tained by recrystallizing a sample from ethanol-ether: mp 216–219°; $\nu_{cm^{-1}}^{Nujol}$ 1660, 1626, 1605; $\lambda_{max}^{CH_3OH}$ 228 mμ (ε 37,300,)258 (7540), 348 (2080), 370 (3280).

Anal. Calcd for $C_{14}H_{13}N_3 \cdot HCl$: C, 64.75; H, 5.43; N, 16.18. Found: C, 64.54; H, 5.73; N, 16.18.

4-Amino-2-benzyl-1,2-dihydroquinazoline (6b).—*o*-Aminobenzamidine hydrochloride[7] (8.4 g, 40 mmol) and 6.65 g of phenylacetaldehyde dimethyl acetal (40 mmol) were refluxed for 3 hr in 170 ml of ethanol. After cooling the reaction mixture, the ethanol was evaporated *in vacuo*, the residue taken up in methylene chloride and washed with an aqueous sodium carbonate solution under an atmosphere of N_2, and the organic layer dried over Na_2SO_4. The solvent was then removed and the residue dissolved in hot benzene. Upon cooling 5.6 g (59%) of product was obtained which after recrystallization from benzene showed mp 145–147°; $\nu_{cm^{-1}}^{Nujol}$ 3455, 3370, 1660, 1620, 1605; $\lambda_{max}^{CH_3OH}$ 232 mμ (ε 50,800), 261 (9100), 359 (2200); nmr (DMSO-d_6) δ 6.4–7.5 (m, 9 H), 5.9 (s, 1 H exchange), 5.4 (s, 2 H exchange), 4.92 (t, J = 6 Hz, 1 H), 3.91 (d, J = 6 Hz, 2 H).

Anal. Calcd for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.97; H, 6.50; N, 17.43.

4-Amino-2-benzyl-1,2-dihydroquinazoline (6b) → 4-Aminoquinazoline (7b). A.—4-Amino-2-benzyl-1,2-dihydroquinazoline (480 mg, 2 mmol) and 120 mg of NaH (55%, washed three times with anhydrous ether) were refluxed under an atmosphere of N_2 in 12 ml of dry diethylene glycol dimethyl ether for a period of 16 hr. After cooling, the reaction mixture was diluted with CH_2Cl_2, washed with dilute $NaHCO_3$ solution, and dried over Na_2SO_4. After removal of the solvent the residue (170 mg) was crystallized from CH_2Cl_2–ether to give 120 mg of 4-aminoquinazoline (**7b**): mp 258–260° (lit.[10] 259–260° and 267°); mass spectrum *m/e* 145 (Calcd for $C_8H_7N_3$: 145.064. Found: 145.063.).

B.—4-Amino-2-benzyl-1,2-dihydroquinazoline (480 mg, 2 mmol) were stirred at room temperature in 20 ml of ethanol with a solution of 3 g of $K_3Fe(CN)_6$ and 1.7 g of K_2CO_3 in 22 ml of water for 2 hr. The solvent was then partially removed and, after the addition of 4 ml of 10 *N* NaOH solution, the mixture was extracted with CH_2Cl_2. From the residue (170 mg), 130 mg of 4-aminoquinazoline (**7b**), mp 257–260°, was obtained (45%).

Registry No.—**2**, 28519-76-8; **3**, 1022-44-2; **4**, 28519-78-0; **4**, 28519-78-0; **6a** HCl, 28607-64-9; **6b**, 28519-79-1; *N*-nitroso-*N*-benzylanthranilonitrile, 28519-75-7.

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Quinazolines and 1,4-Benzodiazepines. LII.[1] Rearrangement of 1-Alkyl-7-chloro-1,3-dihydro-3-acetoxy-3-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-ones with Base

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The preparation and rearrangement of the title compounds (**2a,b**) to 2,5-epoxy-1,4-benzodiazepin-3-ones (**3a,b**) are described. The further rearrangement of the 2,5-epoxy compound **3a** to the corresponding 3-hydroxy-1,4-benzodiazepin-2-one **4a** is shown, and the possible mechanisms involved in these conversions are discussed. The determination of the structure of **3a** by single X-ray diffraction analysis is also presented.

Although considerable attention has been devoted to 3-substituted 1,4-benzodiazepines, 3-hydroxy-3-methyl derivatives are not reported in the literature. Bell and coworkers[2] attempted the preparation of 7-chloro-1,3-dihydro-3-hydroxy-3-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one by hydrolysis of the corresponding 3-acetoxy derivative. Using either acid or base, they obtained only 2-acetyl-6-chloro-4-phenylquinazoline.

Since 1,4-benzodiazepines bearing an alkyl substituent in the 1 position cannot undergo a similar rearrangement to quinazolines, we were able to prepare 7-chloro-1,3-dihydro-1,3-dimethyl-3-hydroxy-5-phenyl-2*H*-1,4-benzodiazepin-2-one (**4a**) by acid hydrolysis of the corresponding acetate **2a** (Scheme I).

