2.0 (m), 4.0 (q), 4.2 (broad). Ethylbenzene was obtained from Fluka.

Thermolysis of Ethyl Azidoformate in Adamantane. (a) In Cyclohexane. Adamantane (204 mg; 1.5 mmol), 144 mg (1.25 mmol) of ethyl azidoformate, and 504 mg (6 mmol) of cyclohexane were placed in a sealed tube and heated at 90 °C for 15 h. GC analysis of the crude product showed that the ratio of **3** to **4** was 4.0 (corrected for numbers of H). The other reaction product cyclohexylurethan does not interfere in the area calculations, showing a shorter retention time.

(b) In Dichloromethane. Adamantane (204 mg; 1.5 mmol), 29 mg (0.25 mmol) of ethyl azidoformate, and 2.5 mL of dichloromethane were placed in a sealed tube and heated at 90 °C for 15 h. The observed tertiary/secondary reactivity ratio was 6.0.

Photolysis of Ethyl Azidoformate in a Cyclohexane Solution of Adamantane. Adamantane (204 mg; 1.5 mmol), 315 mg (2.75 mmol) of ethyl azidoformate, and 1.625 mL (15 mmol) of cyclohexane were photolyzed[7] in a quartz vessel using a medium pressure Hanovia PCR lamp for 6 h. The observed tertiary/secondary reactivity ratio was 4.1.

Thermolysis of Ethyl Azidoformate in Ethylbenzene. Ethylbenzene (1 mL) and 0.1 mL of ethyl azidoformate were placed in a sealed tube and heated at 90 °C for 15 h. The crude mixture was analyzed by GC–MS. The first three peaks (61) were attributed to the isomeric azepines **5–7;** their mass spectra were very similar and the only prominent peaks were at *m/e* 193 (M), 120 (M − EtOCO), and 91 (tropylium ion). The following peak (16) had the same retention time and coincident MS with **8,** synthesized by EtOCOCl treatment of 1-phenylethylamine, obtained by Na/EtOH reduction of acetophenone oximes: *m/e* 193 (M, 36), 178 (92), 164 (73), 147 (16), 132 (37), 120 (58), 106 (100), 105 (71), 91 (12), 79 (92), 77 (60). For synthesized **8:** IR 3440 (NH) and 1720 cm^{-1} (CO); NMR δ 1.2 (t), 1.5 (d), 4.0 (q), 4.8 (broad), 7.3 (s). The following two peaks (23) had the same retention time and coincident MS with meso and *d,l* mixtures of 2,3-diphenylbutanes (**13** and **14**) reported:[15] *m/e* 210 (M), 105 (base peak). The last peak (<0.5%) had the same retention time and coincident MS with **9,** synthesized by EtOCOCl treatment of commercial 2-phenylethylamine (Fluka): *m/e* 193 (M, 16), 164 (7), 120 (7), 104 (38), 102 (100), 91 (74), 77 (10), 65 (10). For synthesized **9:** IR 3450 (NH) and 1725 cm^{-1} (CO); NMR δ 1.2 (t), 2.8 (t), 3.4 (sextet), 4.0 (q), 4.5 (broad), 7.3 (s).

Thermolysis of Ethyl Azidoformate in Ethylbenzene and Dichloromethane. Ethyl azidoformate (0.1 mL), 1 mL of ethylbenzene, and 10 mL of dichloromethane were placed in a sealed tube and heated at 90 °C for 15 h. The crude mixture was analyzed by GC–MS. The major peaks (80%) were the isomeric *N*-ethylphenylurethans **10–12,** as confirmed by the identity of retention times and MS with those obtained by EtOCOCl treatment of the amines coming from Sn/HCl reduction of the isomeric nitroethylbenzenes:[16] *m/e* 193 (M), 178, 147, 134, 132, 120, 106, 91, 77, 65.

