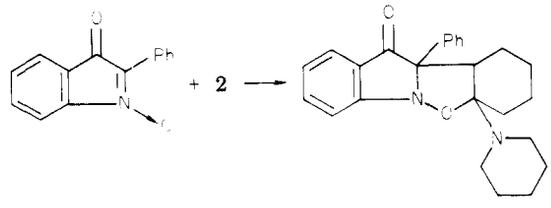
with aqueous hydrochloric acid under the same conditions under which **3** reacts.



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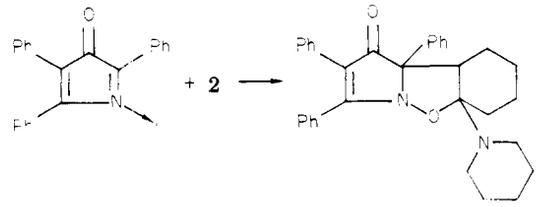

7

Experimental Section

Synthesis of Enamine Adducts (Table I). All of the adducts were prepared in the following manner. To a slurry of 2 g (7.0 mmol) of 2,5-diphenyl-3,4-diazacyclopentadienone 3,4-dioxide[5] in 30 mL of CH_2Cl_2 was added 2 mL of *N*-cyclohexenylpiperidine. This mixture was warmed on a steam bath for 15 min, and then allowed to stand at room temperature for 5 min. The solvent was evaporated, and the dark yellow oily residue was triturated with methanol to produce a yellow solid. Recrystallization from CH_2Cl_2–petroleum ether gives bright yellow crystals: mp 143–145 °C dec; yield 2.9 g (90%); IR (Nujol) 1725 (C=O), 1550 cm^{-1} (C=N(→O)–); ^1H NMR ($CDCl_3$) δ 1.2–1.5 (br d, 16 H), 2.6 (m, 3 H), 7.2–7.6 (m, 6 H), 7.7–7.9 (m, 2 H), 8.6–8.8 (m, 2 H); *m/e* (70 eV) 431 (M^+, 1), 300 (34), 115 (100), 105 (77).

Adduct 6 was prepared by the same general procedure as that used above from 0.3 g of 2-phenylisatogen:[9] yield 0.45 g (87%); mp 163–165 °C; IR (Nujol) 1718, 1600 cm^{-1}; NMR ($CDCl_3$) δ 7.7, 7.3 (m, 9), 3.2, 2.7, 2.3 (m, 19).

Anal. Calcd for $C_{25}H_{25}N_2O_2$: C, 77.29; H, 7.27; N, 7.21. Found: C, 77.18; H, 7.07; N, 7.47.

Upon prolonged standing in light, this adduct took on an orange color suggesting reversion to free isatogen.

Adduct 7 was prepared in two diastereomeric forms by the same procedure as that used above from 0.1 g of 2,4,5-triphenyl-3*H*-pyrrol-3-one 1-oxide[10] and separated by thick layer chromatography on silica; yield 0.125 g (83%).

7a: mp 172–174 °C; IR (Nujol) 1669, 1660 cm^{-1}; NMR ($CDCl_3$) δ 0.8–2.8 (br m, 18), 3.3 (m, 1), 7.3 (m, 13), 7.8 (m, 2); *m/e* (70 eV) M^+ 490 (15), 462 (2), 407 (3), 378 (3), 350 (3), 325 (7), 178 (30), 165 (100).

Anal. Calcd for $C_{33}H_{34}N_2O_2$: C, 80.78; H, 6.98; N, 5.71. Found: C, 79.09; H, 6.86; N, 5.60.

7b: mp 194–196 °C; IR (Nujol) 1710, 1600 cm^{-1}; NMR ($CDCl_3$) δ 1.2–2.6 (m, 18), 3.45 (m, 1), 7.25 (m, 11), 7.8 (4); mass spectrum identical with that of **7a**.

Anal. Calcd for $C_{33}H_{34}N_2O_2$: C, 80.78; H, 6.98; N, 5.71. Found: C, 80.69; H, 6.88; N, 5.70.

