8: ^{1}H NMR ($CDCl_3$) δ 7.63-7.1 (m, 8 H), 3.97 (s, 2 H), 1.88 (s, 6 H).

Oxidation of **7** and **8** by *m*-chloroperbenzoic acid[20] leads to the mixture of dimers **3a-c** and **3'a-c**, respectively. These dimers can be separated by thin-layer preparative chromatography on SiO_2; they were identified by cyclobutanic hydrogen atoms and methyl signals in the ^{1}H NMR ($CDCl_3$): **3a**, δ 4.13 (2 H), 1.1 (6 H); **3b**, δ 4.77 (1 H), 3.70 (1 H), 1.25 (3 H), 1.05 (3 H); **3c**, δ 4.66 (2 H), 1.32 (6 H); **3'a**, δ 4.45 (2 H), 2.0 (6 H); **3'b** δ 4.23 (1H), 4.10 (1 H), 2.15 (3 H), 1.88 (3 H); **3'c**, δ 4.37 (2 H), 2.07 (6 H).

Irradiations. Preparative irradiations were carried out in a 300-mL-capacity photolysis vessel equipped with a nitrogen inlet and Pyrex immersion well. The solutions were previously purged with dry nitrogen for 30 min and then irradiated with a Type 125W Philips HPK mercury arc lamp. Direct irradiations at 313 nm were performed through a K_2CrO_4/K_2CO_3 filter solution[26] circulating around the immersion well. Irradiations at 366 nm for sensitization studies were carried out with the lamp emission filtered by 0.7 M $Cu(NO_3)_2$ solution.[23]

Direct irradiations for concentration, quenching, and sensitization studies were carried out with a Hanovia 450-W mercury arc lamp in a merry-go-round apparatus[30] with interference filters allowing the selection of individual bands. Pyrex tubes (10 × 100 mm) were filled with 3.5 mL of the solution to be irradiated; the samples were then degassed (10^{-6} torr) by using several freeze-thaw cycles before the tubes were sealed. All runs were carried out under low-conversion conditions. After irradiation the amount of unreacted monomer was determined simultaneously by quantitative spectrophotometric UV analysis and by quantitative ^{1}H NMR analysis with dioxane as an internal reference.

Actinometry. The actinometer used was the benzophenone-benzhydrol system according to the described method.[31] Actinometer solutions were irradiated in parallel with the reaction mixtures.

Preparative Dimerization of 3-MeBTO (1). Direct irradiation of **1** (6.08 mM) in 280 mL of dry benzene at 313 nm for 15 h gave (50%) of a mixture of the two dimers **1a** and **1b** with a **1a** to **1b** ratio of 5:3 and a small amount of the third dimer **1c**. After evaporation of the solvent under vacuum, these dimers were separated by thin-layer preparative chromatography on SiO_2 (eluent ether-methanol, 95:5).

Sensitized irradiation of **1** at 366 nm for 4 h, with benzophenone as the sensitizer, gave the same isomers in the same amount with an overall yield of 80%. Anal. Calcd for $C_{18}H_{16}O_2S_2$: C, 65.85; H, 7.41. Found: C, 65.7; H, 7.5.

1a: F 224-226 °C; IR ($CDCl_3$) 1060, 1040, 1025 cm^{-1}; mass spectrum (70 eV), *m/e* 328, 312, 296, 148; ^{13}C NMR ($CDCl_3$); 9 peaks) δ 22.4 (CH_3), 51.5 (C_2, $C_{2'}$), 57.0 (C_3, $C_{3'}$), 125.4 (C_6, $C_{6'}$), 128.0 (C_7, $C_{7'}$), 129.8 (C_4, $C_{4'}$), 132.4 (C_5, $C_{5'}$), 145.1 and 146.2 (C_{3a}, $C_{3'a}$, C_{7a}, $C_{7'a}$).

1b: F 250 °C dec; IR ($CDCl_3$) 1055-1045 cm^{-1}; mass spectrum (70eV), *m/e* 328, 311 148; ^{13}C NMR ($CDCl_3$; all the carbons are different, giving 18 different peaks) δ 23.8, 24.2 (CH_3), 57.6, 58.1 (C_2, $C_{2'}$), 56.4, 60.1 (C_3, $C_{3'}$), 126.0, 126.6, (C_6, $C_{6'}$), 128.2, 128.5 (C_7, $C_{7'}$), 129.7, 130.1 (C_4, $C_{4'}$), 132.3, 132.6 (C_5, $C_{5'}$), 143.9, 144.4, 146.0, and 147.2 (C_{3a}, $C_{3'a}$, C_{7a}, $C_{7'a}$).

