of acetic anhydride in absolute ethanol. The effectiveness of this method of monoacetylation[12] should be noted.

## Experimental Section

**3-Hydroxy-3-methyl-2-butanone.** To a warm vigorously stirred solution of 65 g of yellow mercuric oxide in 500 ml of water and 90 ml of concentrated sulfuric acid was added dropwise 420.5 g (5.0 mol) of 2-methyl-3-butyn-2-ol[8] during 1.5 hr. The mixture was then heated to 70° for 30 min, cooled, and filtered through a Celite layer. The organic product was extracted into ether and the ether layer washed with water and $NaHCO_3$ solution. After pouring through a layer of $MgSO_4$ the solvent was removed and the residue distilled to yield 409.5 (80%) of 3-hydroxy-3-methyl-2-butanone, bp 137.8–139.0° (750 mm).

**1-Acetylcyclohexanol.** In a similar way 620 g of 1-ethynylcyclohexanol[8] was converted into 640 g (90%) of 1-acetylcyclohexanol, bp 100–101° (25 mm).

**3-Hydroxy-3-methyl-2-butanone Oxime.** To a well-stirred solution of 102.1 g (1.0 mol) of 3-hydroxy-3-methyl-2-butanone, 112 g of hydroxylamine hydrochloride, 400 ml of ethanol, and 50 ml of water was added portionwise 80 g of NaOH pellets. After heating to reflux for 10 min after the NaOH had all dissolved the reaction mixture was cooled and diluted with 500 ml of water, and the product isolated by ether extraction. On distillation 90 g (84%) of the oxime, mp 86–87°, was obtained.

**1-Acetylcyclohexanol Oxime.** In a manner similar to the above 142 g of 1-acetylcyclohexanol was converted into the oxime which was isolated by crystallization from benzene instead of distillation. The product, mp 104–105°, was obtained in 90% yield.

**3-Amino-2-methyl-2-butanol (1).** A solution of 23.4 g (0.2 mol) of 3-hydroxy-3-methyl-2-butanone oxime in 125 ml of freshly distilled absolute ethanol was shaken with 1.25 g of 5% rhodium-on-alumina[12] at about 40 psi for 9.5 hr. After removal of the catalyst by filtration through Celite, there was obtained 19.0 g (94%) of **1**, bp 59–61° (2 mm), as a colorless oil. The vacuum should be broken through a KOH tower in order to prevent access of $CO_2$ which produces a colorless solid immediately on contact with **1**. For acetylation 10.3 g (0.1 mol) of the freshly distilled amine was dissolved in 75 ml of ethanol and treated dropwise with 10.2 g (0.1 mol) of acetic anhydride. After refluxing the mixture for 30 min the alcohol was removed under reduced pressure. Vacuum distillation afforded a white solid which was recrystallized from benzene–hexane to yield 13.3 g (92%) of 3-acetylamino-2-methyl-2-butanol, mp 83.5–84.5°. This compound proved identical with that prepared previously by Liang[13] by the hydrolysis of 4,5,5-trimethyloxazolidone to **1** followed by acetylation essentially as above.

*Anal.*[14] Calcd for $C_7H_{15}NO_2$: C, 57.9; H, 10.4. Found: C, 58.1; H, 10.3.

**1-(1-Aminoethyl)cyclohexanol (2).** A solution of 31.4 g (0.19 mol) of 1-acetylcyclohexanol oxime in 150 ml of freshly distilled ethanol was reduced for 48 hr at 60–65° over 5% rhodium-on-alumina at 40–50 psi. The reaction mixture was worked up as for **1** to yield 25.7 g (90%) of **2**, bp 150–153° (40 mm), sensitive to $CO_2$. For acetylation 21.5 g (0.14 mol) of **2** in 100 ml of ethanol was treated with 15.4 g (0.15 mol) of acetic anhydride as in the case of **1**. After isolation as above there was obtained the acetylamino compound which distilled at 138–140° (4.5 mm). The solid distillate was recrystallized from acetone–benzene to yield 24.6 g (90%) of 1-(1-acetylaminoethyl)cyclohexanol: mp 107–108°; nmr ($CDCl_3$) $\delta$ 1.14 (d, 3 H, $CHCH_3$), 1.50 (m, 10 H, cyclohexyl protons), 1.99 (s, 3 H, $COCH_3$), 3.27 (s, 1 H, OH), 4.00 (m, 1 H, $CHCH_3$), and 6.70 (m, 1 H, NH); ir (KBr) 3.00 (NH and OH) and 6.10 $\mu$ (>C=O).

