(12) D. J. Raber, G. J. Kane, and P. v. R. Schleyer, *Tetrahedron Lett.*, 4117 (1970).
(13) Marion Babcock, Brown University, unpublished results.
(14) J. O. Halford, *J. Chem. Phys.*, **24**, 830 (1956).
(15) C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964); P. v. R. Schleyer, *ibid.*, **86**, 1854 (1964).
(16) Infrared spectra were determined with either a Perkin-Elmer 247 grating infrared spectrometer or a Perkin-Elmer 237 spectrometer using sodium chloride optics. The nmr determinations were carried out on a Varian Associates A-60A spectrometer; approximately 20% solutions in $CDCl_3$ were employed with tetramethylsilane as the internal standard. Gas chromatography was accomplished with a Perkin-Elmer 881 flame ionization gas chromatograph fitted with a Golay capillary column adapter. Columns used were all 50 ft Support Coated Open Tubular (SCOT) columns with supports as noted. The mass spectra were carried out on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Microanalyses were performed by Baron Consulting Co., Orange, Conn. Melting points were uncorrected.
(17) T. Sadaki, S. Eguchi, and T. Toru, *J. Org. Chem.*, **35**, 4109 (1970).
(18) The addition of concentrated base to this strongly acid solution caused an exotherm which could be controlled by cautious, slow addition.
(19) Aldrich Chemical Co.
(20) H. C. Brown and P. Heim, *J. Amer. Chem. Soc.*, **86**, 3566 (1964).
(21) N. Schwartz and J. Blumbergs, *J. Org. Chem.*, **29**, 1976 (1964).
(22) K. Bowden, I. Heilbron, E. R. H. Jones, and B. Weedon, *J. Chem. Soc.*, 39 (1946).
(23) S. W. Pelletier, *Chem. Ind. (London)*, 1034 (1953).
(24) S. Winstein and R. Boschan, *J. Amer. Chem. Soc.*, **72**, 4669 (1950).

Studies on 4-Quinazolinones. VII.[1] Some Novel Transformations

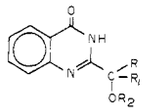
S. C. Pakrashi* and A. K. Chakravarty[2]

Indian Institute of Experimental Medicine, Calcutta-700032, India

Received June 10, 1974

2-(1′-Hydroxydiphenylmethyl)-4-quinazolinone (**1**) or the *O*-acetate (**2**) on refluxing with acetic anhydride and sodium acetate yielded 1,1-diphenyl-3-methylene-9-oxo-9*H*-oxazolo[3,4-*a*]quinazoline (**3**), which gave 1-acetyl-2-(1′-ethoxydiphenylmethyl)-4-quinazolinone (**6**) with ethanolic acetic acid. Both **3** and **6** regenerated the *O*-acetate (**2**) upon treatment with hydrochloric acid. Treatment of **3** or **6** with sodium borohydride in ethanol under reflux furnished 2-methyl-3-(*o*-hydroxymethylphenyl)-4-imino-5,5-diphenyloxazolidine (**13**) by an unusual amide reduction to a primary alcohol with concomitant hydrogenolytic cleavage of the 3,4-bond of the 4-quinazolinone system. Further hydrogenolysis of **13** in the presence of 10% Pd/C and perchloric acid gave **14**.

In continuation of our investigations of the reactions of 4-quinazolinones[1,3-5] we attempted the acetylation of 2-(1′-hydroxydiphenylmethyl)-4-quinazolinone (**1**)[4] with refluxing acetic anhydride in the presence of fused sodium acetate. The major product obtained was a new compound A, mp 163–164°, in approximately 60% yield in addition to 22% of the desired *O*-acetate **2.** The acetate **2** which also afforded compound A under the same condition was, however, the only isolable product in *ca.* 60% yield when **1** was refluxed with acetic anhydride alone.



