Studies in Nonpyridinoid Aza-Aromatic Systems. V. The Methylation–Deprotonation Route to 4-Methyl-4*H*-cyclopenta[*b*]quinoline and Its 1,2-Dihydro Derivative[1]

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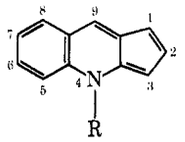
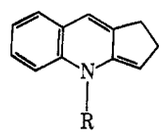
Received August 15, 1972

The synthesis of the fully conjugated, azulene-like heterocycle, 4-methyl-4*H*-cyclopenta[*b*]quinoline (**1c**), was attempted in two different approaches: (a) methylation of the tautomeric mixture of 1*H*-, 3*H*-, and 4*H*-cyclopenta[*b*]quinolines (**1a** and **3**), followed by deprotonation; and (b) dehydrogenation of 2,4-dihydro-4-methyl-1*H*-cyclopenta[*b*]quinoline (**2b**) by DDQ or by triphenylmethyl fluoroborate (**13**). The former route to **1c** was partially successful, but the methylation step involved N-protonation of **3**, C-methylation of **1a**, and probably some dimerization of **3** as side reactions. The latter approach from **2b** failed because **2b** formed an adduct with DDQ instead of simply dehydrogenating, and the **1c** formed from **2b** and **13** was further tritylated by **13**. As a model system for the C-methylation of **1a** observed in the former approach, the enamine system **2b** was found to undergo smooth C-methylation. The most reliable synthesis of **1c** involved the exclusive N-methylation of 3-acetoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (**16**) with dimethyl sulfate, the dehydracetoxylation by brief heating with concentrated sulfuric acid, and the liberation of **1c** only in a strongly basic medium. In its visible and nmr spectra and in its behavior toward nucleophilic or electrophilic attack, **1c** shows itself to be a close electronic relative of azulene and the benzazulenes.

Although several syntheses of substituted cyclopenta[*b*]quinolines (benzo[*b*][1]pyrindines) have been reported,[3–5] only recently has the unsubstituted cyclopenta[*b*]quinoline nucleus been synthesized[6] and its tautomeric character fully described.[7,8] Of special interest was the detection of the 4*H* tautomer (**1a**, *ca.* 0.1%) in the cyclopenta[*b*]quinoline isolated. The fully conjugated, azulene-like character of **1a** was revealed in its deep violet color[6] and in the electrophilic attack that its lithium salt **1b** underwent at C_1 and C_3.[7] To obtain exclusively a derivative of the aromatic 4*H* tautomer, we next wished to synthesize 4-methyl-4*H*-cyclopenta[*b*]quinoline (**1c**). Two general approaches



1a, R = H
b, R = Li
c, R = CH_3



2a, R = Li
b, R = CH_3
c, R = H

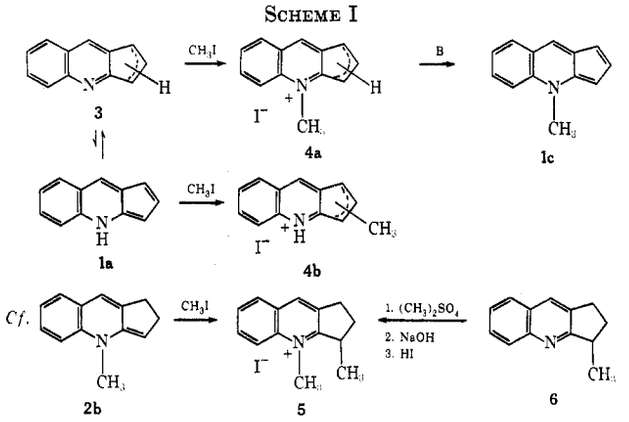
appeared feasible: (1) as with the related 1-pyrindine nucleus,[9] quaternization of cyclopenta[*b*]quinoline and deprotonation of the resulting salt or, alternatively, treatment of **1b** with methyl iodide; and (2) the dehydrogenation of 2,4-dihydro-4-methyl-1*H*-cyclopenta[*b*]quinoline (**2b**). This report describes the interesting chemistry encountered with each of these approaches and, in addition, presents a reliable route to **1c**.

Results

Methylation.—In contrast with the success claimed for the N-methylation of the sodium salt of 1*H*-1-pyrindine with methyl iodide, the lithium salt of benzo[*b*][1]pyrindine (**1b**) gave, as the only isolable products, a mixture of products mono- and dimethylated at C_1 and C_3.[7] Even the lithium salt of 2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (**2a**) underwent methylation in almost a quantitative fashion at C_3. In neither case did the crude, undistilled product reveal any nmr signal ascribable to the NCH_3 of **1c** (3.97 ppm) or of **2b** (2.75 ppm), respectively. Hence, the deprotonation–methylation sequence was inapplicable.

The methylation–deprotonation sequence to **1c** (Scheme I) required the quaternization of cyclopenta[*b*]quinoline (**3**) with methyl iodide. Although the quaternization was conducted at room temperature, infrared and nmr spectral analysis of the isolated methiodide **4a** showed it to be contaminated with N-protonated and probably both C-methylated (**4b**) and dimeric side products. On the basis of previous

SCHEME I



(1) Part IV of this series: J. J. Eisch and G. Gupta, *Tetrahedron Lett.*, 3273 (1972).

(2) Inquiries should be addressed to this author at the Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901.

(3) *Cf.* ref 6 for leading literature citations prior to 1970.

(4) L. E. Kholodov, I. F. Tishchenkova, and V. G. Yashunskii, *Tetrahedron Lett.*, 1535 (1970).

(5) V. N. Gogte, A. G. Namjoshi, and B. D. Tilak, *ibid.*, 4305 (1971).