Reaction of Adduct 3 and Hydrochloric Acid. To 1 g of adduct **3** in 50 mL of CH_3OH was added 6 mL of concentrated HCl, and this mixture was allowed to stand at room temperature overnight. Water was added and **5**, a white solid (mp 188–190 °C), was collected: yield 0.8 g (91%); IR (Nujol) 1770 cm^{-1} (C=O, 5-membered ring), 1700 (C=O, 6-membered ring), 1570 (–N=N(→O)–); NMR ($CDCl_3$) δ 1.4–2.5 (m, 8), 3.48 (m, 1), 7.18–7.5 (m, 9), 7.93 (m, 1); *m/e* (CI) $M^+ + 1$, 383 (20), 385 (5), 348 (24), 326 (22), 324 (61), 303 (100), 250 (48), 119 (68), 105 (39).

Anal. Calcd for $C_{21}H_{19}ClN_2O_3$: C, 65.87; H, 5.00; Cl, 9.27; N, 7.31. Found: C, 65.68; H, 4.90, Cl, 9.47, N. 7.27.

(9) F. Kröhnke and M. Meyer-Delius, *Chem. Ber.*, **84**, 932 (1951).
(10) E. P. Kohler and C. R. Addinall, *J. Am. Chem. Soc.*, **52**, 1590 (1930).

Reduction of Adduct 3. A solution of 1.25 g of **3** in 30 mL of tetrahydrofuran was stirred at room temperature under 1 atm of H_2 in the presence of 0.1 g of Pd/C. After 2 h, the mixture was filtered and concentrated. The residue was chromatographed on silica gel, and the product was eluted with $CHCl_3$. Recrystallization from $CHCl_3$–Skelly B gave **4**: yellow needles: mp 187–189 °C; yield 0.7 g (70%); IR (Nujol) 3220, 1700, 1540 cm^{-1}; *m/e* (70 eV) M^+, 348 (11), 250 (10), 236 (80), 119 (95), 105 (100).

Anal. Calcd for $C_{21}H_{20}N_2O_3$: C, 72.41; H, 5.74; N, 8.04. Found: C, 72.30, H, 5.56; N, 7.89.

Registry No. **1**, 17952-96-4; **2**, 2981-10-4; **3** (R = R^1 = C_6H_5; Am = piperidine), 71964-78-8; **3** (R = R^1 = C_6H_5; Am = morpholine), 71964-79-9; **3** (R = C_6H_5; R^1 = CH_3; Am = morpholine), 71964-80-2; **3** (R = R^1 = C_6H_5; Am = pyrrolidine), 71964-81-3; **3** (R = C_6H_5; R^1 = CH_3CH_2; Am = pyrrolidine), 71964-82-4; **3** (R = C_6H_5; R^1 = CH_3; Am = pyrrolidine), 71964-83-5; **4**, 71964-84-6; **5**, 71964-85-7; **6**, 71964-86-8; **7**, 71964-87-9; 2-methyl-5-phenyl-3,4-diazacyclopentadienone 3,4-dioxide, 16901-38-5; 2-ethyl-5-phenyl-3,4-diazacyclopentadienone 3,4-dioxide, 16858-30-3; *N*-cyclohexenylmorpholine, 670-80-4; *N*-cyclohexenylpyrrolidine, 1125-99-1; 2-phenylisatogen, 1969-74-0; 2,4,5-triphenyl-3*H*-pyrrol-3-one 1-oxide, 62224-74-2.

Sodium–Ethanol: A Superior Reagent for the Reductive Dehalogenation of Polychlorinated Alicyclic Molecules

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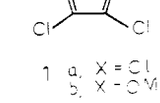
Diels–Alder reactions of hexachlorocyclopentadiene (**1a**) and 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**1b**) with a wide range of dienophiles generally give excellent yields of adducts with a high degree of stereospecificity. For these reasons **1a** and **1b** are often used as synthons for cyclopentadiene and cyclopentadienone, respectively.[1-5] Unfortunately, the attractiveness of these synthons is offset by the necessity to reductively dechlorinate the resulting adducts. The Gassman–Pape method[4] (Na, *tert*-butyl alcohol, THF), a modification of the Bruck–Thompson–Winstein procedure[2] (Li, *tert*-butyl alcohol, THF), is currently the most popular way of carrying out reductive dechlorinations of adducts of both **1a** and **1b**. However,



1 a, X = Cl
b, X = OMe

this method, carried out on a large scale, suffers from several disadvantages: it is time consuming, the workup procedure is inconvenient and hazardous, and the yields are often less than 50%.[6] The Birch reduction (Na, liquid NH_3, EtOH) has shown promise in reductively dechlorinating adducts of **1b**.[5] However, we have applied this method to a series of adducts of hexachlorocyclopentadiene

