Epoxyamines. III. Synthesis and Reactions of 2-(1-Aziridinyl)-2-phenyl-3,3-dimethyloxirane and 2-(1-Aziridinyl)-2-phenyl-1-oxaspiro[2.4]heptane[1,2]

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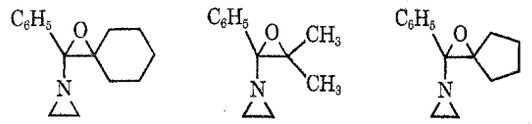
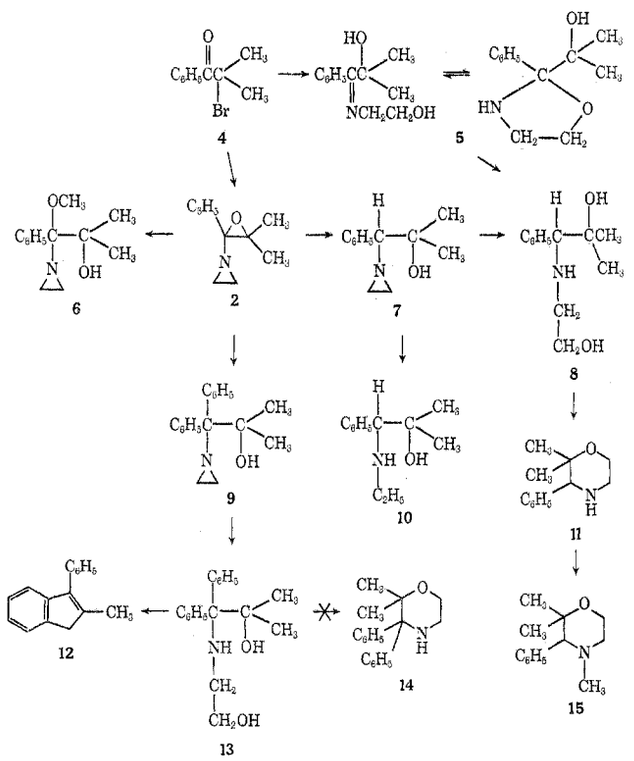
Two new epoxyamines, 2-(1-aziridinyl)-2-phenyl-3,3-dimethyloxirane (**2**) and 2-(1-aziridinyl)-2-phenyl-1-oxaspiro[2.4]heptane (**3**), are synthesized. Reactions of **2** with sodium borohydride, methanol, and phenyllithium are discussed. Hydrolysis of 1-(1-aziridinyl)-1,1-diphenyl-2-methyl-2-propanol (**9**) with 1 *N* perchloric acid followed by treatment with concentrated sulfuric acid yielded 2-methyl-3-phenylindene (**12**) and not the expected morpholine derivative, **14**. The structure of **12** was confirmed by an independent synthesis, and the previous data on **12** are corrected. Epoxyamine **3** was rearranged to give 2-(1-aziridinyl)-2-phenylcyclohexanone (**21**), which on reduction with sodium borohydride gave the *trans*-aziridinyl alcohol, **22**. The formation of various other derivatives is discussed.

After the isolation and characterization of 2-(1-aziridinyl)-2-phenyl-1-oxaspiro[2.5]octane (**1**), the first



1 **2** **3**

stable epoxyamine reported,[1a] attempts were made to synthesize other epoxyamines by similar methods. We now report the preparation, reactions, and rearrangement of two new epoxyamines, 2-(1-aziridinyl)-2-phenyl-3,3-dimethyloxirane (**2**) and 2-(1-aziridinyl)-2-phenyl-1-oxaspiro[2.4]heptane (**3**).



