hydrolysis of the acetyl group of VII, with subsequent loss of formaldehyde and ring closure.

Heating VII in ethanol produced a compound (VIII) which retained an amide peak (5.94 μ) but no longer showed an ester peak in the infrared spectrum. The n.m.r. ($CDCl_3$) peaks at δ 2.19 (s) (N-acetyl), 4.63 (s) (methylene), 1.22 (t), and 3.60 (q) (ethoxy), together with the infrared data, indicated that the structure of VIII was 4′-chloro-2′-(α-ethoxymethyliminobenzyl)acetanilide, resulting from solvolysis of the acetoxy group in VII. Compound VIII, an N,O-acetal, was stable when treated with hot alkali, but when refluxed in alcoholic hydrochloric acid was converted to the hydrochloride salt of III. The ultraviolet absorption spectra of VII [$\lambda_{max}^{CHCl_3}$ 240 mμ (ϵ 36,700), 333 (7320)] and VIII [λ_{max}^{EtOH} 238 mμ (ϵ 29,100), 332 (2950)] were characteristic of *o*-acylaminobenzophenone imines.[9]

3-Acetoxy-7-chloro-1,3-dihydro-5-phenyl-2H-1,4-benzodiazepin-2-one, prepared by rearrangement of I with acetic anhydride,[3] underwent further acetylation at the 1-position upon strong heating with acetic anhydride to form 3-acetoxy-1-acetyl-7-chloro-1,3-dihydro-5-phenyl-2H-1,4-benzodiazepin-2-one (IX). Interestingly, IX also gave III when treated with sodium hydroxide. It seems likely that the diazepine ring of IX, being unstable to alkali, undergoes hydrolytic cleavage to form the intermediate VII, which is thereupon converted into III.

In the reaction of II with phenylchloroformate, no pure intermediate was isolated. Treatment of the crude reaction product with bicarbonate gave 6-chloro-4-phenyl-2(1H)-quinazolinone (X).[10] A route leading to X could be proposed, similar to that discussed above for the formation of III.

Experimental Section[11]

2-Acetamido-5-chloro-α-phenylbenzylideneaminoacetic Acid N-Oxide (VI).—A mixture of 1.0 g. of II, 1 ml. of acetic anhydride, and 15 ml. of chloroform was refluxed for 15 min. The solution was concentrated to dryness *in vacuo*, and the residue was recrystallized from carbon tetrachloride, giving 0.6 g. of product, m.p. 155–156°.

Anal. Calcd. for $C_{17}H_{15}ClN_2O_4$: C, 58.88; H, 4.35; Cl, 10.23; N, 8.16. Found: C, 58.72; H, 4.41; Cl, 10.0; N, 8.18.

4′-Chloro-2′-(α-acetoxymethyliminobenzyl)acetanilide (VII).—A mixture of 5.0 g. of II and 50 ml. of acetic anhydride was heated on the steam bath, with stirring, for 30 min. During this time most of the solid dissolved and gas was evolved. The reaction mixture was cooled, filtered from impurities, and concentrated to dryness *in vacuo*. The residue was treated with a small amount of cold alcohol, and the resultant solid was filtered, giving 2.3 g. of VII, m.p. 123–125°. Recrystallization from cyclohexane did not change the melting point.

Anal. Calcd. for $C_{18}H_{17}ClN_2O_3$: C, 62.65; H, 4.96; Cl, 10.30; N, 8.12. Found: C, 62.71; H, 5.01; Cl, 10.25; N, 8.15.

6-Chloro-2-methyl-4-phenylquinazoline (III). A.—To a suspension of 0.5 g. of VII in 10 ml. of ethanol was added 4 ml. of 4 *N* sodium hydroxide. The resultant solution was diluted with water to give 0.2 g. of III, m.p. 105–107°, identical with an authentic sample.[8]

B.—To 2.0 g. of VII was added 15 ml. of 6 *N* hydrochloric acid and 30 ml. of ethanol. The compound dissolved, and after several minutes a solid precipitated out. There was filtered off 0.8 g. of the hydrochloride salt of III.

C.—To a suspension of 0.3 g. of VIII in 3 ml. of alcohol, 1 ml. of 6 *N* hydrochloric acid was added and the resultant clear solution was heated to reflux. After several minutes a solid separated. The reaction mixture was cooled, and 0.15 g. of solid, m.p. 183–185°, was collected and found to be identical with the product formed by B.

D.—To a suspension of 1.0 g. of IX in 25 ml. of ethanol was added 3 ml. of 4 *N* sodium hydroxide. The reaction mixture darkened at first but after several minutes became lighter. After standing for 1 hr. the solution was diluted with 50 ml. of water, and the precipitate was collected, yielding 0.6 g. of III, m.p. 105–106°.