*Anal.*[14] Calcd for $C_{10}H_{19}NO_2$: C, 65.0; H, 10.2; N, 7.6. Found: C, 64.9; H, 10.4; N, 7.5.

**Registry No.**—**1**, 6291-17-4; **2**, 3183-55-9; **3a**, 115-19-5; **3b**, 78-27-3; 3-hydroxy-3-methyl-2-butanone, 115-22-0; 1-acetylcyclohexanol, 1123-27-9; 3-hydroxy-3-methyl-2-butanone oxime, 7431-25-6; hydroxylamine hydrochloride, 5470-11-1; 1-acetylcyclohexanol oxime, 53336-53-1; 3-acetylamino-2-methyl-2-butanol, 53336-55-3; 1-(1-acetylaminoethyl)cyclohexanol, 53336-54-2.

## References and Notes

(1) This work was supported by Grant No. GP-12445 from the National Science Foundation.
(2) Work done as undergraduate chemistry research problem.
(3) S. N. Danilov and K. A. Ogloblin, *Zh. Obshch. Khim.*, **22**, 2113 (1952); *Chem. Abstr.*, **48**, 1944i (1954).
(4) A. Lambert and A. Lowe, *J. Chem. Soc.*, 1517 (1947).
(5) B. Tchoubar, *C. R. Acad. Sci.*, **237**, 1006 (1953).
(6) I. Elphimoff-Felkin, *Bull. Soc. Chim. Fr.*, 784 (1955).
(7) J. Maillard, M. Vincent, M. Rapin, Vo-Van-Tri, and G. Renaud, *Bull. Soc. Chim. Fr.*, 2110 (1967).
(8) We thank the Airco Chemicals and Plastics Division of the Air Reduction Company, Inc., for gifts of these two compounds.
(9) R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworths Scientific Publications, London, England, 1955, p 40 ff.
(10) G. W. Stacy and C. A. Hainley, *J. Amer. Chem. Soc.*, **73**, 5911 (1951).
(11) Engelhard Industries, Inc.
(12) M. S. Newman and Z. ud Din, *Syn. Commun.*, **1**, 247 (1971); *J. Org. Chem.*, **38**, 547 (1973).
(13) From the Ph.D. Thesis of W. C. Liang, The Ohio State University, 1972.
(14) Analyses by Galbraith Analytical Laboratories, Knoxville, Tenn.

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# Lithium Aluminum Hydride Reduction of 9b-(4-Chlorophenyl)-1,2,3,9b-tetrahydro-5*H*-imidazo[2,1-*a*]isoindol-5-one in Tetrahydrofuran

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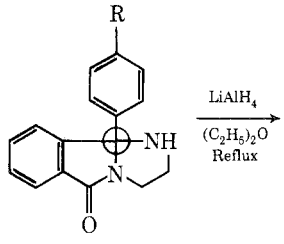
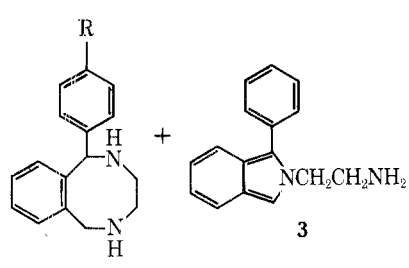
*Received June 14, 1974*

The lithium aluminum hydride ($LiAlH_4$) reduction of the 9b-aryl-1,2,3,9b-tetrahydro-5*H*-imidazo[2,1-*a*]isoindol-5-ones (**1a** and **1b**) in refluxing diethyl ether has been reported to give the 1-aryl-1,2,3,4,5,6-hexahydro-2,5-benzodiazocines (**2a** and **2b**)[1-4] and 2-(2-aminoethyl)-1-phenylisoindole (**3**)[3].