Treatment of α-bromoisobutyrophenone (**4**) with the lithium salt of ethylenimine yielded 83% of epoxyamine **2** as a clear, colorless liquid. Reactions of **2** were analogous to those reported for epoxyamine **1**.[1b] Thus reduction of **2** with sodium borohydride in methanol yielded the aziridinyl alcohol **7**, which on hydrogenation in the presence of palladium on carbon as catalyst gave the known amino alcohol[4] **10** characterized as its hydrochloride. Compound **7** was further characterized by its reaction with 1 *N* perchloric acid to give the amino diol **8** (74%), which was also formed in 64% yield by the reduction of **5** with sodium borohydride. Compound **5**, which was formed by the action of ethanolamine on **4**, has been assigned the oxazolidine structure, as the crystalline material did not show an imine absorption in an infrared spectrum on a potassium bromide pellet. However, as it can be reduced with sodium borohydride, a part of **5** may be existing as the imine in solution. In fact, an infrared spectrum of **5** in chloroform did show a weak imine absorption at 1650 cm^{-1}. Treatment of epoxyamine **2** with methanol without any catalyst opened the epoxide ring to yield 60% of 1-(1-aziridinyl)-1-methoxy-1-phenyl-2-methyl-2-propanol (**6**). Opening of the epoxide without rupturing the aziridine ring was also accomplished by treating **2** with phenyllithium. 1-(1-(Aziridinyl)-1,1-diphenyl-2-methyl-2-propanol (**9**) thus obtained was converted to the amino diol **13** by treatment with 1 *N* perchloric acid.

As amino diols like **8** and **13** have been used for the synthesis of substituted morpholines[5] and since 3-phenylmorpholines are rather uncommon, the conversion of these amino diols to morpholines was attempted. Thus **8** on treatment with concentrated sulfuric acid gave 50% of 2,2-dimethyl-3-phenylmorpholine (**11**) characterized as its hydrogen *p*-toluenesulfonate. Methylation of **11** with formaldehyde and formic acid afforded the *N*-methyl derivative **15**, characterized as its hydrochloride.

Treatment of amino diol **13** with concentrated sulfuric acid did not yield the expected 2,2-dimethyl-3,3-diphenylmorpholine (**14**) but gave 51% of a neutral, crystalline material which was subsequently shown to be 2-methyl-3-phenylindene (**12**). Although elemental

(1) Previous papers in this series: (a) C. L. Stevens and P. M. Pillai, *J. Amer. Chem. Soc.*, **89**, 3084 (1967); (b) C. L. Stevens and P. M. Pillai, *J. Org. Chem.*, **37**, 173 (1972).

(2) A preliminary account of a part of this work has been reported: C. L. Stevens, T. R. Potts, and P. M. Pillai, Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, No. S-92.

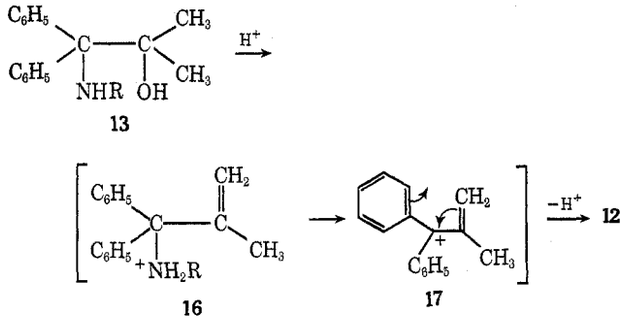
(3) Abstracted in part from the Ph.D. Dissertation of J. M. Cahoon; Frank Knoller Predoctoral Fellow, 1970–1971.

(4) C. L. Stevens, P. Blumbergs, and M. Munk, *J. Org. Chem.*, **28**, 331 (1963).

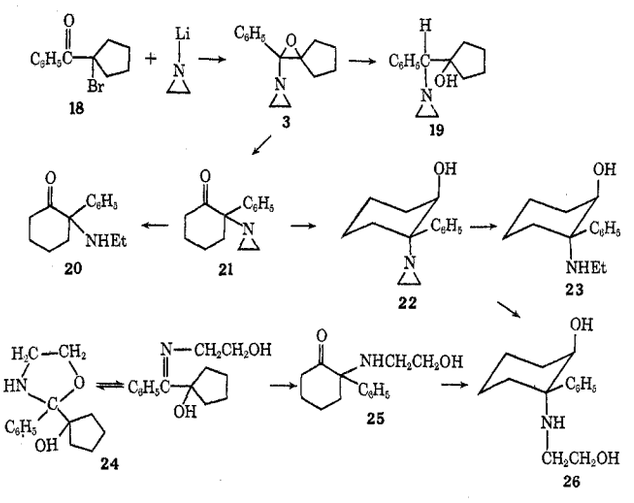
(5) C. L. Stevens, M. E. Munk, C. H. Chang, K. G. Taylor, and A. L. Schy, *ibid.*, **29**, 3146 (1964).

