(1*S*,2*S*)-**Phenyl-2-piperidylcarbinol (2b).**—CD measurements were made at 6.55×10^{-5} *M* (ethanol): $[\theta]_{274}$ 0, $[\theta]_{268}$ −414, $[\theta]_{265}$ −222, $[\theta]_{261}$ −455, $[\theta]_{258}$ −253, $[\theta]_{255}$ −333, $[\theta]_{251}$ −121, $[\theta]_{249}$ −162, $[\theta]_{242}$ −30, $[\theta]_{240}$ −40.

Registry No.—**1a,** 5583-31-3; **1a** HCl, 5583-32-4; **1b,** 5583-35-7; **1b** HCl, 5583-36-8; **2a,** 31002-84-3; **2b,** 30882-77-0.

Anomalous Diborane Reductions of Benz[c]acridines[1]

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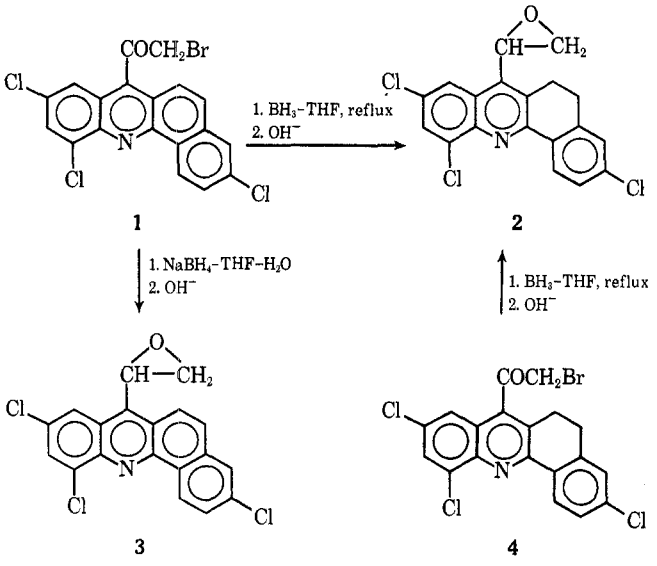
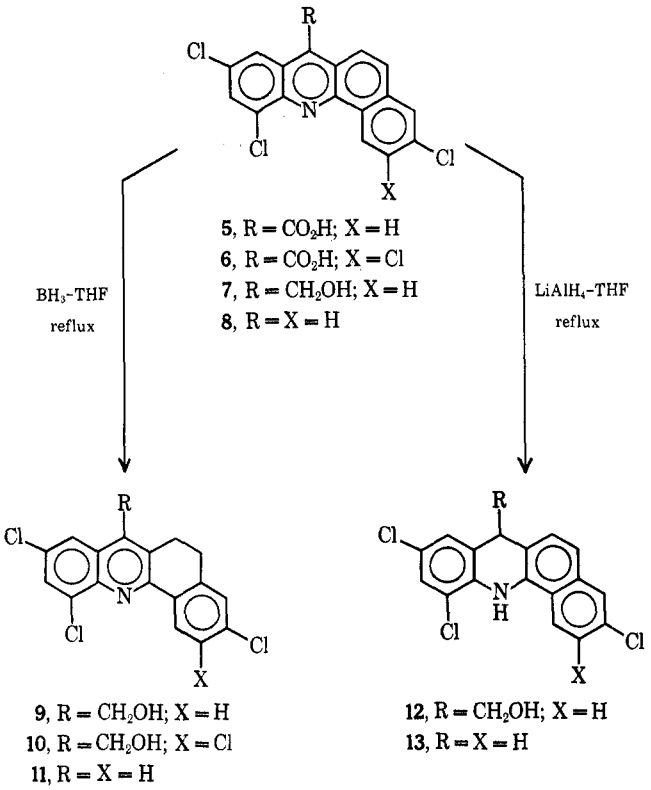
During the course of our work on the synthesis of benz[*c*]acridinemethanols as potential antimalarials,[2] we encountered an unusual diborane reduction of the benz[*c*]acridine ring system. Treatment of 7α-bromoacetyl-3,9,11-trichlorobenz[*c*]acridine (**1**) with diborane in refluxing tetrahydrofuran, followed by an alkaline work-up, unexpectedly yielded the 5,6-dihydro epoxide **2** instead of the desired aromatic product **3**. The identity of **2** was established beyond doubt by comparison with an authentic specimen prepared by reduction of the 5,6-dihydro bromomethyl ketone **4**.[2] Reduction of **1** with sodium borohydride in aqueous tetrahydrofuran at room temperature afforded the aromatic epoxide **3**.[2,3]