1, R = R$_1$ = Ph, R$_2$ = H **7**, R = H, R$_1$ = Ph, R$_2$ = H
2, R = R$_1$ = Ph, R$_2$ = Ac **8**, R = R$_1$ = Me, R$_2$ = H
5, R = R$_1$ = Ph, R$_2$ = Et **9**, R = H, R$_1$ = Ph, R$_2$ = Ac
10, R = R$_1$ = Me, R$_2$ = Ac

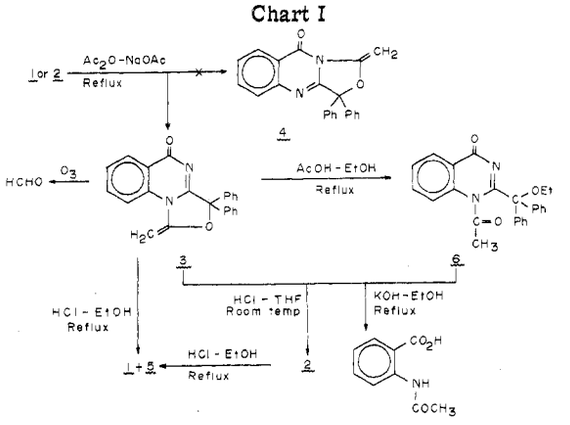
Compound A was analyzed for $C_{23}H_{16}N_2O_2$. Although the mass spectrum did not exhibit the molecular ion, the peak at *m/e* 310 (base peak) in the highest mass region corresponding to $C_{21}H_{14}N_2O$ conceivably could arise by facile expulsion of ketene in the primary fragmentation. The intense bands at 1686, 1694 (sh), 1624, and 1594 cm^{-1} in the ir spectrum (Nujol) indicated the intact 4-quinazolinone moiety in the compound. The nmr spectrum showed a one-proton multiplet at δ 8.46 assignable to an aromatic proton peri to the carbonyl,[6] signals for 13 other aromatic protons, and a pair of sharp doublets at δ 4.67 and 5.6 (J = 3 Hz) attributed to an *exo*-methylene function. This latter assignment was confirmed by the isolation of formaldehyde on ozonolysis.

Treatment of compound A with 1% ethanolic acetic acid at room temperature resulted in recovery of starting material. However, upon refluxing it afforded a product, $C_{25}H_{22}N_2O_3$, mp 158–159°, characterized as 1-acetyl-2-(1′-ethoxydiphenylmethyl)-4-quinazolinone (**6**). The nmr spectrum deserves special mention. Apart from the signals for 14 aromatic protons and a singlet at δ 2.11 for a $-COCH_3$ group, it exhibited a typical ABC_3 pattern composed of a three-proton triplet at δ 1.18 and a centrosymmetric two-proton multiplet around δ 3.38 for the $-O-CH_2-CH_3$ group clearly indicating the $-CH_2-$ protons to be diastereotopic. The first-order analysis of the AB part of the spectrum gave δ_A and δ_B values of 3.51 and 3.26, respectively, and the coupling constants J_{AB} = 9.5 Hz and J_{AC} = J_{BC} = 7 Hz were in excellent agreement with those recorded for the nonequivalent methylene protons of acetaldehyde diethyl acetal.[7] Since the nonequivalence was found to be temperature independent in the range of 30–86° and the corresponding deacetyl derivative (**5**) showed a simple A_2X_3 spectrum, the nonequivalence of the methylene protons presumably results from restricted rotation due to the presence of the acetyl function at N_1 rather than to different populations of the rotamers.[8]

Alkaline hydrolysis of either compound A or **6** with 5% alcoholic KOH furnished *N*-acetylanthranilic acid.

All the above observations (Chart I) appear best explained by the assignment of structure **3** (1,1-diphenyl-3-methylene-9-oxo-9*H*-oxazolo[3,4-*a*]quinazoline) to compound A and not the other possible alternative structure **4.**

Chart I

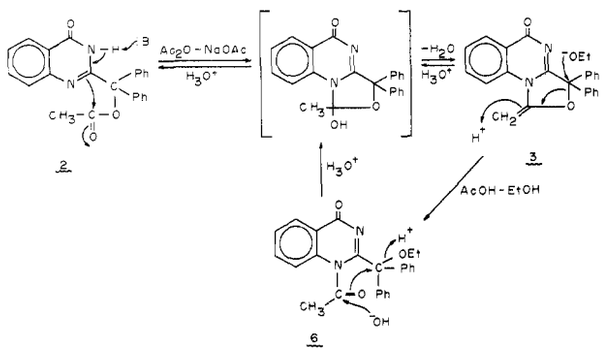


The observed transformation seems to require two phenyl substituents on the same carbon atom to favor cyclization at N-1. Thus, 2-(α-hydroxybenzyl)- and 2-(1′-hydroxyisopropyl)-4-quinazolinones (**7** and **8**) under the specified condition yielded the respective *O*-acetates (**9** and **10**), which regenerated the original alcohols on hydrolysis with dilute ammonia.