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Registry No.—**1,** 281-23-2; **2,** 100-41-4; **3,** 25192-03-4; **4,** 17778-75-5; **5,** 31536-49-9; **6,** 66085-10-7; **7,** 66085-11-8; **8,** 1623-51-4; **9,** 6970-83-8; **10,** 28352-95-6; **11,** 66085-12-9; **12,** 28238-56-4; **13,** 4613-11-0; **14,** 2726-21-8; ethyl azidoformate, 817-87-8; dichloromethane, 75-09-2.

References and Notes

(1) P. A. Tardella, L. Pellacani, G. Di Stazio, and M. Virgillito, *Gazz. Chim. Ital.*, **104,** 479 (1974).
(2) R. C. Belloli, M. A. Whitehead, R. H. Wollenberg, and V. A. LaBahn, *J. Org. Chem.*, **39,** 2128 (1974).
(3) D. S. Breslow and E. I. Edwards, *Tetrahedron Lett.*, 2041 (1972).
(4) R. C. Belloli and V. A. LaBahn, *J. Org. Chem.*, **40,** 1972 (1975).
(5) H. Takeuchi, K. Kinoshita, S. M. A. Hai, M. Mitani, T. Tsuchida, and K. Koyama, *J. Chem. Soc., Perkin Trans. 2,* 1201 (1976).
(6) H. Takeuchi, N. Murata, Y. Nagakawa, T. Tsuchida, and K. Koyama, *J. Chem. Soc., Perkin Trans. 2,* 80 (1977).
(7) P. A. Tardella and L. Pellacani, *J. Org. Chem.*, **41,** 2034 (1976).
(8) D. S Breslow, E. I. Edwards, R. Leone, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **90,** 7097 (1968).
(9) It is impossible to carry out the decomposition of $EtOCON_3$ in pure adamantane (mp 286 °C). Although cyclohexane is a reactive solvent, it should not affect the reactivity ratio, but only the yield. See, for example, Table 2 of ref 1.
(10) J. M. Photis, *J. Heterocycl. Chem.*, **8,** 167 (1971).
(11) Probably acid catalyzed; see K. Hafner, *Angew. Chem.*, **75,** 1041 (1963); *Angew. Chem., Int. Ed. Engl.*, **3,** 165 (1964).
(12) W. Lwowski and R. L. Johnson, *Tetrahedron Lett.*, 891 (1967).
(13) Product **9** was always detectable, but its peak was difficult to integrate, due to its very low amount; for this reason it was not computed.
(14) W. Lwowski and T. W. Mattingly, Jr., *J. Am. Chem. Soc.*, **87,** 1947 (1965).
(15) M. S. Kharash, H. C. Mc Bay, and W. H. Urry, *J. Org. Chem.*, **10,** 401 (1945).
(16) J. R. Knowles, R. O. C. Norman, and G. H. Radda, *J. Chem. Soc.*, 4885 (1960).

2,3-Bis(trimethylsilyloxy)-1,3-butadiene as a Useful Reactive Diene in the Diels–Alder Reaction[1]

David Richard Anderson and Tad H. Koch*

Department of Chemistry, University of Colorado, Boulder, Colorado 80309

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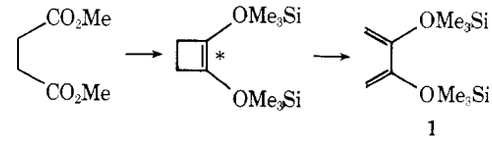
In the course of our present work we have needed to synthesize a number of substituted phthalimides, among them 4,5-dimethoxyphthalimide (**5**) (methahemipinimide). Our synthetic approach to **5** employs a Diels–Alder reaction utilizing the novel diene 2,3-bis(trimethylsilyloxy)-1,3-butadiene (**1**).[2] Further investigation has demonstrated that **1** is indeed a synthetically useful, versatile diene in the Diels–Alder reaction.

2,3-Bis(trimethylsilyloxy)-1,3-butadiene was prepared by the method of Bloomfield and co-workers (Scheme I) although we were able to increase the yield of **1** from 76 to 84% by the addition of 2% by weight hydroquinone to inhibit polymerization during the pyrolysis of the cyclobutene.