(1) H. E. Ungnade and E. T. McBee, *Chem. Rev.*, **58**, 249 (1958).
(2) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind. (London)*, 405 (1960); P. Bruck, *Tetrahedron Lett.*, 449 (1962).
(3) J. Haywood-Farmer, H. Malkus, and M. A. Battiste, *J. Am. Chem. Soc.*, **94**, 2209 (1972).
(4) (a) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964); (b) P. G. Gassman and J. L. Marshall, *Org. Synth.*, **48**, 68 (1968).
(5) M. E. Jung and J. P. Hudspeth, *J. Am. Chem. Soc.*, **99**, 5508 (1977).
(6) For example, the reductive dechlorination of **6a** via this method required 38 h of reaction time to give **6b** in only ca. 31–43% yield.[3b]

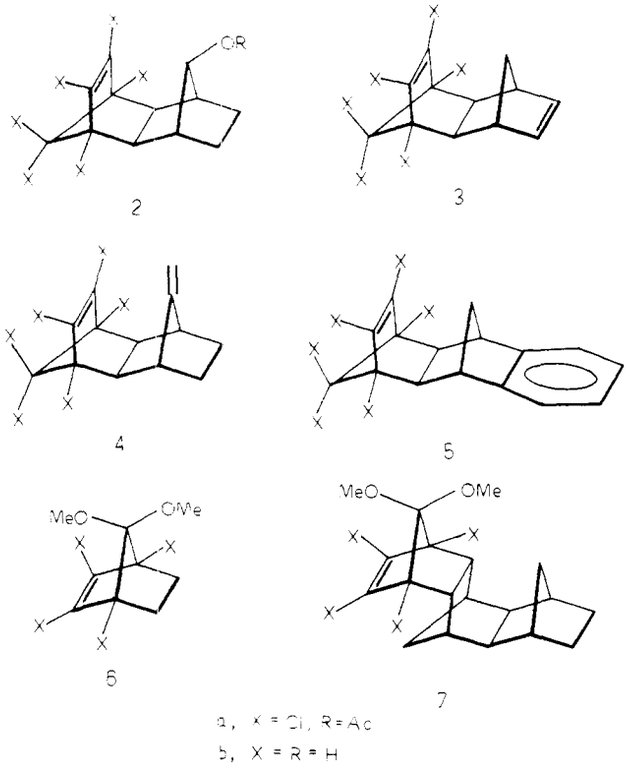
0022-3263/79/1944-4979$01.00/0

Table I. Reaction Conditions for Reductive Dechlorinations

substrate (amt, mmol)	Na-EtOH reaction: amt of Na, mmol	amt of EtOH, mL	reaction time, h	product	isolated yield, %[a]	Gassman-Pape isolated yield, %[a]	Birch reduction isolated yield, %[a]
2a (47)	2174	300	3	**2b**	70	24-50[b]	<10[c,f]
3a (13.7)	521	75	3	**3b**	69	50[d]	2[c,g]
4a (5.3)	304	40	3	**4b**	70		
5a (7.9)	317	50	3	**5b**	80		<15[c]
6a (20.5)	1000	100	3	**6b**	70	31-43[e]	67[f]
7a (4.7)	239	24	2	**7b**	62		60[f]

[a] >98% pure by GLC or TLC. [b] 24-50%;[3] 45%, H. K. Patney unpublished results. [c] Estimated by GLC. [d] Reference 2. [e] Reference 4b. [f] H. K. Patney, unpublished data. [g] P. A. Keogh, unpublished data.

(**1a**) i.e., **2a**–**5a**, without success—only small amounts of desired products were obtained in each case; the remainder



2 3 4 5 6 7

a, X = Cl, R = Ac
b, X = R = H

was polymeric material.

Fritz and his co-workers have noted that a tetrachlorotetraasterane was reductively dechlorinated to tetraasterane by using sodium in refluxing ethanol.[7] We are pleased to report that this reagent reductively dechlorinates Diels–Alder adducts from **1a** and **1b** in good yields. This method offers a number of advantages over that of Gassman and Pape in that the reaction is more rapid, product isolation is simpler, and the yields are generally better.