When diborane reduction in refluxing tetrahydrofuran was carried out with 3,9,11-trichlorobenz[*c*]acridine-7-carboxylic acid (**5**) or the 2,3,9,11-tetrachloro analog **6** (Scheme I), attack at the 5,6 double bond occurred again, with formation of alcohols **9** and **10**, respectively. Reduction of **5** with diborane at room temperature, on the other hand, afforded the aromatic alcohol **7** only, whereas reduction with lithium aluminum hydride in refluxing tetrahydrofuran yielded the 7,12-dihydro alcohol **12**.

SCHEME I



While it is well known that acridines can undergo reduction of the hetero ring upon treatment with metal hydrides[4] or diborane,[5] there appears to be no precedent in the literature for reduction of a carbocyclic aromatic ring by diborane. We considered the possibility that 5,6-dihydro compounds such as **2**, **9**, and **10** were perhaps being formed *via* reduction to the 7,12-dihydro compounds, which could then undergo rearrangement during work-up. This appeared feasible, at first, because alkaline conditions were used in the work-up of these compounds. However, inasmuch as reduction of **5** to **9** also proceeded with a neutral work-up, we were led to conclude that diborane is able to attack the double bond directly.[6]

Further evidence militating against the intermediacy of 7,12-dihydro compounds in the formation of 5,6-dihydro products was obtained by deliberate prolonged treatment of **12** with alkali. Two products were isolated, 7-methyl-3,9,11-trichlorobenz[*c*]acridine (**14**) and 3,9,11-trichlorobenz[*c*]acridine (**8**); however, no

(1) This investigation was supported in part by Research Contract DA-49-193-MD-3008 from the U. S. Army Medical Research and Development Command, Office of the Surgeon General. This is publication No. 871 from the Army Research Program on Malaria.

(2) A. Rosowsky, M. Chaykovsky, S. A. Yeager, R. A. St. Amand, M. Lin, and E. J. Modest, *J. Heterocycl. Chem.*, in press.

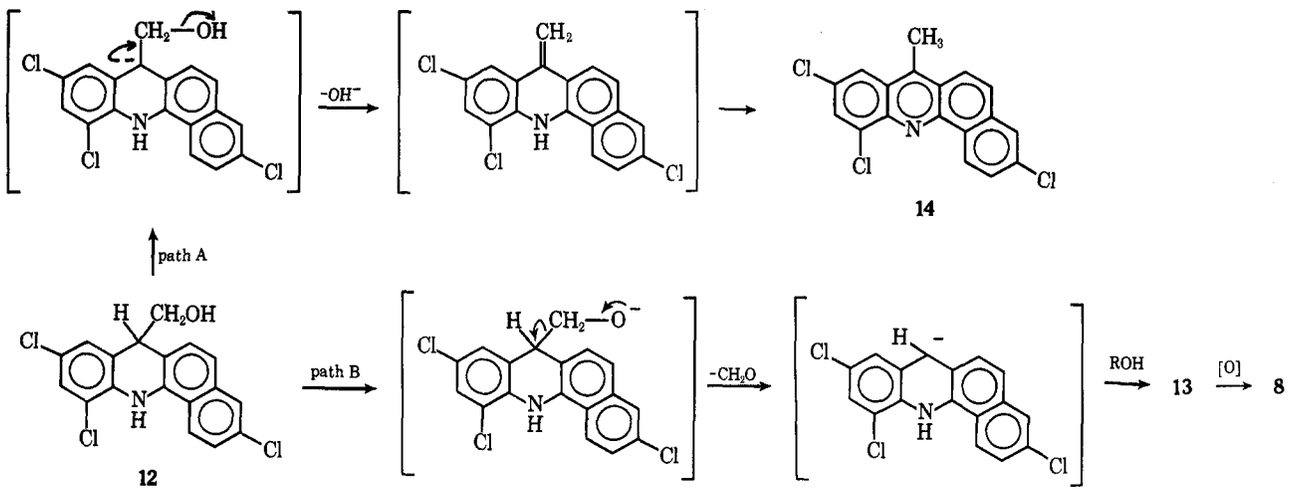
(3) It is of interest to note that reduction of 7α-bromoacetyl-2,3,9,11-tetrachlorobenz[*c*]acridine with sodium borohydride under these same conditions resulted in reduction of the hetero ring to give the 7,12-dihydro epoxide.[2]