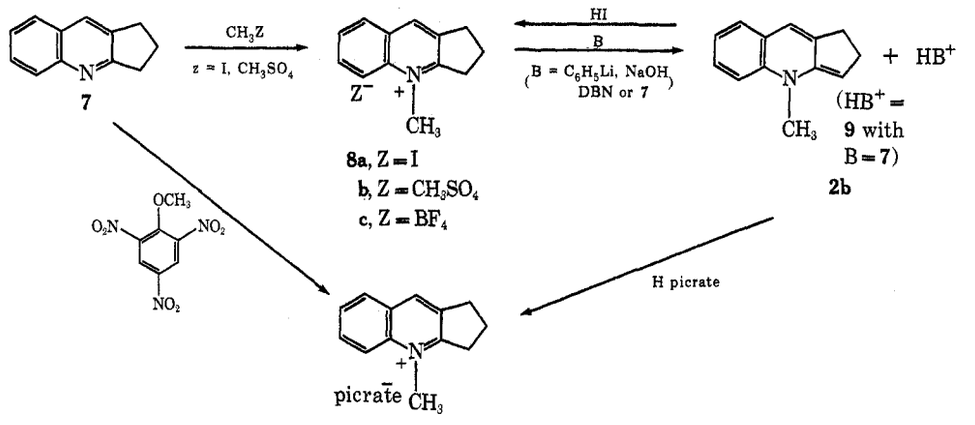
(6) J. J. Eisch and F. J. Gadek, *J. Org. Chem.*, **36**, 2065 (1971).

(7) J. J. Eisch and F. J. Gadek, *ibid.*, **36**, 3376 (1971).

(8) Contemporaneous with our report, I. F. Tishchenkova, L. E. Kholodov, and V. G. Yashunskii, *Khim. Geterotsikl. Soedin.*, **7**, 102 (1971) [*Chem. Abstr.*, **75**, 35668z (1971)] reported the synthesis of cyclopenta[*b*]quinoline involving the treatment of 3-bromo-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (*cf.* ref 6) dissolved in dimethylformamide with triethylamine. The oily product was neither distilled nor crystallized, but the nmr and uv spectral data seem to be in general agreement with our findings. However, their failure to observe a purple component in their product or to note the variable intensities of the 1-CH_2 and 3-CH_2 proton signals remains unexplained. In addition, the picrate of their product (mp 177–181°) melted much lower than the picrate of **3** (mp 217°).

(9) A. G. Anderson, Jr., and H. L. Ammon, *Tetrahedron*, **23**, 3601 (1967).

SCHEME II



nmr correlations for methyl derivatives of **3**, C-methylation is assumed to have occurred at C_3 (**4b**). The formation of **4b** can readily be explained by the presence of the 4*H* tautomer **1a** in **3**, for such an enamine would be expected to undergo C-methylation.[10] In support of this assumption, **2b**, the dihydro relative of **1c**, was found to undergo smooth C-methylation with methyl iodide. The resulting product **5** was prepared by an independent route from 2,3-dihydro-3-methyl-1*H*-cyclopenta[*b*]quinoline (**6**), in order to confirm its identity (Scheme I).

Assurance that quaternization of **3** did give largely the monomeric methiodide **4a**, rather than principally dimeric products as reported for the case of 1*H*-1-pyrindine,[9] was gained in two ways: (a) the nmr spectrum of **4** gave as its most intense singlet a sharp signal at 4.80 ppm (*cf.* ref 9 where the dimeric products displayed NCH_3 signals at 4.36 and 4.45 ppm); and (b) deprotonation yielded largely 4-methyl-4*H*-cyclopenta[*b*]quinoline (Scheme I, **4a** → **1c**) (*cf. infra*). However, because of the contaminants in **4a**, this method was not a completely satisfactory route to **1c**.

A satisfactory synthesis of **1c**, either by the methylation route or by the dehydrogenation route, demanded a suitable N-methylation procedure. In order to achieve N-methylation, exclusively and cleanly, it was necessary to start with a derivative of 2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (**7**). Even in this approach, quaternization had to be conducted so as to avoid contamination with the acid salt of the amine (**9**, Scheme II). Purified methyl iodide in ether at 25° or dimethyl sulfate in benzene at 80° proved to be suitable.

The preparation of pure 2,4-dihydro-4-methyl-1*H*-cyclopenta[*b*]quinoline (**2b**) for dehydrogenation studies was achieved from **8a** or **8b**. Although the preparation of **2b** *in situ* has frequently been reported,[11] its isolation has not. In our hands, the usual method of deprotonating **8a** or **8b**, namely, treatment with aqueous sodium hydroxide, gave the lowest isolated yield of **2b**. The use of phenyllithium proved convenient for deprotonating large batches of **8a** in yields of *ca.* 50%. For small-scale preparations of highly pure **2b**, deprotonation with 1,5-diazabicyclo[4.3.0]-non-5-ene (DBN), conducted under anhydrous conditions, proved superior (Scheme II). The structure and purity of **2b** were ensured by spectral data and by its conversion with hydriodic acid into **8a** and with picric acid into **10**. Structure **10**, in turn, was made independently from **7** and 2,4,6-trinitroanisole.

Dehydrogenation.—Since 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) has been shown to effect the 1,2-dehydrogenation of certain cyclopenta[*b*]quinoline systems,[7] **2b** was treated with DDQ. However, a 1:1 adduct was formed initially whose high melting point (>300°) and insolubility is suggestive of a polymer.[12] No 2,3-dichloro-5,6-dicyanohydroquinone, indicative of dehydrogenation, was detectable by thin layer chromatography.

The removal of hydride ion from tertiary amines by triphenylmethyl fluoroborate[13] (**13**), followed by deprotonation, seemed to be an appealing way to dehydrogenate **2b** (Scheme III). The high yields of triphenylmethane (60–100%, depending upon the order of addition) confirmed that **2b** did undergo hydride loss on contact with **13**, but no pure product could be isolated by column chromatography (under N_2) of the resulting violet-colored oils (presumably **1c** and its dimer or tritylated products). When 1 equiv of **2b** was added to 2 equiv of triphenylmethyl fluoroborate (**13**) an air-sensitive purple solid was isolated that seemed to be a bistrityl derivative of 4-methyl-4*H*-cyclopenta[*b*]quinoline (possibly **12**). With a 1:1 reaction mixture of **2b** and **13**, the trityl groups were essentially accounted for by the 62% yield of triphenylmethane and 33% yield of **11**. One-half of the starting **2b** was accounted for as the fluoroboric acid salt (**8c**, 20%) and 3-trityl salt (**11**, 33%). Accordingly, 47% of **2b** furnished at least 62% of the hydride ion; this is consistent with the dimerization of **1c** and the further loss of one hydride per dimer (*ca.* 40% + 20%). Thus, although the dehydrogenation proceeded readily, this route to benzo[*b*][1]pyrindines seems to fail because of their acid sensitivity.