The diene **1** was found to readily cycloadd to the dienophiles listed in Table I with the indicated yields. The cisoid conformation of **1** is apparently easily attained since the Diels–Alder cycloadditions occurred under fairly mild conditions. In a typical experiment, 1 equiv each of **1** and the dienophile were either refluxed in dry toluene under a nitrogen atmosphere or heated to 150–200 °C in a sealed combustion tube for 24 h. The products were isolated by fractional vacuum distillation or fractional sublimation.

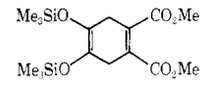
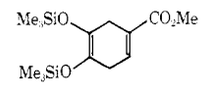
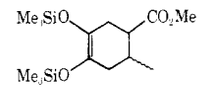
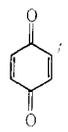
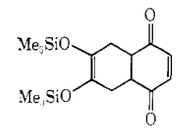
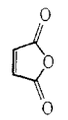
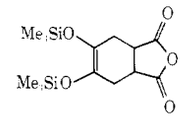
Our original aim was the synthesis of methahemipinimide (**5**), so the cycloadduct **2** was oxidized and further transformed

Scheme I



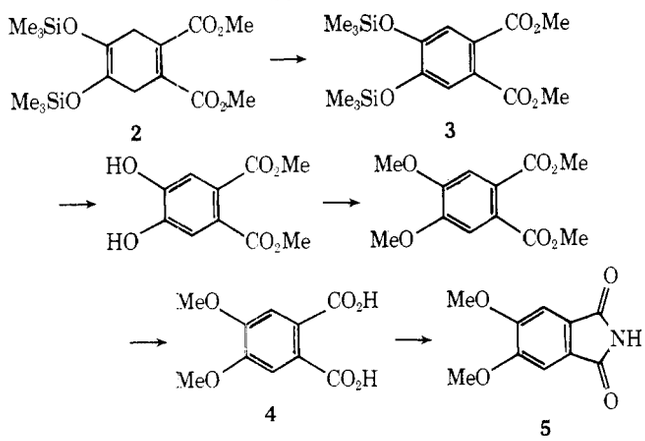
1

Table I. Diels–Alder Cycloadditions to 2,3-Bis(trimethylsilyloxy)-1,3-butadiene

Dienophile	Registry no.	Reaction conditions	Adduct[a]	Registry no.	Yield,[b] %
$MeO_2CC{\equiv}CCO_2Me$	762-42-5	*c*	 **2**	66322-98-3	82
$MeO_2CC{\equiv}CH$	922-67-8	d, 150 °C		66322-99-4	81
	623-43-8	d, 200 °C		66323-00-0	42, 80[e]
	106-51-4	*c*		66323-01-1	78
	108-31-6	*c*		65005-70-1	61

[a] Satisfactory analytical data were obtained for all adducts listed, except 2 (see Experimental Section). [b] Isolated yields. [c] Refluxing toluene. [d] Combustion tube. [e] Based on recovered starting material. [f] Three equivalents of quinone were used.

Scheme II



into metahemipinic acid (4) and the imide according to the synthetic sequence outlined in Scheme II.

Heating the cycloadduct 2 with 1 equiv of sulfur to 210 °C for 15 min yielded the aromatic compound 3 in 95% yield. Hydrolysis of the trimethylsilyloxy groups of 3 with water[4] at room temperature gave a quantitative yield of the diphenol. Subsequent methylation of the diphenol with dimethyl sulfate[5] (94% yield) followed by saponification of the methyl esters with 10% aqueous sodium hydroxide (88% yield) and imide formation by heating the diacid with 2.0 equiv of urea[6] to 180 °C in ethylene glycol (95% yield) gave the desired product, metahemipinimide (5).

