ml of methanol, with a solution of 7.6 g (0.21 mol) of HCl in 25 ml of methanol gave a solution which was concentrated at 30° (20 mm) to a viscous syrup and then treated with 400 ml of ethyl acetate. The precipitate was collected after 2 hr, washed with ethyl acetate, and air dried, giving 50.0 g of the hydrochloride as a white powder (97% yield): mp 154–155° dec; equiv wt (0.1 *N* aqueous NaO, phenolphthalein) 262 (calcd, 258.5); ir (KBr) 1680 cm^{-1} (aminimide salt carbonyl);[2] NMR (D_2O) δ 4.00 [s, 6, $-N(CH_3)_2$], 4.1–4.6 [m, 4, $-N^+(Me)_2CH_2CH_2O-$].

Rearrangement. A solution of 4.44 g (20 mmol) of 1,1-dimethyl-1-(2-hydroxyethyl)amine-*p*-toluimide in 25 ml of ice-cooled 10 *N* aqueous HCl was kept at room temperature during 6 hr. The $-N^+(CH_3)_2$ singlet had by now completely shifted from δ 4.0 to 3.66 (see below). After evaporation in vacuo to dryness at room temperature (0.2 mm), the residue was dissolved in 15 ml of methanol, and the solvent evaporated again. The crystalline residue was recrystallized from 2-propanol–ethyl acetate and dried in vacuo over solid NaOH, giving 3.2 g **2a**, mp 154–156°. Anal. Calcd: Cl^-; 13.71. Found: Cl^-, 13.55. Ir (KBr) 1710 (ester carbonyl) and 1615 cm^{-1} ($-NH_2$); NMR (D_2O) δ 3.73 [s, 6, $-N(CH_3)_2$], 4.1–5.1 [d of m, 4, $-N^+(Me)_2CH_2CH_2O-$].

Kinetics by NMR. 1,1-Dimethyl-1-(2-hydroxyethyl)amine-*p*-toluimide (860 mg, 3.88 mmol) was dissolved under cooling in 5 ml of 10 *N* aqueous HCl, giving a 0.75 *M* solution. The solution was quickly brought to room temperature and was monitored by NMR, using the $-N^+(CH_3)_2$ singlet at δ 4.0 for unrearranged aminimide hydrochloride and at δ 3.66 for the rearranged product. The *p*-$CH_3C_6H_4$ singlet at δ 2.42 is a useful internal standard. Water of the aqueous acid does not interfere, since its signal is offset, and a spectrum can be recorded from 6 ppm upfield.

Acknowledgment. The author is indebted to Dr. P. J. Menardi of the Analytical Department (Ashland) for numerous NMR spectra and their interpretation.

Registry No.—**1a**, 57428-01-0; **1b**, 57428-02-1; **2a**, 57428-03-2; **2b**, 57428-04-3; bis[1,1-dimethyl-1-(2-hydroxypropyl)amine]fumaroylbisimide, 57428-05-4; dimethyl maleate, 624-48-6; 1,1-dimethylhydrazine, 57-14-7; propylene oxide, 75-56-9; dimethyl fumarate, 624-49-7; 1,1-dimethyl-1-(2-hydroxyethyl)amine-*p*-toluylimide, 57428-06-5; ethylene oxide, 75-21-8; methyl *p*-toluate, 99-75-2.

References and Notes

(1) R. C. Slagel, *J. Org. Chem.*, **33**, 1374 (1968).
(2) W. J. McKillip, E. A. Sedor, B. M. Culbertson, and S. Wawzonek, *Chem. Rev.*, **73**, 255 (1973).
(3) B. M. Culbertson and N. A. Randen, *J. Appl. Polym. Sci.*, **15**, 2609 (1971); H. J. Langer, unpublished work.

Preparation and Condensations of 3-Lithiomethylquinoline

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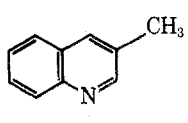
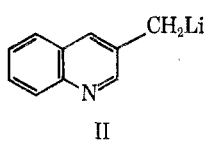
Though the chemical literature abounds with examples of metalation of 2- and 4-methylquinoline,[1] there appear to be no reports of similar reactions on 3-methylquinoline (I). This is perhaps not surprising when it is considered that, although the α carbanions from the 2- and 4-methyl isomers are stabilized by resonance directly involving the ring nitrogen atom, II from the 3-methyl isomer is incapable of such stabilization. Also, the known propensity of quinoline rings unsubstituted at the 2 and/or 4 positions to undergo addition at these positions by bases strong enough to effect metalation[1a] has probably discouraged further investigation.