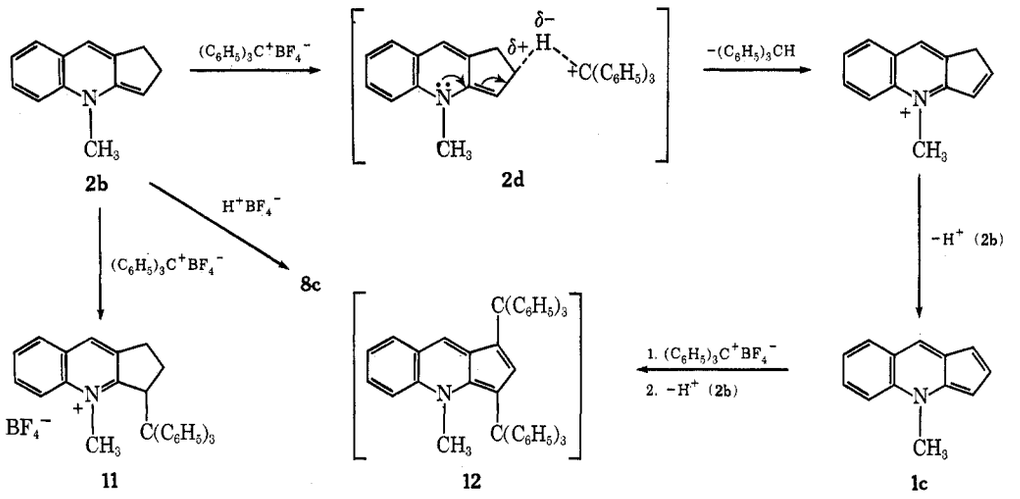
(10) G. H. Alt in "Enamines: Synthesis, Structure, and Reactions," A. G. Cook, Ed., Marcel Dekker, New York, N. Y., 1969, pp 116 ff.

(11) (a) W. Treibs, *Naturwissenschaften*, **49**, 37 (1962); (b) L. E. Kholodov, I. F. Tishchenkova, I. V. Persianova, and V. G. Yashunskii, *Reakts. Sposobnost Org. Soedin.*, **6**, 1000 (1969); *Chem. Abstr.*, **72**, 121751r (1970); (c) I. F. Tishchenkova, L. E. Kholodov, and V. G. Yashunskii, *Khim.-Farm. Zh.*, **5**, 16 (1971); *Chem. Abstr.*, **74**, 125361c (1971); (d) I. F. Tishchenkova, L. E. Kholodov, and V. G. Yahsunskii, *Khim. Geterotsikl. Soedin.*, **7**, 87 (1971); *Chem. Abstr.*, **75**, 35656u (1971).

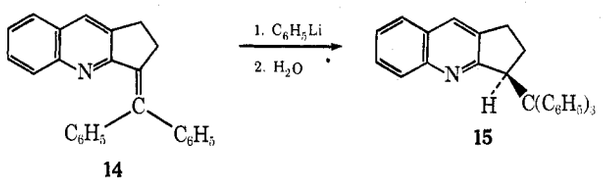
(12) S. Kanda and H. A. Pohl in "Organic Semiconducting Polymers," J. E. Katon, Ed., Marcel Dekker, New York, N. Y., 1969, p 118 ff.

(13) R. Damico and C. D. Broaddus, *J. Org. Chem.*, **31**, 1607 (1966).

SCHEME III



The remarkably easy electrophilic tritylation of **2b** by **13** to yield **11** posed the question of whether the trityl attachment was through methyl [$(C_6H_5)_3C$–] or, owing to better steric accessibility, through a para position [$-C_6H_4CH(C_6H_5)_2$]. The strong similarity between the nmr spectrum of **11** and that of the addition product (**15**) of phenyllithium to 2,3-dihydro-



3-diphenylmethylene-1*H*-cyclopenta[*b*]quinoline (**14**)[7] permits the conclusion that in **11** the trityl group is attached through methyl.[14]

The structure of model compound **15** can, in turn, be readily deduced from its mass spectrum: prominent peaks at *m*/*e* 243 and P − 243 show the clean fragmentation into trityl and quinindanyl moities. Such fragmentation rules out the possibility that **14** underwent phenylation at C_2 or C_9 with rearrangement.

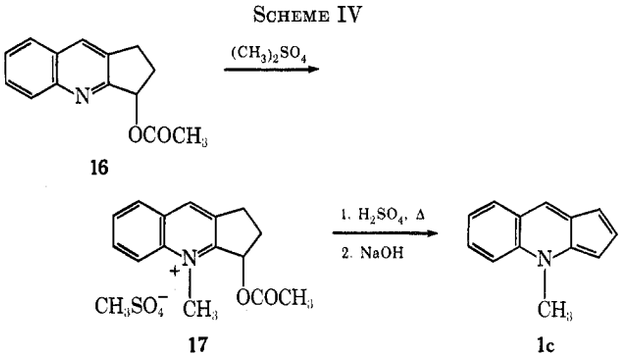
Attempts to dehydrogenate **2b**, by refluxing in xylene with 10% palladium on charcoal or by free-radical bromination at C_1 or C_2 with *N*-bromosuccinimide, failed. In the latter case, **2b** was transformed into a higher molecular weight green solid, similar to the acid-promoted product formed from **2b** upon storage (*cf.* Experimental Section).

Preparation of 4-Methyl-4*H*-cyclopenta[*b*]quinoline.—This synthesis succeeded by achieving exclusively N-methylation with a derivative of **7** suitable for the subsequent introduction of a double bond. Thus, 3-acetoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (**16**) was quaternized with dimethyl sulfate and the resulting methosulfate **17** was heated briefly with concentrated sulfuric acid to eliminate acetic acid. Liberation of deep violet 4-methyl-4*H*-cyclopenta[*b*]-quinoline (**1c**) with base was conducted under an atmosphere of nitrogen (Scheme IV).

