1,1-Dimethylaminoisomaleimide (14g) and N,N-Dimethylaminomaleimide (15g).—*N,N*-Dimethyl-2-(3-carboxyacryloyl)-hydrazine (5.0 g) was slowly added to 120 ml of acetic anhydride, the mixture was stirred under anhydrous conditions for 48 hr, and the solvent was removed *in vacuo*. The residue was extracted with four 25-ml portions of petroleum ether (bp 30–60°) and the combined ether extracts were concentrated to about 25 ml giving yellow crystals. Recrystallization from petroleum ether gave 2.12 g of a product, mp 58–59°. The nmr data (Table I) showed this to be a mixture of maleimide and isomaleimide in the ratio of 2:1.

Anal. Calcd for $C_6H_5N_2O_2$: C, 51.43; H, 5.71; N, 20.00. Found: C, 51.15; H, 5.75; N, 19.91.

A mixture of the maleimide and isomaleimide (0.80 g) was refluxed for 2 hr in glacial acetic acid. Work-up of the resulting solution gave pure maleimide (0.66 g).[31]

Preparation of Maleimides 15.—The maleimides were prepared by the methods described for the preparation of the pyridazinones:[1,2] *N*-acetylaminomaleimide,[1,8] *N*-benzenesulfonylaminomaleimide,[2] and *N*-(2,4-dinitrophenyl)aminomaleimide.[2]

***N,N*-Dimethylaminomaleimide (15g).**—Glacial acetic acid (100 ml) was added to 5.0 g of *N,N*-dimethyl-2-(3-carboxyacryloyl)hydrazine. The mixture was refluxed for 2 hr during which time the color changed from light green to light red. The resulting solution was concentrated *in vacuo* and the remaining oil was extracted with four 10-ml portions of petroleum ether (bp 30–60°). The combined ether extracts were concentrated and gave yellow crystals which after recrystallization from petroleum ether gave 1.6 g of a yellow powder, mp 83–84°.

Anal. Calcd for $C_6H_5N_2O_2$: C, 51.43; H, 5.71; N, 20.00. Found: C, 51.28; H, 5.83; N, 20.14.

2-Ethyl-6-hydroxy-3(2*H*)-pyridazinone (13b).—Glacial acetic acid (150 ml) and maleic anhydride (7.9 g) were mixed and 4.3 g of ethylhydrazine was added dropwise over 5 min while stirring and keeping the temperature below 30°. The solution turned light green and then yellow during the addition. Stirring for 15 min, concentrating *in vacuo*, and recrystallizing the resulting solid from 95% ethanol gave 3.0 g of **13b**, mp 143.5–145°.

Anal. Calcd for $C_6H_8N_2O_2$: C, 51.43; H, 5.71; N, 20.00; neut equiv, 140. Found: C, 51.72; H, 5.91; N, 20.25; neut equiv, 138.8.

2-Ethyl-6-acetoxy-3(2*H*)-pyridazinone.—The pyridazinone **13b** (0.3 g) was added to 25 ml of acetic anhydride and refluxed for 1 hr, and the solvent was removed *in vacuo*. The residue was recrystallized from hexane giving 0.3 g of product, mp 76–77°.

Anal. Calcd for $C_8H_{10}N_2O_3$: C, 52.74; H, 5.49; N, 15.38. Found: C, 52.89; H, 5.60; N, 15.33.

2-Methyl-6-hydroxy-3(2*H*)-pyridazinone (13a).—Following a similar procedure as described for the preparation of **13b** gave **13a**, mp 215–216° (lit.[30] mp 210–211°). Acetonitrile was also found to be a suitable solvent for the reaction.

Anal. Calcd for $C_5H_6N_2O_2$: C, 47.63; H, 4.80; N, 22.22. Found: C, 47.56; H, 4.68; N, 22.46.

2-Methyl-6-acetoxy-3(2*H*)-pyridazinone melted at 90.5–92.0° (benzene).

Anal. Calcd for $C_7H_8N_2O_3$: C, 50.00; H, 4.80; N, 16.66. Found: C, 49.91; H, 4.76; N, 16.48.

2-Phenyl-6-hydroxy-3(2*H*)-pyridazinone (13c).—The procedure similar to that described for **13b** gave 2.3 g of **13c**, mp 262–263° (lit.[32] mp 259–260°).

(31) We are indebted to Mr. Michael Parnarouskis of Lowell Technological Institute for providing this data in response to the suggestion of one of the referees.

Registry No.—2-Methyl-6-acetoxy-3(2*H*)-pyridazinone, 31443-72-8.

Acknowledgment.—One of the authors (H. R.) is indebted to the National Science Foundation for their support of some of this work by an NSF academic year extension grant for 1969–1970. We would like to thank Dr. Arthur C. Waterson and Dr. John B. Grutzner for their helpful discussions of the nmr data during the preparation of this manuscript.

(32) S. Druey, *et al.*, *Helv. Chim. Acta*, **37**, 510 (1954).

Studies in Nonpyridinoid Aza-Aromatic Systems. II. Reactions of the Anions of Benzo[*b*][1]pyrindine and Its 1,2-Dihydro Derivative[1]

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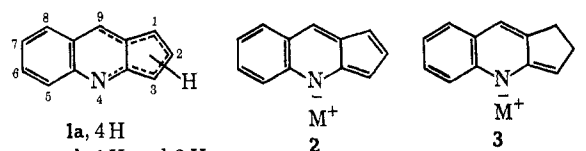
The reactivities of the anions of benzo[*b*][1]pyrindine (**1**) and of its 1,2-dihydro derivative **4** toward electrophilic reagents, such as methyl iodide, 9-fluorenone, and benzophenone, were investigated. The azulene-like, delocalized anion **2** underwent only C-methylation at C_1 and C_3 in almost equal proportions; the 1,2-dihydro anion **3** underwent exclusive methylation at C_3. Both anions reacted with benzophenone in a reversible fashion at C_3 and probably also at the nitrogen center to form a labile aminocarbinolate. The behavior of **2** is in accord with the chemical behavior expected of a nitrogen isostere of an azulene. Access to derivatives of the benzo[*b*][1]pyrindine system, starting from **4**, was gained by the synthesis of 3-methylene derivatives of **4**, followed either by a dehydrogenation with DDQ to yield a fulvene **13** or by base-promoted hydrogen transfer to provide a pyrindine **28**. Finally, abortive and partially successful attempts to dehydrogenate 1,2-dihydro anion **3** did uncover an apparently general, alternative approach to 3-methylene derivatives of **4**.