1c: F 230 °C; IR ($CDCl_3$) 1055-1040 cm^{-1}.

Preparative Dimerization of 3-PhBTO (2). Irradiation of **2** (1.33 mM in 280 mL of benzene) at 366 nm, with benzophenone as the sensitizer, led to a mixture of dimers. It was very difficult to separate the more stable dimers **2a** and **2b** by SiO_2 thick-layer chromatography because of their lack of solubility in all common organic solvents. **2a** and **2b** were identified by their ^{1}H NMR spectra (CF_3COOH-$CDCl_3$).

Mixture of the dimers **2a-c**: IR ($CDCl_3$) 1060-1040 cm^{-1}; mass spectrum (70eV), *m/e* 452, 433, 404, 209. Anal. Calcd for $C_{28}H_{20}O_2S_2$: C, 74.33; H, 4.42. Found: C, 73.9; H, 4.4.

Irradiation of 2-MeBTO (3). Direct irradiation of **3** (2.81 mM) at 313 nm and sensitized irradiation at 366 nm, with benzophenone as the sensitizer, were performed in 280 mL of dry benzene. After removal of the solvent, the products of the reaction were separated by chromatography on SiO_2, leading to 10% of 2-methylbenzothiophene (**3d**) and 50% of unreacted sulfoxide **3**.

Irradiation of 2-PhBTO (4). Irradiation of **4** (0.88 mM) in benzene solution (280 mL) was carried out for 4 h at 366 nm, with benzophenone as the sensitizer. Evaporation of the solvent under vacuum and chromatography on SiO_2 gave the corresponding sulfide **4d** (5%), the head to head dimer **4a** (or **4c**; 60%), and the unreacted sulfoxide **4**: IR (KBr) 1070, 1035, 1030 cm^{-1}; mass spectrum (70 eV), *m/e* 452, 338, 232, 216. Anal. Calcd for $C_{28}H_{20}O_2S_2$: C, 74.33; H, 4.42. Found: C, 73.9; H, 4.5.

Irradiation of 2,3-Me$_2$BTO (5). Direct irradiation and sensitized irradiation of **5** (2.8 mM) in benzene solution (280 mL) were performed at 313 and at 366 nm, respectively. Removal of the solvent and chromatography on SiO_2 gave 180 mg (35%) of the corresponding sulfide **5d**.

Registry No. **1**, 51500-43-7; **1a**, 67282-05-7; **1b**, 67336-09-8; **1c**, 67336-10-1; **2**, 70445-87-3; **2a**, 78592-67-3; **2b**, 78655-25-1; **2c**, 78655-26-2; **3**, 33945-86-7; **3a**, 78592-68-4; **3b**, 78655-27-3; **3c**, 78655-28-4; **3'a**, 78592-69-5; **3'b**, 78655-29-5; **3'c**, 78655-30-8; **4**, 70445-86-2; **4** HTH dimer, 78592-70-8; **5**, 70445-88-4; **6** (2-Cl), 57147-28-1; **6** (2-Br), 57147-27-0; **6** (3-Cl), 63724-95-8; **6** (3-Br), 57147-26-9; **7**, 78592-71-9; **8**, 78592-72-0.

(30) The measurements have been made in the Laboratoire des Composés Azotés Polyfonctionnels, Université Paul Sabatier, Toulouse (Professor A. Lattes and Dr. J. C. Micheau).

(31) W. M. Moore and M. Ketchum, *J. Am. Chem. Soc.*, 84, 1368 (1962).

Mannich Reaction Product of Dihydrocodeinone[1]

Joseph O. Polazzi

Chemistry Department, Corporate Research, Miles Laboratories, Inc., Elkhart, Indiana 46515

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The Mannich reaction with dihydrocodeinone (1) was previously reported to give the dimeric product 7,7'-methylenebis(dihydrocodeinone) (2). Investigation revealed that this structural assignment was incorrect. The product formed, dimer **5**, [3-methoxy-17-methyl-4,5α-epoxy-6,7-didehydromorphinan[6,7-*e*]-3,4-dihydropyran-2-spiro-7'-(3'-methoxy-17'-methyl-4',5'α-epoxymorphinan-6'-one)], results from a Diels-Alder 1,4-cycloaddition between two molecules of 7-methylenedihydrocodeinone (**4**).