The benzodiazepine structure assigned to **4a** is based on spectroscopic data which would not satisfy the alternate 2-acetyl-2-hydroxy-1,2-dihydroquinazoline structure (intermediate A in Schemes II and III). The uv spectra of **4a** and **2a** do not differ from those of other related benzodiazepine derivatives. The intermediate A would be expected to show the uv characteristics of compound **7**, the hydrochloride of which has a strong maximum at 450–454 mμ.[3] An absorption of this kind is not observed for compound **4a** in 0.1 *N* hydrochloric acid. The carbonyl band at 1660 cm^{-1} in the ir spectrum of **4a** certainly speaks for the benzodiazepine structure. The same argument holds for the chemical shift of the methyl group which is not compatible with an acetyl group free of unusual shielding. The conformational equilibrium observed in dimethyl sulfoxide solution gives additional support to the assigned structure, for such conformational equilibria have been found with other benzodiazepines.[4]

Surprisingly, the use of sodium methoxide in methanol did not lead to the 3-hydroxybenzodiazepine **4a** but to compound **3a**. The same reagent also effected the conversion of **4a** to **3a**. A plausible mechanism for these rearrangements is shown in Scheme II. If R represents hydrogen, the intermediate A would convert readily to 2-acetyl-6-chloro-4-phenylquinazoline (**6**) by dehydration.

We were able to reverse this rearrangement and obtained the 3-hydroxy-3-methylbenzodiazepine **4a** by treatment of compound **3a** with hydrogen chloride in ethanol. The proposed mechanism is shown in Scheme III and is envisioned as proceeding through the same intermediate A.

We also looked into the possible formation of 7-chloro-1,3-dihydro-3-hydroxy-3-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one by controlled acid-catalyzed ethanolysis of the 1-methoxymethyl derivative **2b**. While mild ethanolysis allowed the preparation of com-

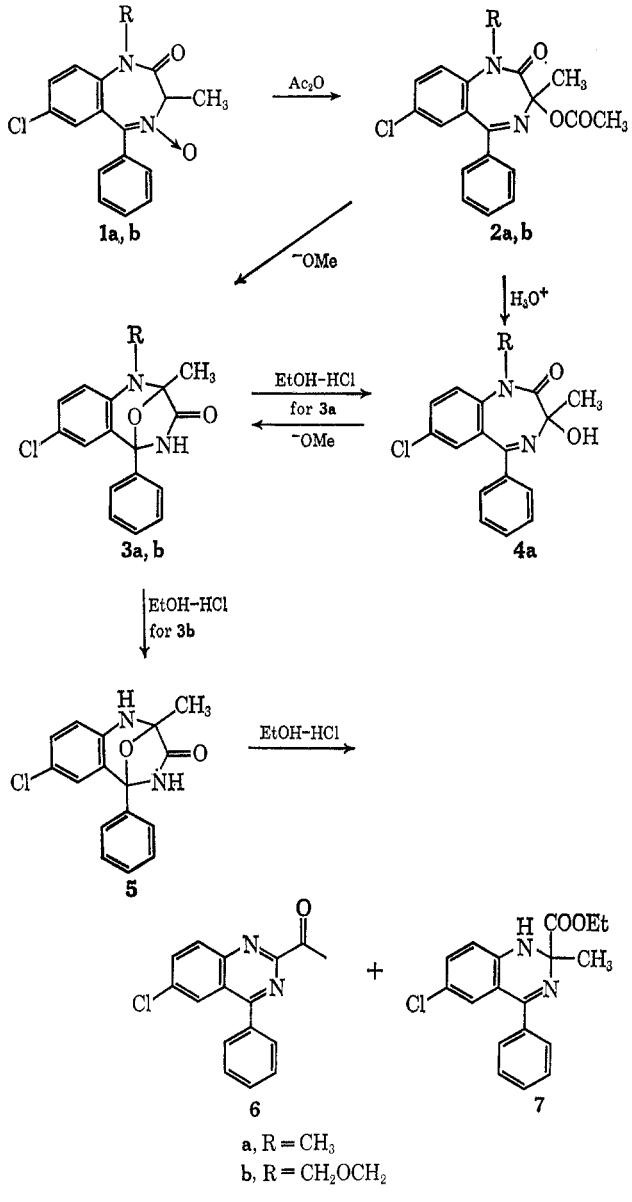
(1) Paper LI: N. W. Gilman and L. H. Sternbach, *J. Heterocycl. Chem.*, **8**, 297 (1971).

(2) S. C. Bell, *et al.*, *ibid.*, **33**, 457 (1968).

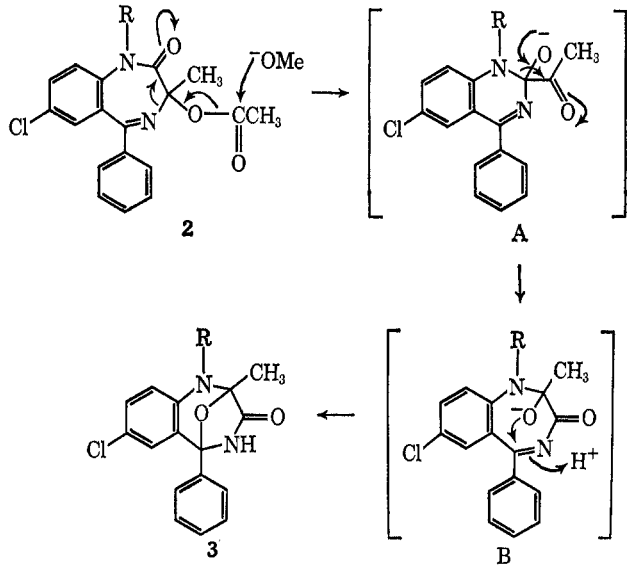
(3) Compare G. F. Field, *Chem. Commun.*, 886 (1969).