The previous study of the synthesis and tautomeric character of benzo[*b*][1]pyrindine (cyclopenta[*b*]quinoline)[1] was prompted by an interest in the aromatic character of the 4H tautomer **1a**. Being a nitrogen isostere of 5,6-benzazulene, **1a** might be expected[2] to undergo electrophilic attack in the five-membered ring and nucleophilic attack in the six-membered nitrogen ring. The latter ring would be a six-π-electron counterpart of the azulene's cyclohepta ring. Since less than 1% of this 4H tautomer is present in benzo[*b*][1]pyrindine, it seemed appropriate to convert the mixture of 1H, 3H, and 4H benzo[*b*][1]pyrindines into their common anion **2** and to examine its chemical behavior toward certain electrophiles. Furthermore, a parallel consideration of its 1,2-dihydro derivative **3** merited



1a, 4 H
b, 1 H and 3 H

2

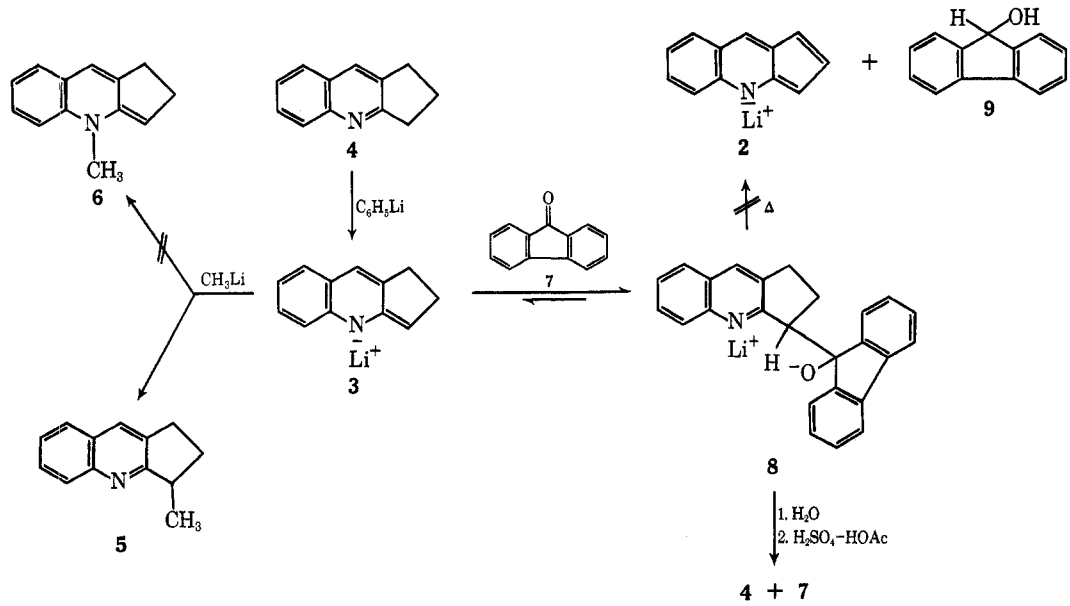
3

attention, in order to compare the chemical responses of a derivative with disrupted conjugation. At the same

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

(2) D. Lloyd, "Carbocyclic Nonbenzenoid Aromatic Compounds," Elsevier, New York, N. Y., 1966.

SCHEME I



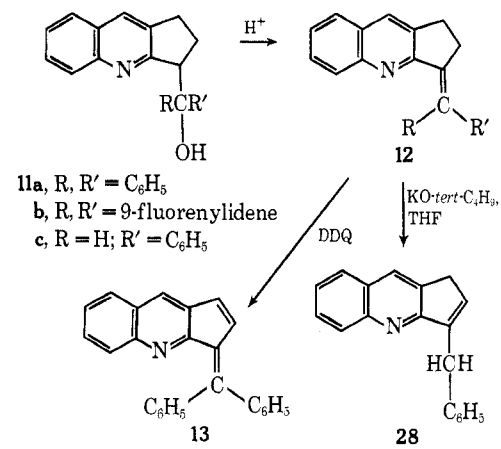
time, the possibility of converting anion **3** or a derivative into the benzo[*b*][1]pyrindine system by means of 1,2 dehydrogenation was attractive for making such azulene-like aromatic systems more accessible. This report, therefore, describes the behavior of the delocalized anions **2** and **3** toward ketones and toward methyl iodide and recounts both successful and abortive attempts to dehydrogenate derivatives of **3**.

Results and Discussion

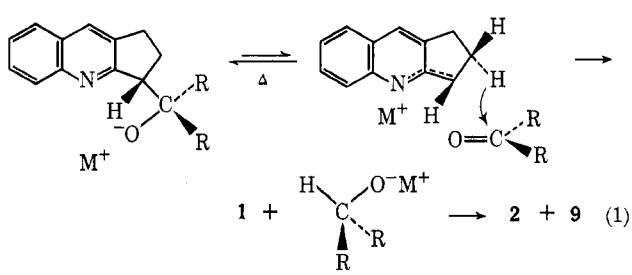
The lithium enaminate salt of 2,3-dihydro-1*H*-benzo[*b*][1]pyrindine (**3**, M = Li) could be prepared in essentially quantitative yield by treating **4** with phenyllithium at 0–25°.[3a] The magnesium salt formed upon refluxing **4** with phenylmagnesium bromide in benzene solution. The pale yellow suspension of **3** reacted cleanly with methyl iodide to furnish a 90% isolated yield of 2,3-dihydro-3-methyl-1*H*-benzo[*b*][1]pyrindine (-cyclopenta[*b*]quinoline, **5**) whose nmr spectrum displayed the expected three-proton doublet due to the methyl group at C_3. The presence of any considerable amount of the N-methylated product, 2,4-dihydro-4-methyl-1*H*-cyclopenta[*b*]quinoline (**6**), could be ruled by the absence of any sharp singlet in the 2.70–2.75-ppm region, where **6** is known to display its N-CH_3 resonance.[3b] Furthermore, the formation of **6** in the methylation reaction and its thermal rearrangement to **5** upon distillative isolation are unlikely, since **6**, prepared by the conventional treatment of **4** methiodide with alkali, could be distilled under nitrogen without decomposition[3b] (Scheme I).