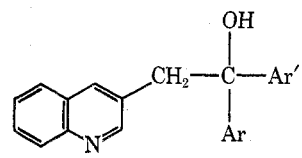


I

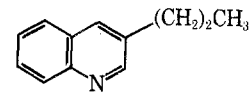


II

This note indicates that lateral metalation of 3-methylquinoline (I) to afford II can indeed be effected provided the proper choice of metalating agent is made. Thus, interaction of I with the strongly basic but weakly nucleophilic lithium diisopropylamide (LDIPA) in THF–HMPA at −78° gives a deep red solution which is apparently due to anion II since subsequent treatment with various electrophiles affords 3-substituted quinolines. For example, II and benzophenone afford III (61%). Similarly, the use of 4,4′-dimethylaminobenzophenone, *p*-chlorobenzophenone, and *p*-chlorobenzaldehyde yields IV (57%), V (36%), and VI (32%), respectively. Likewise, treatment of II with chalcone gives the 1,2-addition product VII (12%). Finally, II and ethyl bromide afford the alkylated product VIII (42%).



III, Ar = Ar′ = C_6H_5
IV, Ar = Ar′ = *p*-$(CH_3)_2NC_6H_4$
V, Ar = C_6H_5; Ar′ = *p*-ClC_6H_4
VI, Ar = *p*-ClC_6H_4; Ar′ = H
VII, Ar = C_6H_5; Ar′ = $CH{=}CHC_6H_5$



VIII

No attempt was made to maximize the conversion of I to II. However, a blank run using the mild conditions described (see Experimental Section) followed by the addition of deuterium oxide resulted in a 75% recovery of deuterated I; the remaining 25% of the material consisted of a tar. Likewise no attempt was made to maximize the yields of III–VIII. All the compounds except VIII are new; VIII was previously prepared (15%) by a Skraup synthesis.[2] Clearly, the preparation of this new organometallic derivative will allow facile synthesis of a variety of additional 3-substituted quinolines.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. All boiling points are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer 237B spectrophotometer and nuclear magnetic resonance spectra were obtained at 60 MHz on a Varian A-60 spectrophotometer using tetramethylsilane as an internal standard. 3-Methylquinoline was prepared by the method of Utermohlen.[3] *n*-Butyllithium was purchased from Apache Chemicals, Rockford, Ill. Commercial anhydrous tetrahydrofuran was distilled from solutions containing calcium hydride after preliminary drying over calcium oxide. Commercial anhydrous HMPA was distilled from solutions containing calcium hydride and stored in septum fitted dark bottles under a positive pressure of purified argon.

General Procedure for the Preparation of 3-Substituted Quinolines. To 0.71 g (0.007 mol) of diisopropylamine in 10 ml of THF at 0° under an argon atmosphere was added 4.4 ml (0.007 mol) of 1.6 *M* *n*-butyllithium in hexane followed, after 30 min, by 1.26 g (0.007 mol) of HMPA. Upon cooling to −78° with a dry ice–acetone bath, the solution was treated during 10 min with 1.0 g (0.007 mol) of 3-methylquinoline to afford a red solution which was stirred for 30 min. This solution was then treated during 5 min with 0.007 mol of an electrophile in 10 ml of THF at −78°. After 1 hr at −78°, the reaction mixture was poured into 100 ml of 10% hydrochloric acid, treated with 30 ml of ether, and made basic with potassium hydroxide pellets, and the product was extracted with three 20-ml portions of ethyl ether. The combined extracts were washed with water, dried (calcium chloride), and concentrated. Specific details follow.

A. Benzophenone. This ketone (1.27 g, 0.007 mol) gave a yellow solid which was recrystallized from aqueous ethanol to afford 1.4 g (61%) of 1,1-diphenyl-2-(3-quinolyl)ethanol (III): mp 178–180°; NMR ($CDCl_3$) δ 3.09–3.25 (s, 1, OH), 3.7 (s, 2, CH_2), 7.1–7.68 (m, 14, ArH), 7.75–8.35 (m, 2, ArH); ir (Nujol) 3200 cm^{-1} (OH).

Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89. Found: C, 85.00; H, 6.07.

B. 4,4′-Dimethylaminobenzophenone. The use of 2.5 g (0.007 mol) of this ketone gave a white solid which was recrystallized from benzene to yield 2.0 g (57%) of 1,1-bis[4-(dimethylamino)phenyl]-2-(3-quinolyl)ethanol (IV): mp 196–197° dec; NMR ($CDCl_3$) δ 2.95 (s, 12, CH_3), 3.72 (s, 2, CH_2), 6.6–6.92 (m, 4, ArH), 7.2–7.73 (m, 9, ArH), 8.38 (m, 1, ArH); ir (Nujol) 3175 cm^{-1} (OH).

Anal. Calcd for $C_{27}H_{29}N_3O$: C, 78.80; H, 7.10. Found: C, 79.07; H, 7.15.

C. p-Chlorobenzophenone. This ketone (1.5 g, 0.007 mol) gave a yellow solid which was recrystallized from aqueous ethanol to yield 0.8 g (32%) of 1-(4-chlorophenyl)-1-phenyl-2-(3-quinolyl)ethanol (V): mp 192.5–193.5°; NMR ($CDCl_3$) δ 3.5 (s, 1, OH), 3.75 (s, 2, CH_2), 7.1–7.84 (m, 13, ArH), 7.9–8.38 (m, 2, ArH); ir (Nujol) 3100 cm^{-1} (OH).

Anal. Calcd for $C_{23}H_{18}ClNO$: C, 76.75; H, 5.04. Found: C, 76.64; H, 5.12.

D. p-Chlorobenzaldehyde. This aldehyde (0.98 g, 0.007 mol) afforded a yellow gum which was recrystallized from methanol to give 0.7 g (34%) of 1-(4-chlorophenyl)-2-(3-quinolyl)ethanol (VI): mp 170–171.5°; NMR (TFA) δ 3.09–3.34 (d, 2, CH_2), 4.85–5.09 (t, 1, CH), 6.93 (s, 4, ArH), 7.59–7.94 (m, 4, ArH), 8.35–8.7 (s, 2, ArH); ir (Nujol) 3215 cm^{-1} (OH).

E. Chalcone. This ketone (1.5 g, 0.007 mol) gave a yellow gum that was recrystallized from benzene–petroleum ether (bp 30–60°) to afford 0.3 g (12%) of 1,3-diphenyl-3-hydroxy-3-(3-quinolylmethyl)-1-propene (VII): mp 215–216°; NMR (Me_2SO) δ 6.9–7.55 (m, ArH); ir (Nujol) 3500 (OH), 1660 (C=C), 965 cm^{-1} (C=CH).

Anal. Calcd for $C_{25}H_{21}NO$: C, 85.44; H, 6.02. Found: C, 85.62; H, 6.21.

F. Ethyl Bromide. This alkyl halide (0.76 g, 0.007 mol) gave 0.5 g (42%) of 3-*n*-propylquinoline (VIII): bp 138–141° (11 mm) [lit.[2] bp 137–140° (11 mm)]; $n^{25}D$ 1.5921; picrate mp 173–174° (lit.[2] picrate mp 174–175°).

Registry No.—I, 612-58-8; II, 57443-81-9; III, 57443-82-0; IV, 57443-83-1; V, 57443-84-2; VI, 57443-85-3; VII, 57443-86-4; VIII, 20668-43-3; VIII picrate, 57443-87-5; LDIPA, 4111-54-0; benzophenone, 119-61-9; 4,4′-dimethylaminobenzophenone, 90-94-8; *p*-chlorobenzophenone, 134-85-0; *p*-chlorobenzaldehyde, 104-88-1; chalcone, 94-41-7; ethyl bromide, 74-96-4.

References and Notes

(1) (a) K. Ziegler and H. Zeiser, *Justus Liebigs Ann. Chem.*, **485**, 174 (1931); (b) F. W. Bergstrom, *J. Am. Chem. Soc.*, **53**, 3027 (1931); (c) F. W. Bergstrom and A. Moffat, *ibid.*, **59**, 1494 (1937); (d) M. J. Weiss and C. R. Hauser, *ibid.*, **71**, 2026 (1949); (e) for a more recent reference, see E. M. Kaiser and W. R. Thomas, *J. Org. Chem.*, **39**, 2659 (1974).
(2) R. W. Brown and G. Dougherty, *J. Am. Chem. Soc.*, **69**, 2232 (1947).
(3) W. P. Utermohlen, Jr., *J. Org. Chem.*, **8**, 544 (1943).