(4) P. Linscheid and J. M. Lehn, *Bull. Soc. Chim. Fr.*, 992 (1967).

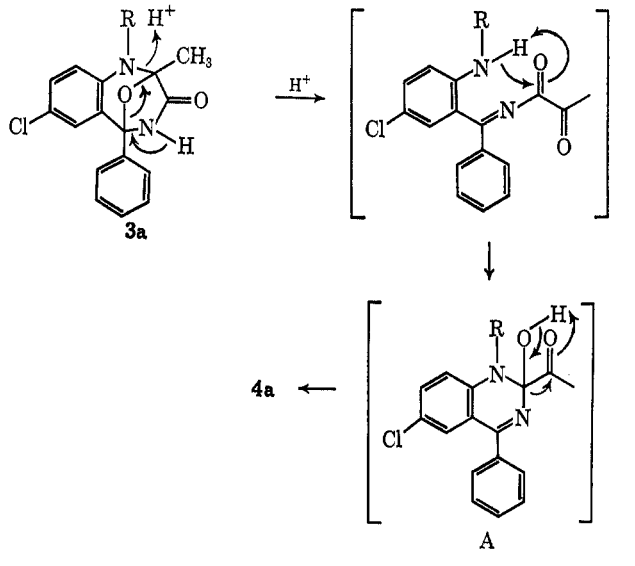
SCHEME I



SCHEME II

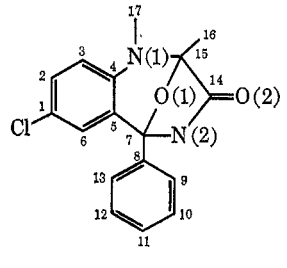


SCHEME III



pound **5**, more vigorous conditions produced a mixture of the anticipated 1,2-dihydroquinazoline **7** and the 2-acetylquinazoline **6**.

The structure of **3a** was established by single-crystal X-ray diffraction analysis. The numbering scheme adopted for the crystallographic analysis is shown below. The bond lengths and angles involving the non-



hydrogen atoms are given in Tables I and II. The average C–H distance is 1.01 Å. N(2) and O(2) participate in intermolecular hydrogen bonding, the N(2)–O(2) distance being 2.99 Å. For the molecule located at (x, y, z), N(2) is hydrogen bonded to O(2) in the molecule located at $(-1/2 + x, 3/2 - y, 1 - z)$ and O(2) is hydrogen bonded to N(2) in the molecule located at $(1/2 + x, 3/2 - y, 1 - z)$, so that the hydrogen bonding network extends in infinite chains parallel to the a axis. Figure 1 is a stereoscopic view of **3a** showing the conformation of the molecule in the solid state.

Determination of the Crystal Structure.—The position of the chlorine atom was determined from a three-dimensional Patterson synthesis. For the initial electron density synthesis based on the phases calculated for the chlorine atom, the x coordinate of the chlorine atom was displaced 0.04 Å from $x = 0$, the value obtained from the Patterson, in order to destroy the additional symmetry that otherwise would have been introduced. A total of four electron density syntheses based on successively more complete partial structures were required to locate all the nonhydrogen atoms. Four cycles of full matrix least squares gave a disagreement index (R) of 9.7% for an isotropic model. Two more cycles of full matrix least squares in which the atoms were assigned anisotropic thermal parameters reduced R to 6.6%. A difference map calculated at this point clearly showed all 15 hydrogen atoms. The structure

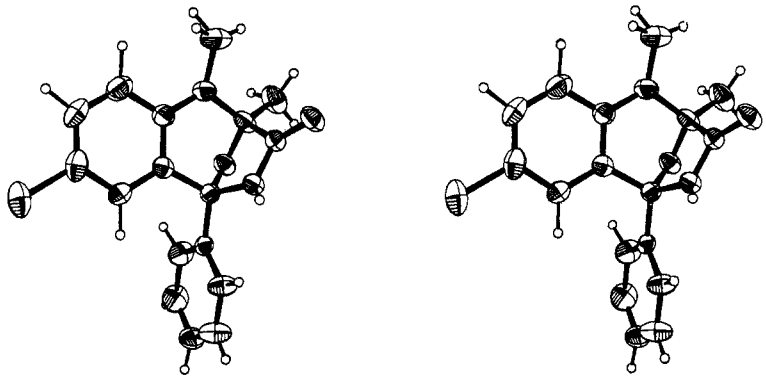


Figure 1.—Stereoscopic view of **3a**. The anisotropic thermal ellipsoids are scaled to include 50% probability; the hydrogens are represented as spheres of arbitrary size.