(4) A. Campbell and E. N. Morgan, *J. Chem. Soc.*, 1711 (1958).

(5) W. J. Wechter, *J. Org. Chem.*, **28**, 2935 (1963).

(6) During the reduction of **5** to **9** with diborane, thin layer chromatography of samples of the reaction mixture on silica gel (2:2:1 benzene–cyclohexane–acetone) showed the formation of **9** with no evidence for the formation of the faster moving **12**. Apparently, partial hydrolysis of the boron intermediate can occur on the tlc plate. The ease of hydrolysis of the boron intermediates involved in 5,6 reduction by aqueous alkali is probably a consequence of the benzylic nature of the boron–carbon bond in these intermediates. The high reactivity of allylic boron derivatives has been reported; see H. C. Brown and H. Nambu, *J. Amer. Chem. Soc.*, **92**, 1761 (1970).

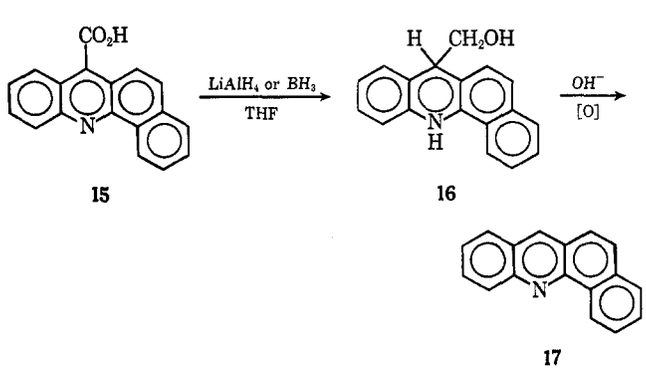
SCHEME II



trace of **7** or **9** could be detected. A plausible pathway for the formation of **14** and **8** is depicted in Scheme II.

In order to determine whether the unexpected diborane reductions observed with compounds **1**, **5**, and **6** might be associated in some fashion with the presence of a side chain at the 7 position, we also investigated the action of reducing agents on **8**. Reduction with lithium aluminum hydride in refluxing tetrahydrofuran or with sodium borohydride in refluxing aqueous tetrahydrofuran afforded the expected 7,12-dihydro product **13**. On the other hand, reduction with diborane in refluxing tetrahydrofuran led once again to the formation of the 5,6-dihydro derivative **11** with only a trace of **13** present. No reaction occurred at room temperature. This evidence tended to rule out the possibility that reduction of the 5,6 double bond involves participation by some intermediate species in which boron is covalently bound to a functional group in the side chain.

It was of interest to determine whether reduction of the 5,6 double bond is related to the presence of halogen atoms, especially at the 11 position. A chlorine substituent at this position would be expected to decrease the basicity of the neighboring ring nitrogen by virtue of its electron-withdrawing effect and also to impede the approach of a Lewis acid such as diborane by virtue of its steric bulk (an example of Brown's F-strain[7]). Such a phenomenon would reduce the ability of nitrogen to serve as an electron sink[5] in the addition of hydride at C-7. In fact, reduction of benz[*c*]acridine-7-carboxylic acid (**15**) did turn out to follow a somewhat different course from the reduction of the halogenated analogs. Like lithium aluminum hydride, diborane effected reduction only in the hetero ring, with formation of 7,12-dihydro-7-hydroxymethylbenz[*c*]acridine (**16**) both at room temperature and at reflux. Prolonged treatment with alkali only yielded benz[*c*]acridine **17** (according to path B, Scheme II).