Thus the diene 1 appears to be synthetically versatile. An extremely electron rich diene, it is apparently reactive despite its bulky 2,3-substituents since it cycloadds to a variety of dienophiles in high yields under mild conditions. In its utility it is comparable to the 1,3-dialkoxy butadiene systems under investigation by Danishefsky[7] and the 2-alkoxy 3-thioalkoxybutadiene system studied by Trost.[8] The easily hydrolyzable trimethylsilyloxy groups afford the possibility of transformation to 1,2-diones or diols, ortho diphenols or quinones, and methoxy, dimethoxy, and methylenedioxy derivatives, to name a few. With oxidation to aromatic derivatives this scheme is immediately attractive as a potential route to the broad class of adrenergic stimulants, the catecholamines, and as a possible entry into the synthesis of a number of CNS agents, among them some derivatives of morphine. It is hoped that this Diels–Alder diene will find wide applicability in the synthesis of a host of biologically important molecules.

Experimental Section

All melting points are uncorrected. IR spectra were determined with a Perkin-Elmer 337 infrared spectrophotometer. NMR spectra were recorded using a Varian Associates EM390 spectrometer and chemical shifts are reported in parts per million on the δ scale from internal Me_4Si. Mass spectral data were obtained at 70 eV using a Varian MAT CH-5 mass spectrometer. Microanalyses were performed by Atlantic Microlab, Inc. Atlanta, Ga.

2,3-Bis(trimethylsilyloxy)-1,3-butadiene (1).[2] 1,2-Bis(trimethylsilyloxy)cyclobutene (83.4 g) and hydroquinone (0.85 g) were placed in a 2.54 cm by 76.2 cm heavy-walled combustion tube and degassed by bubbling argon through the solution for 5 min. The tube was cooled to liquid nitrogen temperature and sealed off under vacuum. Heating to 180 °C for 6 h and vacuum distillation of the product at 10 mm, 77–79 °C, yielded 70.0 g (84%) of 1 which gave the following spectral absorptions: NMR (CCl_4) δ 0.20 (s, 18 H), 4.23 (s, 2 H), and 4.74 ppm (s, 2 H).

Diels–Alder Cycloadditions: Method A. One equivalent each of the diene 1 and the dienophile were refluxed in dry tolune (distilled from sodium) for 10–24 h under a nitrogen atmosphere. Rotary evaporation of the solvent and vacuum distillation as described or sublimation at 110 °C (0.002 mm) yielded the product. **Method B.** One equivalent each of the diene 1 and the dienophile were placed in a 1.3 cm by 20.3 cm heavy-walled combustion tube, degassed by bubbling argon through the mixture, sealed off under vacuum, and heated to 150–200 °C for 24 h. Vacuum distillation as described or sublimation at 110 °C (0.002 mm) yielded the product.

Cycloaddition of 1 to Dimethyl Acetylenedicarboxylate. Method A (10 h) yielded 82% of a clear liquid 1,2-bis-(trimethylsilyloxy)-4,5-bis(carbomethoxy)-1,4-cyclohexadiene (bp 117–120 °C (5 μm)). The adduct gave the following spectral absorptions: IR (neat) 3.4, 5.8, and 6.0 μm; NMR (CCl_4) δ 0.18 (s, 18 H), 3.04 (s 4 H), and 3.73 (s, 6 H); mass spectrum *m/e* (rel intensity) 372 (46), 341 (19), 251 (70), and 73 (100). The product could not be sufficiently purified for elemental analysis.

Cycloaddition of 1 to Methyl Acetylenecarboxylate. Method B (150 °C, 24 h) yielded 81% of a clear liquid, 1,2-bis(trimethylsilyloxy)-4-carbomethoxy-1,4-cyclohexadiene, after Kugelrohr distillation at 115 °C (0.002 mm). The product gave the following spectral absorptions: IR (neat) 3.4, 5.8, and 5.85 μm; NMR (CCl_4) δ 0.14 (s, 9 H), 0.18 (s, 9 H), 2.97 (m, 4 H), 3.73 (s, 3 H), and 6.80 (m, 1 H); mass spectrum m/e (rel intensity) 314 (37), 193 (22), 147 (29), 75 (27), and 73 (100). The product could not be purified satisfactorily for elemental analysis.