TABLE I

BOND LENGTHS (Å)[a] IN **3a** AVERAGED OVER THERMAL MOTION[b]

C(1)-Cl	1.734 (6)	C(2)-C(3)	1.367 (9)
		C(3)-C(4)	1.410 (8)
C(7)-O(1)	1.461 (6)	C(4)-C(5)	1.395 (7)
C(15)-O(1)	1.417 (7)	C(5)-C(6)	1.402 (7)
C(14)-O(2)	1.246 (6)	C(5)-C(7)	1.519 (7)
		C(7)-C(8)	1.498 (7)
C(4)-N(1)	1.397 (7)	C(8)-C(9)	1.406 (7)
C(15)-N(1)	1.476 (8)	C(8)-C(13)	1.417 (7)
C(17)-N(1)	1.490 (8)	C(9)-C(10)	1.395 (9)
C(7)-N(2)	1.477 (6)	C(10)-C(11)	1.373 (10)
C(14)-N(2)	1.341 (6)	C(11)-C(12)	1.381 (10)
		C(12)-C(13)	1.361 (9)
C(1)-C(2)	1.382 (9)	C(14)-C(15)	1.536 (7)
C(1)-C(6)	1.381 (8)	C(14)-C(16)	1.522 (8)

[a] Estimated standard deviation of last significant figures appears in parentheses. [b] Second atom is assumed to ride on first: W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **17**, 142 (1964).

TABLE II

BOND ANGLES (DEGREES)[a] IN **3a**

Cl-C(1)-C(2)	119.5 (4)	C(9)-C(8)-C(13)	119.3 (5)
Cl-C(1)-C(6)	118.0 (5)	C(8)-C(9)-C(10)	119.5 (5)
C(6)-C(1)-C(2)	112.5 (5)	C(9)-C(10)-C(11)	121.4 (5)
C(1)-C(2)-C(3)	119.0 (5)	C(10)-C(11)-C(12)	118.2 (5)
C(2)-C(3)-C(4)	121.7 (5)	C(11)-C(12)-C(13)	121.9 (5)
C(3)-C(4)-C(5)	117.6 (5)	C(12)-C(13)-C(8)	119.6 (5)
C(3)-C(4)-N(1)	121.8 (5)	C(15)-C(14)-N(2)	105.6 (4)
C(5)-C(4)-N(1)	120.6 (5)	C(15)-C(14)-O(2)	126.1 (4)
C(4)-C(5)-C(6)	121.0 (5)	N(2)-C(14)-O(2)	128.2 (5)
C(4)-C(5)-C(7)	116.0 (4)	C(14)-C(15)-C(16)	115.2 (4)
C(6)-C(5)-C(7)	123.0 (4)	C(14)-C(15)-N(1)	107.3 (4)
C(5)-C(6)-C(1)	118.1 (5)	C(14)-C(15)-O(1)	101.7 (4)
C(5)-C(7)-C(8)	116.4 (4)	C(16)-C(15)-N(1)	115.2 (5)
C(5)-C(7)-N(2)	109.9 (4)	C(16)-C(15)-O(1)	108.4 (5)
C(5)-C(7)-O(1)	104.8 (4)	N(1)-C(15)-O(1)	108.1 (5)
C(8)-C(7)-N(2)	114.7 (4)	C(4)-N(1)-C(15)	117.1 (4)
C(8)-C(7)-O(1)	108.1 (4)	C(4)-N(1)-C(17)	119.7 (5)
N(2)-C(7)-O(1)	101.2 (4)	C(15)-N(1)-C(17)	117.6 (5)
C(7)-C(8)-C(9)	121.0 (4)	C(7)-N(2)-C(14)	110.0 (4)
C(7)-C(8)-C(13)	119.7 (4)	C(7)-O(1)-C(15)	103.9 (4)

[a] Estimated standard deviation of last significant figure appears in parentheses.

was further refined by block diagonal least squares (9 × 9 blocks for the heavy atoms and 4 × 4 blocks for the hydrogen atoms) until the shifts in all parameters of the heavy atoms were less than one-fifth of the corresponding standard deviations. The final R value is 4.3%. A difference Fourier based on the final parameters has no features greater than 0.3 e/A^3 in magnitude. The final atomic parameters and the observed and calculated structure factors appear in the microfilm edition of this journal.[5]

Experimental Section

Melting points were determined microscopically on a hot stage. The uv spectra were measured in 2-propanol on a Cary Model 14 spectrophotometer; nmr spectra were recorded with a Varian A-60 instrument. Ir spectra were determined on a Beckman IR-9 spectrometer. Silica gel Merck (70–135 mesh) was used for chromatography. Petroleum ether refers to a fraction of bp 30–60°.

7-Chloro-1,3-dihydro-1-methoxymethyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one 4-Oxide.—A solution of 28.6 g (0.1 mol) of 7-chloro-1,3-dihydro-5-phenyl-2*H*-1,4-benzodiazepin-2-one 4-oxide[6] in 150 ml of dimethylformamide was cooled to −20° with stirring under nitrogen. After addition of 8.1 g (0.15 mol) of sodium methoxide, the temperature was lowered to −40° and 12 ml (0.15 mol) of chloromethyl methyl ether was added dropwise. Cooling was discontinued and when the temperature had reached 0° the reaction mixture was poured into ice water. The precipitate was collected by filtration, washed with water, and dissolved in methylene chloride. The solution was dried over sodium sulfate and evaporated. Crystallization of the residue from methanol yielded 22.4 g (68%) of product. The analytical sample was recrystallized from ethanol, mp 164–166°.