The mass and nmr spectral data on this violet solid give unequivocal proof of its identity as **1c**, free of any

(14) The detection of triphenylmethane in this reaction supports the occurrence of an autoxidation of **15** to form the 3-hydroxy derivative, which then suffers the loss of $(C_6H_5)_3CH$.

SCHEME IV



dimeric or C-methylated contaminants. Its visible spectral maximum at 525 nm (broad absorption between 495 and 555 nm in CCl_4) compares favorably with the absorptions ascribed to **1a** (470–540 nm in C_6H_6) and **1b** (468–530 nm in C_6H_6).[6]

Discussion

Our attempts to dehydrogenate 2,4-dihydro-4-methyl-1*H*-cyclopenta[*b*]quinoline (**2b**) should be compared with those found in two recent reports claiming the synthesis of 1,3-disubstituted 4-methyl-4*H*-cyclopenta[*b*]quinolines from derivatives of **2b** or **8a** and *p*-benzoquinones.[4,5] Benzo[*b*][1]pyrindine systems are postulated to be formed by dehydrogenation with either DDQ or chloranil and these nuclei then are assumed to be attacked by additional substituted benzoquinone to yield, with elimination of hydrogen chloride, 1,3-disubstituted derivatives of **1c**. The high decomposition ranges of our product from **2b** and DDQ and those reported for the above products (230–350°) suggests that such products may be charge-transfer polymers.[12] Mass spectral measurements of molecular weights are necessary to support the monomolecular nature claimed[4,5] for these solids.

Regardless of the molecular weight, however, there seems little doubt that **2b** can undergo dehydrogenation with benzoquinones or with triphenylmethyl fluoroborate (**13**). The nmr spectra of the 1,3-disubstituted 4-methyl-4*H*-cyclopenta[*b*]quinolines reported[4,5] display only aromatic and NCH_3 protons (solutions in DMSO, CF_3COOH, or $AsCl_3$). In our work, treatment of **2b** with **13** gave high yields of triphenylmeth-

ane. A recent mechanistic study points to a similarity in mechanism between the behavior of DDQ and that of **13**: the rapidity with which DDQ transforms tropylidene into the tropenium ion is ascribed to the hydridic transfer of the hydrogen to DDQ.[15] Thus, either in the attack of DDQ or **13** on **2b** the ease with which dehydrogenation occurs can be related to the ease with which hydride ion can be lost from C_2. The developing positive charge at C_2 can be stabilized by the nitrogen center (**2d** in Scheme III). The competing tritylations leading to **11** and presumably to **12** observed with **2b** and **13** are similar to the postulated electrophilic attack of DDQ or chloranil on C_1 or C_3 of benzo[*b*][1]pyrindines.[4,5]

The deprotonation–methylation approach to **1c**, apparently so successful for the synthesis of 1-methyl-1*H*-1-pyrindine from the sodium salt of 1-pyrindine and methyl iodide,[9] was not pursued, since the lithium salt **1b** gave only C-alkylation with methyl iodide. This sharp contrast between the behavior of the salts of pyrindine and benzopyrindine cannot readily be attributed just to the difference in metal ion. Perhaps in **1b** the peri interaction of the C_5 H with the methyl iodide hinders N-methylation. However, it should be observed that a wide variety of anions derived from 2-methylpyridines[16] and 1,2-dihydropyridines[17] undergo C-methylation preferentially.

The methylation–deprotonation route to **1c**, as applied to **3**, seems destined to unavoidable difficulties. Not only can the enamine **1a** compete with **3**, leading to C- and N-methylations, but the acidic methiodide **4a** can easily transfer a proton to unquaternized **3**, leading to salts of **3** and, eventually, dimers of **3**. These difficulties are obviated in the approach to **1c** from the 3-acetoxy derivative **16**. N-Methylation is performed with no such competitive processes and the acid-sensitive system in **1c** is generated only in a strongly basic medium.

In conclusion, the spectral properties of pure 4-methyl-4*H*-cyclopenta[*b*]quinoline (**1c**) provide decisive evidence for the azulene-like character of this heterocycle. The visible spectral absorptions of **1c** ($\lambda_{max}^{Et_2O}$ 525 nm) and of the lithium salt **1b** ($\lambda_{max}^{C_6H_6}$ 530 nm) compare favorably with that of 5,6-benzazulene ($\lambda_{max}^{c\text{-}C_6H_{12}}$ 557 nm).[6] A comparison of the nmr spectrum of **1c** with that of its 1,2-dihydro relative **2b** (in which the conjugation, and hence the ring current, is disrupted) shows the deshielding effect of complete conjugation: aromatic and vinyl protons absorb at 5.83–8.1 ppm in **1c** and at 4.15–7.1 ppm in **2b**, and the NCH_3 group occurs at 3.97 ppm in **1c** but at 2.75 ppm in **2b**. In addition, the ready electrophilic attack that **1b** (and probably also **1c**) undergoes at C_1 and C_3 and the nucleophilic attack that **1c** undergoes at C_9[1] also speak for the azulene-like, aromatic character of the benzo[*b*][1]pyrindine nucleus (**1a–c**).

Experimental Section[18]

2,3-Dihydro-4-methyl-1*H*-cyclopenta[*b*]quinolinium Iodide (8a).—Treatment of **7** in warm ethanolic or ethereal solution with 3 molar equiv of methyl iodide eventually led to the deposition of 98% of the yellowish-green needles of **8a**, mp 209–211° (lit. mp 207°). Recrystallization from 95% ethanol gave dark green needles, mp 212–214°. Extended extraction with hot benzene did not reveal by glpc that any free **7** was present. Spectral data follow: ir_{max}^{KBr} 4.0–4.25 and 5.0–5.3 (weak, $^+$NH), 6.15, 6.25, 8.2, 11.45, and 12.70 μ; nmr (CF_3COOH) 2.72 (q, 2 H), 3.74 (quintet, 4 H), 4.96 (s, <3 H), 8.2–8.7 (m, 4 H), and 9.1 ppm (s, 1 H). From this measurement it was estimated that 1–5% of the hydrogen iodide of **7** was admixed with **8a**. Purer samples resulted from quaternization at room temperature in ether.