Cycloaddition of 1 to Methyl Crotonate. Method B (200 °C; 24 h) yielded 42% (80% relative to unreacted starting material as determined by NMR of the crude reaction mixture) of a clear liquid, 1,2-bis(trimethylsilyloxy)-4-carbomethoxy-5-methyl-1-cyclohexene, after Kugelrohr distillation at 105 °C (0.002 mm). The adduct gave the following spectral data: IR (neat) 3.4, 5.75, and 5.86 μm; NMR (CCl_4) δ 0.12 (s, 9 H), 0.14 (s, 9 H), 0.92–1.03 (m, 3 H), 1.67–2.50 (m, 6 H), and 3.68 (s, 3 H); mass spectrum *m/e* (rel intensity) 330 (100), 230 (18), 182 (20), 165 (16), 147 (48), 73 (99), 58 (14), 43 (48), and 28 (17). Anal. Calcd for $C_{15}H_{30}O_4Si_2$: C, 54.50; H, 9.14. Found: C, 54.25; H, 9.13.

Cycloaddition of 1 to Benzoquinone. Method A (24 h) using 3 equiv of benzoquinone to minimize 2:1 cycloadduct formation yielded 78% of a yellow solid 6,7-bis(trimethylsilyloxy)-5,8,9,10-tetrahydro-1,4-naphthoquinone (mp 81.5–83 °C) which gave the following spectral absorptions: IR (KBr) 3.4 and 6.0 μm; NMR (CCl_4) δ 0.13 (s, 18 H), 2.0–2.75 (m, 4 H), 3.05–3.35 (m, 2 H), and 6.63 (s, 2 H); mass spectrum *m/e* (rel intensity) 338 (50), 147 (23), 73 (100), and 45 (13). Anal. Calcd for $C_{16}H_{26}O_4Si_2$: C, 56.77; H, 7.74. Found: C, 56.54; H, 7.81.

Cycloaddition of 1 to Maleic Anhydride. Method A (24 h) yielded 61% of a white solid, 4,5-bis(trimethylsilyloxy)-1,2,3,6-tetrahydrophthalic anhydride (mp 51–51.5 °C), with the following spectral absorptions: IR (KBr) 3.4, 5.4, and 5.75 μm; NMR ($CDCl_3$) δ 0.16 (s, 18 H), 2.57–2.67 (m, 4 H), and 3.33–3.47 (m, 2 H); mass spectrum *m/e* (rel intensity) 328 (31), 167 (18), 147 (43), 75 (24), 73 (100), and 45 (13). Anal. Calcd for $C_{14}H_{24}O_5Si_2$: C, 51.19; H, 7.36. Found: C, 50.96; H, 7.40.

Oxidation of Cycloadduct 2. The cycloadduct **2** (65.8 g, 0.177 mol) and sulfur (5.66 g, 0.177 equiv) were heated with stirring in a 250-mL round-bottom flask fitted with a condenser. At 210 °C the mixture vigorously evolved hydrogen sulfide gas. The vessel was maintained at 210 °C for 15 min and then cooled. The reaction mixture was diluted with 100 mL of carbon tetrachloride and 35 g of copper power (previously washed with dilute hydrochloric acid, water, acetone, and finally carbon tetrachloride) was added to remove any unreacted sulfur. The solid materials were filtered off, the solvent was rotary evaporated, and the product was distilled under vacuum (0.002 mm, 120–125 °C) to yield 62.44 g (95.3%) of a clear liquid, dimethyl 4,5-bis(trimethylsilyloxy)phthalate (**3**). The phthalate derivative showed the following spectral absorptions: IR (neat) 3.4 and 5.8 μm; NMR (CCl_4) δ 0.27 (s, 18 H), 3.83, (s, 6 H), and 7.17 (s, 2 H); mass spectrum *m/e* (rel intensity) 370 (92), 339 (17), 251 (100), and 73 (92). Anal. Calcd for $C_{16}H_{26}O_6Si_2$: C, 51.86, H, 7.07. Found: C, 51.77; H, 7.08.