Anal. Calcd for $C_{17}H_{15}ClN_2O_3$: C, 61.73; H, 4.57; N, 8.47. Found: C, 61.55; H, 4.60; N, 8.50.

7-Chloro-1,3-dihydro-1-methoxymethyl-3-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one 4-Oxide (1b).—Potassium *tert*-butoxide (23 g, 0.2 mol) was added to a solution of 50 g (0.15 mol) of 7-chloro-1,3-dihydro-1-methoxymethyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one 4-oxide in 250 ml of dimethylformamide cooled to −30°. After stirring under nitrogen for 5 min, 12.5 ml (0.2 mol) of methyl iodide was added. The temperature was allowed to reach 0° and the reaction mixture was then poured into ice water. The collected precipitate was dissolved in methylene chloride and the solution was dried and evaporated. Crystallization of the residue from ethanol gave 28.8 g (55%) of product: mp 133–136° after recrystallization from ethanol; nmr ($CDCl_3$) δ 1.68 (d, 3, J = 6.5 Hz, C_3 CH_3), 3.4 (s, 3, OCH_3), 4.52 (q, 1, J = 6.5 Hz, C_3 H), 5.03 5.45 (AB, 2, J = 10 Hz, NCH_2O), 7–7.8 (m, 8).

Anal. Calcd for $C_{18}H_{17}ClN_2O_3$: C, 62.70; H, 4.97; N, 8.12. Found: C, 62.79; H, 4.89; N, 8.12.

3-Acetoxy-7-chloro-1,3-dihydro-1,3-dimethyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one (2a).—A mixture of 15.8 g (0.015 mol) of 7-chloro-1,3-dihydro-1,3-dimethyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one 4-oxide,[7] 150 ml of toluene, and 75 ml of acetic anhydride

(5) Listings of structure factors, coordinates, and thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.

(6) L. H. Sternbach and E. Reeder, *J. Org. Chem.*, **26**, 4936 (1961).

(7) Paper L: A. Walser, G. Silverman, R. Ian Fryer, L. H. Sternbach, and J. Hellerbach, *ibid.*, **36**, 1248 (1971).

was heated under reflux for 3 hr. During this time, 110 ml of toluene was removed by distillation. The reaction mixture was evaporated under reduced pressure and the residue was crystallized from a mixture of methylene chloride and hexane to yield 7.2 g of product. Chromatography of the concentrated mother liquor on 250 g of silica gel using 10% (v/v) ethyl acetate in methylene chloride for elution afforded an additional 4.6 g of **2a**: yield 66%; mp 150–152; ir ($CHCl_3$) 1730, 1680 cm^{-1} (C=O); uv max 235–237 mμ (ϵ 28,200), infl 260 (16,300), max 325–328 (2280); nmr ($CDCl_3$) δ 1.35 (s, C_3 CH_3), 2.14 (s, 3, $COCH_3$), 3.45 (s, 3, NCH_3).

Anal. Calcd for $C_{19}H_{17}ClN_2O_3$: C, 63.96; H, 4.80; N, 7.85. Found: C, 63.87; H, 4.89; N, 7.83.

3-Acetoxy-7-chloro-1,3-dihydro-1-methoxymethyl-3-methyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one (2b).—A mixture of 17.3 g (0.05 mol) of **1b** was dissolved in a mixture of 200 ml of toluene and 75 ml of acetic anhydride and was heated for 3 hr with distillation of 150 ml of solvent. Work-up of the reaction mixture as for **2a** afforded 11 g of product which was crystallized from a mixture of ether and hexane. The analytical sample was recrystallized from a mixture of methylene chloride, ether, and hexane: mp 154–157°; ir ($CHCl_3$) 1730, 1680 cm^{-1} (C=O); nmr ($CDCl_3$) δ 1.4 (s, 3, C_3 CH_3), 2.12 (s, 3, $COCH_3$), 3.48 (s, 3, OCH_3), 4.86, 5.60 (AB, 2, J = 10 Hz, NCH_2O).

Anal. Calcd for $C_{20}H_{19}ClN_2O_4$: C, 62.10; H, 4.95; N, 7.24. Found: C, 62.11; H, 4.74; N, 7.39.