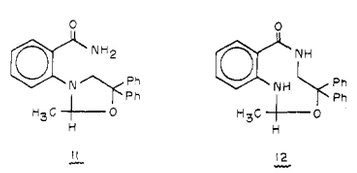
The reverse process was also observed upon treatment of **3** or **6** with dilute acid in THF to afford the *O*-acetate (**2**). On the other hand, hydrolysis of **3** with 5% ethanolic HCl under reflux yielded **1** and a compound, mp 200–202°, for which the nmr and the mass spectral data were in good agreement with 2-(1′-ethoxydiphenylmethyl)-4-quinazolinone (**5**). The apparent intermediacy of the *O*-acetate (**2**) was confirmed by conversion to both **1** and **5** on similar treatment.

The mechanism envisaged for the formations of **3** and **6** from **2** and the reverse process is given in Scheme I.

Scheme I

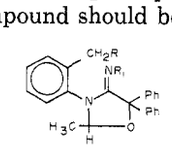


Both **3** and **6** on treatment with $NaBH_4$ in refluxing ethanol afforded compound B, mp 150–151°. It analyzed for $C_{23}H_{22}N_2O_2$ indicating the addition of six hydrogen atoms to **3** during reduction. The presence of a $-CH(CH_3)-O-CPh_2-$ moiety in the compound was revealed by the mass spectrum (high resolution) which showed intense peaks at 210 ($C_{15}H_{14}O$), 209 ($C_{15}H_{13}O$), 166 ($C_{13}H_{10}$), and 165 ($C_{13}H_9$) besides primary loss of CH_3CHO and Ph_2CO. Either structure **11** or **12** was thus considered[10] likely for



compound B, since disubstituted 4-quinazolinones are known[5,9] to undergo reductive ring cleavage at the 1,2- or 2,3-bond on similar treatment with metal hydrides.

Structure **11** was incompatible with the nmr spectrum which was in accord with structures **12** or **13**, since a broad two-proton singlet centered at δ 4.34 converted to a pair of AB doublets at δ 4.3, and δ 4.38 (J = 13 Hz) on deuteration showed the presence of a $-CH_2-$ coupled with a NH or OH proton. That the compound should be represented by the



13, R = OH, R_1 = H
4, R = R_1 = H
15, R = OAc, R_1 = Ac
16, R = H, R_1 = Ac

unexpected structure **13** [2-methyl-3-(*o*-hydroxymethylphenyl)-4-imino-5,5-diphenyloxazolidine] became apparent from the following evidences: (i) compound B formed an *O,N*-diacetate (**15**), the mass spectrum of which showed a low-intensity peak at M − 73 for a CH_2OAc function; and (ii) on catalytic hydrogenation with 10% Pd/C in the presence of perchloric acid B underwent hydrogenolysis to **14**, $C_{23}H_{22}N_2O$ (M^+ 342), forming a *N*-monoacetate (**16**). The nmr spectrum of **14** exhibited a three-portion singlet for a deshielded $C-CH_3$ group at δ 1.89 at the expense of the signals for $-CH_2OH$. Appearance of a peak at 1345 cm^{-1} in the ir spectrum of **14** also supported the assignment.

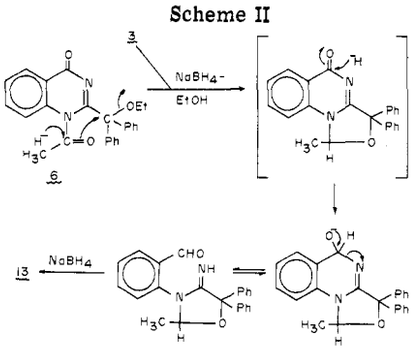
The ir absorption at 1650 cm^{-1} of both **13** and **14** could now be assigned to the C=NH group, the reluctance of which toward further reduction or hydrolysis is probably due to the steric hindrance caused by the vicinal *gem*-diphenyl groups.

Though the reduction of the amide carbonyl, normally resistant to borohydride, to primary alcohol with concomitant hydrogenolytic cleavage of the 3,4-bond of the 4-quinazolinone system is novel, it is not without analogy in the literature. Witkop and his coworkers[11–14] reported the conversion of cyclic imides, *viz.*, succinimide, glutarimides including phthalimidoglutarimides, and 5,6-dihydro-2,4-dioxopyrimidines principally to amido alcohols by the same reagent.