The interaction of the lithium enaminate salt **3** with aromatic ketones, such as benzophenone[3b] and 9-fluorenone, was of twofold interest; not only did the resulting adducts (*e.g.*, **8**) promise to lead to benzo[*b*][1]-pyrindines in practical steps (*cf.* Scheme II), but hopefully these ketones might dehydrogenate **3** directly by hydrogen transfer. Since the addition of either benzophenone or 9-fluorenone to **3** proved to be reversible,

SCHEME II



it was reasoned that eventually hydride transfer might be able to compete[4] (eq 1). Although no such hydride



transfer was observed with the lithium salt **3** and benzophenone or 9-fluorenone (Scheme I), a significant amount of reduction (10–20%) was achieved when the magnesium salt of **3** (M = MgZ) was heated with benzophenone.[5] Unfortunately, the method is unsuitable for the preparation of the benzo[*b*][1]pyrindine system (**1**, R = H), because the proportion of hydride transfer is modest and since it is now known that **1** cannot survive prolonged contact with strong bases.[1]

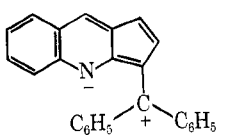
(3) (a) *Cf.* K. Ziegler and H. Zeiser, *Justus Liebigs Ann. Chem.*, **485**, 174 (1931), for the behavior of the lithium salt of 2-methylquinoline toward ketones and alkyl halides; (b) J. J. Eisch and F. J. Gadek, unpublished work.

(4) *Cf.* H. Gilman and C. W. Bradley, *J. Amer. Chem. Soc.*, **60**, 2335 (1938), for the ready loss of lithium hydride from organolithium compounds.

(5) *Cf.* M. S. Kharasch and S. Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

In attempting to convert such carbinols to fulvenes related to the benzo[*b*][1]pyrindine nucleus, an interesting consequence of steric hindrance to ring coplanarity was uncovered. The synthetic approach required the dehydration of the carbinol to the 3-methylene derivative of **4** and the dehydrogenation of the latter by 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) to yield the completely unsaturated fulvene (Scheme II). With the carbinol derived from 9-fluorenone (2,-3-dihydro-3-(9-hydroxy-9-fluorenyl)-1*H*-cyclopenta[*b*]-quinoline, **11b**), however, even mild acid treatment led only to decomposition into **4** (β-quinindane) and **7** (Scheme I). No dehydration into the 3-methylene derivative could be effected with a wide variety of experimental procedures. In contrast, the adduct from benzophenone (2,3-dihydro-α,α-diphenyl-1*H*-cyclopenta[*b*]quinoline-3-methanol, **11a**) could be dehydrated to **12a** in satisfactory yield by use of a warm solution of concentrated sulfuric acid in glacial acetic acid. Admittedly, even here some reversal to **4** and benzophenone occurred as a side reaction. The dehydration of **11b** to yield **12b** apparently is strongly disfavored by the steric repulsion between the C–H bond at C_1 of the coplanar fluorenylidene group and the (protonated) nitrogen of the quinoline ring. With **12a** the dehydration is possible, because the phenyl group syn to the (protonated) nitrogen can rotate into a conformation where its plane is at a right angle to that of the quinindane nucleus.

Once compounds of type **12** were obtained, however, they could be smoothly converted into derivatives of the benzo[*b*][1]pyrindine nucleus. The 1,2 dehydrogenation of **12a** with DDQ to yield **13** illustrates one successful approach; the isomerization of **12c** to **28** under the agency of potassium *tert*-butoxide also proved to be practical. In the latter case, a pyrindine anion of type **2** is undoubtedly an intermediate, as is evident by the deep violet color present before hydrolysis. In the former case, the bathochromic shift observed in passing from **12a** to **13** can be ascribed to the importance of resonance contributions, such as **14**, in lowering the

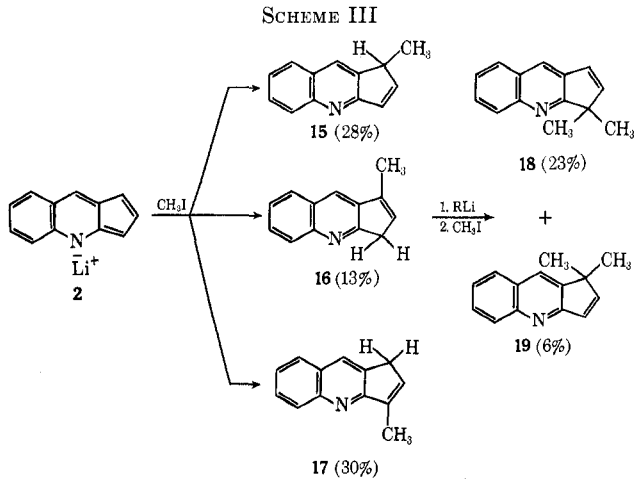


14

energy of $\pi \rightarrow \pi^*$ transitions. Since the conjugate acid of **14** might be expected to be formed in strong acid and thereby to accentuate the spectral shift, it should be noted that no bathochromic shift in the orange color of **13a** was observed, even in concentrated sulfuric acid. Furthermore, a red picrate was obtained, rather than the expected yellow form. The weak basicity of **13a** and its red complex with picric acid are reminiscent of the behavior of carbazole.[6] Stuart–Briegleb models show that the phenyl group syn to the nitrogen could easily block protonation by strong acids. Presumably the picric acid forms instead a π complex with the benzopyrindine nucleus.