**1a**, R = H
**b**, R = Cl




**3**

**2a**, R = H
**b**, R = Cl

We have carried out the $LiAlH_4$ reduction of **1** in tetrahydrofuran (THF) at 20–25° and found that the reaction leads to different products. In the present report, our findings with 9-(*p*-chlorophenyl)-1,2,3,9b-tetrahydro-5*H*-imidazo[2,1-*a*]isoindol-5-one (**1b**) are given.[5]

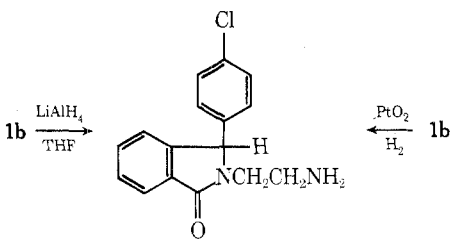
Compound **1b** was treated with $LiAlH_4$ in THF at 20–25° and then hydrolyzed with aqueous sodium hydroxide. After standing for about 4 hr at room temperature, the mixture was dried with anhydrous $Na_2SO_4$ to give a compound with ir and nmr spectrum in agreement with the phthalimidine (**4**). The same phthalimidine was obtained when **1b** was hydrogenated in the presence of platinum.

When the reduction was carried out as above and treated immediately after hydrolysis with anhydrous $Na_2SO_4$, a labile solid compound A, isomeric with **4**, was isolated in 95% yield.

**Table I**
**$^{13}$C-Nmr Chemical Shifts**

| Compd[a] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 1b | | 5 | | 9 | | 10 | | 11 | |
| Ppm | C-Atom[b,c] | Ppm | C-Atom[c] | Ppm | C-Atom[c] | Ppm | C-Atom[d] | Ppm | C-Atom[d] |
| 21.5 | 5 | 48.4 | 9a* | 49.3 | 1′ | 53.0 | | 51.7 | 1′ |
| 45.3 | 9a | 49.5 | 5a* | 49.9 | 1 | 64.0 to 65.0 | 2′,3′,4′ | 64.5 to 65.0 | 2′,3′,4′ |
| 53.4 | 1′ | 51.0 | 11 | 63.2 | 2,6 | | 5′,6′ | | 5′,6′ |
| 59.3 | 4′ | 59.5 | 4′ | | 2′,6′* | 94.6 | 1 | 107.9 | 2 |
| 60.0 | 8 | 60.4 | 8 | 60.9 | 4 | 127.7 | 5 | 136.8 | 5 |
| 60.4 | 5a | 63.6 | 2′,6′* | 64.7 | 3,5 | 138.1 | 4 | 147.9 | 4 |
| 63.2 | 7 | 64.3 | 7 | | 3′,5′* | 154.1 | $NCH_3$ | 154.0 | $NCH_3$ |
| 64.1 | 2′,6′* | 65.1 | 3′,5′* | 65.4 | 4′ | | | | |
| 64.6 | 3′,5′* | 68.8 | 6* | 116.1 | C-$\alpha$ | | | | |
| 68.8 | 6* | 69.7 | 9* | 148.5 | $N(CH_3)_2$ | | | | |
| 69.1 | 9* | 98.1 | 9b | | | | | | |
| 103.0 | 9b | 98.8 | 5 | | | | | | |
| 141.8 | 3 | 139.5 | 3 | | | | | | |
| 150.6 | 2 | 144.6 | 2 | | | | | | |

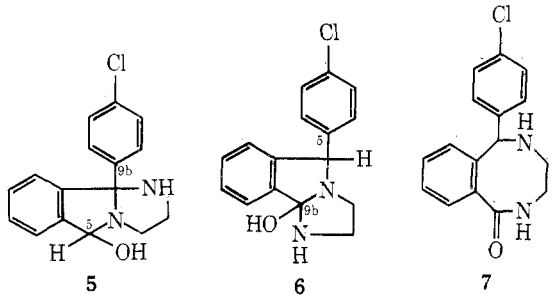
[a] The solvent was DMSO-$d_6$/$CHCl_3$. See ref 11 for experimental procedure. [b] The assignment of those C atoms marked with an asterisk (*) is uncertain. [c] The $^{13}$C nmr of toluene and chlorobenzene were used as references to assist in these assignments. [d] The $^{13}$C nmr of tetrahydrofuran and *N*-methylpyrrolidine were used as references to assist in these assignments.




