Reduction of 1.—Stirred together in 100 ml of toluene and in an atmosphere of hydrogen was 0.3 g (0.6 mmol) of 1 and 0.7 g of 5% palladium on charcoal. After only 18.2 ml (0.81 mmol) of H_2 had been taken up, the reaction was stopped, the mixture was filtered, and the filtrate was evaporated to an orange mass which was chromatographed on acid-washed alumina. Three bands were eluted with toluene which were, in order of elution, 1 (trace); 0.1 g of decachlorohydrazobenzene (**3**); and 0.15 g of pentachloroaniline. **3** recrystallized from toluene as light yellow needles which darkened to a copper color at 150° and at 195° began to disproportionate to pentachloroaniline (identified by ir and melting point) and to a red liquid (1). Spectral data for **3**: ir (mull) 2.92 (w), 6.28 (m), 7.08 (m), 7.28 (w), 7.45 (br m), 7.58 (m), 13.16 (br), 13.60 μ (br, w).

Anal. Calcd for $C_{12}H_2Cl_{10}N_2$: C, 27.23; H, 0.38. Found: C, 27.13; H, 0.19.

Reduction of 2.—A solution of 0.5 g (0.9 mmol) of **2** dissolved in 80 ml of benzene and 40 ml of toluene was stirred with 1 g of 5% palladium on charcoal in an atmosphere of H_2. Hydrogen uptake was very slow and, after 26 hr, the reaction was worked up as described above to yield 0.45 g of a white solid, melting between 160 and 240° and containing only a small amount of **3**. The solid was mainly pentachloroaniline as determined by ir spectroscopy.

Pentachloronitrosobenzene (4).—A two-phase liquid system containing 5.0 g (19 mmol) of pentachloroaniline, 20 ml of 90% formic acid, 100 ml of chloroform, and 5 ml of 98% hydrogen peroxide was stirred under reflux for 6 hr. After the deep green mixture cooled, white granular crystals settled and were collected. The green filtrate was washed with water, dried, and evaporated to yield 3.4 g of crude pentachloroaniline. The filtered crystals, after recrystallization from toluene, afforded 1.5 g (30% conversion) of **4**: mp 168–170°; ir (mull) 6.70 (w), 7.41 (s), 7.75 (s), 8.19 (m), 8.85 (w), 10.40 (w), 12.60 (w), 13.92 μ (s).

Anal. Calcd for C_6Cl_5NO: C, 25.78; Cl, 63.48. Found: C, 26.09; Cl, 63.57.

A. Typical Condensation of 4 with an Amine.—A solution of 1.0 g (3.6 mmol) of **4**, 0.64 g (5.0 mmol) of 4-chloroaniline, and 70 ml of glacial acetic acid was refluxed for 3 hr. Water was added to the reaction mixture and the precipitated solid was collected *via* suction filtration. Elution of this material with benzene on a column (1 × 22 in.) of acid-washed alumina (110 g) produced 0.74 g (53%) of 2,3,4,4′,5,6-hexachloroazobenzene and 0.25 g (25%) of pentachloroaniline. The product was recrystallized from ethanol: mp 168–170°; uv max (EtOH) 212 nm (ϵ 31,300), 226 (sh, 23,000), 307 nm (14,300); ir (mull) 6.35 (w), 6.73 (m), 7.13 (m), 7.44 (s), 7.61 (m), 8.71 (m), 9.11 (m), 9.90 (m), 11.30 (m), 12.00 (s), 13.72 (m), 13.85 (m), 13.92 μ (s).