We believe, however, that the observed unusual transformation requires the oxazoloquinazolinone rather than the 4-quinazolinone system itself since 3-phenylquinazol-2,4-dione has been reported[14] to be inert to borohydride reduction and we also did not encounter any such product during our metal hydride reduction studies[5] on variously substituted 4-quinazolinones. Moreover, the same product **13** from both compounds **3** and **6** suggests that the reaction most probably proceeds through a common intermediate.

Thus, the mechanism of the observed transformation is envisaged in Scheme II, the amide reduction being analo-

Scheme II



gous to the one suggested by Witkop, *et al.*[11] Though the intermediate carbinolimine or its ring-chain tautomeric iminoaldehyde was not obtained by us perhaps due to the vigorous conditions used, Kondo and Witkop[14] actually isolated, at least in some cases, the carbinolamide expected in their systems.

Experimental Section[15]

2-(1′-Acetoxydiphenylmethyl)-4-quinazolinone (2) from 1. 2-(1′-Hydroxydiphenylmethyl)-4-quinazolinone[4] (**1**, 0.1 g) was heated on a steam bath with acetic anhydride (1 ml) and pyridine (0.5 ml) for 4 hr. Usual work-up led to quantitative recovery of the starting material.

However, compound **1** (0.1 g) when refluxed with acetic anydride (1 ml) alone for 2 hr afforded a deep-green gum which on repeated crystallizations from benzene and then from ethanol furnished the *O*-acetate (**2**, 65 mg): mp 219–221° dec; ir 1757, 1661, 1642, 1600, and 1210 cm^{-1}.

Anal. Calcd for $C_{23}H_{18}N_2O_3$: C, 74.50; H, 4.90; N, 7.56. Found: C, 74.60; H, 5.03; N, 7.66.

1,1-Diphenyl-3-methylene-9-oxo-9*H*-oxazolo[3,4-*a*]quinazoline (3) from 1. A mixture of compound 1 (4 g), acetic anhydride (20 ml), and anhydrous sodium acetate (2 g) was refluxed for 6 hr. A dark-brown solid was obtained on decomposition of excess reagent with water. It was filtered, dissolved in chloroform (100 ml), washed successively with 5% Na_2CO_3 solution and water, dried, and evaporated. The crude product on crystallization from benzene yielded the major part of *O*-acetate (**2**, 0.75 g), recrystallized from alcohol in transparent plates, mp 219–221° dec.

The mother liquor from the above crystallization was then subjected to column chromatography. Benzene–petroleum ether (1:1, 1.2 l.) eluted **3** (2.5 g, 60%) crystallizing out of alcohol in fine needles: mp 164–165°; ir 1694 sh, 1686, 1623, 1594 cm^{-1}; nmr δ 4.67 and 5.6 (a pair of doublets, 1 H each, $=CH_2$, J_{AB} = 3 Hz), 7.3–8.6 (m, 14, ArH); *m/e* (rel intensity) 310 (100), 233 (4), 165 (6), 105 (9), 77 (10).

Anal. Calcd for $C_{23}H_{16}N_2O_2$: C, 78.38; H, 4.58; N, 7.95. Found: C, 78.70; H, 4.80; N, 8.16.

Further elution with benzene (1 l.) afforded a viscous oil which on crystallization from alcohol furnished an additional amount of the *O*-acetate (**2**, 0.25 g), the total yield being 22%.

Repetition of the same experiment using the *O*-acetate **2** (2 g), acetic anhydride (10 ml), and anhydrous sodium acetate (1 g) as the reactants yielded the same oxazoloquinazolinone **3** (1 g), and part of the starting material (0.5 g) was recovered unchanged.

Formaldehyde from 3 by Ozonolysis. Ozonized oxygen was bubbled through a solution of **3** (0.15 g) in chloroform (10 ml) at −5 to 0° for 2.5 hr. The reaction mixture was then poured into a slurry of zinc dust and water and rapidly steam distilled. The aqueous part of the distillate was treated with a solution of dimedone (0.2 g) in alcohol (10 ml), concentrated, and extracted with chloroform, and the solvent was evaporated. The major unreacted dimedone was recovered by crystallization of the residue from benzene and the mother liquor on chromatography yielded methylenebisdimedone (18 mg), mp 188–189°, identical (mmp) with an authentic specimen prepared from formaldehyde and dimedone.

The residue remaining after steam distillation yielded unconverted **3** (75 mg) on extraction with chloroform and chromatography.