It is significant that diborane treatment at room temperature sufficed to reduce both the carboxyl function and the hetero ring in **15**, but reduced only the carboxyl function in the 3,9,11-trichloro analog **5**, and effected no reduction in **8**. We believe that these findings are consistent with the view that the 11-chloro substituent retards diborane reduction for reasons stated above. Apparently, reduction of the 5,6 double bond of **1**, **5**, **6**, and **8** with diborane at the reflux temperature of tetrahydrofuran is seen because "normal" reduction of the hetero ring is energetically unfavorable.

Finally, in this connection, we became interested in the effect of lithium ions on the course of diborane reduction of the 11-chloro substituted compounds. We anticipated that the small size of the lithium cation would allow it to penetrate the steric barrier of the 11-chloro substituent and to coordinate with the ring nitrogen, thus facilitating hydride addition at C-7 and promoting reduction of the hetero ring. In fact, reduction of **8** with diborane in the presence of lithium iodide (1:3:3) yielded a mixture of reduced products consisting of about 40% of the 7,12-dihydro isomer and 60% of the 5,6-dihydro isomer. Increasing the amount of lithium iodide (1:3:6) led to a mixture containing about 60% of the 7,12-dihydro isomer. Thus, lithium cations lower the energy barrier for the "normal" diborane reduction of **8** sufficiently to allow the 7,12-dihydro isomer to become the predominant product.

Experimental Section[8]

Starting Materials.—The synthesis of compounds **1**, **5**, **6**, and **15** has been described.[2] Compound **8** was prepared by heating **5** to its melting point (280°) for several minutes to effect decarboxyla-

(7) H. C. Brown and R. B. Johannesen, *J. Amer. Chem. Soc.*, **85**, 16 (1953).

(8) Ultraviolet spectra were measured with Cary Model 11 and Model 15 spectrophotometers. Infrared spectra were taken in potassium chloride disks with a Perkin–Elmer Model 137B double-beam recording spectrophotometer. Nmr spectra were determined on a Varian A-60 instrument, with tetramethylsilane as the internal reference. Melting points were measured in Pyrex capillary tubes in a Mel-Temp apparatus (Laboratory Devices, Inc., Cambridge, Mass.) and are uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Werby Laboratories, Boston, Mass.

tion; recrystallization from benzene gave pale yellow needles, mp 228–230°.

Anal. Calcd for $C_{17}H_8Cl_3N$: C, 61.38; H, 2.42; N, 4.21; Cl, 31.98. Found: C, 61.32; H, 2.42; N, 4.07; Cl, 32.06.

5,6-Dihydro-3,9,11-trichloro-7-benz[*c*]acridinyloxirane (2).—A solution of borane in tetrahydrofuran[9] (60 ml, 0.06 mol) was added to a slurry of bromomethyl ketone **1** (12.0 g, calculated by nmr to contain 0.0208 mol of bromomethyl ketone and 0.0069 mol of methyl ketone) in dry tetrahydrofuran[10] (200 ml). After 2 hr of refluxing, the mixture was cooled to room temperature, and a solution of potassium hydroxide (15.7 g, 0.28 mol) in water (50 ml) and ethanol (150 ml) was added slowly. After 15 min of stirring, water (200 ml) was added, and after another 15 min the mixture was poured into cold water (400 ml). The precipitated solid was filtered, washed with water, and dried, yield 6.8 g, mp 228–231° dec. The solid was chromatographed on silica gel (250 g), with benzene as eluent. The oxirane **2** was eluted in the first few fractions, the more polar alcohols being retained on the column: yield 4.5 g (58% based on bromomethyl ketone); light tan solid, mp 234–240° dec. This product proved to be identical (ir, mixture melting point) with the compound obtained by borane reduction of **4**.[2] The nmr spectrum ($CDCl_3$) showed a pair of multiplets centered at δ 2.95 and 3.30 (total of 6 H) and a multiplet centered at δ 4.26 (1 H).

