Acid Amide (6d): bp 140–141 °C (0.1 mm); IR (neat) 1660 (amide), 1600, 1580, 1500 cm^{-1} (aromatic); ^1H NMR ($CDCl_3$) 7.3 (s, 5 H), 4.6 (s, 2 H), 3.95 (t, 2 H, J = 14 Hz), 5.55 (ddd, 1 H, J = 47, 15, 7 Hz), 3.35 (q, 4 H, J = 7 Hz), 1.1 (t, 6 H); ^{19}F NMR ($CDCl_3$) 121 (dt, 2 F, J = 10, 14 Hz), 122 (ddd, 1 F, J = 294, 15, 16 Hz), 127 (ddd, 1 F, J = 13, 7 Hz), 200 (m, 1 F); mass spectrum m/e (rel intensity) 353 ($M^{\cdot+}$, 43), 334 (M − F, 12), 297 (M − $2C_2H_4$, 10), 262 (M − C_7H_7, 42), 247 (M − C_7H_7 − CH_3, 100).

Anal. Calcd for $C_{16}H_{20}F_5NO_2$: C, 54.38; H, 5.70; N, 3.96. Found: C, 54.65; H, 5.55; N, 3.77.

The enamine **5d** (1-diethylamino-5*H*,5*H*-5-benzyloxyhexafluoropentene-1) was isolated from the crude reaction mixture by evaporation of the solvent before hydrolysis: ^{19}F NMR 117 (tt, 2 F), 122 (m, 2 F), 120 (dt, 1 F, J = 12, 7 Hz), 115 (dt, 1 F, J = 12 Hz).

***N,N*-Diethyl-2*H*,7*H*-7-ethylenedioxynonafluoroheptanoic Acid Amide (6e):** bp 139–140 °C (0.1 mm); IR (neat) 1660 cm^{-1} (amide); ^1H NMR ($CDCl_3$) 3.5 (q, 4 H, J = 7 Hz), 1.25 (t, 6 H), 3.95 (m, 4 H), 4.9 (ddd, 1 H, J = 34, 13, 6 Hz), 5.1 (m, 1 H); ^{19}F NMR 119–121–124 (m, 8 F), 197 (dm, 1 F); mass spectrum m/e (rel intensity) 405 ($M^{\cdot+}$, 10), 361 (M − OC_2H_4, 18), 346 (M − OC_2H_3, 100), 332 (M − $C_3H_5O_2$, 36).

Anal. Calcd for $C_{13}H_{16}F_9NO_3$: C, 38.53; H, 3.98; N, 3.46. Found: C, 38.68; H, 3.84; N, 3.46.

Registry No.—**1a,** 355-37-3; **1b,** 336-07-2; **1c,** 60895-94-5; **1d,** 60895-95-6; **1e,** 60895-96-7; **5d,** 60895-97-8; **6a,** 60895-98-9; **6b,** 60895-99-0; **6c,** 60934-65-8; **6d,** 60896-00-6; **6e,** 60896-01-7.

References and Notes

(1) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969, p 417; L. H. Slaugh and E. Bergman, *J. Org. Chem.*, **26,** 3158 (1961).
(2) T. J. Brice, W. H. Pearlson, and J. H. Simmons, *J. Am. Chem. Soc.*, **68,** 968 (1946).
(3) W. A. Severson and T. J. Brice, *J. Am. Chem. Soc.*, **80,** 2313 (1958); V. C. R. McLoughlin, *Tetrahedron Lett.*, 4761 (1968).
(4) S. Andreades, *J. Am. Chem. Soc.*, **86,** 2003 (1964).
(5) J. D. Lazerte and R. J. Koshar, *J. Am. Chem. Soc.*, **77,** 910 (1955).
(6) Peninsular Chemical Research, Gainesville, Fla.
(7) S. Nagase, H. Baba, K. Tanake, and T. Abe, *Kogyo Kagaku Zasshi*, **67,** 2062 (1964); C. Fuller and J. C. Tatlow, *J. Chem. Soc.*, 3198 (1961); P. Robson, J. Roylance, R. Stephens, J. C. Tatlow, and R. E. Worthington, *ibid.*, 5748 (1964); R. R. Twelves and V. Weinmayr, U.S. Patent 3 076 041 (1963); W. Bloechl, Netherlands Appl. 6 414 504 (1965).
(8) N. O. Brace, *J. Org. Chem.*, **26,** 4005 (1961).
(9) R. M. Joyce, Jr., U.S. Patent 2 559 628 (1951).
(10) H. J. Dauben, Jr., B. Loken, and H. J. Ringold, *J. Am. Chem. Soc.*, **76,** 1359 (1954).
(11) PCUK, Produits Chimiques Ugine Kuhlman; PCR, Peninsular Chem Research, Gainesville Fla.; DGRST, Déléguation Générale à la Recherche Scientifique et Technique.