Hydrolysis of 3. A. Formation of 2-(1′-Ethoxydiphenylmethyl)-4-quinazolinone (5) and 1. Compound **3** (0.1 g) was refluxed with 5% ethanolic HCl (6 ml) for 4 hr. After cooling, the solid product was filtered, washed with water, dried, and chromatographed. Elution with 25% chloroform in benzene (250 ml) yielded 60 mg of **5**, crystallizing from benzene–petroleum ether in prisms: mp 200–202°; ir 3144, 3039, 1672 and 1607 cm^{-1}; nmr δ 1.32 (t, 3, $-CH_2-CH_3$, J = 7 Hz), 3.28 (q, 2, $-CH_2-CH_3$, J = 7 Hz), 7.3–8.0 (m, 13, ArH), 8.45 (dt, 1, C_5H), 10.33 (br, 1, –CONH); *m/e* (rel intensity) 356 (M^+, 3), 328 (8), 327 (30), 314 (3), 313 (22), 312 (100), 311 (15), 310 (10), 211 (8), 183 (10), 165 (13), 152 (3), 105 (72), 78 (60), 77 (59).

Anal. Calcd for $C_{23}H_{20}N_2O_2$: C, 77.51; H, 5.66; N, 7.87. Found: C, 77.90; H, 5.74; N, 7.63.

Further elution with chloroform (150 ml) afforded **1** (30 mg).

B. Formation of 1-Acetyl-2-(1′-ethoxydiphenylmethyl)-4-quinazolinone (6). Compound **3** (50 mg) was refluxed with 1% ethanolic acetic acid (5 ml) for 4 hr. It was concentrated and cooled when **6** (51 mg) was separated as colorless plates: mp 158–159°; ir 1705, 1695, 1630, and 1605 cm^{-1}; nmr δ 1.18 (t, 3, $-O-CH_2-CH_3$, J = 7 Hz), 2.11 (s, 3, $-COCH_3$), 3.38 (a centrosymmetric multiplet, 2, $-O-CH_2-CH_3$), 7.2–8.0 (m, 13, ArH), 8.37 (dd, 1, C_5H, J = 7.5, 1.5 Hz).

Anal. Calcd for $C_{25}H_{22}N_2O_3$: C, 75.36; H, 5.57; N, 7.04. Found: C, 75.40; H, 5.61; N, 6.98.

C. Formation of *N*-Acetylanthranilic Acid. Compound **3** (0.2 g) was refluxed with 5% ethanolic KOH (12 ml) for 1 hr. After cooling and dilution with water, it was extracted with chloroform. The oily product (0.11 g) was chromatographed to yield benzophenone (45 mg) and **1** (65 mg).

The aqueous part was acidified with HCl and extracted with chloroform, and the solvent was evaporated. The residue (68 mg) on crystallization from benzene–methanol furnished *N*-acetylanthranilic acid as fine colorless flakes (35 mg), mp 183–184°, identified by direct comparison with a synthetic specimen.

***N*-Acetylanthranilic Acid from 6.** Compound **6** (0.1 g) was hydrolyzed with 5% ethanolic KOH (6 ml) for 0.5 hr yielding benzophenone (32 mg), **1** (10 mg), and *N*-acetylanthranilic acid (35 mg).

Attempted Hydrogenation of 3. A solution of compound **3** (0.2 g) in ethanol (50 ml) was stirred in an atmosphere of hydrogen in the presence of 10% Pd/C (75 mg) for 3 hr. It was filtered, and the filtrate was concentrated and allowed to crystallize to obtain the unconverted starting material (0.19 g).

Transformation of 3 and 6 to *O*-Acetate 2. When solutions of **3** or **6** in ethyl acetate with a few drops of $HClO_4$ or in THF with concentrated HCl were stirred separately at room temperature for 1 hr, the *O*-acetate **2** was obtained in quantitative yield in each case.

However, compound **3** was recovered unchanged when stirred with 1% ethanolic acetic acid at room temperature for 2 hr.

Conversion of 2 to 1 and 5. Compound **2** (0.1 g) was refluxed with 5% ethanolic HCl for 4 hr. The crude product obtained after usual work-up on chromatographic resolution furnished **1** (55 mg) and **5** (30 mg).