The results of the reductive dechlorinations of the adducts **2a**–**7a** using Na–EtOH are presented in Table I together with the available data from the Gassman–Pape and the Birch reduction methods. In every case where a comparison can be made, product yields from the Na–EtOH method are superior to those of the Gassman–Pape procedure, and the reaction times are shorter. It is worth noting from the data that double bonds and aromatic rings are not reduced by Na–EtOH. The Birch reduction method is useless for dechlorinating hexachloro adducts, i.e., **2a**–**5a**, but appears to be as good as Na–EtOH in dechlorinating tetrachloro adducts **6a** and **7a**.

In summary, Na–EtOH appears to be the method of choice for reductively dechlorinating polychlorinated alicyclic compounds.

Experimental Section

General Methods. All melting points are uncorrected and were recorded on a Gallenkamp melting point apparatus. The 60-MHz ^{1}H NMR spectra were obtained by using a Varian T-60 spectrometer; tetramethylsilane was used as an internal standard, and the resonances are quoted in δ units. Mass spectra were measured on an AEI MS902 mass spectrometer at 70 eV. All preparative thin-layer chromatography was carried out on plates with silica gel as adsorbent. Column chromatographic separations used neutral alumina as adsorbent. All solvents were freshly distilled before use. GLC analyses were carried out on a Bendix 1200 instrument (flame-ionization detector) with a 4 m × 32 mm column containing 10% SE-30 on Chromosorb W (A/W), 60/80 mesh. Microanalyses were performed by The Australian National University Microanalytical Service under the direction of Miss B. Stevenson and Dr. J. E. Fildes.

2a was prepared by the method of Haywood-Farmer et al.[3] and **6a** by a modification of the method of Gassman and Marshall.[4b,8] Aldrin (**3a**, Shell) was recrystallized from methanol. **4a** and **7a** were obtained from the cycloaddition of **1a** and **1b** onto 7-methylenenorbornene and the dimethanooctahydronaphthalene, respectively.[9]

***endo,exo*-1,2,3,4,11,11-Hexachloro-1,4,4a,9,9a,10-hexahydro-1,4:9,10-dimethanoanthracene (5a).** A mixture of hexachlorocyclopentadiene (10 g, 36 mmol) and benzonorbornadiene (4.3 g, 30 mmol) was heated at 150–160 °C for 1.5 h after which it was cooled and triturated with methanol (20 mL). The resulting solid was collected and recrystallized from acetone to give **5a**: 8 g, 61%; mp 134 °C; ^{1}H NMR ($CDCl_3$) δ 1.57 (d, J = 11 Hz, 1 H, H12 syn to aromatic ring), 1.93 (d of t, J = 11 and ca. 1.5 Hz, 1 H, H12 anti to aromatic ring), 2.79 (s, 2 H, H4a and H9a), 3.4 (m, J = ~1.5 Hz, 2 H, H9, H10), 7.1 (m, 4 H, aromatic). Anal. Calcd for $C_{16}H_{10}Cl_6$: C, 46.31; H, 2.43; Cl, 51.26. Found: C, 46.40; H, 2.40; Cl, 51.45.

Na–EtOH Dechlorinations. The typical procedure is as follows (the quantities of reagents and substrate and the reaction times for the reduction of each substrate are given in Table I). Small pieces of cleaned sodium metal were added to a refluxing solution of the substrate in absolute ethanol over 2 h after which time refluxing was continued for a further 1 h (or until all sodium had been reacted). The cooled mixture was treated with crushed ice (10 g/mmol of substrate). After the ice had melted, the solution was extracted with petroleum ether (40–60 °C fraction). The petroleum extract was dried (Na_2SO_4) and evaporated under reduced pressure. The resulting product was purified either by distillation or by recrystallization. The following data were recorded.

(i) Reduction of 2a gave the alcohol **2b** (from pentane), mp 109–110 °C (lit.[3] mp 108–109 °C), in 70% yield. ^{1}H NMR data for **2b** are identical with the literature values.[3]

(7) H.-G. Fritz, H.-M. Hutmacher, H. Musso, G. Ahlgren, B. Akermark, and R. Karlsson, *Chem. Ber.*, **109**, 3781 (1976).

(8) We found that the reaction between **1b** and ethene proceeded quantitatively by heating the reagents in a Parr Mini Reactor at 150 °C for ca. 5 min.[9]

(9) H. K. Patney and M. N. Paddon-Row, unpublished data.