Synthesis and Activity of 29-Hydroxy-3,11-dimethyl-2-nonacosanone, Component B of the German Cockroach Sex Pheromone

Albert W. Burgstahler,* Leland O. Weigel, Mark E. Sanders, and Craig G. Shaefer

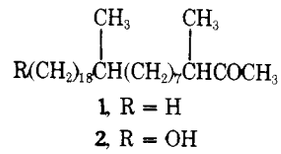
Department of Chemistry, The University of Kansas, Lawrence, Kansas 66045

William J. Bell and Susan B. Vuturo

Department of Entomology, The University of Kansas, Lawrence, Kansas 66045

Received June 2, 1976

In a previous report,[1] we described a synthesis of 3,11-dimethyl-2-nonacosanone (**1**), an active component of the contact mating pheromone present in the cuticle of the female German cockroach (*Blattella germanica*). Recently, Ishii and co-workers, who first isolated and synthesized this substance,[2] have identified a closely related second component, 29-hydroxy-3,11-dimethyl-2-nonacosanone (**2**).[3] In connection with

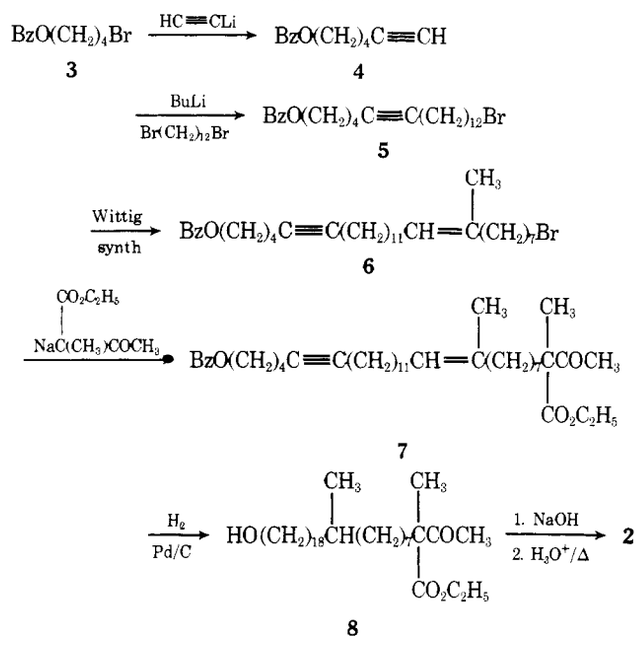


1, R = H
2, R = OH

studies on the behavioral responses of cockroaches to pheromones,[4] we undertook and now describe a synthesis of **2** together with some preliminary bioassays.

As shown in Chart I, the benzyl ether (**3**) of 4-bromo-1-butanol was used to assemble the terminal hydroxy chain.

Chart I



This derivative was selected because of its greater stability and convenience for removal compared to the alternative tetrahydropyranyl ether and because its distinctive spectral features made it especially useful for monitoring subsequent steps. The preparation of **3** was achieved in 88% yield by the phase-transfer catalyzed reaction[5] of 1,4-dibromobutane (5 equiv) with sodium benzyloxide. By alkylation with lithium acetylide (as the ethylenediamine complex), **3** was converted almost quantitatively into the acetylenic ether **4.** Monoalkylation of 1,12-dibromododecane (3 equiv) with the lithium salt of **4** then provided the acetylenic bromo ether **5** in 84% yield.