analysis and nmr spectrum were consistent with the structure, the reported characteristics[6] of 2-methyl-3-phenylindene [liquid, uv λ_{max}^{alc} 263 nm (log ϵ 3.87)] were substantially different from our findings [crystals, mp 58–59°, uv λ_{max}^{EtOH} 254 nm (log ϵ 4.01)]. This compound was therefore synthesized by essentially the same route used by Christol and coworkers[6] and the crystalline product obtained in 58% yield from 2-methyl-1-indanone was shown to be identical with our sample **12** in all respects.

The formation of **12** from **13** can be brought about by the ionization of both the hydroxyl and amine functions by the strong sulfuric acid medium. If a carbonium ion was formed on the benzilic position first, the product would have been 2,2-diphenyl-3-butanone, as obtained from the pinacol rearrangement of 1,1-diphenyl-2-methyl-1,2-propanediol.[7] In order to form **12**, the tertiary hydroxyl group in **13** should be eliminated first to give the olefin intermediate **16**. The ionization of the protonated amine group from **16** can be envisaged as taking place in a strong acid medium to give an extremely stable cation, **17**, which can then close with the loss of a proton to form the indene derivative **12**.



Treatment of α-bromocyclopentyl phenyl ketone[8] (**18**) with the lithium salt of ethylenimine in ether at room temperature gave 2-(1-aziridinyl)-2-phenyl-1-oxaspiro[2.4]heptane (**3**) in 78% yield. Further characterization of **3** was achieved by its reduction with sodium borohydride in methanol to give 85% of the aziridinyl alcohol **19**. Rerrangement of **3** in *o*-dichlorobenzene at 185° for 15 hr gave 2-(1-aziridinyl)-2-phenylcyclohexanone (**21**) in 80% yield. The direction of this rearrangement is in complete agreement with previous findings.[1] Upon catalytic hydrogenation in ethyl acetate in the presence of 10% palladium on carbon as catalyst, **21** was selectively reduced to the known 2-*N*-ethylamino-2-phenylcyclohexanone[9] (**20**) characterized as its hydrochloride. Reduction of **21** with sodium borohydride in methanol gave *trans*[10]-2-(1-aziridinyl)-2-phenylcyclohexanol[11] (**22**) in 75% yield. Catalytic hydrogenation of **22** in ethyl acetate in the presence of 10% palladium on carbon afforded the known *trans*-2-*N*-ethylamino-2-phenylcyclohexanol[12] (**23**) characterized as its hydrochloride. Treatment of **22** with 1 *N* perchloric acid gave the *trans*-β-hydroxyethylamino alcohol **26**. Compound **26** was also obtained by sodium borohydride reduction of the amino ketone **25**, which in turn was obtained by the thermal rearrangement[13] of **24**. Compound **24**, which was prepared by the general method[4] involving the action of ethanolamine on the α-bromo ketone **18**, did not show an imine absorption in an infrared spectrum on a potassium bromide pellet and therefore has been assigned the oxazolidine structure.



Attempted rearrangement of epoxyamine **2** did not yield any clean products; when a solution of **2** in *o*-dichlorobenzene was heated at 185° for several hours, it decomposed into many products, none of which could be characterized.

Experimental Section

Melting points were taken on a Thomas-Hoover melting point apparatus using capillary tubes and are uncorrected. Nmr spectra were obtained on a Varian A-60 or T-60 spectrometer using tetramethylsilane as internal standard. The ultraviolet spectra were recorded on a Cary 14 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer (Model 237B) grating spectrophotometer. Elemental analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

2-(1-Aziridinyl)-2-phenyl-3,3-dimethyloxirane (2).—A solution of 9.05 g (39.9 mmol) of α-bromoisobutyrophenone (**4**) in ether was treated with a suspension of the lithium salt of ethylenimine[1b] in ether according to the procedure of Stevens and Pillai.[1b] The product after distillation yielded 6.25 g (83%) of **2** as a colorless liquid: bp 55–57° (0.1 mm); nmr (CCl_4) δ 7.1–7.6 (m, 5 H, phenyl), 1.5 (s, 6 H, methyl), 0.9 (s, 4 H, methylene).

Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.31; H, 8.19; N, 7.67.

2-(2-Hydroxy-2-propyl)-2-phenyloxazolidine (5).—A mixture of 22.7 g (0.1 mol) of bromo ketone **4** was stirred with 50 ml of 2-aminoethanol for 46 hr. The product was extracted with ether, and the ether layer was washed with water, dried (K_2CO_3), and evaporated to dryness. The crude product was crystallized from ether–hexane to give **5**: mp 93–95°; ir (KBr) 3475 cm^{-1} (OH); ir ($CHCl_3$) 1650 cm^{-1} (weak, C=N); uv λ_{max}^{EtOH} 207 nm (log ϵ 3.78). The mother liquor was recycled with more 2-aminoethanol to obtain a total yield of 13.3 g (64.4%).

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.53; H, 8.27; N, 6.76. Found: C, 69.77; H, 8.32; N, 6.98.

(6) H. Christol, C. Martin, and M. Mousseron, *Bull. Soc. Chim. Fr.*, 1696 (1960).

(7) T. E. Zalesskaya and I. K. Lavrova, *Zh. Org. Khim.*, **4**, 2070 (1968); *Chem. Abstr.*, **70**, 67788b (1969).

(8) C. L. Stevens, R. D. Elliot, and B. L. Winch, *J. Amer. Chem. Soc.*, **85**, 1464 (1963).

(9) C. L. Stevens, A. B. Ash, A. Thuillier, J. H. Amin, A. Balys, W. E. Dennis, J. P. Dickerson, R. P. Glinski, H. T. Hanson, M. D. Pillai, and J. W. Stoddard, *J. Org. Chem.*, **31**, 2593 (1966).

(10) Trans heteroatom substituents.

(11) The authors thank Mr. Kenneth J. TerBeek for establishing the stereochemistry of this reduction.

(12) C. L. Stevens, H. T. Hanson, and K. G. Taylor, *J. Amer. Chem. Soc.*, **88**, 2769 (1966).

(13) For a review on amino ketone and hydroxyimine rearrangements, see C. L. Stevens, P. M. Pillai, M. E. Munk, and K. G. Taylor in "Mechanisms of Molecular Migrations," B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1971, p 271.

1-(1-Aziridinyl)-1-methoxy-1-phenyl-2-methyl-2-propanol (6).—Epoxyamine **2** (3.38 g, 17.9 mmol) was dissolved in 25 ml of absolute methanol and after the solution had been left at room temperature for 3 hr it was evaporated to dryness. The residue was recrystallized from hexane to give 2.05 g (60%) of **6**: mp 63–65°; nmr (CCl_4) δ 7.2–7.7 (m, 5 H, phenyl) 3.2 (s, 3 H, OCH_3), 2.4 (s, 1 H, OH), 2.0 and 1.8 (m, 4 H, aziridinyl), 1.2 (s, 3 H, CH_3), 1.0 (s, 3 H, CH_3).

Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found: C, 70.45; H, 8.81; N, 6.48.

1-(1-Aziridinyl)-1-phenyl-2-methyl-2-propanol (7).—A solution of 4.51 g (23.9 mmol) of **2** in 5 ml of ether was added to a solution of 5.6 g of $NaBH_4$ in 130 ml of CH_3OH at 0°. After 2 hr at 0° and 16 hr at room temperature, most of the CH_3OH was evaporated. The solution was diluted with water, extracted with ether, and dried (K_2CO_3) and solvent was expelled. The residue was recrystallized from ether–pentane to give 3.326 g (73.8%) of **7**, mp 52–53°, ir (KBr) 3340 cm^{-1}.

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.44; H, 8.92; N, 7.22.