2,4-Dihydro-4-methyl-1*H*-cyclopenta[*b*]quinoline (2b). Method A.—To a suspension of 72.8 g (234 mmol) of **8a** in 250 ml of dry benzene was added dropwise an ethereal solution of phenyllithium (246 mmol, 5% excess) at 0° over a period of 2.5 hr. The red-brown solution was then allowed to warm to room temperature with stirring over a 16-hr period. The hydrolysis of the reaction mixture was carried out with deoxygenated water at 0° and the separated organic layer was kept at all times under a nitrogen atmosphere. The organic extract was dried with powdered K_2CO_3 and the solvent was removed with a rotary film evaporator. Distillation under reduced pressure gave a main fraction of an orange-red oil consisting of principally **2b**, bp 133–135° (0.34 mm), for a yield of 46%. Upon standing under a nitrogen atmosphere this oil solidfied to a mass of stout yellow rods. Forerun and afterrun contained **2b**, contaminated with biphenyl and three other products.[19] The main fraction was analyzed by glpc on a 2-ft column (10% silicone gum rubber on firebrick, column temperature 175°, 60 ml/min He) and was shown to display peaks for **7** (192 sec) and **2b** (360 sec) in a 1:9 ratio. A further peak at a longer retention time (480 sec) appeared to be an oxidation product, since its area increased with time of storage and with conscious exposure of the sample to air. Also, oxidation caused the sharp diminution of the peak at 360 sec and the development of new peaks at 384 and 672 sec. However, the absolute amount of **7** in a distilled sample of anhydro base was undoubtedly only about a maximum of 5%, for the neat infrared spectrum did not show the characteristic, intense bands of **7** at 10.55, 11.05, and 12.9 μ, nor did the nmr spectrum display the prominent broad multiplet at 3.2 ppm, characteristic of the 1-CH_2 and 3-CH_2 groups. The presence of sharp singlets at 2.83 and 2.95 ppm, in addition to the principal NCH_3 singlet at 2.75 ppm due to **2b**, revealed the presence of NCH_3-containing components in a sample that had stood for 2 days under nitrogen. The relative intensities of 1.0 (2.95), 1.0 (2.83), and 2.8 (2.75), taken together with the glpc ratio of 1:9 for **7** and **2b**, leads to a minimum composition for this fraction of 55% **2b**, 5% **7**, and 40% of the components having the NCH_3 signals at 2.83 and 2.95 ppm. The latter peaks increased with time, so their origin was ascribed to dimerization or oxidation products of the anhydro hase (*cf. infra*). Samples for further reactions or for spectral measurements, accordingly, were freshly distilled under a nitrogen atmosphere just before use.

Spectral data follow: ir (neat) 2.9–3.1 (clear), 3.3–3.4, 6.1 (C=C str), 6.3, 6.7, 6.9, 7.5, 7.7, 7.8, 8.2, 8.8, 9.15, 9.6, 9.7, 10.8, 11.4, 11.55, and 13.5 (s); nmr (CCl_4) 2.48 (br s, 4 H), 2.75 (s, NCH_3), 4.15 (br s, C_3 H), 5.85 (br s, C_9 H) and 6.5–7.1 ppm (aromatic m). Signals attributable to further chemical reaction developed at 2.1–2.4, 2.83, 2.95, 3.6, and 5.0 ppm.

A solution of **2b** in dry, degassed methylene chloride was warmed with an excess of 45% aqueous hydriodic acid. Upon cooling the methiodide **8a** was formed and identified by melting point, mixture melting point, and infrared spectrum.

Admixture of ethanolic solutions of **2b** and of picric acid led to an immediate precipitation. Collection of the solid revealed a mixture of green and red needles which were mechanically separated. The green, rod-shaped crystals (**10**) melted at 138.0–139.5° after recrystallizations from ethanol and proved to be the methopicrate of **7**. Spectral data: ir_{max}^{KBr} 6.2, 6.45, 6.7, 6.8, 6.9, 7.05, 7.4–8.1, 8.7, 9.3, 11.05, 12.75, 12.95, 13.25, 13.45, 13.9, and 14.2 μ; nmr (CF_3COOH) 2.70 (c of quartet, 2-CH_2), 3.55 (c of quintet, 1-CH_2 and 3-CH_2), 4.6 (s, NCH_3), and 8.0–8.34 (m, 5 H).

Anal. Calcd for $C_{19}H_{16}N_4O_7$: C, 55.34; H, 3.91; N, 13.58. Found: C, 55.06; H, 4.02; N, 13.68.

(15) P. Müller and J. Rocĕk, *J. Amer. Chem. Soc.*, **94**, 2716 (1972).

(16) K. Ziegler and H. Zeiser, *Justus Liebigs Ann. Chem.*, **485**, 174 (1931).

(17) C. S. Giam and J. L. Stout, *Chem. Commun.*, 478 (1970).

(18) Details of the general manipulative procedures and the instrumental methods are given in ref 6.

(19) The higher boiling fractions (150–200°, 0.34 mm) were dissolved in petroleum ether and concentrated to yield a colorless solid, mp 115°, whose infrared (13.5 and 14.4 μ, C_6H_5) and mass [261 (P), 245 (P − 16)] spectra are consistent with the addition of a phenyl group to **8a**.

It is interesting to note that the separated dark red needles melted at 140.5–142.0° when recrystallized from ethanol and that a mixture melting point with the green methopicrate **10** was slightly depressed (134.5–135.5°). However, since the mass, ir, and nmr spectra were essentially identical, these differences may stem from polymorphism.

Method B.—A solution of 42.2 g (250 mmol) of **7** in 100 ml of dry toluene was heated to reflux under a nitrogen atmosphere and then a solution of 93.8 g (750 mmol) of freshly distilled dimethyl sulfate dissolved in 50 ml of toluene was introduced dropwise. The heat of reaction sustained the temperature. The solution was cooled and filtered with exclusion of moisture (if required to be hydrate-free) to give a quantitative yield of the methosulfate **8b**. A tlc examination of the almost colorless solid, even after digestion with hot toluene, still showed the presence of some **7**.