5,6-Dihydro-7-hydroxymethyl-3,9,11-trichlorobenz[*c*]acridine (9).—A solution of borane in tetrahydrofuran (2.34 ml, 2.34 mmol) was added to a solution of **5** (220 mg, 0.585 mmol) in tetrahydrofuran (10 ml). The solution was refluxed for 3 hr and cooled to room temperature, and a solution of potassium hydroxide (336 mg, 6.0 mmol) in water (5 ml) was added slowly. After 20 min, water (40 ml) was added and the precipitated solid was filtered, washed with water, and dried: yield 160 mg (75.1%); mp 220–224° dec. Recrystallization from benzene gave almost colorless plates, mp 222–224° dec. The same compound was produced by borane reduction of the 5,6-dihydro-7-carboxylic acid:[2] nmr (deuteriopyridine) A_2B_2 multiplet centered at δ 3.0 (4 H), 5.25 (s, CH_2OH).

Anal. Calcd for $C_{18}H_{12}Cl_3NO$: C, 59.28; H, 3.32; N, 3.84; Cl, 29.17. Found: C, 59.45; H, 3.28; N, 3.79; Cl, 29.01.

5,6-Dihydro-7-hydroxymethyl-2,3,9,11-tetrachlorobenz[*c*]acridine (10).—Reduction of **6** (205 mg, 0.5 mmol) with borane in tetrahydrofuran (2.0 mmol) and treatment with KOH (280 mg, 5.0 mmol) as described above yielded **10** (163 mg, 81.6%), mp 235–239° dec. Recrystallization from benzene gave almost colorless needles, mp 245–248° dec. This compound was identical with the product formed on borane reduction of the 5,6-dihydro-7-carboxylic acid:[2] nmr (deuteriopyridine) A_2B_2 multiplet centered at δ 3.0 (4 H), 5.28 (s, CH_2OH); uv λ_{max} (95% EtOH) 222 mμ (ϵ 37,670), 268 (33,400), 276 (48,300), 312 (9780), 327 (11,800), 341 (16,110), 356 (17,500).

5,6-Dihydro-3,9,11-trichlorobenz[*c*]acridine (11).—Reduction of **8** (166 mg, 0.5 mmol) with borane in tetrahydrofuran (1.5 mmol) and treatment with KOH (280 mg, 5.0 mmol) as described above yielded **11** (155 mg, 93%); mp 221–223° dec. Tlc analysis (silica gel, 1:1 benzene–hexane) showed only a trace of compound **13**. Recrystallization from benzene gave pale yellow needles, mp 243–246° dec. The same compound was formed by decarboxylation of the 5,6-dihydro-7-carboxylic acid[2] by heating to 280°. The nmr spectrum ($CDCl_3$) showed a multiplet at δ 3.02 ($-CH_2CH_2-$).

Anal. Calcd for $C_{17}H_{10}Cl_3N$: C, 61.01; H, 3.01; N, 4.19; Cl, 31.79. Found: C, 61.20; H, 2.96; N, 4.12; Cl, 31.61.

7-Hydroxymethyl-3,9,11-trichlorobenz[*c*]acridine (7).—When **5** was reduced with borane in tetrahydrofuran for 3 hr at room temperature by the standard procedure, compound **7** was formed (84%), mp 225–235° dec. Recrystallization from benzene gave yellow needles: mp 247–250° dec; nmr (deuteriopyridine) δ 5.70 (s, CH_2OH).

Anal. Calcd for $C_{18}H_{10}Cl_3NO$: C, 59.61; H, 2.78; N, 3.86; Cl, 29.33. Found: C, 59.24; H, 2.61; N, 3.68; Cl, 29.25.