A small portion of **7** dissolved in ether was treated with a saturated solution of HCl in ethyl acetate to give 1-(2-chloroethylamino)-1-phenyl-2-methyl-2-propanol hydrochloride, mp 198–200° after recrystallization from methanol–ether.

Anal. Calcd for $C_{12}H_{19}Cl_2NO$: C, 54.55; H, 7.25; Cl, 26.84; N, 5.30. Found: C, 54.77; H, 7.45; Cl, 26.56; N, 5.37.

Catalytic hydrogenation of 300 mg (1.7 mmol) of **7** in ethyl acetate in the presence of 50 mg of 10% Pd/C for 3 hr gave 302 mg (83.5%) of 1-*N*-ethylamino-1-phenyl-2-methyl-2-propanol (**10**) hydrochloride, mp 199–200°, identical with an authentic sample.[4]

1-(2-Hydroxyethylamino)-1-phenyl-2-methyl-2-propanol (8).

A. By the Hydrolysis of 7.—A solution of 200 mg (1.04 mmol) of **7** in 50 ml of 1 *N* $HClO_4$ was heated on a steam bath for 12 hr. The mixture was cooled and extracted with ether. The aqueous layer was basified with NaOH, extracted with chloroform, dried (K_2CO_3), and evaporated to dryness. The residue was recrystallized from methanol–ether to give 163 mg (74.5%) of **8**, mp 102–104°.

Anal. Calcd for $C_{12}H_{19}NO_2$: C, 68.87; H, 9.15; N, 6.69. Found: C, 68.93; H, 9.16; N, 6.79.

B. From the Reduction of 5.—A solution of 10.2 g (49.3 mmol) of **5** in 150 ml of CH_3OH was reduced with 7.9 g of $NaBH_4$ with stirring. The reaction was worked up after standing overnight to give 7.93 g (76.9%) of **8**, mp 104–106°. A mixture melting point with a sample from A above was undepressed.

1-(1-Aziridinyl)-1,1-diphenyl-2-methyl-2-propanol (9).—A solution of 4.65 g (24.6 mmol) of **2** in 60 ml of pure dry ether was cooled to 0° and 23 ml of a 2.11 *M* solution of phenyllithium in ether was added slowly with stirring. Another 20 ml of ether was added and the mixture was stirred overnight. It was poured into water and extracted with $CHCl_3$. The crude product was distilled under reduced pressure to give 6.33 g (96.2%) of **9** as a pale yellow liquid, bp 120–130° (0.2 mm).

A solution of 507 mg of **9** in ether was treated with an excess of HCl in ethyl acetate and the product was recrystallized from methanol–ether to give 419 mg (65%) of 1-(2-chloroethylamino)-1,1-diphenyl-2-methyl-2-propanol hydrochloride, mp 214–215° dec.

Anal. Calcd for $C_{18}H_{23}Cl_2NO$: C, 63.53; H, 6.81; Cl, 20.84; N, 4.12. Found: C, 63.32; H, 6.88; Cl, 20.79; N, 4.16.

2,2-Dimethyl-3-phenylmorpholine (11).—A mixture of 3.25 g (15.5 mmol) of **8** and 100 ml of cold concentrated H_2SO_4 was stirred at 0° for 3 hr. The solution was poured into ice, the neutrals were extracted with ether, and the aqueous layer was basified with NaOH. The product was extracted with ether, the ether solution was dried (K_2CO_3), and the solvent was evaporated. The residue was redissolved in ether and treated with anhydrous *p*-toluenesulfonic acid to give 2.86 g (51%) of **11** as the hydrogen *p*-toluenesulfonate. Recrystallization from acetone gave an analytical sample: mp 200–202°; nmr ($CDCl_3$) of free base, δ 7.2–7.6 (m, 5 H, aromatic), 3.5–4.3 (m, 3 H, benzilic and OCH_2), 2.9–3.2 (m, 2 H, NCH_2), 1.8 (s, 1 H, NH), 1.2 (s, 3 H, CH_3), 1.1 (s, 3 H, CH_3).

Anal. Calcd for $C_{19}H_{25}NO_4S$: C, 62.78; H, 6.93; N, 3.85; S, 8.82. Found: C, 62.53; H, 6.85; N, 4.08; S, 8.96.