Rapoport and Small[2] reported that the Mannich reaction with dihydrocodeinone (1) unexpectedly gave the dimeric product 7,7'-methylenebis(dihydrocodeinone) (2). The isolation of the intermediate Mannich base **3** or the corresponding eliminated 7-methylene compound **4** (see

(1) Analgesic Narcotic Antagonists. 12. For part 11 see: Leland, D. L. *J. Heterocycl. Chem.*, in press.

(2) Rapoport, H.; Small, L. *J. Org. Chem.* **1947**, *12*, 834.

0022-3263/81/1946-4262$01.25/0

Chart I

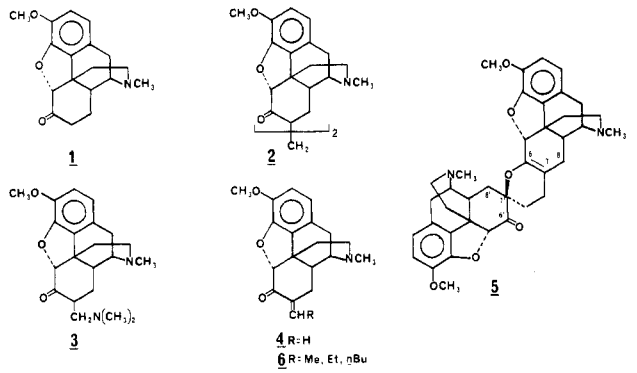

Chart I) would provide a valuable intermediate for the synthesis of 7-substituted dihydrocodeinones.[3]

To initiate studies toward this end, we examined reaction of the milder Mannich reagent, *N,N,N′,N′*-tetramethylmethanediamine[4] with **1**. We also repeated the procedure of Rapoport and Small.[2] With either set of reaction conditions, the only isolatable product was a dimer. This dimer had similar physical characteristics (melting point, $[\alpha]^{20}_D$, analysis) to those reported[2] for **2**. The unsymmetrical nature of both the ^1H NMR and the C^{13} NMR spectra[5] and the observed molecular ion of *m/e* 622 in the mass spectrum, however, ruled out structure **2** (*m/e* 610).

The product of both reactions is dimer **5**. Compound **5** results from a Diels–Alder 1,4-cycloaddition[6] between two molecules of **4**. The stereochemistry of this product is based on Alder's rule of maximum accumulated centers.[7] Thus, dimerization of **4** in the endo configuration yields **5**. The reasons for the instability of Mannich adduct **3**, or the eliminated product **4**, are not immediately apparent.

The preparations of 7-alkylidene compounds **6** were previously reported.[3] These substituted exocyclic methylene compounds, where R is a small alkyl group, are unstable. During recrystallization or chromatography varying quantities of dimeric products are obtained. These dimers are structurally similar to **5** as indicated by NMR.

Thus, on the basis of evidence presented in this report, the previously reported structure for the Mannich reaction product **2** should be revised to **5**.

(3) Kotick, M. P.; Leland, D. L.; Polazzi, J. O.; Howes, J. F.; Bousquet, A. R. *J. Med. Chem.*, in press.
(4) DeSolms, S. J. *J. Org. Chem.* **1976**, *41*, 2650.
(5) For a discussion of the C^{13} NMR spectra of the morphine alkaloids see: Carroll, F. I.; Moreland, C. G.; Brine, G. A.; Kepler, J. A.; *J. Org. Chem.* **1976**, *41*, 996.
(6) For a review of α,β-unsaturated carbonyl compounds as dienes see: Colonge, J.; Descotes, G. In "1,4-Cycloaddition Reactions, Organic Chemistry Series"; Hammer, J., Ed.; Academic Press: New York, 1967; Vol. 8, pp 219–253.
(7) Alder, K. *Ann. Chem.* **1951**, *571*, 157. Alder, K.; Offermans, H.; Ruden, E. *Chem. Ber.* **1941**, *74*, 905. Alder, K.; Stein, G. *Angew. Chem.* **1937**, *50*, 510.