6-Chloro-4-phenylquinazoline (IV).—To a solution of 10 ml. of 98–100% formic acid and 5 ml. of acetic anhydride was added 1.0 g. of II. The solution was stirred at room temperature for 1 hr., heated at 60° for 30 min., cooled, and diluted with a large volume of water. A sticky precipitate was separated from the aqueous layer and recrystallized from an alcohol–water mixture, giving 0.3 g. of IV, m.p. 136–138°.

Anal. Calcd. for $C_{13}H_9ClN_2$: C, 69.84; H, 4.74; Cl, 14.73; N, 11.65. Found: C, 69.42; H, 4.51; Cl, 14.30; N, 11.81.

4′-Chloro-2′-(α-ethoxymethyliminobenzyl)acetanilide (VIII).—A solution of 2.3 g. of VII was refluxed in 50 ml. of ethanol for 30 min. and chilled. The precipitate (1.3 g., m.p. 114–116°) was recrystallized from cyclohexane. After drying to constant weight the product had a melting point of 118–120°.

Anal. Calcd. for $C_{18}H_{19}ClN_2O_2$: C, 65.38; H, 5.80; Cl, 10.72; N, 8.48. Found: C, 65.45; H, 5.69; Cl, 10.60; N, 8.42.

6-Chloro-4-phenyl-2(1H)-quinazolinone (X).—To a solution of 1.0 g. of II in 15 ml. of dioxane was added, with stirring, 2.0 ml. of phenylchloroformate. The solution was diluted with water, neutralized with sodium bicarbonate solution, and extracted with ether. The ether was evaporated, alcohol was added to the residue, and the product was filtered off, yielding 0.7 g. of X, m.p. >300°, identical with an authentic sample.[10]

3-Acetoxy-1-acetyl-7-chloro-1,3-dihydro-5-phenyl-2H-1,4-benzodiazepin-2-one (IX).—A mixture of 5.0 g. of I and 50 ml. of acetic anhydride was refluxed for 1 hr. The solvent was removed *in vacuo*, and the residue was recrystallized twice from cyclohexane, giving 3.8 g. of IX, m.p. 170–172°.

Anal. Calcd. for $C_{19}H_{15}ClN_2O_4$: C, 61.54; H, 4.08; N, 7.56. Found: C, 61.69; H, 4.34; N, 7.15.

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(11) The melting points are uncorrected. The infrared spectra were determined in KBr pellets. The n.m.r. spectra were obtained on a Varian A-60 spectrometer using tetramethylsilane as the internal reference.

Isomerization of *o*-Phenylphenol to *m*-Phenylphenol

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We recently had occasion to attempt a Friedel–Crafts acylation of *o*-phenylphenol using aluminum chloride as catalyst and isolated, as a major product of the reaction, *m*-phenylphenol. This represents a further example of phenyl group migration, a reaction that has been studied recently by Olah[1] and Wynberg[2] and is of further significance because *m*-phenylphenol has been, to date, a relatively inaccessible chemical.

The isomerization of *o*-phenylphenol to *m*-phenylphenol proceeds rapidly at 100° in the presence of

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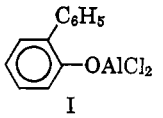
(2) H. Wynberg and A. P. Wolf, *J. Am. Chem. Soc.*, **85**, 3308 (1963).

greater than molar amounts of aluminum chloride. The phenolic hydroxyl group reacts initially with aluminum chloride with evolution of hydrogen chloride and it is evidently then the species (I)[3] which isomerizes



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in the presence of excess aluminum chloride to the more stable *meta* isomer. Water is presumably a promoter in this reaction, as in the previously described cases[1,2]; however, its effect on the present reaction has not been studied. It is interesting to note that no *p*-phenylphenol is detectable in the reaction and furthermore that *p*-phenylphenol under the same conditions, even for extended periods of time, does not appear to be appreciably affected. In the isomerization of terphenyls[1] the same equilibrium mixture of *meta* and *para* isomers is obtained starting with any of the three terphenyls.