4

The ir spectrum of A gave an NH or OH band at 3.10 $\mu$ and no absorption in the carbonyl region. The nmr spectrum in DMSO-$d_6$ gave two sets of 2 H multiplets between $\delta$ 2.6 and 3.2, a broad singlet at 3.40, a 2 H quartet[6] centered at 5.60, and 8 aromatic protons. On treatment with $D_2O$, the 1 H singlet at $\delta$ 3.40 exchanged and the 2 H quartet at 5.60 collapsed to a 1 H singlet at 5.62.

To account for the above data, we considered A to have either structure **5** or **6**. Compound **5** is obtained by direct

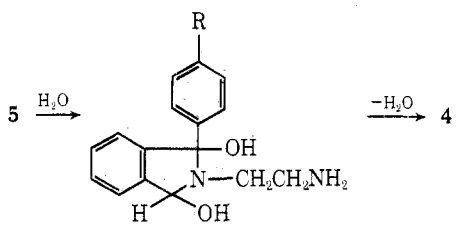



5 6 7

reduction of the carbonyl group in **1b**, whereas **6** is a tautomeric form of 6-*p*-chlorophenyl-3,4,5,6-tetrahydro-2,5-benzodiazocin-1(2*H*)-one (**7**), an intermediate proposed[4] in the diethyl ether–$LiAlH_4$ reduction of **1b** to **2b**.

When A was dissolved in THF–$H_2O$ (9:1), a solvent system approximating that which gave **4**, and maintained at room temperature for *ca.* 20 hr, it was transformed into **4**. The rearrangement of **5** (compound A) to **4** has previously been reported by Sulkowski.[7]

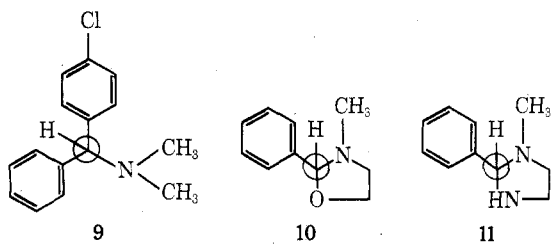
The formation of **4** may proceed by a hydration–dehydration pathway *via* the dihydroxyisoindoline (**8a**). The same type of intermediate (**8b**) has been proposed by Metlesics[8] to account for the formation of the dechloro analog of **4** from *o*-benzoylbenzaldehyde and ethylenediamine in aqueous alcohol.




**8a**, R = Cl
**b**, R = H

Structure **5** is more consistent with the nmr spectrum, whereas the formation of **4** from A in THF–$H_2O$ is better explained by structure **6**. To distinguish between these structures, we turned to a $^{13}$C nmr investigation. The two most significant C atoms for study in these compounds, C-5 and C-9b, are in such dissimilar environments that comparison of A with relevant model compounds should distinguish the structures. The model compounds selected for comparison with A were **1b**, **9**, **10**, and **11**.

The $^{13}$C nmr of A gave the C-5 and C-9b carbon atom signals at 98.1 and 98.8 ppm upfield from $CS_2$. The relevant $^{13}$C signals (circled atoms) in the model compounds were found at 103 ppm in **1b**, 116.1 ppm in **9**, 94.6 ppm in **10**, and 107.9 ppm in **11**.




9 10 11

Comparison of these values with A clearly establishes **5** as the correct structure.[9,10] The 94.6-ppm C atom in **10** is in an environment similar to C-5 in **5** and can be related with the 98.1-ppm signal in A. The 103-ppm C atom signal in **1b** is in an environment similar to C-9b in **5** and can be related with the 98.8-ppm signal in A. The 116.1-ppm C atom in **9** and the 107.9-ppm C atom in **11** are related to C-5 and C-9b, respectively, in **6** and are sufficiently different from the signals in A to eliminate **6** as a possible structure.