Compared with the behavior of the lithium salt **3** of β-quinindane (**4**), the lithium salt of benzo[*b*][1]pyrindine (**2**) reacted very indiscriminantly with 1 equiv of methyl iodide. Due to the rapidity with which the monomethylbenzo[*b*][1]pyrindine products (**15**, **16**, and **17**) themselves formed anions and underwent methylation, a mixture of monomethylated (71%) and dimethylated (29%) benzopyrindines was obtained by distillation. Based upon known spectral shifts for such systems and relative shifts reported for methylindenes, the nmr spectrum of this mixture could be used to verify the presence of 28% of the 1-methyl-1H (**15**), 13% of the 1-methyl-3H (**16**), and 30% of the 3-methyl-1H (**17**) derivatives; in addition, 23% of the 3,3-dimethyl-3H (**18**) and 6% of the 1,1-dimethyl-1H (**19**) derivatives were estimated to be present (Scheme III).

SCHEME III

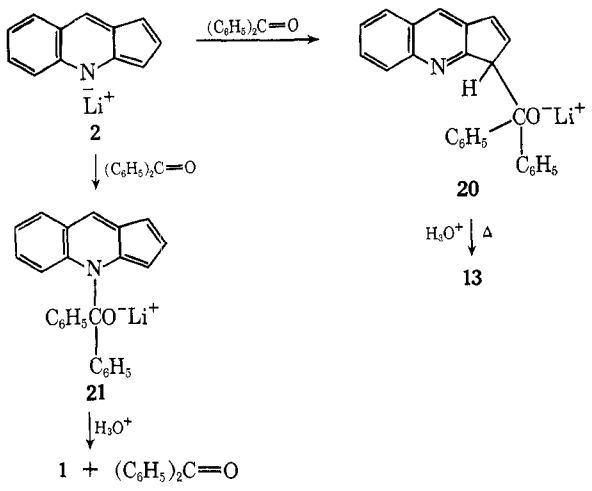


Interestingly, the total of all C_3 mono- and dimethylated products was 53% *vs.* 47% for C_1 methylation. Possible isomers which were not detected, such as 3-methyl-1H and 1,3-dimethyl-1H (or -3H) derivatives, might have been present in subordinate amounts. Moreover, since this nmr analysis was performed on a representative distilled sample, the tendency of benzopyrindines to polymerize thermally[1] might have led to losses of small amounts of certain isomers during distillation. In the one case where both the 1H and 3H tautomers were detected and measured (1-methybenzo-[*b*][1]pyrindines, **15** and **16**), the ratio of the 1H and 3H isomers, 62:38, compared favorably with the equilibrium ratio of tautomers for benzo[*b*][1]pyrindine itself, 67:33.[1] In any event, the results support the conclusion that the electrophilic methyl iodide seems to attack C_1 and C_3 of **2** with almost equal facility but that the lithium salt of **17** undergoes further methylation faster than the lithium salt of **15** or **16**.

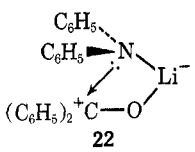
Treatment of the red lithium salt of benzo[*b*][1]-pyrindine (**2**) with benzophenone was accompanied by the appearance of a vivid purple color, but subsequent hydrolytic work-up yielded much recovered benzophenone. Careful column chromatography led to the isolation of 14% of **13** in the form of its picrate. Apparently the carbinol precursor **20** underwent dehydration under the action of acid (*cf.* **11a** → **12a**). The generation of the intense purple color during the reaction proper can best be explained by a competing N-alkylation leading to carbinol amide salt **21**, whose chromophoric system would be the same as the known, purple-colored 4*H*-benzo[*b*][1]pyrindine[1] and its 4-methyl derivative[3] (Scheme IV). Failure to isolate the

(6) S. Coffey, Ed., "Rodd's Chemistry of Carbon Compounds," Vol. III, Elsevier, New York, N. Y., 1964, p 123.

SCHEME IV



carbinolamine can be ascribed to the ready regeneration of benzo[*b*][1]pyrindine and benzophenone from **21** upon hydrolytic work-up. An alternative explanation can be drawn from the studies of Wittig and Wulff,[7] who observed that the colorless components, benzophenone and lithium diphenylamide, formed a red, diamagnetic 1:1 complex, possibly of the charge-transfer type, whose structure most reasonably was that of the "ate" salt **22**. Titrimetric discharge of the red



22

color with methanol was followed by the quantitative recovery of the ketone and the amine. In the present situation it is not only likely that **21** reverts to its components upon hydrolysis, but also that **20** is labile as well (*cf.* reversibility of carbinolates such as **11a** and **11b**, eq 1).

In summarizing the comparative behavior of anions **2** and **3**, then, it is seen that essentially only C-methylation occurs with methyl iodide and on those sites of benzo[*b*][1]pyrindine which are analogous to the C_1 and C_3 sites of azulene. For both azulene and its nitrogen counterpart (**1** and **2**), these are just those carbon atoms where the π-electron density distributions would favor electrophilic attack. For benzophenone, only products of C_3-alkylation could be isolated from either anion **2** or **3**. It is quite credible that a N-alkylation occurred with the benzopyrindine anion **2** because of the purple color of the reaction solution. With its dihydro anion **3**, such N-alkylation may also have occurred, since the yield of carbinol **11a** amounted only to 68–70%, despite prolongation of reaction times. With either anion, of course, the nitrogen atom would have the highest electron density and hence be prone to reversible alkylation.