In the next step, a Wittig reaction of 9-bromo-2-nonanone[2] with the triphenylphosphorane derivative of **5** gave the olefinic bromo ether **6** as a mixture of *Z* and *E* isomers in 56% yield. Alkylation of **6** with ethyl 2-methylacetoacetate then furnished the required benzyloxy keto ester **7** in 91% yield. Finally, hydrogenation–hydrogenolysis of **7** gave the saturated hydroxy keto ester **8** (97% yield), mp 30–32 °C, which, when hydrolyzed and decarboxylated, afforded, in 71% yield from **8,** the desired hydroxy ketone **2** as a mixture of diastereoisomers, mp 41.5–43 °C.

Bioassay by antennation[1,2] showed that synthetic **2** readily evoked the characteristic precopulatory wing raising and 180°-turning response in isolated adult male German cockroaches. Male roaches isolated from their parent colonies were housed and tested in groups of five. In the tests their antennae were stroked intermittently (~10 s/min) with freshly ablated American cockroach (*Periplaneta americana*) antennae that had been dipped for 1–2 s into a carbon tetrachloride solution of the test substance and then allowed to dry.[6] All tests were performed at 24–25 °C during a period of 2.5–4.0 h into the dark phase of a 12/12-h photocycle.

In 3-min tests on males isolated for 2–4 days, synthetic **2** at a concentration of 250 μg/ml exhibited about half the activity of synthetic **1** (23% vs. 48% response; $n = 60$ in each group). With longer periods of isolation and extended testing times considerable increase in response sensitivity was observed. Thus after isolation for 24 days, 40% of 25 males responded to **1** at 100 μg/ml when intermittently antennated for up to 8 min each. Similarly, a low molecular weight analogue, 3-methyl-2-heneicosanone, found previously to be devoid of activity at 500 μg/ml toward males isolated for 2–4 days,[1] produced ~10% response in 8-min tests at 100 μg/ml and ~70% response at 1000 μg/ml in 24-day isolates.

With an isolation period of only 2–4 days and testing for up to 3 min, the response to **1** dropped to ~5% at 70 μg/ml,[1,7] whereas the activity of **2** did not decrease to this level until diluted to ~5 μg/ml. Moreover, under these conditions 3:1 and 1:1 mixtures of **1** and **2** at a total concentration of 250 μg/ml evoked 63 and 60% response, respectively, while a 1:3 mixture showed only 48% response ($n = 60$ in each group). Neither the solvent alone nor the synthetic intermediates **7** or **8** produced any sexual display.

These findings, therefore, not only confirm the pheromonal activity of **2**, but they also suggest a synergistic effect between **1** and **2**. Further study of these compounds is continuing.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137B Infracord spectrophotometer. Proton magnetic resonance (^{1}H NMR) spectra were taken on a Varian A-60A instrument in carbon tetrachloride with tetramethylsilane as internal reference. Electron impact mass spectra (MS) were obtained at 70 eV with a Varian CH-5 spectrometer by Mr. Robert Drake, University of Kansas Department of Chemistry. All reactions were conducted under dry argon or nitrogen; organic extracts were dried over anhydrous magnesium sulfate. Homogeneity assays were made by TLC (silica gel 60F-254, 0.25 mm layer), GLC (Varian A90-P3 instrument, 6 ft × 0.25 in. stainless steel column packed with 10% OV-17 on 100–120 mesh Gas-Chrom Q), or HPLC (Waters 6000A unit, 25-cm column of 10 μ Partisil 10 ODS). Preparative layer chromatography (PLC) was conducted on precoated F-254 silica gel plates (20 × 20 × 0.2 cm). Elemental analyses were performed on an HP-185C CHN analyzer by Mr. Tho Nguyen, University of Kansas Department of Medicinal Chemistry microanalyst.