7-Chloro-1,2-dimethyl-2,5-epoxy-5-phenyl-1,2,4,5-tetrahydro-3*H*-1,4-benzodiazepin-3-one (3a).—A solution of 7.2 g (0.02 mol) of **2a** in 200 ml of warm methanol was treated with 2.7 g (0.05 mol) of sodium methoxide. The reaction mixture was heated to boiling and the solvent was partly removed under reduced pressure. The residue was diluted with water, and the precipitated crystals were collected, washed with water, dried, and recrystallized from a mixture of methylene chloride and methanol to yield 4.7 g (74%) of product: mp 227–230° dec; ir (KBr) 3260 (NH), 1730, 1705 cm^{-1} (C=O); uv infl 207 mμ (ϵ 33,000), max 265–266 (12,900), 310–313 (2580); nmr (DMSO-*d*) δ 1.73 (s, 3, C_2 CH_3), 2.98 (s, 3, NCH_3), 6.18 (d, 1, J = 2.5 Hz, C_6 H), 6.9 (d, 1, J = 9 Hz, C_9 H), 7.3 (q, 1, J_{AB} = 9 Hz, J_{AX} = 2.5 Hz, C_8 H), 7.53 (s, 5, C_6H_5), 10.3 (broad s, 1, NH).

Anal. Calcd for $C_{17}H_{15}ClN_2O_2$: C, 64.86; H, 4.80; N, 8.90; Cl 11.26. Found: C, 64.93; H, 5.14; N, 9.10; Cl, 11.32.

This compound was also obtained from **4a** under the same conditions.

7-Chloro-2,5-epoxy-1-methoxymethyl-2-methyl-5-phenyl-1,2,-4,5-tetrahydro-3*H*-1,4-benzodiazepin-3-one (3b).—A solution of 7.75 g (0.02 mol) of **2b** in 200 ml of warm methanol was cooled to 30° when 2.25 g (0.04 mol) of sodium methoxide was added. The mixture was kept at room temperature for 15 min. The solvent was partly removed *in vacuo* and the residue was partitioned between water and methylene chloride. The methylene chloride layer was dried over sodium sulfate and evaporated. The crystalline residue was slurried with ether and filtered to yield 6.4 g (93%) of product: mp 220–225° dec after recrystallization from a mixture of methylene chloride and hexane; ir (KBr) 3240 (NH), 1730, 1690 cm^{-1} (C=O); uv max 253 mμ (ϵ 13,000), 300 (2400); nmr (DMSO-*d*) δ 1.76 (s, 3, C_2 CH_3), 3.33 (s, 3, OCH_3), 4.79 (s, 2, OCH_2N), 6.3 (d, 1, J = 2.5 Hz, C_6 H), 7.05 (d, 1, J = 9 Hz, C_9 H), 7.3 (q, 1, J_{AB} = 9 Hz, J_{AX} = 2.5 Hz, C_8 H), 7.53 (s, 5, C_6H_5), 10.3 (broad s, 1, NH).

Anal. Calcd for $C_{18}H_{17}ClN_2O_3$: C, 62.70; H, 4.97; N, 8.12. Found: C, 62.59; H, 4.99; N, 8.08.

7-Chloro-1,3-dihydro-1,3-dimethyl-3-hydroxy-5-phenyl-2*H*-1,4-benzodiazepin-2-one (4a). 1.—A mixture of 3.6 g (0.01 mol) of **2a** and 30 ml of concentrated sulfuric acid was stirred at room temperature until solution was complete. The mixture was then poured on ice and made alkaline by the addition of ammonia. The precipitated product was collected, washed with water, and dissolved in methylene chloride. The solution was dried and evaporated. Crystallization of the residue from a mixture of methylene chloride and hexane gave 2.5 g (79%) of **4a**: mp 156–158° dec; ir ($CHCl_3$) 3450 (OH), 1660 cm^{-1} (C=O); uv max 232–234 mμ (ϵ 28,750), infl 260 (1400), max 321–327 (1800); nmr ($CDCl_3$) δ 1.15 (s, 3, C_3 CH_3), 3.56 (s, 3, NCH_3), 5.5 (s, 1, OH), 7.2–7.9 (m, 8); nmr (DMSO-*d*) mixture of two conformers.

Anal. Calcd for $C_{17}H_{15}ClN_2O_2$: C, 64.87; H, 4.80; N, 8.90. Found: C, 64.93; H, 4.64; N, 8.95.

2.—A mixture of 2 g of **3a**, 20 ml of methylene chloride, and 20 ml of (1.6 *N*) ethanolic hydrogen chloride was heated under reflux for 27 hr. After evaporation of the solvents, the residue was partitioned between aqueous sodium bicarbonate and methylene chloride. The organic layer was separated, dried, and concentrated. Partial crystallization of the residue from a mixture of ether and petroleum ether yielded 0.5 g (25%) of product identical in every respect with the compound described above.

7-Chloro-2,5-epoxy-2-methyl-5-phenyl-1,2,4,5-tetrahydro-3*H*-1,4-benzodiazepin-3-one (5).—A mixture of 1 g of **3b**, 20 ml of methylene chloride, 20 ml of ethanol, and 5 ml of (1.6 *N*) ethanolic hydrogen chloride was heated under reflux for 1 hr. The orange-colored solution was diluted with water and extracted with methylene chloride. The organic layer was washed with 1 *N* hydrochloric acid, dried over sodium sulfate, and evaporated. The crystalline residue was slurried in ether, collected, and recrystallized from a mixture of acetone and hexane to yield 0.5 g (57.5%) of product. The analytical sample was recrystallized from methanol: mp 220–225°; ir (KBr) 1720 cm^{-1} (C=O); uv max 261–262 mμ (ϵ 10,800), 309–310 (2340); nmr (DMSO-*d*) δ 1.57 (s, 3, C_2 CH_3), 6.2 (d, 1, J = 2 Hz, C_6 H), 6.67 (d, 1, J = 8 Hz, C_9 H), 7.14 (q, 1, J_{AB} = 8 Hz, J_{AX} = 2 Hz, C_8 H), 7.5 (s, 5, C_6H_5), 7.62 (s, 1, NH), 10.02 (broad s, 1, NHCO).