## Experimental Section[11]

**Lithium Aluminum Hydride Reduction of 9b-*p*-Chlorophenyl-1,2,3,9b-tetrahydro-5*H*-imidazo[2,1-*a*]isoindol-5-one (1b).** A stirred mixture of 1.68 g (0.044 mol) of $LiAlH_4$ and 100 ml of dry THF, maintained under $N_2$, was cooled to an internal temperature of 15° and treated dropwise (10 min) with a solution of 10.0 g (0.035 mol) of **1b** in 75 ml of THF while maintaining the temperature at 20–25°. Approximately 5 min after addition was complete, the mixture was cooled to an internal temperature of 10° and treated dropwise in turn with 2 ml of $H_2O$, 5 ml of 15% NaOH, and 5 ml of $H_2O$ while maintaining the temperature below 15°. The resultant mixture was allowed to stand for *ca.* 4 hr at room temperature and then treated with 10 g of anhydrous $Na_2SO_4$ and filtered. The salts were washed with 25 ml of anhydrous THF and the combined filtrate was concentrated *in vacuo* at a water bath temperature of 35°. The resultant solid was stirred in anhydrous diethyl ether and filtered to give 8.1 g (80%) of 2-(2-aminoethyl)-3-(*p*-chlorophenyl)phthalimidine (**4**): mp 83–85° ($Et_2O$–hexane); ir (KBr) 2.95 ($NH_2$), 5.87 $\mu$ (C=O); uv (95% EtOH) maxima 225 m$\mu$ ($\epsilon$ 23,800), 253 (3000) and 279 (1700); nmr ($CDCl_3$) $\delta$ 1.20 (2 H, $NH_2$, $D_2O$ exchangeable), 3.7 ($H_A$), 2.6–3.1 ($H_B$ + $2H_C$, $ABC_2$ m, $HCH_AH_BCH_CH_CNH_2$), 5.52 (1 H, s, ArCHAr) 6.85–7.95 (8 H, m, aromatic H).

*Anal.* Calcd for $C_{16}H_{15}ClN_2O$: C, 67.0; H, 5.3; Cl, 12.4; N, 9.8. Found: C, 67.1; H, 5.3; Cl, 12.3; N, 9.8.

The reduction was repeated as above through the hydrolysis stage. The resultant mixture was treated immediately after hydrolysis with 10 g of anhydrous $MgSO_4$. The mixture was stirred for *ca.* 5 min, and then filtered. The salts were washed with 25 ml of anhydrous THF and the combined filtrate was concentrated *in vacuo* at a water bath temperature of 35° to give 9.6 g (95%) of 9b-*p*-chlorophenyl-1,2,3,9b-tetrahydro-5*H*-imidazo[2,1-*a*]isoindol-5-ol (**5**): mp 133–135° (lit.[7] mp 144–146° dec or 135°); ir (KBr) 3.05–3.10 $\mu$ (NH, OH); nmr (DMSO-$d_6$) $\delta$ 2.6–3.2 (4 H, 2 sets of multiplets, $NCH_2CH_2N$), 3.40 (1 H, broad s, $D_2O$ exchangeable, NH), 5.60 (2 H, q, 1 H, $D_2O$ exchangeable, OH, $C^9H$), 6.80–8.05 (8 H, $C_6H_4$, 4-$ClC_6H_4$); uv (95% EtOH) maxima 224 m$\mu$ ($\epsilon$ 19,400), 249 (3000), and 281 (1850); $^{13}C$ nmr in Table I.

*Anal.* Calcd for $C_{16}H_{15}ClN_2O$: C, 67.0; H, 5.3; Cl, 12.4; N, 9.8. Found: C, 67.1; H, 5.2; Cl, 12.3; N, 9.7.