Finally, the results of some unsuccessful attempts to convert the dihydrobenzopyrindine anion **3** into the benzopyrindine system merit brief comment. Predicated on the known tendency of certain organolithium compounds to eliminate lithium hydride upon heating,[4] suspensions of **3** were heated in refluxing xylene with hope of forming **1** or its anion **2**. However, there was no significant evidence of hydride formation nor any hydrogen gas evolution (*i.e.*, from LiH to **1a**). Heating **3** with triphenylborane, which hopefully would complex at C_3, did yield a small amount of hydride elimination in the form of a complex with the triphenylborane but this route was impractical as an approach to the parent benzopyrindine. Therefore, to foster boration at C_3, the anion **3** was treated with phenylboron dichloride with the intention of oxidizing the resulting 3-bora-2,3-dihydro derivative **23** with trimethylamine oxide.[8] The 3-hydroxy derivative **24** expected upon hydrolysis would then serve as an excellent source of **1** through an established dehydration.[1] However, no trace of **24** was formed by attempted oxidation in refluxing benzene and in refluxing toluene a 38% yield of only 3-methylene-2,3-dihydro-1*H*-benzo[*b*][1]pyrindine (**25**) was realized instead. The failure to observe the formation of any 3-hydroxy derivative **24** convincingly rules out any C_3-boration (**23**) of **3** with phenylboron dichloride and hence favors only N-boration (**26**) (Scheme V). The formation of **25** from **26** can be explained by the slow thermal decomposition of trimethylamine oxide above 100° to yield formaldehyde[9] and the reaction of the latter with **26**. The generality of the reaction of **26** with carbonyl reagents to yield methylene derivatives of β-quinindane directly was supported by treating **26** with benzophenone. The resulting 28% yield of **12a** in this single procedure compares favorably with the 38% overall yield for the usual two-step method (**3** → **11a** → **12a**). Again the absence of any benzhydrol among the products argues against any hydride transfer by **26** (*cf.* eq 1). Utilization of this approach for the synthesis of 3-methylene derivatives of benzo[*b*][1]pyrindine and a study of their behavior under nucleophilic attack will be the subject of a subsequent report.

Experimental Section[10]

Lithium Salt of 2,3-Dihydro-1*H*-cyclopenta[*b*]quinoline (3, 6,7-Dihydro-5*H*-benzo[*b*][1]pyrindine). A. With Methyl Iodide.—The tan-colored slurry of **3** was prepared by treating 8.45 g (50.0 mmol) of **4** in 100 ml of dry benzene with 60 mmol of phenyllithium in 75 ml of ether at 0°. After being stirred at 25° for 3 hr, the suspension was recooled to 0° and treated with 6.42 g (60.0 mmol) of methyl iodide in 50 ml of dry benzene. The dark brown mixture was stirred at 25° overnight and then refluxed for 2 hr. After the usual hydrolytic work-up the isolated crude product was distilled to yield 8.21 g (90%) of colorless 2,3-dihydro-3-methyl-1*H*-cyclopenta[*b*]quinoline (**5**), bp 113–117° (0.64 mm), which turned yellow upon standing but did not solidify. A second distillation provided a colorless sample: bp 111° (0.37 mm). Spectral data: ir λ_{max}^{neat} 9.8, 10.5, 11.0, 11.6, 12.7, and 13.3 μ; nmr (CCl_4) 1.46 (d, J = 7 Hz, CH_3), 2.0–2.7 (m, CH_2), 2.75–3.5 (m, CH, CH_2), 7.2–7.75 (m, 4 H), 8.1–8.25 ppm (d, 1 H). The picrate was composed of yellow granules: mp 182.5–184.5°; nmr (CF_3CO_2H) 1.6 ppm (d).

Anal. Calcd for $C_{13}H_{13}N$: C, 85.20; H, 7.15; N, 7.64. Found: C, 85.40; H, 7.49; N, 7.47.

B. With 9-Fluorenone.—To a tan slurry of **3**, prepared from 100 mmol of **4** according to the foregoing procedure, was added a

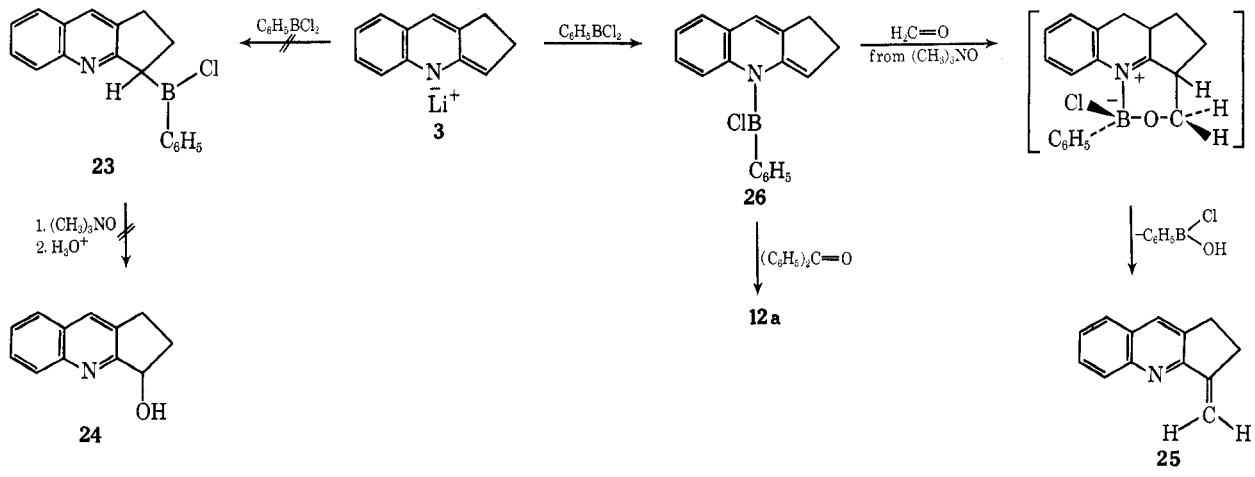
(7) G. Wittig and H. Wulff, *Proc. Robert A. Welch Found. Conf. Chem. Res., 9th, 1965*, 31, (1966).

(8) This reagent performs the quantitative oxidation of a wide variety of carbon–boron linkages and hence serves as an excellent diagnostic tool for such linkages. *Cf.* R. Köster and Y. Morita, *Justus Liebigs Ann. Chem.*, **704**, 70 (1967).

(9) E. Müller, Ed., "Houben-Weyls Methoden der Organischen Chemie," Band XI/2, Thieme Verlag Stuttgart, 1958, pp 191–193.

(10) Details of the general manipulative procedures and the instrumental methods are given in the previous article, ref 1.