A solution of 7.4 g (25 mmol) of **8b** in 125 ml of degassed water was treated with 70 ml of a 10% aqueous potassium hydroxide solution at 0° and under nitrogen. A yellow-green precipitate formed promptly. The slurry was stirred for 1 hr at 25° and then filtered through a coarse glass frit under nitrogen. Repeated washing of the precipitate under nitrogen with degassed water seemed to cause solubilization of some **2b**. Drying overnight *in vacuo* yielded only 18% of the anhydro base **2b**. Its apparent content of **7** by glpc was about the same as that from method A and its ir spectrum was also in agreement with that recorded above. A melting point taken in a sealed tube was 54–57°.

Method C.—A suspension of **8a** (500 mg, 1.60 mmol) in 50 ml of anhydrous, purified tetrahydrofuran was treated with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 200 mg, 1.61 mmol, freshly distilled from calcium hydride) with vigorous stirring under an atmosphere of nitrogen for 2.5 hr. The cooled suspension was filtered through a glass frit under nitrogen and the filtrate was then subjected to reduced pressure evaporation to yield **2b** as a pale yellow solid, 257 mg, 87%. The nmr and infrared spectra were recorded immediately under a nitrogen atmosphere. The infrared spectrum was identical with those of **2b** prepared by methods A and B. The nmr spectrum (CCl_4) was free of any peaks attributable to impurities. The absence of the sharp singlets of equal intensity at 2.83 and 2.95 ppm, noted in the spectrum of **2b** made according to method A, is noteworthy. When the DBN was not dried just before use, these peaks also appeared in the **2b** isolated. Such peaks can be assigned to NCH_3 groups in a dimer of **2b**, apparently formed owing to a moisture-promoted reaction. The progress of such a reaction could be discerned by the eventual deposition of a green solid from a solution of **2b** in CCl_4. In contrast with freshly prepared **2b**, which gave a mass spectrum at 70 eV showing peaks at *m/e* 183 (P), 182 (P − 1), 168 (P − 15), and 167 (P − 16), this green solid gave weak peaks over *m/e* 500 and prominent peaks between *m/e* 330 and 370.

2,3-Dihydro-4-methyl-1*H*-cyclopenta[*b*]quinolinium Methopicrate (10).—Gentle heating of 1.0 g (5.9 mmol) of **7** with 1.46 g (6.0 mmol) of 2,4,6-trinitroanisole at 75° for 10 min yielded a dark green solid from which, by recrystallization from ethanol, 1.9 g (78%) of authentic, dark green needles of **10** was isolated, mp 138.0–139.5°.

Action of Triphenylmethyl Fluoroborate (13) on the Anhydro Base 2b.—A solution of freshly distilled **2b** (5.3 g, 29 mmol) in 100 ml of dry, degassed methylene chloride was treated dropwise with a solution of triphenylmethyl fluoroborate (**13**, 9.55 g, 29 mmol) in 125 ml of the same solvent over a period of 15 min at 0°. The dark solution was then stirred at room temperature for 10 hr, after which time tlc monitoring showed the consumption of **2b** and **13**. After evaporation of the solvent from the reaction mixture, the residue was extracted exhaustively with anhydrous ethyl ether to remove the triphenylmethane (4.4 g, 62% by melting point and ir).[20]

Fractional recrystallization of the residue from the previous extraction from acetone yielded two substances. (A) Colorless needles of 2,3-dihydro-4-methyl-3-triphenylmethyl-1*H*-cyclopenta[*b*]quinolinium fluoroborate (**11**) were obtained after several recrystallizations: mp 184.5–185.5°; 4.9 g (33% yield); ir_{max}^{KBr} 8.8–9.8 (BF_4^-), 13.0–13.4 and 14.3 μ [$(C_6H_5)_3C$]; nmr (CF_3CO_2H) 1.6 (m, 1 H), 2.7 (m, 3 H), 3.87 (s, 3 H), 5.58 (m, 1 H), 7.3 (s, 15 H), 8.05–8.2 (4 H), and 8.3 ppm (1 H). *Cf.* nmr spectral discussion under the section describing the action of phenyllithium on **14**.

Anal. Calcd for $C_{32}H_{28}BF_4N$: C, 74.86; H, 5.50. Found: C, 74.81; H, 5.83.

(B) Pale green needles of 2,3-dihydro-4-methyl-1*H*-cyclopenta[*b*]quinolinium fluoroborate (**8c**) were obtained after several recrystallizations, mp 170–171°, 1.6 g (20%). An authentic sample of **8c** was prepared by admixing aqueous solutions of **8a** (1.0 g, 3.3 mmol) and silver fluoroborate (0.9 g, 3 mmol). After collection of the silver iodide and concentration of the filtrate, colorless needles of **8c** were deposited, mp 171.5–172.0°.

Anal. Calcd for $C_{13}H_{14}BF_4N$: C, 57.60; H, 5.20. Found: C, 57.61; H, 5.50.

The dark mother liquor from these recrystallizations was evaporated under reduced pressure while under a nitrogen atmosphere. Addition of sodium hydroxide and extraction with benzene gave a deep purple organic layer. Passing gaseous hydrogen bromide into the dried benzene solution discharged the violet color and yielded a yellow-orange solution.

When a purple benzene solution was extracted with concentrated sulfuric acid, the purple color was discharged. However, dilution of the sulfuric acid layer with water did not regenerate the purple color. When the extraction of the purple benzene layer was repeated with 85% orthophosphoric acid, the color was again discharged but in this case dilution of the acid layer with water did restore the purple color. However, the purple-violet oils and solids obtained from such attempts at isolation could not be obtained pure.