7,12-Dihydro-7-hydroxymethyl-3,9,11-trichlorobenz[*c*]acridine (12).—Compound **5** (735 mg, 2.0 mmol) was added in portions to a mixture of lithium aluminum hydride (228 mg, 6.0 mmol) in tetrahydrofuran (30 ml). The mixture was refluxed for 2 hr, cooled to room temperature, and treated dropwise with saturated aqueous sodium chloride (2.0 ml). The mixture was filtered and the filtrate was evaporated to leave a red oil which was dissolved in methylene chloride, washed with 5% aqueous sodium hydroxide, rinsed with water, dried over sodium sulfate, and evaporated. Recrystallization of the yellow solid from benzene gave almost colorless prisms (520 mg, 71.4%): double mp 168–170° and 189–190°; nmr (deuteriopyridine) δ 3.95 (d, CH_2OH) and 4.30 (quartet, CH); uv λ_{max} (EtOH) 263 mμ (ϵ 24,300), 283 infl (15,800), 290 infl (12,970), 343 (9940), 385 (1400).

Anal. Calcd for $C_{18}H_{12}Cl_3NO$: C, 59.28; H, 3.32; N, 3.84; Cl, 29.17. Found: C, 59.11; H, 3.55; N, 3.59; Cl, 29.18.

7,12-Dihydro-3,9,11-trichlorobenz[*c*]acridine (13). A. By $LiAlH_4$ Reduction.—A mixture of **8** (998 mg, 3.0 mmol) and lithium aluminum hydride (228 mg, 6.0 mmol) in dry tetrahydrofuran (30 ml) was refluxed for 3 hr. The mixture was cooled and saturated aqueous sodium chloride (2.0 ml) was added slowly, followed by dilution with tetrahydrofuran (30 ml) and filtration. Evaporation of the filtrate left a yellow solid which was recrystallized from benzene: yield 550 mg (55%); yellow needles, mp 210–213°. A second recrystallization gave the analytical sample: mp 214–215°; nmr (deuteriopyridine) δ 4.08 (s, CH_2); uv λ_{max} (EtOH) 263 mμ (ϵ 23,100), 280 infl (13,740), 287 infl (12,540), 345 (9100), 365 infl (7390), 383 infl (2400).

Anal. Calcd for $C_{17}H_{10}Cl_3N$: C, 61.01; H, 3.01; N, 4.19; Cl, 31.79. Found: C, 61.08; H, 2.97; N, 4.12; Cl, 31.92.

B. By $NaBH_4$ Reduction.—A mixture of **8** (166 mg, 0.5 mmol), sodium borohydride (280 mg, 5.0 mmol), tetrahydrofuran (10 ml), and water (3 ml) was refluxed for 6 hr, cooled, and treated with potassium hydroxide (280 mg, 5.0 mmol) in water (5 ml). After 20 min, water (30 ml) was added and the precipitated solid was filtered, washed with water, and dried, yield 150 mg (95.2%), mp 200–204°. Two recrystallizations from benzene gave the pure compound, mp 214–215°.

Reduction of 8 with Borane in the Presence of Lithium Iodide.—To a solution of **8** (166 mg, 0.5 mmol) and anhydrous lithium iodide (201 mg, 1.5 mmol) in tetrahydrofuran (15 ml) was added borane in tetrahydrofuran (1.5 ml, 1.5 mmol). The mixture was refluxed for 3 hr, cooled to room temperature, and treated slowly with potassium hydroxide (280 mg, 5.0 mmol) in water (5 ml). After 20 min, water (30 ml) was added and the precipitated yellow solid was filtered, washed with water, and dried, yield 155 mg, mp 198–220°. Thin layer chromatography (silica gel, 1:1 benzene–hexane) showed the presence of **11** and **13** (the latter being the faster moving spot). Nmr analysis (deuteriopyridine) showed bands at δ 2.87 ($-CH_2CH_2-$ in **11**) and 4.08 ($-CH_2-$ in **13**). The amount of **13** was calculated to be about 40 mol %. When the reaction was run again under the same conditions but with twice the amount of lithium iodide (402 mg, 3.0 mmol) a product was isolated, mp 195–200°, which contained about 60% **13** and 40% **11**.