SCHEME V



solution of 9-fluorenone (19.0 g, 100 mmol) in 200 ml of dry benzene. The mixture was stirred for 2 hr and hydrolyzed with a saturated aqueous solution of sodium bicarbonate, and the crude 2,3-dihydro-3-(9-hydroxy-9-fluorenyl)-1*H*-cyclopenta[*b*]quinoline (**11b**) was filtered off and washed with some hexane, 58.6 mmol (59%). Three recrystallizations from a chloroform–petroleum ether (bp 30–60°) pair afforded colorless crystals of an analytical sample of **11b**, mp 166.5–167.5°. Infrared spectral band at 2.95 μ (CH_2Cl_2).

Anal. Calcd for $C_{25}H_{19}NO$: C, 85.93; H, 5.48. Found: C, 85.72; H, 5.47.

C. With Phenylboron Dichloride, Followed by Trimethylamine Oxide in Benzene.—To a slurry of **3**, prepared from 25.0 mmol of **4**, was added a solution of 4.30 g (27.0 mmol) of phenylboron dichloride in 50 ml of dry benzene. The tan solution was stirred at room temperature for 20 hr and thereupon the ether was distilled off by the slow addition of more benzene during refluxing. To the refluxing and stirred reaction mixture was added 6.36 g (84.5 mmol) of anhydrous trimethylamine oxide in portions over a period of 45 min. During a further heating period of 100 min a nitrogen stream was used to sweep the liberated trimethylamine into a known amount of standard acid. Titration revealed that 1.5 equiv of $(CH_3)_3N$ or $(CH_3)_2NH$ had been liberated. Thereupon, 20 ml of methanol was added and the reaction mixture heated to reflux for 1 hr. The $(CH_3O)_3B$ and methanol were distilled off and the residue was hydrolyzed. The organic layer was extracted with 1 *N* hydrochloric acid, the acid extracts were separated and made basic, and the liberated amines were taken up in benzene. Separation of the organic layer, drying over anhydrous calcium sulfate, removal of solvent, and distillation under reduced pressure afforded a 71% recovery of **4** (melting point and ir). By examination of the amine fraction before distillation by tlc, the absence of cyclopenta[*b*]quinoline (**1a**) and 2,3-dihydro-3-hydroxy-1*H*-cyclopenta[*b*]quinoline (**24**) could be demonstrated.

D. With Phenylboron Dichloride, Followed by Trimethylamine Oxide in Toluene.—Exactly as in the preceding section, **3** was treated with the boron halide, but the ether–benzene was distilled off with the simultaneous addition of 175 ml of dry toluene. Also, a 6-hr reflux followed the addition of trimethylamine oxide. A total of 2.3 equiv of amine ($(CH_3)_3N$ or $(CH_3)_2NH$) was liberated. Usual work-up furnished an amine fraction (3.5 g) that by tlc contained neither **1a** nor **24**. Column chromatography on neutral alumina with a petroleum ether (bp 30–60°) eluent gave back **4** and 1.73 g (38.2%) of 2,3-dihydro-3-methylene-1*H*-cyclopenta[*b*]quinoline (**25**). An analytical sample was obtained by recrystallizations from petroleum ether as colorless flakes, mp 103–105°. Spectral data: ir λ_{max}^{Nujol} 6.25, 6.45 μ (arom conj C=CH_2); nmr (CCl_4) 2.88 (s, 4 H, CH_2CH_2), 5.20 (br s), and 6.21 (br s, C=CH_2), and 7.2–8.1 ppm (m, 5 H).

Anal. Calcd for $C_{13}H_{11}N$: C, 86.15; H, 6.16; N, 7.73. Found: C, 85.80; H, 6.18; N, 7.74.

E. With Phenylboron Dichloride, Followed by Benzophenone.[11]—To a tan slurry of **3**, prepared from 100 mmol of **4**, according to the foregoing procedure, was added a solution of 7.94 g (50.0 mmol) of phenylboron dichloride in 50 ml of dry benzene. After a 5-hr stirring period a solution of benzophenone (18.2 g, 100 mmol) in 100 ml of benzene was added and the mixture refluxed 16 hr. Examination by tlc showed the presence of carbinol **11a** but definitely no benzhydrol. Distillative replacement of the benzene and ether by toluene, a 44-hr reflux period, and hydrolytic work-up gave crude, bright yellow 2,3-dihydro-3-diphenylmethylene-1*H*-cyclopenta[*b*]quinoline (**12a**), 11.3 g. Recrystallizations from 95% ethanol gave 9.3 g (28%), mp 161.5–162°. For spectral data, *cf.* section on **12a**.

Anal. Calcd for $C_{25}H_{19}N$: C, 89.87; H, 5.73. Found: C, 89.71; H, 5.63.

F. With Triphenylborane.—To a slurry of **3**, prepared from 25 mmol of **4**, was added a solution of triphenylborane[12] (6.05 g, 25 mmol) in 50 ml of dry benzene. The dark mixture was heated at the reflux temperature for 22 hr and then treated water at 0° (no gas evolution). The separated organic layer was extracted with dilute sodium hydroxide to remove any boron compounds, dried over anhydrous calcium sulfate, and heated *in vacuo* to remove the solvent. Column chromatography of the residue on neutral alumina and elution with petroleum ether permitted recovery of 3.33 g (79%) of **4**, as verified by melting point and ir spectrum. No **1a** was detected in any of the fractions.

The aqueous layer of the hydrolyzed reaction mixture was filtered and then treated with an aqueous solution of 2.67 g (28 mmol) of trimethylammonium chloride. A white solid which was thought to be principally trimethylammonium triphenylborohydride was deposited immediately, 1.8 g (21%). The colorless solid melted at *ca.* 120°, decomposing with gas evolution and resolidifying to a colorless material, mp 150–152° [$(C_6H_5)_3B$ lit.[12] mp 151–152°]. Solution in ethanol and addition of dilute hydrochloric acid gave an evolution of hydrogen. Its infrared spectrum in KBr showed broad bands between 4.0 and 5.6 μ (BH and HCr_3^+) and other bands at 6.8 (BC_6H_5) 13.5 and 14.2 μ (C_6H_5).