Action of the Anhydro Base 2b on an Excess of Triphenylmethyl Fluoroborate (13).—To a solution of 5.88 g (17.9 mmol) of **13** in 125 ml of dry, degassed methylene chloride was added dropwise a solution of 1.56 g (8.5 mmol) of **2b** in 50 ml of the same solvent at 0°. After a 7-hr stirring period at room temperature a solution of 4.32 g (42.6 mmol) of dry, degassed triethylamine in 40 ml of methylene chloride was added to the dark mixture at 0°. The blue-purple mixture was concentrated *in vacuo* with warming to 55° and the residue, dissolved in methylene chloride, was chromatographed on an alumina–petroleum ether (bp 30–60°) column that was prepared and operated under a nitrogen atmosphere. Elution with petroleum ether yielded 2.63 g (60%) of triphenylmethane (melting point and ir spectrum). Use of petroleum ether–benzene yielded 0.50 g of a purple-violet solid, mp 160–170°, that by tlc was shown to contain some triphenylmethane. Spectral data follow: ir (mineral oil) 13.3, 13.5, and 14.35 μ [strong, $(C_6H_5)_3C$]; nmr ($CDCl_3$) 3.72 (s, NCH_3), 6.65 (s, 2 H, possibly C_2H and C_9H), 7.05–7.75 with spike at 7.75 ppm for $(C_7H_5)_3C$ (m, *ca.* 40 H). Although this compound could not be obtained analytically pure because of its air sensitivity, it seemed to be a 1,3-bistrityl derivative of 4-methyl-4*H*-cyclopenta[*b*]quinoline (**12**). It showed a behavior, on extraction of its benzene solution with acids, similar to that shown by the previous purple-colored products.

Successive elution with benzene, methylene chloride, and ether yielded 2.8 g of material composed of unknown solids, together with triphenylmethanol.

Action of 2,3-Dichloro-5,6-dicyanobenzoquinone on the Anhydro Base 2b.—A solution of 8.5 g (46 mmol) of **2b** in 50 ml of dry, degassed benzene was heated to reflux for 27 hr under nitrogen with a solution of 10.5 g (46 mmol) of DDQ in 500 ml of benzene. The cooled mixture was diluted with 500 ml of petroleum ether, in order to precipitate selectively any 2,3-dichloro-5,6-dicyanohydroquinone. However, the precipitated black solid was a quantitative yield of a 1:1 adduct of **2b** and DDQ: mp 192–202°, after one recrystallization from ethanol; mp >330°; ir (KBr) 2.80 (str OH), 4.40 (C≡N), and 6.3 μ (C=O).

Methylation of Anhydro Base 2b.—A solution of 250 mg (0.80 mmol) of freshly prepared **2b** in 40 ml of anhydrous tetrahydrofuran was heated at reflux under nitrogen for 24 hr with a threefold excess of methyl iodide. The dark green mixture was filtered to give 240 mg of product (92%). Recrystallization from methanol, after treatment with charcoal, afforded yellow crystals of **5**, mp 172–173°.

The identity of the product as the methiodide of 3-methyl-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (**5**) was established by preparing an authentic sample from the known 3-methyl derivative **6**. Although attempted quaternization with methyl iodide proceeded poorly, an indirect route proved successful. Thus, 200 mg (0.61 mmol) of **6** dissolved in benzene was heated with a

(20) In two runs where 1 equiv of **2b** was added dropwise to a solution of 1 equiv of **13**, yields of 95–100% of triphenylmethane were realized. However, again only intractable, violet-colored material resulted.

twofold excess of freshly purified dimethyl sulfate for 3 hr. The resulting mixture was treated with 10 *N* aqueous sodium hydroxide at 20°. The separated benzene layer was treated with 48% aqueous hydriodic acid. The precipitated yellow solid was collected and recrystallized from methanol, mp 172–173° (tends to darken above 60°). A mixture melting point with the methylation product of **2b** was undepressed.

Action of Phenyllithium on 2,3-Dihydro-3-diphenylmethylene-1*H*-cyclopenta[*b*]quinoline (14).[21]—A solution of 6.60 g (20 mmol) of **14** in 40 ml of benzene was treated with 26 mmol of phenyllithium dissolved in 25 ml of ethyl ether. An immediate exothermic reaction accompanied the formation of a red-brown solution. After an 18-hr stirring period at 25° the solution was hydrolyzed and 2.6 g of an insoluble greenish precipitate was collected, mp 175–215°. The separated, dried, and evaporated organic layer was taken up in benzene and addition of ethanol then precipitated a yellow solid that was mostly **14**.

The original crude product (mp 175–215°) was recrystallized from a benzene–petroleum ether pair to yield colorless crystals of **15**, mp 221–222° dec, 28%. Recrystallization from acetone was necessary to avoid occluded benzene. Spectral data follow: $ir_{max}^{CS_2}$ 3.2, 13.3, and 14.3 μ (C_6H_5); nmr (CS_2) 1.5 (m, 1 H), 2.4 (m, 3 H), 5.13 (d of d, 1 H), and 6.9–7.6 ppm (m, 20 H); mass spectrum (70 eV) *m/e* 411 (P and base), 334 (P − 77), 243 [$(C_6H_5)_3C$], 168 ($C_{12}H_{10}N$), and 165 (9-fluorenyl). The proton at 1.5 ppm is ascribed to the 2-H trans to the 3-trityl group; the three-proton multiplet to the 2-H cis to the trityl group (causing deshielding) and to the two 1-H protons. The 3-H proton occurs at 5.13 ppm. The mass spectral peaks at *m/e* 334, 243, and 168 are of equal intensity and are the most prominent after the parent and base peak.

Anal. Calcd for $C_{31}H_{25}N$: C, 90.48; H, 6.12. Found: C, 90.41; H, 6.29.

The mother liquors from the separation of **15** and from the recovery of **14** were combined and freed of solvent. Column chromatography on neutral alumina and elution with petroleum ether yielded 100 mg of triphenylmethane, mp 91–92°, identified by mixture melting point and infrared criteria. An unidentified yellow solid, mp 225–240°, was also isolated.

4-Methyl-1*H*-cyclopenta[*b*]quinolinium Iodide (4).—A freshly distilled, 2.77-g sample of 1*H*- (and 3*H*- and 4*H*-) cyclopenta[*b*]-quinoline (**3**) (16.6 mmol) was treated at room temperature and under a nitrogen atmosphere with 5 ml of dry, degassed methyl iodide. The solution turned dark green and, upon standing overnight, a chartreuse-colored solid was deposited. This solid was collected, washed with petroleum ether, powdered, and then thoroughly dried in an Abderhalden pistol at 42° under reduced pressure for 60 hr, 4.7 g (92%), mp 221–236° (sealed tube). Although this methiodide was contaminated with N-protonated and probably both C-methylated and dimeric by-products, purification by washing had to suffice. No satisfactory recrystallization could be performed from acetonitrile, ethyl acetate, alcohols, or water, for decomposition ensued with the formation of purple solutions.