**Hydrogenation of 1b.** A mixture of 14.2 g (0.05 mol) of **1b**, 0.30 g of platinum oxide, and 150 ml of glacial acetic acid was placed in a Parr hydrogenation bottle and then attached to a Parr hydrogenation apparatus. The bottle was evacuated and then filled with hydrogen to a total pressure of 50 psi. After 3.0-hr agitation at room temperature, the hydrogen uptake (1 equiv of $H_2$) ceased. The catalyst was filtered off and the filtrate concentrated *in vacuo*. The residue was treated with 2 *N* NaOH until the aqueous phase had pH 9. It was then extracted with chloroform, dried with anhydrous $MgSO_4$, filtered, and concentrated to give 12.2 g (85%) of **4**, mp 84–85°. This substance gave ir and nmr spectrum identical with **4** prepared by $LiAlH_4$ reduction of **1b**.

**Conversion of 5 to 4.** A solution of 1.0 g of **5** in 25 ml of THF–$H_2O$ (9:1) was stirred for *ca.* 20 hr at room temperature. The tlc analysis ($CHCl_3$–$CH_3OH$, 9:1) revealed that **5** had been converted into a new substance. The solvent was removed *in vacuo* to give 0.91 g of a substance that gave ir and $^1H$ nmr and mp (83–85°) identical with **4** obtained in the $LiAlH_4$ reduction of **1b**.

**1-(*p*-Chlorophenyl)-1-phenyl-*N,N*-dimethylmethylamine (9).** A solution of 10.4 g (0.05 mol) of 4-chlorbenzhydrol, 30 ml of thionyl chloride and 150 ml of dry chloroform was stirred and refluxed until gas evolution (HCl, $SO_2$) had ceased. The solvent was removed *in vacuo* and the crystalline residue dissolved in 150 ml of dry tetrahydrofuran, cooled in an ice bath, and treated dropwise with 50 ml of 2 *N* dimethylamine (0.10 mol) in tetrahydrofuran. The mixture was allowed to stand at room temperature for *ca.* 7 days and then concentrated *in vacuo*. The residue was treated with 100 ml of 5 *N* HCl and 50 ml of benzene. The acid layer was separated, cooled in an ice bath, and treated with 50% KOH until the aqueous phase had pH 9.0. The mixture was extracted with 50 ml of toluene, dried with anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give 3.1 g (25%) of **9** as a viscous oil: ir ($CHCl_3$) no OH bond; $R_f$ 0.6 ($CHCl_3$–$CH_3OH$, 98:2).

*Anal.* Calcd for $C_{15}H_{16}ClN$: C, 73.5; H, 6.5; Cl, 14.5. Found: C, 73.3; H, 6.6; Cl, 14.3.

**3-Methyl-2-phenyloxazolidine (10).** A mixture of 13.1 g (0.123 mol) of benzaldehyde, 9.2 g (0.123 mol) of *N*-methylethanolamine and 50 ml of benzene were stirred and refluxed in a flask with a Dean–Stark water separator until the water level in the separator remained constant (*ca.* 1 hr). The mixture was distilled to give 17.1 g (85%) of **10**: bp 55° (1.0 mm); ir ($CHCl_3$), no C=O bond; tlc [$CHCl_3$–$CH_3OH$ (98:2)], one component; lit.[12] bp 110–115° (18 mm).

*Anal.* Calcd for $C_{10}H_{13}NO$: C, 73.6; H, 8.0; N, 8.6. Found: C, 73.8; H, 7.9; N, 8.4.

**1-Methyl-2-phenylimidazolidine (11).** A mixture of 10.6 g (0.10 mol) of benzaldehyde, 7.5 g (0.10 mol) of *N*-methylethylenediamine, and 50 ml of benzene were treated as in the preparation of **9** to give 13 g (80%) of **11**: bp 100° (1.0 mm); ir ($CHCl_3$), no C=O bond; tlc [$CHCl_3$–$CH_3OH$ (98:2)], one component.

*Anal.* Calcd for $C_{10}H_{14}N_2$: C, 74.0; H, 8.7; N, 17.3. Found: C, 74.3; H, 8.8; N, 17.2.

