on resin samples which were exposed to Cu^{++} for 6 days and then eluted for 6 days. They have only qualitative, descriptive significance, since equilibrium was not reached and since the adsorbed Cu^{++} was probably not uniformly distributed through the resin. When the 3 *m* resin was eluted with 0.10 *M* $NaNO_3$ for 6 days, relatively small amounts of Cu^{++} were extracted into the aqueous phase (curve b). When the 2 *m* resin was treated for 6 days with a solution containing enough HNO_3 to make the resin 3 *m* in H^+, more Cu^{++} was eluted, although curve B was not reached.

The results of the experiments on the adsorption of Hg^{++} are shown in Table I. To avoid possible precipitation of basic mercuric salts, the solutions initially were at a *p*H of *ca.* 2 and the resin was 4 to 5 *m* in H^+. After 8 days, a large fraction of the mercuric ion was taken up by the resin. The ratio of H^+ liberated/Hg^{++} adsorbed was above unity. Table I and the data of Fig. 1 show that on a charge basis Hg^{++} and H^+ are about equally effective in increasing the acid constant of the resin.

TABLE I

ADSORPTION OF Hg^{++} BY AMBERLITE IR-4B

1 g. resin/100 ml. aqueous phase; constant stirring; temp., 28.3°; ionic strength, 0.09 to 0.10; 8 days equilibration.

m Hg^{++} in resin	*M* Hg^{++} in soln.	*m* H^+ in resin	*M* H^+ in soln.	H^+ liberated / Hg^{++} adsorbed
0	0	4.52	0.0040	..
.22	.000025	4.12	.0077	1.7
.50	.00049	3.84	.0100	1.2
.67	.0043	3.35	.0142	1.5
.81	.0029	3.35	.0142	1.2[a]
1.01	.0120	2.55	.0207	1.7
1.13	.0218	2.24	.0221	1.6

[a] 16 days equilibration.

The resin did not appreciably change color on adsorbing Hg^{++}. The greater affinity of the resin for Hg^{++} as compared to Cu^{++} is in accordance with the relative affinity of NH_3 for these two ions; $Hg^{++} + NH_3 = HgNH_3^{++}$, $\log K = 8.8$; $Cu^{++} + NH_3 = CuNH_3^{++}$, $\log K = 4.15$.[3b]

Acknowledgment.—We are grateful to the Atomic Energy Commssion for support of this research under Contract AT(11-1)-188. We are grateful to Dr. A. Adamson for helpful criticisms made in the process of refereeing this paper.

CONTRIBUTION NO. 1798 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY
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p-Dimethylaminophenylquinaldylcarbinol

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RECEIVED JUNE 18, 1953

Bahner and Pace[2] were unable to isolate *p*-dimethylaminophenylquinaldylcarbinol from the reaction mixture of quinaldine and *p*-dimethylaminobenzaldehyde. Other substituted benzaldehydes did combine with quinaldine under the same conditions. From the Elderfield[3] summary of the various procedures used for the synthesis of these carbinols it is evident that *p*-dimethylaminobenzaldehyde will not condense.

Three of these carbinols were made[4] by treating the lithium derivative of 6-ethoxyquinaldine, 6-methoxyquinaldine and quinaldine itself with *p*-dimethylaminobenzaldehyde. Although the yields were only fair, the by-products formed presented no difficulty in the purification. These carbinols were easily dehydrated to the corresponding styryl derivatives by heating with acetic anhydride or hydrochloric acid.