7,12-Dihydro-7-hydroxymethylbenz[*c*]acridine (16).—To a solution of **15** (2.73 g, 10 mmol) in tetrahydrofuran (20 ml) was added dropwise a solution of borane in tetrahydrofuran (30 ml, 30 mmol) with slight external cooling. After 3 hr of stirring at room temperature, 4 *N* hydrochloric acid (20 ml) was added slowly. The tetrahydrofuran was removed under vacuum, water (20 ml) was added, and the pH of the mixture was adjusted to 7 with concentrated aqueous potassium hydroxide. The mixture was extracted with methylene chloride and the extracts were washed with 5% aqueous potassium hydroxide, rinsed with water, dried over sodium sulfate, and evaporated. Recrystallization of the brown solid from benzene–hexane (charcoal) yielded **16** (1.9 g, 73.4%) as light tan crystals, mp 153–156°. Almost identical results were obtained when the reaction was carried out at reflux. The pure compound had mp 157–159° and was identical (ir, mixture melting point) with the product obtained on lithium aluminum hydride reduction of **15**.

Benz[*c*]acridine (17).—A solution of **16** (1.30 g, 5.0 mmol) and potassium hydroxide (1.12 g, 20 mmol) in absolute ethanol (45 ml) was stirred at room temperature in an open flask for 24 hr (after about 2 hr a precipitate began to form). The mixture was concentrated to about 20 ml under vacuum and filtered, and the solid was washed with dilute aqueous ethanol and dried, yield 860 mg (75%), mp 105–108°. Recrystallization from ethanol gave **17** as yellow needles, mp 107–108° (lit.[11] mp 108°).

(9) A 1.0 *M* solution of "borane" in tetrahydrofuran was supplied by Alfa Inorganics, Inc., Beverly, Mass.

(10) Matheson Coleman and Bell tetrahydrofuran was dried over molecular sieves (Linde 3A) and used without distillation.

(11) A. Albert, "The Acridines," 2nd ed, Edward Arnold, London, 1966, p 279.

Anal. Calcd for $C_{17}H_{11}N$: C, 89.05; H, 4.83; N, 6.11. Found: C, 89.02; H, 4.64; N, 5.87.

7-Methyl-3,9,11-trichlorobenz[c]acridine (14).—A solution of **12** (364 mg, 1.0 mmol) and potassium hydroxide (561 mg, 10 mmol) in absolute ethanol (60 ml) was refluxed for 3 hr. After about 1 hr a precipitate began to form. The mixture was cooled and the solid was filtered, washed with water, and dried, yield 300 mg, mp 208–213°. Two recrystallizations from benzene gave pale yellow needles, mp 234–237°, nmr (deuteriopyridine) δ 2.82 (s, CH_3).

Anal. Calcd for $C_{18}H_{10}Cl_3N$: C, 62.36; H, 2.91; N, 4.04; Cl, 30.69. Found: C, 62.17; H, 21.87; N, 3.93; Cl, 30.45.

The mother liquor from the first recrystallization, upon standing, deposited 20 mg of crystals, mp 215–220°. Further recrystallization from benzene gave pale yellow needles, mp 227–230°. This proved to be **8** (ir and mixture melting point).

Registry No.—**2**, 30885-38-2; **7**, 30885-39-3; **8**, 30885-40-6; **9**, 30885-41-7; **10**, 30885-42-8; **11**, 30885-43-9; **12**, 30885-44-0; **13**, 30885-45-1; **14**, 30953-15-2; **16**, 30885-46-2.

A New Method for the Controlled Hydroxymethylation of Ketones

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The attachment of a single hydroxymethyl substituent adjacent to a ketone or other electron-withdrawing function is most often accomplished by base-catalyzed aldol condensation of the active methylene compound and formaldehyde. Unfortunately, the process is usually difficult to control at the monoalkylation stage, resulting in complex mixtures containing polycondensation products as well as Cannizzaro-type reduction products.[1]

One well-used alternative to this process is the Mannich Reaction[2] which results in formation of the β-amino carbonyl derivative.