Experimental Section

Melting points were taken in open capillary tubes on a Thomas-Hoover apparatus and are not corrected. IR spectra were recorded on a Perkin-Elmer Model 237 spectrophotometer and are calibrated relative to the 1601-cm^{-1} stretch of polystyrene. ^1H NMR were determined in $CDCl_3$ by using a Varian T-60A. Chemical shifts are reported in parts per million downfield from tetramethylsilane. ^{13}C NMR were recorded in $CDCl_3$ by using a JEOL FX 90Q. Optical rotations were observed on a Perkin-Elmer Model 141 polarimeter. Elemental Analysis was performed by Analytical Services, Chemistry Department, Miles Laboratories. The high-resolution mass spectra were determined on an Associated Electronic Industries MS 9 at the Department of Chemistry, University of Notre Dame.

3-Methoxy-17-methyl-4,5α-epoxy-6,7-didehydromorphinan[6,7-*e*]-3,4-dihydropyran-2-spiro-7′-(3′-methoxy-17′-methyl-4′,5′α-epoxymorphinan-6′-one) (5). To a suspension of 3.0 g (10 mmol) of **1** in 10 mL of *N,N,N′,N′*-tetramethylmethanediamine was added dropwise 10 mL of acetic anhydride. The reaction temperature was maintained below 90 °C by ice-bath cooling. After the addition was complete, the mixture was cooled to room temperature and stirred for a total of 2 h. The mixture was slowly added to 100 mL of ice–H_2O, made basic with NH_4OH, and extracted with $CHCl_3$. The combined organic phases were washed with H_2O, dried ($MgSO_4$), filtered, and evaporated under reduced pressure. Crystallization of the residue from acetone gave 1.6 g (53%) of **5** (mp 165–172 °C), which after being dried under vacuum at 100 °C had the following: mp 170–173 °C (lit.[2] mp 174–175 °C), $[\alpha]^{20}_D$ −254.9° (*c* 1.0, dioxane) (lit.[2] $[\alpha]^{20}_D$ −314° (*c* 0.943, dioxane)); IR (KCl pellet) 3400, 2920, 1737 (C=O), 1498, 1437, 1275, 1255, 1150, 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.67 (d, 4 H, *J* = 1.5 hz, aromatic), 5.11 (s, 1 H), 4.80 (s, 1 H), 3.96 (s, 3 H, OCH_3), 3.92 (s, 3 H, OCH_3), 2.42 (s, 3 H, NCH_3), 2.40 (s, 3 H, NCH_3); ^{13}C NMR ($CDCl_3$) 206.6 (s), 145.5 (s), 145.4 (s) 143.2 (s), 143.1 (s), 142.5 (s), 129.5 (s), 127.7 (s), 127.3 (s), 126.8 (s), 119.8 (d), 118.5 (d), 115.5 (d), 115.0 (d), 113.1 (s), 92.3 (d), 88.8 (d), 80.4 (s), 58.8 (d), 57.3 (q), 57.2 (q), 48.5 (s), 47.1 (t), 46.4 (t), 43.0 (q), 42.9 (s), 39.3 (q), 38.0 (t), 35.8 (t), 35.2 (t), 28.9 (t), 26.5 (t), 23.2 (t), 20.6 (t), 20.2 (t); mass spectrum, calcd *m/e* 622.306, obsd 622.304.

Anal. Calcd for $C_{38}H_{42}N_2O_6$: C, 73.29; H, 6.80; N, 4.50. Found: C, 73.53; H, 6.87; N, 4.51.

By use of the procedure of Rapoport and Small,[2] from 3.16 g (10.6 mmol) of **1** was obtained 2.4 g (80%) of **5** by crystallization of the residue from acetone and chromatography of the resultant mother liquor over silica gel G (E. Merck) with 15:1 $CHCl_3$–CH_3OH containing 0.5% NH_4OH v/v as the eluant. Recrystallization from acetone gave analytically pure **5**: mp 170–173 °C; $[\alpha]^{20}_D$ −264.3° (*c* 1.0, dioxane); IR, ^1H NMR, and ^{13}C NMR identical with those reported above; mass spectrum, *m/e* obsd 622.306.

Anal. Found: C, 73.06; H, 7.02; N, 4.45.

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Registry No. 1, 125-29-1; 5, 78672-87-4.