Anal. Calcd for $C_{13}H_{12}IN$: C, 50.50; H, 3.91. Found: C, 49.85; H, 4.16.

Spectral data follow: ir (mineral oil) 4.0–5.7 (HNR_3^+); nmr (CF_3COOH) 2.10 (s), 4.0–4.75 (br m), 4.80 (s), 8.2–8.8 (m), and 9.0–9.2 ppm (m). On the basis of the signal at 9.0–9.2 as one C_5H, the ratio of all vinylic H to all aliphatic H (4.0–4.8 ppm) is 7.0:8.0. Compound **4** would require a ratio of 7.0:5.0. It is concluded that the observed ratio signifies the formation of some dimer of **3** (*cf.* ref 8 and 9), causing loss of vinyl H and gain of aliphatic H. Comparison of signals at 2.10 (CCH_3) and 4.80 (NCH_3) ppm suggests a maximum of 15% C-methylation. Although methyl iodide also absorbs around 2.10 ppm, the thorough drying of **4** at 42° *in vacuo* assures its absence. Furthermore, repetition of the quaternization of **3** in benzene or in absolute ethanolic solution gave identical results.

4-Methyl-4*H*-cyclopenta[*b*]quinoline (1c). Method A.—Under a nitrogen atmosphere a yellow slurry of 380 mg (1.2 mmol) of **4** in 15 ml of degassed methylene chloride was slowly admixed with degassed, aqueous sodium carbonate solution at 0°. The blue-violet mixture was warmed to 25° with stirring. The organic layer was separated and the solvent was evaporated, all under a nitrogen atmosphere. The nmr spectrum of this product showed it to contain 4-methyl-4*H*-cyclopenta[*b*]quinoline (**1c**). Treatment with picric acid dissolved in ethanol gave a dark green picrate, mp 127–132°, whose nmr spectrum in CF_3COOH again displayed both *C*-methyl (2.10 ppm) and *N*-methyl (4.60 ppm) signals.

Method B.—A mixture of 400 mg (1.75 mmol) of 3-acetoxy-2,3-dihydro-1*H*-cyclopenta[*b*]quinoline (**16**) and 1 ml of freshly distilled dimethyl sulfate dissolved in 10 ml of benzene was stirred at 25° for 24 hr. Removal of the benzene and excess dimethyl sulfate under reduced pressure afforded an off-white methosulfate (**17**). (After this point all operations were conducted under nitrogen.) The solid was dissolved in 30 ml of concentrated sulfuric acid and the resulting solution was heated for 4 min in an oil bath maintained at 115–120°. The solution was poured over cracked ice. While the mixture was further chilled in an ice bath, 100 ml of ethyl ether was added and the system was made basic by the slow addition of 50% aqueous sodium hydroxide solution. After the ether layer was separated, the aqueous layer was extracted with three 100-ml portions of ether. All ether extracts were dried over anhydrous magnesium sulfate and the solvent was then removed to afford **1c** as a violet solid, 175 mg (55%). Although solutions in degassed ether or CCl_4 were stable under nitrogen <0°. the violet color of **1c** rapidly disappeared upon exposure to air and, in the solid state, **1c** tended to form an insoluble, apparently polymeric (no mass spectral peaks at 25°) black solid.

Its spectral data are in complete accord with the assigned structure: (A) mass spectrum (70 eV) with the probe at 25° (mass, rel intensity, assignment) 181 (64, P), 167 (100, P − CH_2), 166 (56, P − CH_3), 146 (18, P − C_2H), 140 (22, P − CH_3 − C_2H), and 139 (18, P − CH_3 − C_2H_2); (B) nmr spectrum in CCl_4 (peak on δ scale with internal TMS): 3.97 (s, N − CH_3), 5.83 [br, C_1 H presumably split by C_2 H (*ca.* 4 Hz) and by C_3 H and C_9 H (~1 Hz)], 6.40 [d of d with higher intensity downfield (C_3 H, J_{23} = 5 Hz, J_{13} = 1.5 Hz)], 7.0–7.4 (two triplets of unequal splitting, C_2 H and C_9 H), 7.5–7.9 (m, 3 H), and 8.1 (br s, C_5-H); (C) visible spectrum in Et_2O, broad maximum between 495 and 555 nm [λ_{max} 525 nm (log ϵ *ca.* 2.5)]; and (D) infrared spectrum in CCl_4 2.5–3.4 (clear), principal band at 3.4–3.6, 6.3–6.6 (br str), 8.0, 9.2, 9.4, 9.9, and 11.6 μ).

Addition compounds were readily formed with *sym*-trinitrobenzene and with both picric acid and hydriodic acid. However, decomposition accompanied these reactions, since only dark green or black products of uncertain composition could be isolated. Moreover, the products from acid treatment of **1c**, when treated with sodium carbonate solution, under a nitrogen atmosphere, did not regenerate the violet 4-methyl-4*H*-cyclopenta[*b*]quinoline (**1c**).

Registry No.—**1c**, 13038-93-2; **1c** picrate, 37160-83-1; **2b**, 31860-33-0; **4a**, 26865-54-3; **8c**, 37164-21-9; **10**, 37160-86-4; **11**, 37164-22-0; **12**, 37160-87-5; **15**, 37160-88-6; adduct (1:1) of **2b** and DDQ, 37160-89-7.

Acknowledgment.—The authors express their gratitude to the National Cancer Institute of the Public Health Service for support of this research through Grant CA-10743. In addition, the collaboration of Dr. Robert L. Harrell, Jr., with certain experiments was most valuable. Finally, a research instrument award of the National Science Foundation (GP-8537) permitted the departmental purchase of the Varian-MAT CH-5 mass spectrometer used in this study.

(21) This experiment was performed by Dr. Robert A. Harrell, Jr.