4-Benzyloxy-1-bromobutane (3). To a magnetically stirred solution of 10 g of sodium hydroxide in 20 g of water cooled to 10 °C were added 5.4 g (50 mmol) of benzyl alcohol, 54 g (250 mmol) of 1,4-dibromobutane, and 0.85 g (2.5 mmol) of tetrabutylammonium hydrogen sulfate[5] (Aldrich). After stirring (~300 rpm) for 10 h at 25 °C, the mixture was poured into 300 ml of water and extracted with pentane, and the dried extracts were evaporated. Slow distillation of the product at 0.3 mm through a 25-cm Vigreux column furnished 40 g of recovered 1,4-dibromobutane and benzyl alcohol (bp 30–40 °C) and 10.7 g (88%) of **3** (>99% by GLC): bp 103–105 °C (0.3 mm); IR (film) 3040, 1215, 1110, 740, and 700 cm^{-1}; ^{1}H NMR δ 7.23 (s, 5 H), 4.43 (s, 2 H), 3.42 and 3.36 (overlapping triplets, $J = 7$ Hz, 4 H), 1.83 (m, 4 H); MS *m/e* (rel intensity) 244 (0.2, $M^+ + 2$), 242 (0.2, M^+), 92 (42), 91 (100). Anal. Calcd for $C_{11}H_{15}OBr$: C, 54.33; H, 6.22. Found: C, 54.53; H, 6.39.

6-Benzyloxy-1-hexyne (4). To a solution of 2.69 g (28.0 mmol) of lithium acetylide ethylenediamine complex (Alpha, 96%) in 56 ml of dimethyl sulfoxide[8] was added 6.82 g (28.0 mmol) of **3** with stirring at 5–10 °C. After stirring for 12 h at 25 °C the mixture was poured into water and the product recovered by extraction with pentane. Short-path distillation gave 5.12 g (97%) of **4** (>99.5% by GLC): bp 85 °C (0.01 mm); IR (film) 3300, 2120, 1110, 740, and 700 cm^{-1}; ^{1}H NMR δ 7.20 (s, 5 H), 4.42 (s, 2 H), 3.42 (t, $J = 7$ Hz, 2 H), 2.15 (t split 2.5 Hz, $J = 7$ Hz, 2 H), 1.79 (t, $J = 2.5$ Hz, 1 H), 1.68 (m, 4 H); MS *m/e* (rel intensity) 188 (1.4, M^+), 91 (100). Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.87; H, 8.59.

1-Benzyloxy-18-bromo-5-octadecyne (5). The monolithium salt of **4** (5.65 mmol in 6 ml of tetrahydrofuran, generated by the method of Schwarz[9]) was added dropwise at 20 °C to a stirred solution of 5.72 g (17.4 mmol) of 1,12-dibromododecane (Aldrich) in 25 ml of hexamethylphosphoramide and 15 ml of tetrahydrofuran. After stirring for 24 h at 25 °C the mixture was diluted with water and extracted with pentane, and the dried pentane extracts were evaporated. Rapid distillation of the residue yielded ca. 4.0 g of recovered dibromide, bp 130 °C (0.005 mm), and then 2.06 g (84%) of **5** (~97% by GLC): bp 238–240 °C (0.005 mm); IR (film) 3340, 1215, 1110, 740, and 700 cm^{-1}; ^{1}H NMR δ 7.21 (s, 5 H), 4.43 (s, 2 H), 3.42 and 3.35 (overlapping triplets, $J = 7$ Hz, 4 H), 2.35–1.87 (broad m, 4 H), 1.87–1.48 (m, 4 H), 1.27 (broad s, 20 H); MS *m/e* (rel intensity) 436 (2.1, $M^+ + 2$), 435 (2.6), 434 (2.3, M^+), 433 (2.2), 91 (100). Anal. Calcd for $C_{25}H_{39}OBr$: C, 68.95; H, 9.03. Found: C, 69.31; H, 9.03.