Treatment of 2-(α-Hydroxybenzyl)- and 2-(1′-Hydroxyisopropyl)-4-quinazolinones (7 and 8) with Acetic Anhydride and Sodium Acetate. Compound **7** (0.1 g) was refluxed with acetic anhydride (2 ml) in the presence of anhydrous sodium acetate (0.05 g) for 2 hr. After usual work-up, the crude product was crystallized from benzene–petroleum ether to get the *O*-acetate (**9**, 94 mg): mp 164–165°; ir 1750, 1220 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}N_2O_3$: C, 69.38; H, 4.80; N, 9.52. Found: C, 69.58; H, 5.06; N, 9.31.

Compound **8** under identical conditions afforded, in quantitative yield, the *O*-acetate **10**: mp 183–184° (benzene–petroleum ether); ir 1745, 1250 cm^{-1}.

Anal. Calcd for $C_{13}H_{14}N_2O_3$: C, 63.39; H, 5.74; N, 11.37. Found: C, 63.53; H, 5.67; N, 11.24.

2-Methyl-3-(*o*-hydroxymethylphenyl)-4-imino-5,5-diphenyloxazolidine (13) from 6 and 3. A solution of 1-acetyl-2-(1′-ethoxydiphenylmethyl)-4-quinazolinone (**6**, 1.3 g) in dry ethanol (20 ml) was refluxed for 5 hr with $NaBH_4$ (1.3 g) with constant stirring. The refluxing was continued for 4 hr more after further addition of borohydride (1.3 g). Most of the alcohol was distilled off under reduced pressure. The crude product (1.05 g) obtained after usual work-up was crystallized from methanol to get the unconverted starting material (0.3 g), mp 158–159°. The mother liquor on purification through chromatography and crystallization afforded **13** (0.60 g, 50%): mp 150–151°; ir ($CHCl_3$) 3525, 3300, 1650, 1582, 995 cm^{-1}; nmr (100 MHz) δ 1.52 (d, 3, $CH-CH_3$, J = 6 Hz), 2.33 (br, 1, –OH), 4.3 and 4.38 (pair of AB doublets, 1 H each, $-CH_2-$, J_{AB} = 13 Hz), 5.67 (q, 1, $CH-CH_3$, J = 6 Hz), 6.8–8.3 (m, 15, ArH and =NH); *m/e* (rel intensity) 358 (M^+, 100), 343 (5), 340 (1), 325 (4), 314 (4), 297 (11), 295 (5), 283 (4), 210 (48), 209 (52), 193 (5), 182 (2), 176 (12), 167 (23), 166 (84), 165 (55), 158 (9), 152 (2), 147 (3), 134 (7), 133 (7), 132 (7), 131 (6), 122 (7), 105 (27), 77 (11).

Anal. Calcd for $C_{23}H_{22}N_2O_2$: mol wt, 358.167480. Found by high resolution mass spectrometry: mol wt, 358.167969.

Anal. Calcd for $C_{23}H_{22}N_2O_2$: C, 77.07; H, 6.19; N, 7.83. Found: C, 77.40; H, 6.35; N, 7.98.

Compound **3** (0.1 g) was also refluxed with $NaBH_4$ (0.2 g) in dry ethanol (10 ml) for 6 hr. The crude oily product (85 mg) on chromatographic resolution gave **13** (50 mg), mp 150–151°, and the unconverted starting material (30 mg), mp 164–165°.

Acetylation of 13 to *O,N*-diacetate (15). Acetic anhydride (0.5 ml) was added to a solution of **13** (0.1 g) in pyridine (0.2 ml) and kept overnight at room temperature. Usual work-up gave an oil which on chromatography afforded the diacetate **15** (95 mg) as a glass: ir 1735, 1680, 1650 sh cm^{-1}; *m/e* (rel intensity) 442 (M^+, 28), 400 (12), 385 (2), 369 (2), 357 (10), 340 (2), 325 (3), 313 (7), 297 (13), 295 (9), 280 (3), 260 (3), 210 (92), 209 (96), 182 (3), 175 (11), 166 (100), 165 (99), 158 (12), 132 (35), 105 (33), 77 (21).