**Acknowledgments.** The authors thank Mr. T. Doyle for synthetic assistance, Dr. Sandor Barcza for obtaining the $^{13}C$ nmr spectra, and Mr. W. Bonkowski for analytical determinations.

**Registry No.**—**1b**, 6038-49-9; **4**, 23227-06-7; **5**, 26800-10-2; **9**, 53370-25-5; **10**, 1630-62-2; **11**, 53370-26-6; $LiAlH_4$, 16853-85-3; THF, 109-99-9; 4-chlorobenzhydrol, 119-56-2; dimethylamine, 124-40-3; benzaldehyde, 100-52-7; *N*-methylethanolamine, 109-83-1; *N*-methylethylenediamine, 109-81-9.

## References and Notes

(1) T. S. Sulkowski, M. A. Willie, A. Mascitti, and J. L. Diebold, *J. Org. Chem.*, **32**, 2180 (1967).
(2) W. Metlesics, T. Anton, and L. H. Sternbach, *J. Org. Chem.*, **32**, 2185 (1967).
(3) M. Winn and H. E. Zaugg, *J. Org. Chem.*, **34**, 249 (1969).
(4) P. Aeberli and W. J. Houlihan, *J. Org. Chem.*, **34**, 1720 (1969).
(5) Additional examples of the $LiAlH_4$–THF reduction of **1** can be found in (a) W. J. Houlihan, U. S. Patent 3,444,181, *Chem. Abstr.*, **71**, 49941n (1969); (b) W. J. Houlihan, Ger. Offen. Patent 1,814,540, *Chem. Abstr.*, **71**, 81368s (1969); (c) P. Aeberli, P. Eden, J. H. Gogerty, W. J. Houlihan, and C. Penberthy, *J. Med. Chem.*, in press.
(6) On several occasions, the nmr spectrum obtained in DMSO-$d_6$ gave this signal as a broad unresolved band.
(7) Compound **5** has also been prepared by treating **1b** with $LiAlH_4$ in diethyl ether at ambient temperature for 0.5 hr. The reported ir, nmr, and uv data are in excellent agreement with our findings. T. S. Sulkowski, Ger. Offen. Patent 1,926,477, *Chem. Abstr.*, **72**, 66920t (1970); T. S. Sulkowski, U. S. Patent 3,555,042.
(8) W. Metlesics, T. Anton, M. Chaykovsky, V. Toome, and L. H. Sternbach, *J. Org. Chem.*, **33**, 2874 (1968).
(9) Structure **6** has previously been incorrectly assigned to the $LiAlH_4$ reduction product of **1b** in THF: G. A. Cooke and W. J. Houlihan, Ger. Offen, Patent 2,023,633, *Chem. Abstr.*, **74**, 42360a (1971).
(10) It has been reported in ref 1 that use of THF or dioxane in the $LiAlH_4$ reduction of **1** results in considerably lower yields of **2** relative to use of refluxing diethyl ether. In the present work, we have been unable to detect the presence of any **2b** in our reduction product using tlc analyses.
(11) Melting points were determined in a Thomas-Hoover capillary melting point apparatus and have not been corrected. The ir spectra (KBr) were determined using a Perkin-Elmer Infracord and the uv spectrum on a Cary Model 15 spectrophotometer. The pmr spectra were obtained on a Varian Associates A-60 spectrometer. The $^{13}C$ nmr spectra were carried out on a Bruker HX-90 spectrometer equipped with a pulse-Fourier transform accessory that included a Fabritch (Nicolet) signal averager and a PDP-8 computer that contained 4K data points in the time domain. The frequency was set at 22.62 MHz with broad band $^1H$ decoupling at 90 MHz and typical sweep width of 5000 Hz with 15-$\mu$sec pulse width. Hexafluorobenzene was added for locking and hexamethyldisiloxane was used as an internal standard, which was taken as 191 ppm upfield of $CS_2$ and 2 ppm downfield of TMS. Thin layer chromatography (tlc) was carried out using glass plates coated with silica gel HF-254 (E. Merck AG).
(12) Miles Laboratories, Inc., British Patent 839,289 (June 29, 1960), *Chem. Abstr.*, **55**, 1450 (1961).