Reaction of 4 with Phenylmagnesium Bromide.—A solution of **4** (16.9 g, 100 mmol) in 100 ml of benzene and 100 mequiv of filtered[13] ethereal phenylmagnesium bromide was stirred for 14 hr at 25° and for 25 hr at reflux. A solution of benzophenone (19.2 g, 105 mmol) in 100 ml of dry benzene was added and the reaction mixture heated at reflux for 4 hr. After the usual hydrolytic work-up (*cf. supra* section B), isolation of the crude solid by filtration, and recrystallization, 16.1 g (46%) of pure 2,3-dihydro-α,α-diphenyl-1*H*-cyclopenta[*b*]quinoline-3-methanol (**11a**) was obtained, mp 153–155° (from methylene chloride). The organic filtrate from this isolation was freed of solvent to leave 20.6 g of dark yellow oil, which contained *ca.* 10% of **11a**, 30% of **4**, 20% of benzophenone, 10% of triphenylcarbinol, and 10% of benzhydrol (vpc and tlc).

Reactions of 11b with Phenylmagnesium Bromide and of 11b with Phenyllithium.—When a solution of **11b** (1.5 g, 4.3 mmol) in 50 ml of dry toluene was heated at reflux with 4.5 mequiv of ethereal phenylmagnesium bromide solution for 45 hr, tlc ex-

(11) This experiment was performed by Dr. Robert L. Harrell, Jr.

(12) G. Wittig and P. Raff, *Justus Liebigs Ann. Chem.*, **573**, 195 (1951).

(13) The Grignard reagent had to be filtered through a sintered glass frit to ensure the absence of magnesium particles, also being able to cause reduction.

amination showed that some reversal to **4** and 9-fluorenone had occurred but that no 9-fluorenol was formed.

Similar treatment of **11b** in toluene with ethereal phenyllithium solution caused the formation of **4** and benzophenone but not the formation of benzhydrol.

2,3-Dihydro-3-diphenylmethylene-1*H*-cyclopenta[*b*]quinoline (12a).—A solution of 13.5 g (38.6 mmol) of carbinol **11a** was dissolved in 200 ml of warm, glacial acetic acid and then 24 ml of concentrated sulfuric acid was added. The solution was brought to a boil for 5 min and then poured over ice. Further dilution with water gave 9.1 g of crude **12a**. After solution in 2 l. of hot ethanol, decolorizing with charcoal, filtering, and cooling, 7.47 g (55%) of fluffy yellow needles was obtained: mp 160–162°; ir λ_{max}^{KBr} 6.20 and 6.5 μ (arom conj C=C); nmr ($CDCl_3$) 3.04 (s, 4 H, CH_2CH_2), 7.3–7.85 ppm (m, 15 H); uv $\lambda_{max}^{95\%\ EtOH}$ 352 mμ (log ϵ 4.31) 282 (4.37), and 228 (4.62).

3-Diphenylmethylene-3*H*-cyclopenta[*b*]quinoline (13, 3-Diphenylmethylene-3*H*-Benzo[*b*][1]pyrindine).—A solution of **12a** (6.64 g, 20.0 mmol) in 200 ml of benzene was mixed at 25° with a solution of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ, 4.56 g, 20.0 mmol) in 250 ml of benzene. The mixture was heated under reflux until (29 hr) tlc analysis showed the DDQ to have been consumed. The cooled mixture was diluted with petroleum ether to precipitate the quinol, DDQ·2H. (Before this considerable amounts of red-brown material had deposited on the walls of the reaction vessel.) The filtrate was treated with charcoal, refiltered, and then concentrated. The resulting reddish precipitate was collected and recrystallized from 95% ethanol. The golden-orange, flaky crystals of **13** melted at 153.5–155.5°, 2.05 g (31%). Spectral data: ir λ_{max}^{KBr} 6.30 and 6.40 μ (arom conj C=C); nmr (CCl_4) 6.87 (s, 2 H) and 7.3–7.8 ppm (m, 15 H); uv $\lambda_{max}^{95\%\ EtOH}$ 402 mμ (log ϵ 3.93), 307 (4.52), and 237 (4.51). The picrate was composed of red, feathery crystals, mp 151–155°.

Anal. Calcd for $C_{25}H_{17}N$: C, 90.60; H, 5.17; N, 4.23. Found: C, 90.50; H, 5.05; N, 4.41.

Attempted Dehydration of 2,3-Dihydro-3-(9-hydroxy-9-fluorenyl)-1*H*-cyclopenta[*b*]quinoline (11b).—When the dehydration of **11b** (6.86 g, 19.8 mmol) with 12 ml of concentrated sulfuric acid in 100 ml of glacial acetic acid was attempted in the manner successful for **11a**, no dehydration was achieved. Usual work-up yielded 94% of 9-fluorenone and 90% of **4** (melting point and infrared spectral identification). Even refluxing a solution of **11b** in benzene with a crystal of *p*-toluenesulfonic acid resulted only in cleavage into 9-fluorenone and **4**.

Lithium Salt of Benzo[*b*][1]pyrindine (2). A. With Benzophenone.—A solution of freshly distilled cyclopenta[*b*]quinoline (1.23 g, 7.38 mmol) in 50 ml of benzene was treated dropwise at 0° with 7.45 mequiv of ethereal phenyllithium solution. After 10 min a solution of benzophenone (1.48 g, 8.1 mmol) in 25 ml of benzene was added at 0° to the deep red solution. The dark purple mixture was stirred at room temperature for 12 hr and then hydrolyzed at 0°. Usual work-up gave 2.9 g of a dark yellow oil which was chromatographed on alumina by use of chloroform and ether eluents. The main fraction (2.2 g) was extracted with 6 *N* hydrochloric acid and these extracts were made basic to yield 0.5 g of a tan-colored solid, mp 220–225°, whose infrared resembled carbinol **11a**, band at 3.05 μ (OH). Because of its higher melting point, compared with that of **11a**, this is thought to have been a tautomer of the expected carbinol **20b**, namely the 3-hydroxydiphenylmethyl-1H derivative but a homogeneous sample could not be obtained.