Hydrolysis of 3. The phthalate **3** (61.8 g, 0.167 mol) was stirred with 100 mL of water at room temperature overnight. The water and hexamethyldisiloxane were rotary evaporated to yield 37.6 g (99.6%) of a white solid, dimethyl 4,5-dihydroxyphthalate. Recrystallization from Skellysolve B/ethyl acetate gave white needles, mp 141.5–142.5 °C, with the following spectral properties: IR (KBr) 2.9, 3.0, 3.4, 5.8, 5.9, and 6.2 μm; NMR (acetone-d_6) δ 3.80 (s, 6 H), 7.25 (s, 2 H), and 8.83 (br s, 2 H); mass spectrum *m/e* (rel intensity) 226 (42), and 195 (100). Anal. Calcd for $C_{10}H_{10}O_6$: C, 53.10; H, 4.46. Found: C, 53.14; H, 4.49.

Conversion of Dimethyl 4,5-Dihydroxyphthalate to Imide 5. Dimethyl 4,5-dihydroxyphthalate (33.47 g, 0.148 mol) was dissolved in 500 mL of dry acetone. Potassium carbonate (90 g, 0.652 mol) and dimethyl sulfate (41 g, 0.326 mol) were added and the solution was refluxed with stirring under a nitrogen atmosphere for 8 h, at which point the solution gave a negative ferric chloride test. The salts were filtered off and the acetone was removed by rotary evaporation. Water (50 mL) was added and the organic product was extracted with three 300-mL portions of ether. The ether layers were combined, washed with water, and dried over magnesium sulfate and the ether was rotary evaporated to yield 35.4 g (94%) of a white solid, dimethyl 4,5-dimethoxyphthalate, mp 88–89 °C, with the following spectral properties: IR (KBr) 3.33, 3.4, 5.78, 5.84, and 6.27 μm; NMR (CCl_4) δ 3.80 (s, 6 H), 3.87 (s, 6 H), and 7.04 (s, 2 H); mass spectrum *m/e* (rel intensity) 254 (66) and 223 (100).

The dimethoxyphthalate (34.35 g, 0.135 mol) was saponified by refluxing in 125 mL of 10% aqueous sodium hydroxide solution for 3 h. The solution was cooled and acidified to pH 1 with concentrated hydrochloric acid and the precipitate was filtered off and dried under vacuum to yield 26.9 g (88%) of a white solid, 4,5-dimethoxyphthalic acid, mp 198–199.5 °C dec (lit.[9] mp 193–199 °C). The phthalic acid derivative (**4**) gave the following spectral absorptions: IR (KBr) 3.1–3.6 (br), 4.2 (br), 5.85, 6.12, and 6.3 μm; NMR (Me_2SO-d_6) δ 3.83 (s, 6 H) and 7.23 (s, 2 H); mass spectrum *m/e* (rel intensity) 226 (100).

The diacid **4** (26.5 g, 0.117 mol), urea (14 g, 0.234 mol), and 250 mL of ethylene glycol were heated with stirring to 180 °C until no more ammonia evolved as tested by pH paper. The solution was cooled and the product was filtered off, washed with water, and dried under vacuum to yield 23.1 g (95%) of a cream-colored solid, 4,5-dimethoxyphthalimide. Recrystallization from acetic acid gave white needles, mp > 320 °C (lit.[10] mp >300 °C), with the following spectral properties: IR (KBr) 3.02, 5.7, 5.8, and 6.25 μm: NMR (Me_2SO-d_6) δ 3.88 (s, 6 H) and 7.33 (s, 2 H); mass spectrum *m/e* (rel intensity) 207 (12), 206 (100), 192 (19), 164 (12), 136 (20), and 121 (22).

Registry No.—**1**, 31411-71-9; **3**, 66323-02-2; **4**, 577-68-4; **5**, 4764-20-9; 1,2-bis(trimethylsilyloxy)cyclobutene, 17082-61-0; hydroquinone, 123-31-9; dimethyl 4,5-dihydroxyphtholate, 66323-03-3; dimethyl 4,5-dimethoxyphthalate, 17078-61-4; urea, 57-13-6.