Methylation of 1.106 g (5.79 mmol) of **11** with formaldehyde and formic acid[5] gave 1.19 g (84.2%) of 2,2,4-trimethyl-3-phenylmorpholine (**15**) hydrochloride: mp 246–247° dec after recrystallization from methanol–ether; nmr (CCl_4) of free base, δ 7.2–7.3 (s, 5 H, aromatic), 3.8 (m, 2 H, OCH_2), 2.8 (s, 1 H, benzylic), 2.4 (m, 2 H, NCH_2), 2.0 (s, 3 H, NCH_3), 1.2 (s, 3 H, CH_3), 1.0 (s, 3 H, CH_3).

Anal. Calcd for $C_{13}H_{20}ClNO$: C, 64.58; H, 8.34; Cl, 14.67; N, 5.79. Found: C, 64.50; H, 8.53; Cl, 14.59; N, 5.78.

1-(2-Hydroxyethylamino)-1,1-diphenyl-2-methyl-2-propanol (13).—A solution of 5.33 g (20 mmol) of **9** in 25 ml of acetone was added to a mechanically stirred solution of 533 ml of 1 *N* $HClO_4$ which was heated on a steam bath. After heating for 10 hr, the solution was cooled and extracted with ether. The aqueous layer was made basic with NaOH, extracted with $CHCl_3$, dried (K_2CO_3), and evaporated to dryness. The residue was dissolved in 150 ml of dry ether and treated with a saturated solution of HCl in isopropyl alcohol. The product was filtered and recrystallized from methanol–ether to give 4.13 g (64%) of **13** as the hydrochloride, mp 202–203° dec.

Anal. Calcd for $C_{18}H_{24}ClNO_2$: C, 67.17; H, 7.52; Cl, 11.02; N, 4.35. Found: C, 66.92; H, 7.39; Cl, 11.16; N, 4.36.

2-Methyl-3-phenylindene (12).—Compound **13** (HCl) (1.0 g, 3.2 mmol) was added in small portions with stirring to 25 ml of concentrated H_2SO_4 at room temperature. After stirring for 3 hr, the reaction mixture was poured into ice and the neutral material was extracted with ether. The ether solution was washed with water and dried (Na_2SO_4), and the solvent was evaporated. The oily residue was crystallized from ether–pentane to give 326 mg (51%) of **12**: mp 59.5–60.5°; nmr (CCl_4) δ 7.0–7.5 (m, 9 H, aromatic), 3.4 (s, 2 H, methylene), 2.1 (s, 3 H, CH_3); uv λ_{max}^{EtOH} 254 nm (log ϵ 4.01). Practically no basic material was isolated from this reaction.

Anal. Calcd for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.19; H, 6.93.

2-Methyl-3-phenylindene (**12**) was also prepared in 57.6% yield from 2-methyl-1-indanone[14] by the addition of phenyllithium followed by mild dehydration.[6] A mixture melting point with the two samples was not depressed and the ir spectra were superimposable.

2-(1-Aziridinyl)-2-phenyl-1-oxaspiro[2.4]heptane (3).—A solution of 9.5 g (37 mmol) of α-bromocyclopentyl phenyl ketone (**18**) in ether was treated with 2 equiv of the lithium salt of ethylenimine according to the previously published procedure.[1b] The product after work-up was crystallized from pentane by cooling in a Dry Ice–acetone bath to give 6.2 g (78%) of **3**, mp 34–35°.

Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.34; H, 8.02; N, 6.65.

1α-(1-Aziridinyl)benzylcyclopentanol (19).—A solution of 1.5 g (6.97 mmol) of epoxyamine **3** was reduced with $NaBH_4$ as described previously.[1b] The product was recrystallized from pentane to yield 1.3 g (86%) of **19**, mp 85–88°.

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.44. Found: C, 77.43; H, 9.03; N, 6.48.