(ii) Reduction of 3a gave **3b**, bp 100 °C (20 mm) [lit.[2] bp 98 °C (17mm)], in 69% yield. ^{1}H NMR data for **3b** are identical with those reported in the literature.[10]

(iii) Reduction of 4a gave **4b**: bp 115 °C (18 mm); 70% yield; ^{1}H NMR ($CDCl_3$) δ 1.0–1.6 (m, 6 H, H10, H2, H3), 2.05 (m, 4 H, H1, H4, H4a, H8a), 2.82 (m, 2 H, H5, H8), 4.33 (s, 2 H, methylene CH_2), 5.66 (t, 2 H, H6, H7). Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.58; H, 9.40.

(iv) Reduction of 5a gave **5b**: bp 79–80 °C (4.7 mm); 80% yield; ^{1}H NMR δ 1.2–1.75 (m, 3 H, H11, H12 syn to the aromatic ring), 2.25 (br s, 2 H, H4a, H9a), 2.83 (m, 3 H, H1, H4, H12 anti to the aromatic ring), 3.20 (s, 2 H, H9, H10), 6.10 (t, 2 H, H2, H3), 6.80–7.20 (m, 4 H, aromatic). Anal. Calcd for $C_{16}H_{16}$: C, 92.25; H, 7.75. Found: C, 92.06; H, 7.50.

This product was identical, in every respect, to that formed from the direct, thermal addition of cyclopentadiene to benzonorbornadiene.[11]

Reduction of 6a gave **6b**, bp 65–72 °C (20 mm) [lit.[4b] bp 58–68 °C (17 mm)], in 70% yield.

Reduction of 7a gave **7b** (from methanol), mp 99 °C, in 62% yield, identical in every respect to authentic material.[9]

Acknowledgment. We gratefully acknowledge the Australian Research Grants Committee for support of this work. We thank Dr. H. K. Patney for helpful discussions and Mr. M. J. Oliver for some assistance.

Registry No. **1a**, 77-47-4; **1b**, 695-77-2; **2a**, 28068-44-2; **2b**, 28068-45-3; **3a**, 309-00-2; **3b**, 15914-94-0; **4a**, 71871-91-5; **4b**, 71871-92-6; **5a**, 52420-67-4; **5b**, 71885-02-4; **6a**, 19448-78-3; **6b**, 875-04-7; **7a**, 71927-69-0; **7b**, 71871-93-7; 7-methylenenorbornene, 694-69-9; dimethanooctahydronaphthalene, 15914-93-9; benzonorbornadiene, 4453-90-1; sodium, 7440-23-5; ethanol, 64-17-5.

(10) A. P. Marchand and J. E. Rose, *J. Am. Chem. Soc.*, **90**, 3724 (1968).
(11) R. Hartcher, M.Sc. Thesis, New South Wales Institute of Technology, 1978.

Stereospecific Synthesis of (+)-Decahydro-$\alpha,\alpha,4a\beta$-trimethyl-β-cyclopropa-[*d*]naphthalene-7β-methanol[1]

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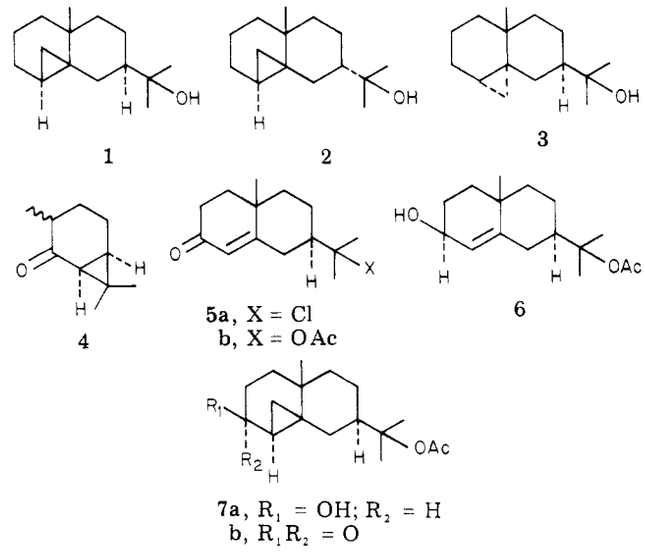
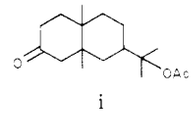
Received July 6, 1979