We now report a convenient two-step procedure capable of performing the desired transformation selectively and in high yield. The reaction sequence is illustrated by the conversion of 4-*tert*-butylcyclohexanone to 2-hydroxymethyl-4-*tert*-butylcyclohexanone.

Treatment of the ketone with sodium hydride and excess ethyl formate in dry dimethoxyethane (25°, 3–5 hr) gave the 2-hydroxymethylene derivative in 95% yield. This material was reduced, without further purification, by a method based on that suggested by Brown in his studies of aluminum hydride.[3] Generation of the sodium enolate by reaction with sodium hydride in tetrahydrofuran, followed by reaction with a tetrahydrofuran solution of aluminum hydride, furnished the desired 2-hydroxymethyl ketone in 90% yield. This material could be further purified by preparative layer chromatography on silica gel or short-path distillation.

The procedure may be varied by the substitution of dimethyl carbonate for ethyl formate, but there seems to be no particular advantage in this change. In fact, in some cases, only the more reactive formate was capable of acylating hindered ketones.

Experimental Section

Acylation with Ethyl Formate.—4-*tert*-Butylcyclohexanone (0.16 g, 1.04 mmol) in 2 ml of dry dimethoxyethane (distilled from lithium aluminum hydride) was added to a slurry of 4.1 mmol of sodium hydride (0.19 g of 55% mineral oil dispersion, washed three times with petroleum ether) in 3 ml of dry, alcohol-free ethyl formate (dried over potassium carbonate, distilled from phosphorus pentoxide) at 25° under argon. Ethanol (0.010 ml) was added, and the mixture was stirred for 5 hr and then poured into half-saturated aqueous ammonium chloride. Extraction with ether and drying of the ethereal extracts over sodium sulfate, followed by evaporation of the solvent, gave 0.18 g (95%) of the hydroxymethylene ketone: nmr (CCl_4) δ 0.92 (s, CH_3, 9 H), 1.0–2.6 (m, 7 H), 8.65 (s, olefinic, 1 H), 14.1 (m, OH, 1 H); ir $\lambda_{max}^{CCl_4}$ 2.7–4.0 (OH), 6.0–6.3 μ (keto enol ether).

Aluminum Hydride Reduction to 2-Hydroxymethyl-4-*tert*-butylcyclohexanone.—The hydroxymethylene ketone (0.17 g, 0.95 mmol) in 4 ml of tetrahydrofuran (distilled from lithium aluminum hydride) was added to a slurry of 1.07 mmol of sodium hydride (0.051 g of 55% mineral oil dispersion, washed three times with petroleum ether) in 2 ml of tetrahydrofuran. After 20 min at room temperature, 1.4 ml (1.05 mmol) of 0.75 *M* aluminum hydride in tetrahydrofuran (prepared from lithium aluminum hydride and 100% sulfuric acid by the method of Brown[3]) was added. After 1.25 hr the reaction mixture was poured into a mixture of ether and half-saturated aqueous ammonium chloride and filtered through Celite. Ether extraction of the filtrate, followed by drying (sodium sulfate) and evaporation of the solvent, gave 0.16 g (90%) of the desired hydroxymethyl ketone: nmr (CCl_4) δ 0.93 (s, CH_3, 9 H), 1.0–2.6 (m, 9 H), 3.65 (m, CH_2OH, 2 H); ir $\lambda_{max}^{CCl_4}$ 2.8 (OH), 5.85 μ (C=O). An analytical sample was prepared by bulb-to-bulb distillation at 90° (0.01 mm).

Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.58; H, 10.86.

Registry No.—Ethyl formate, 109-94-4; 2-hydroxymethylene-4-*tert*-butylcyclohexanone, 22252-96-6; 2-hydroxymethyl-4-*tert*-butylcyclohexanone, 31354-38-8.

Acknowledgment.—This work was supported by the National Science Foundation.

(1) *Cf.* H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York, N. Y., 1965, p 230.

(2) F. F. Blicke, *Org. React.*, **1**, 303 (1942).

(3) N. M. Yoon and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 2927 (1968).