2-(1-Aziridinyl)-2-phenylcyclohexanone (21).—A solution of 4.0 g of **3** in 25 ml of *o*-dichlorobenzene was refluxed under a N_2 atmosphere on a metal bath at 190–195° for 15 hr. The mixture was cooled and the solvent was removed under vacuum. The residue was crystallized from hexane to give 3.23 g (80.7%) of **21**, mp 95–97°, ir ($CHCl_3$) 1710 cm^{-1} (C=O). A small portion of **21** was dissolved in ether and treated with excess HCl in isopropyl alcohol to give 2-(2-chloroethylamino)-2-phenylcyclohexanone hydrochloride, mp 197–201° dec, ir (KBr) 1720 cm^{-1} (C=O).

Anal. Calcd for $C_{14}H_{19}Cl_2NO$: C, 58.33; H, 6.64; N, 4.86. Found: C, 58.04; H, 6.82; N, 5.02.

Hydrogenation of 50 mg (0.23 mmol) of **21** in ethyl acetate in the presence of 20 mg of 10% Pd/C followed by treatment with HCl in isopropyl alcohol gave 51 mg (85%) of 2-*N*-ethylamino-2-phenylcyclohexanone (**20**) hydrochloride,[11] mp 239–240°. A mixture melting point with an authentic sample was undepressed.

trans-**2-(1-Aziridinyl)-2-phenylcyclohexanol (22).**—A solution of 100 mg (0.46 mmol) of **21** in methanol was reduced with $NaBH_4$ according to the previously reported procedure[1b] to give 76 mg (75%) of **22**, mp 111–112° after recrystallization from hexane.

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.44. Found: C, 77.21; H, 8.60; N, 6.32.

(14) G. Baddeley, J. W. Rasburn, and R. Rose, *J. Chem. Soc.*, 3168 (1958).

A solution of 11.8 mg (0.054 mmol) of **22** in ethyl acetate was hydrogenated in the presence of 10% Pd/C and the product was treated with HCl in isopropyl alcohol to give 11.2 mg (81%) of *trans*-2-*N*-ethylamino-2-phenylcyclohexanol (**23**) hydrochloride,[12] mp 207–209°, identical with an authentic sample.

2-(1-Hydroxycyclopentyl)-2-phenyloxazolidine (24).—Treatment of 15.0 g (59.3 mmol) of bromo ketone **18** with 100 ml of 2-aminoethanol as in the preparation of **5** gave 11.5 g (83.6%) of **24** after recrystallization from hexane: mp 94–95°; ir (KBr) 3475 cm^{-1} (OH); ir ($CHCl_3$) 1650 cm^{-1} (weak, C=N); uv λ_{max}^{EtOH} 208 nm (log ϵ 3.80).

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.01. Found: C, 71.81; H, 8.23; N, 6.03.

2-(2-Hydroxyethylamino)-2-phenylcyclohexanone (25).—A solution of 3.04 g (13 mmol) of **24** in 60 ml of freshly distilled *o*-dichlorobenzene was heated at 175° under a N_2 atmosphere for 6 hr. After cooling, the mixture was diluted with ether and extracted with 1 *N* HCl. The aqueous layer was separated, basified with NaOH, and reextracted with ether. The product crystallized from ether on concentration to give 1.06 g (35%) of **25**, mp 97–99°, ir (KBr) 1710 cm^{-1} (C=O).

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.01. Found: C, 72.27; H, 8.40; N, 6.23.

Treatment of the mother liquor with picric acid yielded 1.18 g (19.3%) more of **25** as the picrate, mp 185–187° dec.

Anal. Calcd for $C_{20}H_{22}N_4O_9$: C, 51.95; H, 4.80; N, 12.12. Found: C, 51.89; H, 5.03; N, 12.29.

A small sample of **25** was converted to the HCl salt, mp 183–185° dec after recrystallization from methanol–ether.

Anal. Calcd for $C_{14}H_{20}ClNO_2$: C, 62.33; H, 7.47; Cl, 13.14; N, 5.19. Found: C, 62.24; H, 7.69; Cl, 12.95; N, 4.93.

***trans*-2-(2-Hydroxyethylamino)-2-phenylcyclohexanol (26).**—Aziridinyl alcohol **22** (407 mg, 1.9 mmol) was hydrolyzed with 150 ml of 1 *N* $HClO_4$ as for the preparation of **8** to give 232 mg (52.7%) of **26**, mp 130–132° after recrystallization from ether–pentane.