Experimental

Quinaldines.—Quinaldine was Eastman Kodak Co., white label grade and was used with no further purification. 6-Methoxyquinaldine was prepared by modifying the procedure of Cocker and Turner.[5]

A solution of 123 g. (1.0 mole) of *p*-anisidine in 200 ml. of concentrated hydrochloric acid was cooled to 0°. With constant stirring, 137 g. (1.0 mole) of paraldehyde was added over a period of one-half hour. Stirring was discontinued, and the reaction mixture was allowed to stand overnight. The brown material was refluxed on a water-bath for four hours (additional paraldehyde was added from time to time to compensate for the unavoidable loss through the condenser). The solution was cooled and poured with vigorous stirring into a large excess of 6 *M* ammonium hydroxide (*ca.* 1000 ml.). The dark viscous oil formed was separated, washed three times with 200-ml. portions of water dissolved in ether and dried over KOH. The ether was removed and the remaining oil was distilled under reduced pressure, b.p. 145–150° (3 mm.).[6] The pale yellow oil solidified in the receiver and formed lemon color cubic crystals. Crystallization from ligroin gave white crystals. Yield was 54 g. (31%); m.p. 64°.

6-Ethoxyquinaldine was made by the above method. From 137 g. (1.0 mole) of *p*-phenetidine, 23 g. of 6-ethoxyquinaldine (12.7%) were obtained by fractionating at 173° at 14 mm., the bath temperature being 248°. A white product was obtained from the ether–petroleum ether crystallization; m.p. 71°.[7]

***p*-Dimethylaminophenylquinaldylcarbinol.**—To a phenyl lithium solution[8] cooled in an ice–salt-bath was added an equivalent amount of the quinaldine dissolved in 20 ml. of dry ether; the color turned brick red. Stirring was continued for one-half hour after the addition of the quinaldine. An equal molar amount of *p*-dimethylaminobenzaldehyde suspended in 35 ml. of ether was added portionwise. The color gradually changed from brick-red to orange and then to yellow. The solution was stirred for two hours and then allowed to warm to room temperature by standing overnight. The lithium salt was decomposed with 95% alcohol. The carbinol was isolated by dilution and crystallized from a dilute alcohol solution. Pale straw-yellow plates were obtained which did not turn red if kept dry. Yield was 14.3%; m.p. 130°.

Anal.[9] Calcd. for $C_{19}H_{20}N_2O$: C, 78.02; H, 6.91. Found: C, 78.10; H, 6.90.

***p*-Dimethylaminophenyl-6-methoxyquinaldylcarbinol** was made as described above, but the mixture was refluxed prior to decomposition of the lithium salt until the color changed to yellow. The salt was hydrolyzed with 50% alcohol, the top layer was separated, and the water layer was extracted

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(2) C. T. Bahner and E. S. Pace, THIS JOURNAL, **74**, 3932 (1952).

(3) R. C. Elderfield, "Heterocyclic Compounds," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1952, p. 295.

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(6) If a sharp fraction is not taken the oil fails to solidify. At times recrystallization from ligroin will give the desired solid, but most of the time two layers separate making redistillation necessary. The dry solid turns pink almost at once and will keep indefinitely. Moist products turn brown and decompose in a matter of days.

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(9) Microanalysis by C. W. Koch, Albany, California.

with two 50-ml. portions of benzene. The solvents were combined, and evaporated to one-half volume on the steam-bath. On cooling a precipitate formed which was recrystallized from alcohol. Yield was 12.5%; m.p. 151.5°.

Anal.[9] Calcd. for $C_{20}H_{22}N_2O_2$: C, 74.48; H, 6.90. Found: C, 74.30; H, 6.82.

p-Dimethylaminophenyl-6-ethoxyquinaldylcarbinol.—The above procedure was followed. The mixture was refluxed for two hours prior to the hydrolysis until the precipitate turned yellow. Yield was 24.9%; m.p. 153.6°.

Anal.[9] Calcd. for $C_{21}H_{24}N_2O_2$: C, 74.94; H, 7.21. Found: C, 74.69; H, 7.33.

Styryls.—The carbinols were dehydrated to the respective styryl derivatives by boiling in 2 *M* hydrochloric acid for one hour; the carbinol dehydrated *ca.* 99%, the 6-methoxy *ca.* 75% and the 6-ethoxy *ca.* 50%. Mixed melting points showed no depression with the corresponding styryl compounds synthesized by procedures in the literature.[10,11]

Acknowledgment.—We should like to thank Dr. H. S. Mosher for helpful comments in the preparation of this manuscript.