Anal. Calcd for $C_{16}H_{13}ClN_2O_2$: C, 63.90; H, 4.35; N, 9.31. Found: C, 63.78; H, 4.22; N, 9.49.

Ethyl 6-Chloro-1,2-dihydro-2-methyl-4-phenylquinazoline-2-carboxylate (7).—A mixture of 2 g of **3b**, 50 ml of methylene chloride, and 50 ml of (1.6 *N*) ethanolic hydrogen chloride was refluxed for 20 hr. The red solution obtained was evaporated and the residue was crystallized from acetone and recrystallized from a mixture of methanol and acetone to yield 0.8 g (38%) of the hydrochloride: mp 150–160° dec; ir (KBr) 1750 cm^{-1} (C=O); uv max 238–240 mμ (ϵ 28,200), 285–290 (9300), 450–454 (3450).

Anal. Calcd for $C_{18}H_{18}Cl_2N_2O_2$: C, 59.19; H, 4.96; N, 7.66. Found: C, 59.23; H, 4.93; N, 7.64.

The free base was crystallized from a mixture of ether and hexane, mp 98–101°. It was found identical with a sample prepared from ethyl pyruvate, 2-amino-5-chlorobenzophenone, and ammonium acetate.

The original mother liquor was evaporated and the residue was partitioned between aqueous sodium carbonate and methylene chloride. The organic layer was separated, dried, and concentrated. Crystallization of the residue from ethanol and recrystallization of the collected material from the same solvent yielded 0.27 g (16%) of the known 2-acetyl-6-chloro-4-phenylquinazoline,[2] mp and mmp 132–134°.

Crystallography.—Crystals of **3a** ($C_{17}H_{15}ClN_2O_2$, mol wt 314.74) were grown from a methylene chloride–methanol mixture. The crystal data are a = 8.413 ± 0.002, b = 7.918 ± 0.001, c = 22.840 ± 0.004 Å (at 21°, λ = 1.5418 Å for Cu Kα), V = 1521.5 Å^3, D_m = 1.40 g cm^{-3}, D_c = 1.38 g cm^{-3} for Z = 4, $F(000)$ = 1256. The space group is $P2_12_12_1$ (D_2^4, no. 19)[8] ($h00$ absent for h odd, $0k0$ absent for k odd, and $00l$ absent for l odd). The intensities of 1066 independent reflections with $2\theta < 140°$ were measured on a Hilger & Watts Model Y290 four-circle diffractometer by a moving crystal-moving counter method using Ni-filtered Cu Kα radiation. The data were corrected for Lorentz and polarization effects but not for absorption (μ = 22.6 cm^{-1}). The crystal used was a rectangular prism with dimensions 0.12 × 0.18 × 0.25 mm.

All calculations were performed on a GE-635 computer. Local modifications of the Busing–Martin–Levy ORFLS[9] crystallographic least-squares program was used for the refinement in which $\Sigma w(|F_o| - |F_c|)^2$ was minimized. In the final cycles of least-squares refinement, the weights were taken as $w = 1/(8.5 + F_o + 0.021F_o^2)$. The scattering curves of Cromer and Waber[10] were used for Cl, O, N, and C and that of Stewart, Davidson, and Simpson[11] for hydrogen.

Registry No.—**1b**, 28506-46-9; **2a**, 28506-47-0; **2b**, 28506-48-1; **3a**, 28506-49-2; **3b**, 28506-50-5; **4a**, 28506-51-6; **5**, 28506-52-7; **7**, 28638-51-9; 7-chloro-1,3-dihydro-1-methoxymethyl-5-phenyl-2*H*-1,4-benzodiazepin-2-one 4-oxide, 28506-53-8.

(8) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965.

(9) W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(10) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965).

(11) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

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Mass Spectra and Pyrolyses of Tetrachloro-*o*-phenylene Carbonate and Tetrachloro-*o*-benzoquinone[1a,b]