Recently, Moss and co-workers[2] reported the synthesis of the tricyclic alcohols **1** (β,β-cycloeudesmol) and **2** (β,α-cycloeudesmol). Independent syntheses of **1** and **2** as well as the tricyclic alcohol **3** (α,β-cycloeudesmol) have also been reported by Ando, Sayama, and Takase.[3] Compounds **1–3** are diastereomers of the structure assigned to cycloeudesmol, an antibiotic cyclopropane containing sesquiterpene, which was isolated from the marine alga *Chondria oppositiclada* Dawson by Fenical and Sims.[4] We wish to report an alternative stereospecific synthesis of the optically active alcohol **1** from the readily available terpene (−)-2-carone (**4**).[5]



Ketone **4** has been previously converted into the bicyclic chloro enone **5a**[6a] by Michael addition to methyl vinyl ketone followed by treatment of the 1,5-diketone product with hydrogen chloride in ethanol to effect opening of the cyclopropane ring and aldol cyclization.[6b] Solvolysis of **5a** in acetic acid containing silver acetate gave **5b** in 42% yield. Reduction of **5b** with lithium tri-*tert*-butoxyaluminum hydride in ether gave exclusively the β allylic alcohol **6** in 86% yield.[7] The NMR spectrum of **6** showed a small coupling constant (ca. 1.0 Hz) between the vinyl proton and the adjacent proton on the carbon atom bearing the hydroxyl group. This was consistent with the assignment of the β configuration to the allylic hydroxyl group.[8] Allylic alcohol **6** was then converted into β-cyclopropanated derivative **7a** in 49% yield by using the Conia modification[9] of the Simmons–Smith reaction.[10] There is a considerable amount of literature precedent which indicates that the β-hydroxyl group in **6** should direct the cyclopropanation in the indicated manner.[2,3,8,10] The structural assignment of the tricyclic hydroxy acetate **7a** was verified by the similarity of its NMR spectral properties (see Experimental Section) to those of closely related tricyclic alcohols.[3,11] Jones oxidation of alcohol **7a** gave the tricyclic acetoxy ketone **7b**[12] in 52% yield. The synthesis of **1** was accomplished in 64% yield by Wolff–Kishner reduction of the carbonyl function of **7b** which was accompanied by

(1) Partial support of the research by a grant from the National Cancer Institute is gratefully acknowledged.
(2) R. A. Moss, E. Y. Chen, J. Banger, and M. Matsuo, *Tetrahedron Lett.*, 4365 (1978).
(3) M. Ando, S. Sayama, and K. Takase, *Chem. Lett.*, 191 (1979).
(4) W. Fenical and J. J. Sims, *Tetrahedron Lett.*, 1137 (1974).
(5) W. G. Dauben, G. W. Shaffer, and E. J. Deviny, *J. Am. Chem. Soc.*, **92**, 6273 (1973).
(6) (a) D. Caine, H. Deutsch, and J. T. Gupton, III, *J. Org. Chem.*, **43**, 343 (1978); (b) see also, D. Caine and J. T. Gupton, III, *ibid.*, **39**, 2654 (1974).
(7) For examples of reductions of related enones to the corresponding β allylic alcohol with this reagent, see: (a) A. W. Burgstahler and I. C. Nordin, *J. Am. Chem. Soc.*, **83**, 198 (1961); (b) J. A. Marshall and J. A. Ruth, *J. Org. Chem.*, **39**, 1971 (1974).
(8) W. G. Dauben and A. C. Ashcraft, *J. Am. Chem. Soc.*, **85**, 3673 (1963).
(9) J. M. Dennis, C. Girard, and J. M. Conia, *Synthesis*, 549 (1972).
(10) H. E. Simmons, T. L. Cairns, and S. A. Vladuchick, *Org. React.*, **20**, 1 (1973).
(11) W. G. Dauben, P. Laug, and G. H. Berezin, *J. Org. Chem.*, **31**, 3869 (1966).
(12) In order to obtain chemical confirmation for the structural assignment of **7b** it was converted in good yield to a decalone derivative which had spectral properties completely consistent with the structure **i** by reductive cleavage of the cyclopropane ring with lithium in liquid ammonia (see W. G. Dauben and J. E. Deviny, *J. Org. Chem.*, **31**, 3794 (1966)).



i

0022-3263/79/1944-4981$01.00/0