Anal. Calcd for $C_{14}H_{21}NO_2$: C, 71.45; H, 9.00; N, 5.95. Found: C, 71.21; H, 8.81; N, 5.79.

Reduction of 504 mg (1.1 mmol) of **25** picrate with $NaBH_4$ also provided 217 mg (84.8%) of **26**, mp 130–132°. A mixture melting point with the two samples was undepressed.

Registry No.—**2**, 35099-50-4; **3**, 35099-51-5; **5**, 35099-52-6; **5** imine form, 35099-53-7; **6**, 35099-54-8; **7**, 35099-55-9; **8**, 35099-56-0; **9**, 35099-57-1; **11**, 35099-58-2; **11** hydrogen *p*-toluenesulfonate, 35099-59-3; **12**, 35099-60-6; **13** HCl, 35099-61-7; **15**, 35099-62-8; **15** HCl, 35099-63-9; **19**, 35099-64-0; **21**, 35099-65-1; **22**, 35099-66-2; **24**, 35099-67-3; **25**, 35099-68-4; **25** picrate, 35099-69-5; **25** HCl, 35099-70-8; **26**, 35099-71-9; 1-(2-chloroethylamino)-1-phenyl-2-methyl-2-propanol HCl, 35099-72-0; 1-(2-chloroethylamino)-1,1-diphenyl-2-methyl-2-propanol HCl, 35099-73-1.

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The Catalytic and Photolytic Decomposition of 1-Chloro-4-diazoalkenes

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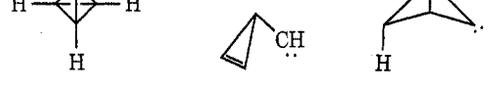
The synthesis of 1-chloro-4-diazo-2,3-dimethyl-1-pentene from 3-methyl-3-penten-2-one and of 1-chloro-4-diazo-2,3-dimethyl-1-butene from methyl acetoacetate is described. The catalytic decomposition of the diazoalkenes was studied; the decomposition of the latter with mercuric iodide gave 1-chloro-2,3-dimethyl-1,3-butadiene, 1-chloro-2-methyl-1,3-pentadiene, and 3-chloro-1,4-dimethylcyclobutene as major products. The mechanism of formation of these products is discussed in terms of the rearrangement of either a metal complexed carbenoid species or a metal complexed bicyclobutane.

The synthesis of tetrahedranes represents a fascinating challenge to the organic chemist.[3] The



availability of such a molecular system would represent a significant development in furthering our understanding of the correlation between chemical bonding and chemical reactivity. Most of the previous unsuccessful approaches evolved around intramolecular insertion of a carbene into a proximate cyclopropene double bond.[3a-c] A more attractive alternative involves intramolecular C–H insertion of a carbene in a suitable bicyclo[1.1.0]butane. Such an intermediate is presumed to be generated in the photodecomposition of carbon suboxide in the presence of cyclopropenes.[3d,e] The subsequent products allow an interpretation of a tetrahedrane intermediate. In an attempt to generate this carbene (or carbenoid) at low temperature in its ground state, we became interested in the synthesis of 2-halobicyclo[1.1.0]butanes.[4] Among the various approaches to such compounds, the catalytic decomposition of diazobutenes appeared particularly suitable.[5,6] We therefore undertook a study of the synthesis and decomposition of 1-chloro-4-diazo-2,3-dimethyl-1-pentene (**1**) and 1-chloro-4-diazo-2,3-dimethyl-1-butene (**2**) as a route to the 2-chlorobicyclo[1.1.0]butanes **3** and **4**. The fascinating rearrangement products obtained relate to the mechanism of decomposition of bicyclobutanes by transition metal catalysis.

Synthesis.—The envisioned precursor of bicyclobutane **3**, 1-chloro-4-diazo-2,3-dimethyl-1-pentene (**1**), was prepared as outlined in Scheme I. Addition of cyanide ion to 3-methyl-3-penten-2-one, saponification of the crude product, and esterification gave the keto ester **5**. Introduction of the chloromethylene group

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