Catalytic Hydrogenation of 13 to 14. Oxazolidine **13** (0.3 g) in ethylacetate (12 ml) containing five drops of perchloric acid was hydrogenated in the presence of 10% Pd/C (75 mg) for 1.5 hr. After filtration, the filtrate was washed successively with dilute ammonia and water, and the solvent was evaporated. The crude product (0.28 g) was crystallized from petroleum ether to get **14** (0.24 g, 84%) as colorless plates: mp 122–123°; ir ($CHCl_3$) 3420, 1650, 1582, 1345 cm^{-1}; nmr δ 1.61 (d, 3, $CH-CH_3$, J = 5.5 Hz), 1.89 (s, 3, $-CH_3$), 5.7 (q, 1, $CH-CH_3$, J = 5.5 Hz), 5.87 (br, 1, =NH), 6.7–8.3 (m, 14, ArH); *m/e* (rel intensity) 342 (M^+, 33), 327 (14), 299 (8), 298 (7), 297 (7), 283 (6), 210 (59), 209 (70), 193 (9), 182 (7), 175 (5), 166 (100), 165 (96), 160 (10), 152 (7), 132 (14), 118 (66), 105 (65), 91 (35), 77 (62).

Anal. Calcd for $C_{23}H_{22}N_2O$: C, 80.67; H, 6.48. Found: C, 80.80; H, 6.81.

Acetylation of 14 to *N*-Monoacetate (16). Compound **14** (50 mg) was heated on a steam-bath with acetic anhydride (1 ml) and

pyridine (0.5 ml) for 2 hr. After work-up, the crude product was crystallized from benzene–petroleum ether to give the acetate **16** (35 mg) in needles: mp 148–149°; ir 1680, 1650 sh cm^{-1}; nmr (100 MHz) δ 1.68 (d, 3, CH–C**H**$_3$, J = 5.5 Hz), 1.74 (s, 3, –CH_3), 2.34 (s, 3, N–CO–CH_3), 5.4 (q, 1, C**H**–CH_3, J = 5.5 Hz), 6.5–7.5 (m, 14, ArH); *m/e* (rel intensity) 384 (M^+, 51), 342 (2), 327 (2), 297 (9), 280 (3), 210 (92), 209 (94), 202 (3), 194 (8), 182 (2), 175 (3), 166 (100), 165 (95), 159 (30), 152 (3), 132 (4), 118 (8), 116 (31), 105 (34), 91 (25), 77 (24).

Anal. Calcd for $C_{25}H_{24}N_2O_2$: mol wt, 384.18376. Found by high resolution mass spectrometry: mol wt, 384.18229.

Attempted Hydrolysis of 13 and 14. Compounds **13** and **14** were recovered unchanged after refluxing with 5% ethanolic HCl or KOH for 2 hr.

Acknowledgment. The authors are grateful to Dr. K. Nagarajan, CIBA Research Centre, Bombay, and Dr. Nitya Anand, CDRI, Lucknow, for the 60-MHz nmr spectra, to Dr. L. J. Durham and Dr. A. Duffield, Stanford University, California, and Dr. C. E. Hignite, M.I.T., Cambridge, for 100-MHz nmr spectra and high resolution mass spectra, to Dr. F. W. Wehrli, Varian AG, Switzerland, for the temperature-dependant nmr spectra, and to CSIR, New Delhi, for a Senior Research Fellowship to A.K.C.

Registry No.—**1,** 18963-82-1; **2,** 18963-83-2; **3,** 52827-39-1; **5,** 52827-40-4; **6,** 52827-41-5; **7,** 13182-44-0; **8,** 52827-42-6; **9,** 13182-40-6; **10,** 52827-43-7; **13,** 52827-44-8; **14,** 52827-45-9; **15,** 52827-46-0; **16,** 52827-47-1; *N*-acetylanthranilic acid, 89-52-1.