The main chromatographic fraction, after the above-mentioned acid extraction, was freed of solvent and the residue was treated with picric acid dissolved in ethanol. The characteristic red picrate of **13** was isolated in 14% yield, as verified by melting point, mixture melting point, and spectral criteria. The mother liquors of the picric acid solution were freed of solvent and the solid was extracted with 5% sodium hydroxide. The residue consisted of 590 mg (40%) of benzophenone.

When lithium salt **2** was allowed to stand for 1 hr at 25° before the addition of the benzophenone, only a trace of **13** (tlc) was obtained in the subsequent reaction. By tlc the only other components were shown to be **1a** and benzophenone.

B. With Methyl Iodide.—To the deep red solution of **2**, prepared as above from 11.5 mmol of **1a** and 11.6 mequiv of phenyllithium, was added dropwise at 0° a solution of methyl iodide (0.77 ml, 12.3 mmol) in 20 ml of benzene. The reddish-purple solution was stirred for 15 min at 0° and 1 hr at 25°. The usual hydrolytic work-up was carried out promptly under a nitrogen atmosphere. The solvent was removed at <40° and the residue immediately distilled *in vacuo*. After a forerun of biphenyl (50 mg) the main fraction distilled at 112–116° (0.46 mm) as a pale-violet-colored oil, 0.80 g. The ir and nmr spectra of this sample (CCl_4) revealed it to be a mixture of monomethyl tautomeric (71%) and dimethyl derivatives (29%) of **1a**. Spectral data: ir λ_{max}^{neat} 2.9 (NH, almost undetectable in a 25% solution in CCl_4), 6.15 and 6.35 (arom conj C=C), 7.25 and 7.35 μ (internal $C(CH_3)_2$); nmr (CCl_4) 1.06 (d, J = 7 Hz, 1-CH_3-1H, 28%), 1.90 (d, J = 2 Hz, 1-CH_3-3H, 13%), 2.18 (br m, 3-CH_3-1H, 30%), 2.90 (br m, 3-CH_3-1-H), 3.26 (m, J = 2 Hz, and m, 1-$CHCH_3$ of 1-CH_3-1H and 3-CH_2 of 1-CH_3-3H), 1.22 (s, 1,1-$(CH_3)_2$-1H, 6%), and 1.32 ppm (s, 3,3-$(CH_3)_2$-3H, 23%); nmr spectrum unchanged after 220 hr.

Anal. Calcd for $C_{13}H_{11}N$: N, 7.73. Calcd for $C_{14}H_{13}N$: N, 7.17. Found: N, 7.73.

The assignment of signals was based upon the following considerations. (1) The doublet at 1.06 ppm arose from either the 1-CH_3-1H or 3-CH_3-CH isomer. In **1** and in **4** the 3-CH_2 lies at a lower field than the 1-CH_2. Since the methyl signal in the 3-CH_3 derivative of **4** occurs at 1.46 ppm, the methyl signal in the 3-CH_3-3H derivative of **1** would occur even lower. Hence, the observed doublet at 1.06 ppm fits the 1-CH_3-1H tautomer better. (2) The same reasoning leads to the assignment of the higher field doublet (1.90 ppm) to the 1-CH_3-3H tautomer and the lower field, broadened signal (2.18 ppm) to the 3-CH_3-1H tautomer. (3) Again, the sharpness of the signals and their chemical shifts prompted the assignments of the signals at 1.22 and 1.38 ppm to the 1,1-dimethyl-1H and to the 3,3-dimethyl-3H derivatives, respectively. (4) The peaks at 2.90 and at 3.26 ppm were confirmatory of the presence of the 3-CH_3-1H and 1-CH_3-1H tautomers, respectively. (5) Finally, the trends in chemical shifts assumed here are consistent with a recent nmr analysis of the methylindenes.[14]

Isomerization of 2,3-Dihydro-3-phenylmethylene-3*H*-cyclopenta[*b*]quinoline (12c).[15]—Under an atmosphere of nitrogen, a stirred, cooled solution of 1.28 g (5 mmol) of **27**[16] in 100 ml of dry tetrahydrofuran was admixed with 0.92 g (10 mmol) of potassium *tert*-butoxide. The reaction mixture promptly became intense violet in color. After a 3-hour stirring period at 0° the reaction mixture was treated with 100 ml of water. The organic product was extracted into ethyl ether, the ethereal extracts were dried over anhydrous calcium sulfate, and the solvent was removed to provide 1.10 g (86%) of crude 3-benzyl-1*H*-cyclopenta[*b*]quinoline (**28**), whose nmr spectrum showed the absence of significant amounts of any other tautomer. Recrystallization from 95% ethanol yielded colorless crystals, mp 72.5–73°. Spectral data: nmr ($CDCl_3$) 3.26 (m, 2 H), 4.10 (m, 2 H), 6.45 (m, 1 H), and 7.10–8.35 ppm (m, 10 H); mass spectrum (*m/e*, relative intensity, assignment) 257, 100, P; 180, 26, P − C_6H_5; 166, 15, P − $C_6H_5CH_2$; 127, 11, P − $C_3H_3(C_6H_5CH_2)$; 91, 30, $C_6H_5CH_2$.

Anal. Calcd for $C_{19}H_{15}N$: N, 5.44. Found: N, 5.61.

Registry No.—**2**, 31330-94-6; **3**, 31330-95-7; **4**, 5661-06-3; **5**, 31330-97-9; **11a**, 29520-62-5; **11b**, 31330-99-1; **12a**, 31331-00-7; **13**, 31331-01-8; **13** picrate, 31331-02-9; **15**, 31331-03-0; **16**, 31331-04-1; **17**, 31331-05-2; **18**, 31331-06-3; **19**, 31331-07-4; **25**, 30479-46-0; **28**, 31331-09-6; methyl iodide, 74-88-4; 9-fluorenone, 486-25-9; phenylboron dichloride, 873-51-8; phenylmagnesium bromide, 100-58-3.

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