Organometallic Chemistry. VIII.[1] Protonated Anisolechromium Tricarbonyl and Its Carbon-13 Nuclear Magnetic Resonance Spectroscopic Study

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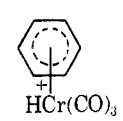
Arenechromium tricarbonyls undergo hydrogen–deuterium exchange in acid media, and it has been proposed that protonated species are intermediates in the reaction.[3] Protonated arenechromium tricarbonyls were first reported by Davison, McFarland, Pratt, and Wilkinson in 1962.[4] The hydrido hydrogen signals were observed at δ −3.5 to −4.0



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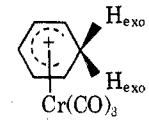

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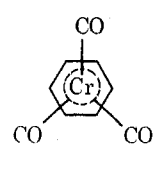
as singlets. Both metal-protonated 1 and ring-protonated 2 structures have been proposed. Based on the width of the hydride hydrogen absorption in comparison with the estimated $J_{exo,endo}$ coupling constants, a recent ^1H NMR study indicated that ring-protonated ion 2 cannot be the major species observed in solution.[5] Chromium protonated structure 1 is also indicated in protonated arenechromium triphenylphosphinedicarbonyls by the splitting of the signal corresponding to the hydrido hydrogen into a doublet due to a coupling with the ^{31}P nucleus.[6] We now report the preparation and carbon-13 NMR study of protonated anisolechromium tricarbonyl. We selected the methoxy substituent to enhance the ring π-donor ability of the system. Data obtained indicate that despite the powerful ring activating substituent the observed long-lived species contains the proton attached exclusively to the metal atom.

Results and Discussion

Anisolechromium tricarbonyl was protonated with FSO_3H in liquid SO_2 at −80° under nitrogen. The carbon-13 NMR spectral data of the protonated species as well of related model compounds are summarized in Table I.

Carbon-13 NMR spectroscopy seems to be a most suitable method for determining the structure of protonated arenechromium tricarbonyls. If protonation occurs on the aromatic ring, the ring carbons should exhibit characteristic shifts similar to areniumiron tricarbonyl cations.[7] The methylene carbon would show pronounced shielding in accordance with the transformation from aromatic sp^2 to aliphatic sp^3 hybridation upon protonation. Furthermore, the methylene carbon should appear as a triplet with J_{C-H} coupling corresponding to the sp^3 hybridization of the carbon. Based on the spectrum shown in Figure 1, the structure of protonated anisolechromium tricarbonyl is not consistent with formation of an arenium ion. If an arenium ion is formed, the C_2 and C_6 carbons should become most deshielded as in the case of the $C_6H_7Fe(CO)_3$ cation (Table I). The chemical shifts of all ring carbons are deshielded by about 8–17 ppm upon protonation, and the pattern of chemical shifts resemble that of the anisolemercurinium ion[14] (Table I), where the aromatic ring is complexed with electron-deficient metal. There is no chemical shift observed corresponding to an aliphatic methylene carbon which would result at the site of protonation due to a change from sp^2 to sp^3 hybridization. There is also no triplet absorption corresponding to a methylene carbon or doublet of doublets corresponding to proton exchange involving ring proton. The increase of J_{C-H} coupling constants of all ring carbons also rules out ring protonation.

The structure of arenechromium tricarbonyls is of considerable interest. Benzenechromium tricarbonyl shows structure 3 with the Cr–CO bonds directed toward the midpoints of the C–C bonds of the ring.[8] Monosubstituted derivatives adopt either an eclipsed configuration 4 or a staggered configuration 5.[9] The temperature dependence of



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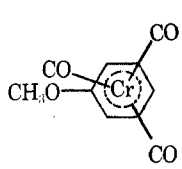

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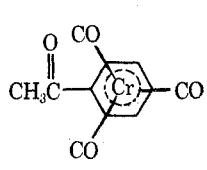

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