References and Notes

(1) Paper VI: S. C. Pakrashi and A. K. Chakravarty, *Indian J. Chem.*, **11,** 122 (1973).
(2) Pool Officer, CSIR, New Delhi.
(3) S. C. Pakrashi and A. K. Chakravarty, *Chem. Commun.*, 1443 (1969).
(4) S. C. Pakrashi, J. Bhattacharyya, and A. K. Chakravarty, *Indian J. Chem.*, **9,** 1220 (1971).
(5) S. C. Pakrashi and A. K. Chakravarty, *J. Org. Chem.*, **37,** 3143 (1972).
(6) S. C. Pakrashi, J. Bhattacharyya, L. F. Johnson, and H. Budzikiewicz, *Tetrahedron*, **19,** 1011 (1963).
(7) L. S. Rattet, L. Mandell, and J. H. Goldstein, *J. Amer. Chem. Soc.*, **89,** 2253 (1967).
(8) D. Nasipuri and A. Bhattacharya, *Indian J. Chem.*, **10,** 799 (1972), and the references cited therein.
(9) W. J. Irwin, *J. Chem. Soc., Perkin Trans. 1,* 353 (1972).
(10) S. C. Pakrashi, S. Chattopadhyay, and A. K. Chakravarty, Abstract of the 8th International Symposium on the Chemistry of Natural Products, Feb 6–12, New Delhi, 1972, p 49.
(11) H. G. Ballé, P. Cerutti, and B. Witkop, *J. Amer. Chem. Soc.*, **88,** 3946 (1966).
(12) Y. Kondo and B. Witkop, *J. Amer. Chem. Soc.*, **90,** 764 (1968).
(13) P. Cerutti, Y. Kondo, W. R. Landis, and B. Witkop, *J. Amer. Chem. Soc.*, **90,** 771 (1968).
(14) Y. Kondo and B. Witkop, *J. Org. Chem.*, **33,** 206 (1968).
(15) All melting points were determined in open capillaries and are uncorrected. Unless otherwise stated, the nmr spectra were recorded in a 60-MHz Varian instrument in $CDCl_3$ with TMS as internal standard, and ir spectra were taken in Nujol mull in a Perkin-Elmer Infracord spectrophotometer (Model 137). Silica gel was used throughout for column chromatography and anhydrous Na_2SO_4 as the drying agent. Microanalyses were done by Dr. R. D. Macdonald, Micro-Analytical Laboratory, University of Melbourne, Australia.

Electrochemical Reductive Acylation of Benzophenone[1]

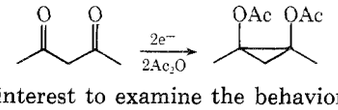
T. J. Curphey,* L. D. Trivedi, and T. Layloff

Department of Chemistry, St. Louis University, St. Louis, Missouri 63156

Received August 14, 1974

Polarographic and cyclic voltammetric studies of benzophenone in acetonitrile were carried out in the presence and absence of acetic anhydride, using tetraethylammonium bromide or perchlorate as supporting electrolytes. From the variation of pertinent parameters in these studies and from the known electrochemical behavior of benzophenone, a mechanism is proposed for the reduction of benzophenone in the presence of acetic anhydride. The results of controlled potential electrolysis substantiate the proposed mechanism.

There are many examples in the literature of electroorganic synthesis, defined as the transformation of one organic molecule into another by the action of an electric current.[2] In a number of cases involving cathodic processes, a radical anion produced by initial electron transfer undergoes followup chemical reactions in which one or more protons are abstracted from the reaction medium. We have for some time been interested in generating reactive species electrochemically and in studying their reactions with reagents other than proton donors. Our initial foray into this area[3] involved the reduction of 1,3-diketones in aprotic solvents in the presence of acetic anhydride, which led ultimately to the formation of 1,2-cyclopropanediol diacetates (eq 1), the products of intramolecular pinacol reduction. It



(1)

was of some interest to examine the behavior of monoketones under similar conditions, and this paper reports the results of our investigation of benzophenone.

Electrochemical reduction of aromatic carbonyl compounds in aqueous and aprotic media has been extensively studied.[4–16] In particular there have been studies of the electrochemical reduction of benzophenone in dimethylformamide[12–14,16] and in pyridine.[15] These studies have shown that in aprotic solvents benzophenone undergoes an initial one electron reduction to form an anion radical intermediate **1.** Further reduction results in the formation of dianion **2.** Utilizing the techniques of polarography, cyclic voltammetry (CV), and large-scale controlled potential electrolysis, we have now studied the electrochemical behavior of benzophenone in acetonitrile containing acetic anhydride with tetraethylammonium bromide (TB) or perchlorate (TP) as the supporting electrolyte. As a result of these studies, we propose the following reaction scheme for the reduction of benzophenone under these conditions.

$$Ph_2C{=}O + e^- \longrightarrow \underset{\mathbf{1}}{[Ph_2C\text{-}O]^{\cdot -}}$$

$$\mathbf{1} + e^- \longrightarrow \underset{\mathbf{2}}{Ph_2\bar{C}\text{-}\bar{O}}$$

$$Ph_2C{=}O + e^- \longrightarrow \mathbf{1} \xrightarrow{Ac_2O} \underset{\mathbf{3}}{Ph_2\dot{C}\text{-}OAc}$$

$$\mathbf{3} + e^- \longrightarrow \underset{\mathbf{4}}{Ph_2\bar{C}\text{-}OAc} \xrightarrow{Ac_2O} \underset{\mathbf{5}}{Ph_2C(COCH_3)\text{-}OAc}$$