Experimental Section

To a 2-l. three-necked round-bottom flask equipped with a stirrer, condenser, and thermometer was added 300 g. (1.77 moles) of *o*-phenylphenol, 500 ml. of chlorobenzene, and 300 g. (2.24 moles) of anhydrous aluminum chloride. The reaction was stirred on the steam bath for 1 hr., then added to dilute hydrochloric acid and ice. The organic layer was separated and washed twice with dilute hydrochloric acid. The solution was then extracted with 10% sodium hydroxide solution and the aqueous alkaline layer was acidified. The oil that separated was taken up in ether; the solution was dried over magnesium sulfate and filtered. The ether was evaporated on the steam bath and the residue distilled at 20 mm. through a short Vigreux column. Two fractions were iso ated: (1) 131.7 g., b.p. 144–164°; (2) 120.9 g., b.p. 164–170°; and 17 g. of tarry residue. Fraction 1 was shown to be a mixture of *o*-phenylphenol (73%) and *m*-phenylphenol (27%) by thin layer chromatography and infrared. Fraction 2 was substantially pure *m*-phenylphenol, m.p. 75–77°. One recrystallization (heptane) raised the melting point to 78° (lit. m.p. 74–75°,[4] 75°[5]). The combined yield of *m*-phenylphenol was 156.4 g. (0.92 mole, 77%).

(3) P. H. Gore in G. A. Olah, "Friedel–Crafts and Related Reactions," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1964, p. 46.
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(5) H. Cassebaum, *J. prakt. Chem.*, **13**, No. 4, 141 (1961).

Photochemical Transformations and Reactions of 3β-Acetoxy-16β-diazoacetylisopregn-5-en-20-one

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We recently described the preparation of 3β-hydroxy-16-diazoandrostan-17-one and its conversion by ultraviolet radiation to the corresponding D-nor carboxylic acid.[1] D-Nor-16-carboxyandrost-5-en-3β-ol can be transformed to the diazoketone, which by treatment with acetic acid affords the D-nor-17-desoxycorticosteroid acetate.[2] These results led us to prepare a steroid 16-diazo ketone and to study its chemical and photochemical reactions.

Discussion

By treating 3β-acetoxyisopregn-5-en-20-one 16-carbonyl chloride with diazomethane there was obtained, in good yield, 16β-diazoacetyl-3β-acetoxyisopregn-5-en-20-one (I).[2] Irradiation of I with a Hanau S-700 mercury lamp in tetrahydrofuran gave 16β-hydroxyacetyl-3β-acetoxyisopregn-5-en-20-one (II). Acetylation of II with acetic anhydride–pyridine gave a compound identical with the product previously obtained by treatment of the diazo ketone I with acetic acid.[3] Irradiation of I in methanol led to an Arndt–Eistert rearrangement affording the methyl ester of 3β-acetoxyisopregn-5-en-20-on-16β-ylacetic acid (III) characterized by its infrared absorptions at 1740 (acetate), 1709 (ester), and 1700 cm.$^{-1}$ (20-ketone), and proton magnetic resonance at 2.06 (methyl ketone), 2.20 (acetate), and 3.68 p.p.m. (CH_3O); the elementary analysis was in agreement with $C_{26}H_{38}O_5$. The β orientation of the C-16 group was confirmed by the optical rotatory dispersion curve, which showed a negative Cotton effect.[3] Also in agreement with this assignment is the resonance frequency of the angular methyl protons at 1.02 p.p.m.[4] Alkali hydrolysis of III gave 3β-hydroxyisopregn-5-en-20-on-16β-ylacetic acid (IV) with infrared absorption at 1690 and 3300–3000 cm.$^{-1}$, a negative Cotton effect curve, and elemental analysis in agreement with $C_{23}H_{34}O_4$.

By treatment with diazomethane IV was transformed to the corresponding methyl ester V with infrared absorption at 1700 and 1735 cm.$^{-1}$ (acetyl and acetate groups) and n.m.r. resonances at 2.17 (21H) and 3.62 p.p.m. (OMe). Compound IV was further characterized as the acetate VI. The latter with diazomethane produced compound III, identical with the compound obtained by irradiation of the diazo ketone I in methanol. To obtain further proof of a photoinduced Wolff rearrangement, the diazo ketone I was allowed to react with freshly prepared silver oxide in methanol leading to compound III. When the compound IV was treated with acetic anhydride and *p*-toluenesulfonic acid, the enol lactone (VII) of 3β-acetoxyisopregn-5-en-20-on-16β-ylacetic acid was obtained showing infrared absorption at 1780 and 1750 cm.$^{-1}$ and proton resonance at 0.92–1.0 (angular methyls), 1.89 (olefinic methyl), and 1.98 p.p.m. (acetate). The end absorption in the ultraviolet at 210 mμ (ε 5340) was also in agreement with the presence of a tetrasubstituted double bond.

Using the usual procedure of the Arndt–Eistert synthesis it was possible to prepare the amide VIII by treating the diazo ketone with ammonia [infrared absorption at 3480 (NH), 1720 (acetate), 1700 (acetyl), 1680 (C=C), and 1595 cm.$^{-1}$ (amide); n.m.r. at 3.5

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