References and Notes

(1) Financial support from the National Institutes of Health under Grant GM 18349 is gratefully acknowledged. D.R.A. thanks the National Science Foundation for a Traineeship.
(2) J. J. Bloomfield, H. M. Frey, and J. Metcalfe, *Int. J. Chem. Kinet.*, **3**, 85 (1971); R. E. K. Winter and M. L. Honig, *J. Am. Chem. Soc.*, **93**, 4616 (1971).
(3) J. Weichet, J. Hodrova, and L. Blaha, *Collect. Czech. Chem. Commun.*, **29**, 197 (1964).
(4) C. A. Brukland, *J. Org. Chem.*, **22**, 592 (1957).
(5) S. Fukushima, A. Ueno, and Y. Akahori, *Chem. Pharm. Bull.*, **12**, 312 (1964).
(6) G. Ya. Kondrat'eva and H. Chih-heng, *Zh. Prikl. Khim. (Leningrad)*, *35*, 119 (1962); J. M. Gulland and R. Robinson, *J. Chem. Soc.*, **127**, 1493 (1925).
(7) S. Danishefsky and T. Kitahara, *J. Am. Chem. Soc.*, **96**, 7807 (1974); S. Danishefsky, R. K. Singh, and R. B. Gammill, *J. Org. Chem.*, **43**, 379 (1978).
(8) B. M. Trost and A. J. Bridges, *J. Am. Chem. Soc.*, **98**, 5017 (1976).
(9) H. R. Arthur and Y. L. Ng, *J. Chem. Soc.*, 3095 (1959).
(10) W. H. Perkin, *J. Chem. Soc.*, **109**, 815 (1916).

Peroxy Acid Oxidation of Alkyl Phenyl Disulfides

Ajit K. Bhattacharya and Alfred G. Hortmann*

Department of Chemistry, Washington University, St. Louis, Missouri 63130

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The oxidation of an unsymmetrical disulfide, RS–SR′, with 2 equiv of a suitable oxidizing agent might yield two possible thiolsulfonates, namely, RSO_2–SR′ and RS–SO_2R′, provided no cleavage of the S–S bond occurs in the course of the oxidation. Depending on the nature of the substituent groups, one might expect to observe a preponderance of one isomeric product over the other.[1] In connection with another study, we found it desirable to establish the relative reactivity of phenyl- vs. alkyl-substituted sulfur atoms toward peroxy acid in such unsymmetrical disulfides. Toward this end, the peroxy acid oxidation of ethyl phenyl disulfide (**1**) and benzyl disulfide (**2**) was studied.

$$\underset{\mathbf{1}}{CH_3CH_2SSC_6H_5} \xrightarrow{\text{MCPBA}} \underset{\mathbf{1a}}{CH_3CH_2SO_2SC_6H_5}$$

$$\underset{\mathbf{2}}{C_6H_5CH_2SSC_6H_5} \xrightarrow{\text{MCPBA}} \underset{\mathbf{2a}}{C_6H_5CH_2SO_2SC_6H_5}$$

Upon oxidation of ethyl phenyl disulfide (**1**) with 2.3 equiv of *m*-chloroperoxybenzoic acid (MCPBA), phenyl ethanethiolsulfonate (**1a**) was formed as the major product in ca. 75 ± 10% yield. Similarly, oxidation of **2** with MCPBA (2.0 equiv) afforded **2a** in ca. 65% yield. In both reactions, considerable amounts of difficultly separable materials were produced; however, none of the possible alternate isomeric products, ethyl benzenethiolsulfonate (**1b**) or benzyl benzenethiolsulfonate (**2b**), respectively, were detectable in the crude oxi-

$$\underset{\mathbf{1b}}{CH_3CH_2SSO_2C_6H_5} \qquad \underset{\mathbf{2b}}{C_6H_5CH_2SSO_2C_6H_5}$$

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