(*Z*)- and (*E*)-26-Benzyloxy-1-bromo-8-methylhexacos-8-en-21-yne (6). A solution of 178 mg (0.409 mmol) of **5** and 108 mg (0.412 mmol) of triphenylphosphine in 1.2 ml of xylene was heated at 140 °C for 20 h. The xylene was removed in vacuo at 20 ° C and the residue washed with three 1-ml portions of dry ether at −78 °C. The vacuum-dried, viscous phosphonium salt (247 mg, 0.354 mmol, 86%) was dissolved in 2 ml of tetrahydrofuran–ether (1:1) and 0.63 ml of 0.57 M methyllithium (in ether) was added slowly at −23 °C, followed by 150 mg (0.678 mmol) of 9-bromo-2-nonanone.[2b,11] After stirring for 0.5 h at −23 °C and then for 6 h at 30 °C the mixture was diluted with water and extracted with pentane. After drying and evaporation of the pentane, PLC (ether–pentane, 1:10) of the residue gave 108 mg (56% from the phosphonium salt) of **6** as a colorless, oily mixture of *Z* and *E* isomers: R_f 0.61; IR (film) 3040, 1215, 1110, 740, and 700 cm^{-1}; ^{1}H NMR δ 7.20 (s, 5 H), 5.05 (t, $J = \sim 6$ Hz, 1 H), 4.42 (s, 2 H), 3.41 and 3.32 (overlapping triplets, $J = 7$ Hz, 4 H), 2.2–1.7 (broad m, 8 H), 1.7–1.5 (m, 7 H), 1.27 (broad s, 28 H); MS *m/e* (rel intensity) 560 (1.2, $M^+ + 2$), 558 (1.2, M^+), 91 (100). Anal. Calcd for $C_{34}H_{55}OBr$: C, 72.96; H, 9.91. Found: 72.87; H, 9.92.

Ethyl (*Z*)- and (*E*)-2-Acetyl-28-benzyloxy-2,10-dimethyloctacos-10-en-23-ynoate (7). By means of a syringe, 480 mg (0.858 mmol) of **6** was added at 25 °C to 1.27 mmol of the sodium hydride generated enolate of ethyl 2-methylacetoacetate (Aldrich, fractionally distilled, 98% by GLC) in 3 ml of benzene–dimethylformamide (2:1). This mixture was stirred at 60 °C for 27 h, poured into 100 ml of water, and extracted with pentane. The washed extracts were dried and evaporated at 20 mm, and the yellow residue (550 mg) was purified by PLC (chloroform, two-developments) to give 489 mg (91%) of **7** as a colorless oil: R_{f2} 0.47; IR (film) 3040, 1740, 1720, 1110, 740, and 700 cm^{-1}; ^{1}H NMR δ 7.20 (s, 5 H), 5.03 (t, $J = \sim 6$ Hz, 1 H), 4.42 (s, 2 H), 4.13 (q, $J = 7$ Hz, 2 H), 3.42 (t, $J = 7$ Hz, 2 H), 2.2–1.7 (broad m, 8 H), 2.03 (s, 3 H), 1.65–1.55 (m, 10 H), 1.26 (broad s, 30 H), 1.23 (t, $J = 7$ Hz, 3 H); MS *m/e* (rel intensity) 622 (0.97, M^+), 91 (100). Anal. Calcd for $C_{41}H_{66}O_4$: C, 79.05; H, 10.68. Found: C, 79.16; H, 10.68.

Ethyl 2-Acetyl-28-hydroxy-2,10-dimethyloctacosanoate (8). A solution of 147 mg (0.236 mmol) of **7** in 15 ml of absolute ethanol was stirred under 1 atm of hydrogen with 50 mg of 30% palladium–carbon until 4 equiv of hydrogen was absorbed (ca. 12 h). Filtration and evaporation (0.1 mm) gave 127 mg (97%) of **8** as a colorless, waxy solid: mp 31–32 °C; IR (melt) 3360, 1740, and 1720 cm^{-1}; ^{1}H NMR δ 4.13 (q, $J = 7$ Hz, 2 H), 3.52 (t, $J = 6.5$ Hz, 2 H), 2.25 (broad s, 1 H), 2.05 (s, 3 H), 1.55 (m, 1 H), 1.27 (t, $J = 7$ Hz, 3 H), 1.25 (m, 51 H), 0.83 (d, $J = 6$ Hz, 3 H); MS *m/e* (rel intensity) 538 (0.99, M^+), 112 (100). Anal. (after PLC, ether–chloroform, 1:2; R_f 0.43) Calcd for $C_{34}H_{66}O_4$: C, 75.78; H, 12.34. Found: C, 75.99; H, 12.45.