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A Stable Chloroform Adduct of 11-Epi-17α-hydroxycorticosterone

BY HELMUTH CORDS

RECEIVED JULY 16, 1953

In view of the recent interest in Δ^4-pregnene-11α,17α,21-triol-3,20-dione,[1-7] the 11-epimer of the most important adrenal secretory product 17α-hydroxycorticosterone, we wish to describe a stable adduct of this substance with chloroform. The adduct is formed readily when the steroid is crystallized from chloroform, in which it is very difficultly soluble. It forms colorless platelets, m.p. 206–209°, $[\alpha]^{23}D$ +88 ± 2° (0.5% in ethanol) (calculated for an adduct containing one mole of chloroform: +87.8°).[8] The substance was analyzed after drying *in vacuo* (1 mm.) at 100° for two hours. *Anal.* Calcd. for $C_{21}H_{30}O_5 \cdot CHCl_3$: C, 54.83; H, 6.49; Cl, 22.08. Found: C, 54.92; H, 6.59; Cl, 21.99.

The infrared spectrum of the chloroform adduct, sampled as nujol mull, differs from that of the free 11-epi-17α-hydroxycorticosterone in that it contains a deep band at 13.28 μ, characteristic for chloroform. Moreover, the C_{21}–carbonyl band shifted from 5.83 μ for the free steroid to 5.88 μ for the adduct.

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(8) The specific rotation of the free steroid is +117° (0.5% in ethanol).

Its low solubility in chloroform, its well formed crystal shape and its stability to heat and vacuum render the chloroform adduct very suitable for purification of 11-epi-17α-hydroxycorticosterone. Microbiological synthesis of Δ^4-pregnene-11α,17α,21-triol-3,20-dione[1] generally yields slightly colored material. Recrystallization of this material from chloroform produces an almost colorless chloroform adduct (well formed platelets). The steroid can be readily freed of chloroform by crystallization from the lower alcohols, acetone or ethyl acetate.

Δ^4-Pregnene-11α,17α,21-triol-3,20-dione 11,21-diacetate[2-6,9,10] forms a similar complex with chloroform, whereas the corresponding 21-monoacetate, which was obtained in crystalline form from acetic acid–water, crystallizes from chloroform without solvate formation.

Another adduct has been observed with 5,16-pregnadiene-3β-ol-20-one and chloroform. One mole of chloroform is attached here to two moles of the steroid. This adduct, colorless platelets, is obtained by crystallization of the steroid from chloroform, and is stable to a vacuum of 1 mm., yet labile to heat. The melting point is unchanged from that of the free compound. The optical rotation, $[\alpha]^{23}D$ 20 ± 2° (0.5% in ethanol) differs, as expected, 19% from that of the free steroid. *Anal.* Calcd. for $C_{21}H_{30}O_2 \cdot {}^1/_2CHCl_3$: C, 69.02; H, 8.22; Cl, 14.22. Found: C, 69.27; H, 8.34; Cl, 14.21.

The adduct shows the strong band at 13.32 μ, characteristic for chloroform, and three additional bands at 10.54, 11.78 and 11.99 μ. The C_{20}-carbonyl shifted from 6.05 to 6.02 μ in the adduct, and four minor bands of the free steroid (8.62, 10.45, 12.41 and 12.52 μ) appeared at slightly lower wave lengths. The band at 9.86 μ is missing in the complex.

$\Delta^{5,16}$-Pregnadiene-3β-ol-20-one acetate does not form a similar adduct.

I am indebted to Dr. N. Coy for the spectrometric measurements and to Mr. J. Alicino for the microanalytical determinations.

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Phenyl Esters

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RECEIVED JUNE 22, 1953

The preparations of phenyl esters have hitherto been rather tedious as they have involved the use of acid chlorides, acid anhydrides or $POCl_3$, or in the case of phenyl esters of reactive acids such as acrylic[1] or methacrylic acid,[2] somewhat circuitous synthetic routes. Phenyl esters even of reactive acids have recently been prepared with trifluoro-

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