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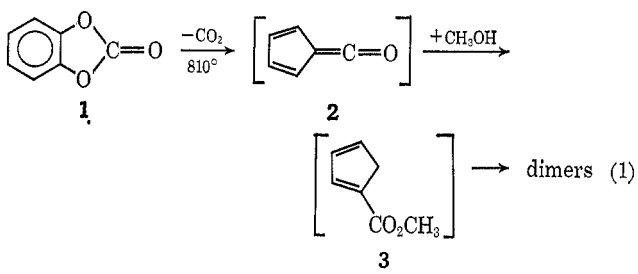
The mass spectra of tetrachloro-*o*-phenylene carbonate (**6**) and of tetrachloro-*o*-benzoquinone (**7**) have been compared. The M − CO ion from **6**, which is part of a minor fragmentation pathway, may be the same as the molecular ion from **7**. The major fragmentation pathway of the molecular ion of **6** involves initial loss of CO_2. When **6** is pyrolyzed in the gas phase by passing it through a heated quartz tube in a stream of nitrogen, products are isolated which can be associated with initial pyrolytic loss of CO_2, and other products can be associated with initial pyrolytic loss of CO. For example, $C_{10}Cl_{10}$, $C_{10}Cl_8$, and C_9Cl_8 compounds have been associated with initial CO_2 loss, whereas tetrachlorobut-1-en-3-yne (**11**) and dichloro-1,3-dibutadiyne (**12**) have been associated with initial CO loss. When **7** is pyrolyzed, **11** and **12** are isolated, as well as the dimer of tetrachlorocyclopentadienone; this indicates **7** is the intermediate formed in that pyrolytic pathway of **6** involving initial CO loss. A ketocarbene could be the intermediate formed in that pyrolytic pathway of **6** involving initial CO_2 loss. Thus, these electron-impact and pyrolytic fragmentations appear to be qualitatively similar.

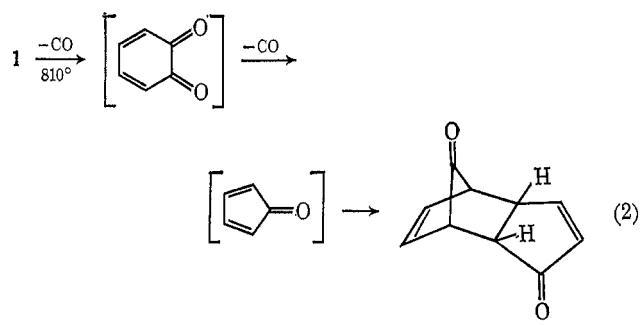
The mass spectra of a number of organic carbonates and cyclic sulfites have been compared with the products isolated from their pyrolyses, and similarities and differences have been noted.[2-6] For example, the mass spectrum of *o*-phenylene carbonate (**1**) shows the loss of CO_2 followed by CO to be the major fragmentation of the molecular ion; a minor path involves successive losses of CO for a total of 3CO lost.[5] When **1** is pyrolyzed in a stream of nitrogen in the presence of methanol, an intermediate ketene **2** is trapped and isolated as dimers of methyl cyclopentadiene-1-carboxylate (**3**) (44% at 810°) (eq 1).[5] This path is similar to



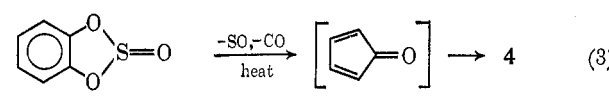
(1)

the major fragmentation of the molecular ion of **1**, *i.e.*, CO_2 is initially eliminated. A dimer **4** of cyclopentadienone is also obtained (14% at 810°) *via* a pathway (eq 2) involving loss of 2CO. This path is similar to the minor fragmentation of the molecular ion of **1**, *i.e.*, CO is initially lost.

The molecular ion of *o*-phenylene sulfite (**5**) eliminates SO followed by CO. When **5** is pyrolyzed, **4** is isolated in 30% yield (eq 3); cyclopentadienone forms *via* loss of SO followed by CO.[6]

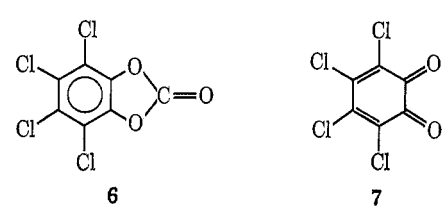


(2)



(3)

Tetrachloro-*o*-phenylene carbonate (**6**) has been studied with pyrolytic and electron-impact techniques, and we report the results in this article. *o*-Benzoquinone (**7**) has also been studied in order to determine the extent to which it functions as one of the intermediates in the pyrolysis of **6**.



Experimental Section

Infrared spectra were recorded with a Perkin-Elmer Infracord. Mass spectra were obtained from an Atlas CH4 or an A.E.I. MS 902 mass spectrometer. All glpc work was carried out with a Hewlett-Packard 5750 research chromatograph with a thermal conductivity detector. Ultraviolet and visible spectra were determined with a Perkin-Elmer 202 or Cary 14 spectrophotometer. Chemical analyses were carried out by Midwest Microlab, Inc., Indianapolis, Ind.

Preparation of Tetrachloro-*o*-phenylene Carbonate (6).—Tetrachlorocatechol (Aldrich), 50 g, was added to a solution of 18 g of

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(2) P. Brown and C. Djerassi, *J. Amer. Chem. Soc.*, **88**, 2469 (1966).

(3) G. G. Smith and B. Koesters, *Chem. Ber.*, **93**, 2400 (1960).

(4) A. David and J. H. Golden, *J. Chem. Soc. B*, 40 (1968).

(5) D. C. DeJongh and D. A. Brent, *J. Org. Chem.*, **35**, 4204 (1970).

(6) D. C. DeJongh, R. Y. Van Fossen, and C. F. Bourgeois, *Tetrahedron Lett.*, 271 (1967).