29-Hydroxy-3,11-dimethyl-2-nonacosanone (2). A solution of 108 mg (0.200 mmol) of **8** in 0.6 ml of 0.8 M ethanolic sodium hydroxide was stirred at 40 °C for 6 h. After acidification with 1% hydrochloric acid and warming to 60 °C, the mixture was diluted with water and extracted with pentane. Evaporation of the pentane followed by PLC (ether–chloroform, 1:2, two developments) afforded 66 mg (71%) of nearly pure **2**, mp 38–40 °C, R_{f2} 0.50. Recrystallization from pentane at −40 °C furnished an analytical sample: mp 41.5–43 °C; IR (melt) 3340, 1710, 1045, and 710 cm^{-1}; ^{1}H NMR δ 3.52 (t, $J = 6$ Hz, 2 H), 2.34 (m, $J = 6.8$ Hz, 1 H), 2.3 (broad s, 1 H), 2.01 (s, 3 H), 1.53 (m, 1 H), 1.23 (broad s, 48 H), 1.04 (d, $J = 6.8$ Hz, 3 H), 0.84 (d, $J = 6$ Hz, 3 H); MS *m/e* (rel intensity) 466 (2.9, M^+), 72 (100). Anal. Calcd for $C_{31}H_{62}O_2$: C, 79.76; H, 13.39. Found: C, 79.64; H, 13.58.

Acknowledgments. Fellowship aid from the Phillips Petroleum Co. to L.O.W. and financial support from the National Science Foundation (BNS75-21019 and SMI76-03094), the National Institute of Mental Health (R03-MH-27545), and the Velsicol Corp. to W.J.B. are gratefully appreciated. We also thank Professor S. Ishii for information concerning results of his investigations in advance of publication.

Registry No.—**2**, 60789-53-9; **3**, 60789-54-0; **4**, 60789-55-1; **4** Li salt, 60789-56-2; **5**, 60789-57-3; *Z*-**6**, 60789-58-4; *E*-**6**, 60789-59-5; *Z*-**7**, 60789-60-8; *E*-**7**, 60789-61-9; **8**, 60815-96-5; benzyl alcohol, 100-51-6;

1,4-dibromobutane, 110-52-1; 1,12-dibromododecane, 3344-70-5; 9-bromo-2-nonanone, 52330-02-6; ethyl 2-methylacetoacetyl enolate, 29537-38-0.

References and Notes

(1) A. W. Burgstahler, L. O. Weigel, W. J. Bell, and M. K. Rust, *J. Org. Chem.*, **40**, 3456 (1975).
(2) (a) R. Nishida, H. Fukami, and S. Ishii, *Appl. Entomol. Zool.*, **10**, 10 (1975); (b) T. Sato, R. Nishida, Y. Kuwahara, H. Fukami, and S. Ishii, *Agric. Biol. Chem.*, **40**, 391 (1976). For other syntheses of **1**, see M. Schwarz, J. E. Oliver, and P. E. Sonnet, *J. Org. Chem.*, **40**, 2410 (1975); also L. D. Rosenblum, R. J. Anderson, and C. A. Henrick, *Tetrahedron Lett.*, 419 (1976).
(3) (a) Reported at the meeting of the Japanese Society of Agricultural Chemistry, Kyoto, Japan, April 1976. (b) **Note Added in Proof.** A synthesis of **2** (diastereoisomeric mixture, mp 40–41 °C) has now also been reported by Professor Ishii's group along with data showing biological activity equivalent to that of the natural pheromone but greater than that of **1**: R. Nishida, T. Sato, Y. Kuwahara, H. Fukami, and S. Ishii, *Agric. Biol. Chem.*, **40**, 1407 (1976).
(4) M. K. Rust, T. Burk, and W. J. Bell, *Anim. Behav.*, **24**, 52 (1976); M. K. Rust and W. J. Bell, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 2524 (1976).
(5) Cf. H. H. Freedman and R. A. Dubois, *Tetrahedron Lett.*, 3251 (1975); J. Dockx, *Synthesis*, 447 (1973).
(6) In our experience, bioassays conducted with either American cockroach antennae[1] or male German cockroach antennae[2] give comparable results.
(7) Although our test results on synthetic **1** are in accord with those in ref 2a, which noted "distinct activity [for both natural **1** and synthetic **1**] at a concentration of 50 μg/ml" in CCl_4 toward "sexually mature males which had been segregated from females for 1 to 2 weeks after their adult emergence", apparently higher activities are recorded in ref 2b. In the latter report, 50% response to synthetic **1** at 1.7 μg/ml ("3.7×10^{-9} mol/ml") and to 3-methyl-2-heneicosanone at 22.4 μg/ml ("6.9×10^{-8} mol/ml") was indicated for males "segregated from females for 12–13 days after their adult emergence".
(8) F. L. M. Pattison and R. E. A. Dear, *Can. J. Chem.*, **41**, 2600 (1963).
(9) M. Schwarz and R. M. Waters, *Synthesis*, 567 (1972).
(10) H. Normant, *Angew. Chem., Int. Ed. Engl.*, **6**, 1046 (1967).
(11) Prepared in 68% overall yield by alkylation of 1,6-dibromohexane (3 equiv) with the NaH-generated enolate (1 equiv) of ethyl acetoacetate in benzene–dimethylformamide (5:1) at 55–60 °C, followed by hydrolysis–decarboxylation at 25–30 °C in 48% HBr–acetic acid (1:1) for 40 h; bp 83–85 °C (0.01 mm).

Selective Reduction of Sulfoxides[1]

Ralph G. Nuzzo, Henry J. Simon, and Joseph San Filippo, Jr.*

Wright and Rieman Chemistry Laboratories, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08903

Received July 30, 1976

Sulfoxides are important intermediates in a variety of synthetic transformations. The successful application of these procedures generally requires the removal of the residual sulfoxide moiety and a number of processes have been devised for achieving such transformations. Ostensibly, one of the simplest of these involves the reduction of the sulfoxide to a sulfide which is then further reduced by treatment with Raney nickel or a reducing metal system such as lithium in liquid ammonia or amine.

The mildest and therefore the most desirable procedures for effecting the reduction of sulfoxides to sulfides involve either their prolonged treatment with triphenylphosphine in refluxing carbon tetrachloride,[2] reaction with titanium(III),[3] or their conversion to an alkoxysulfonium salt, which in turn is reduced by reaction with borohydride[4a] or (more selectively) cyanohydride borate.[4b] Each of these procedures possess disadvantages: the former two have limited selectivity, the latter are inconvenient at best.

We wish to report that the reaction of sulfoxides with various complex ions of molybdenum(II), -(III), and tungsten(III) provides a procedure for the reduction of a sulfoxide to the corresponding sulfide that is facile, efficient, and highly selective. This procedure seems applicable to the reduction of a broad spectrum of sulfoxides under mild conditions. Although water is generally a good solvent, the use of methanol as a solvent or cosolvent resulted in improved yields in those instances where (1) the sulfoxide has only a very limited solubility in water or (2) the complex ion is relatively unstable in neutral water as, for example, are salts of octachlorodimolybdenum(II) ion, $Mo_2Cl_8^{4-}$.

Numerous reagents are capable of effecting deoxygenations of various organic substrates. Most of these are not specific. Thus, for example, phosphites and phosphines, two of the most commonly employed deoxygenating agents, will reduce a variety of functional groups including nitrile oxides to nitriles,[6] epoxides to olefins,[7] and certain alkyl halides to the corresponding hydrocarbon. In addition, these reagents also react in less well-defined ways with *N*-oxides, nitro, nitroso, and related functional groups.[8] In contrast, the reduction of sulfoxides to sulfides by the reagents reported here appears to be highly specific. Thus, organic halides (*n*-octyl iodide and benzotrichloride), sulfones, phosphine oxides, epoxides (cyclohexene oxide), ketones, (including α,β-unsaturated ketones), esters, nitriles, and nitro compounds (nitrobenzene) can all be recovered unchanged under the reduction conditions outlined in Table I. It is clear from the results presented that these reagents afford a mild, efficient, and highly selective procedure for the reduction of sulfoxides.

Sharpless and co-workers[9] have studied the deoxygenation of epoxides, aldehydes, and ketones using lower valent tungsten complexes of an undefined nature. The mechanism(s) of these conversions as well as the reduction of sulfoxides by $Mo_2Cl_8^{4-}$, $Mo_2Cl_8H^{3-}$, $MoCl_6^{3-}$, and $W_2Cl_9^{3-}$ is still unclear. However, it is reasonable to assume that the successful utilization of the lower valent complexes of titanium, molybdenum, and tungsten in effecting the deoxygenation of certain organic molecules is in substantial part a consequence of the unusually high thermodynamic stability of titanium–, molybdenum–, and tungsten–oxo bonds.[10,11]

Experimental Section[14]

Tripotassium ennachloroditungstate(III),[5] $K_3W_2Cl_9$, pentaammonium nonachlorodimolybdenum(II) monohydrate,[12] $(NH_4)_4Mo_2Cl_8 \cdot NH_4Cl \cdot H_2O$, and tricesium 1,1,1,2,2,2-hexachloro-μ-(hydrido)bis-μ-(chloro)dimolybdenum(III),[13] $Cs_3Mo_2Cl_8H$, were prepared according to literature procedures. Tripotassium hexachloromolybdenum(III), K_3MoCl_6, was obtained from Climax Molybdenum.

Procedures for Reduction. Similar procedures were used to carry out the reductions for all the sulfoxides examined. Representative procedures for each sulfoxide follow.

Reduction of Diphenyl Sulfoxide Using $K_3W_2Cl_9$. Tripotassium ennachloroditungstate(III) (1.40 g, 1.74 mmol) was placed in a 50-ml flask equipped with a condenser and containing a Teflon-coated stirrer bar, 10 ml of water, and 1 ml of methanol. Diphenyl sulfoxide (0.250 g, 1.26 mmol) and a known amount of hexadecane (GLC internal standard) were added and the flask heated at 60 °C with stirring for 3 h under a static head of nitrogen. Additional water (15 ml) was added and the resulting mixture extracted with three 10-ml portions of chloroform. The combined organic extracts were dried ($MgSO_4$), gravity filtered, and analyzed by GLC.

Reduction of Di-*n*-butyl Sulfoxide with $(NH_4)_4Mo_2Cl_8 \cdot NH_4Cl \cdot H_2O$. In a typical experiment, 1.12 g (1.80 mmol) of pentaammonium ennachlorodimolybdenum(II) monohydrate was placed in a 50-ml flask containing a Teflon-coated stirrer bar. Methanol (10 ml) was added along with 0.260 g (1.61 mmol) of di-*n*-butyl sulfoxide. The flask was equipped with a condenser stoppered with a rubber septum and flushed with nitrogen. The resulting mixture was stirred under a static head of nitrogen for 2 h at 50 °C. Upon cooling to room temperature, 0.180 g of tridecane (GLC internal standard) was added. Water (25 ml) was added and the resulting mixture extracted with three 5-ml portions of chloroform. The combined extracts were dried ($MgSO_4$) and analyzed by GLC.

Reduction of Benzyl Methyl Sulfoxide Using $Cs_3Mo_2Cl_8H$. Into a 50-ml flask equipped with condenser capped with a rubber septum and containing a Teflon-coated stirrer bar was placed benzyl methyl sulfoxide (0.250 g, 1.61 mmol) and $Cs_3Mo_2Cl_8H$ (1.58 g, 1.80 mmol). The contents of the flask were flushed with nitrogen before adding