An Improved Condensation of 4 with Aniline.—Aniline (0.5 g, 5 mmol) was added rapidly to a solution of 1.0 g (3.6 mmol) of **4** and 50 ml of toluene–acetic acid solution (4% glacial acetic acid in toluene) maintained at 40°. After 18 hr the reaction temperature was increased slowly to 75° over an additional 12-hr period. Evaporation of the solvent gave a red solid, which was chromatographed twice (acid-washed alumina, benzene). Obtained was 1.08 g (85%) of 2,3,4,5,6-pentachloroazobenzene: mp 117–118°; uv max (EtOH) 215 nm (ϵ 24,000), 229 (23,000), 293 (12,600); ir (mull) 3.28 (w), 6.71 (m), 7.44 (s), 7.65 (m), 8.15 (m), 8.70 (s), 11.28 (m), 12.88 (m), 13.10 (s), 13.78 (m), 13.95 (m), 14.72 (s), 15.05 μ (vr).

A Typical Oxidation of the 2,3,4,5,6-Pentachloroazobenzenes.—A two-phase liquid system of 0.3 g (0.85 mmol) of 2,3,4,5,6-pentachloroazobenzene, 3 ml of trifluoroacetic anhydride, 2 ml of 98% hydrogen peroxide, and 20 ml of $CHCl_3$ was stirred at reflux for 2 hr. The red solution faded to a light yellow almost immediately. On cooling, the mixture was washed with water; the organic layer separated and was evaporated to give 0.3 g (96% yield) of crude 2,3,4,5,6-pentachloroazoxybenzene. The product was recrystallized three times from hexane as fine, yellow needles: mp 148–150°; uv max (EtOH) 214 nm (ϵ 50,000), 260 (11,900); ir (mull) 6.99 (s), 7.43 (s), 12.92 (s), 13.85 (s), 14.90 μ (s).

Pentadeuterioazo- and -azoxybenzenes.—Pentadeuteronitrosobenzene (obtained from Merck Sharp and Dohme of Canada Ltd.) was condensed with the appropriately substituted aniline in acetic acid–benzene solution. The resulting pentadeuterioazobenzenes were oxidized in chloroform with peracetic acid solution, prepared from glacial acetic acid and 98% hydrogen peroxide. The α and β isomers of each azoxy mixture were partially resolved by elution chromatography on alumina and brought to constant melting point by repeated recrystallizations (methanol) of the initial and final chromatographic fractions.

Registry No.—**1**, 35159-27-4; **2**, 35159-28-5; **3**, 35191-77-6; **4**, 13665-49-1; pentachloroaniline, 527-20-8.

Acknowledgment.—The authors are indebted to the Allied Chemical Corp. for financial support of the work and to R. G. Cooks for his assistance with the mass spectra interpretation.

Studies on 4-Quinazolinones. V.[1] Reductive Ring Cleavage by Metal Hydrides

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Metal hydride reductions of some substituted 4-quinazolinones have been studied under various conditions. Though the reduction was found to be facile in the *N*-methylated compounds under ordinary conditions irrespective of the substitution at position 2, the C=N function in those with a free NH group proved to be extremely resistant to the reducing agents and led to unusual products under forcing condition. 2,3-Disubstituted 4-quinazolinones and only the 3-phenyl derivative among the monosubstituted ones studied underwent ring cleavage at the bond between C_2 and the tertiary nitrogen. Reduction of the carbonyl group could only be brought about by lithium aluminum hydride in tetrahydrofuran under reflux in all cases.

While the carbonyl function of indoloquinazolinones is known[3] to be fully reduced by lithium aluminum hydride at room temperature, 1-methyl-2-benzyl-4-quinazolinone (**1**), a naturally occurring alkaloid[4] known as arborine, under the same condition afforded[5] only its 2,3-dihydro derivative **2**. We therefore investigated the metal hydride reduction of a series of variously substituted simple 4-quinazolinones under different conditions, and the results are summarized in Scheme I.

The reduction of 2-benzyl-3-methyl-4-quinazolinone (**3a**) with the same reagent at room temperature re-

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(2) Senior Research Fellow, CSIR, New Delhi.

(3) I. J. Pachter, R. F. Raffauf, C. E. Ullyot, and O. Ribeiro, *J. Amer. Chem. Soc.*, **82**, 5187 (1960).

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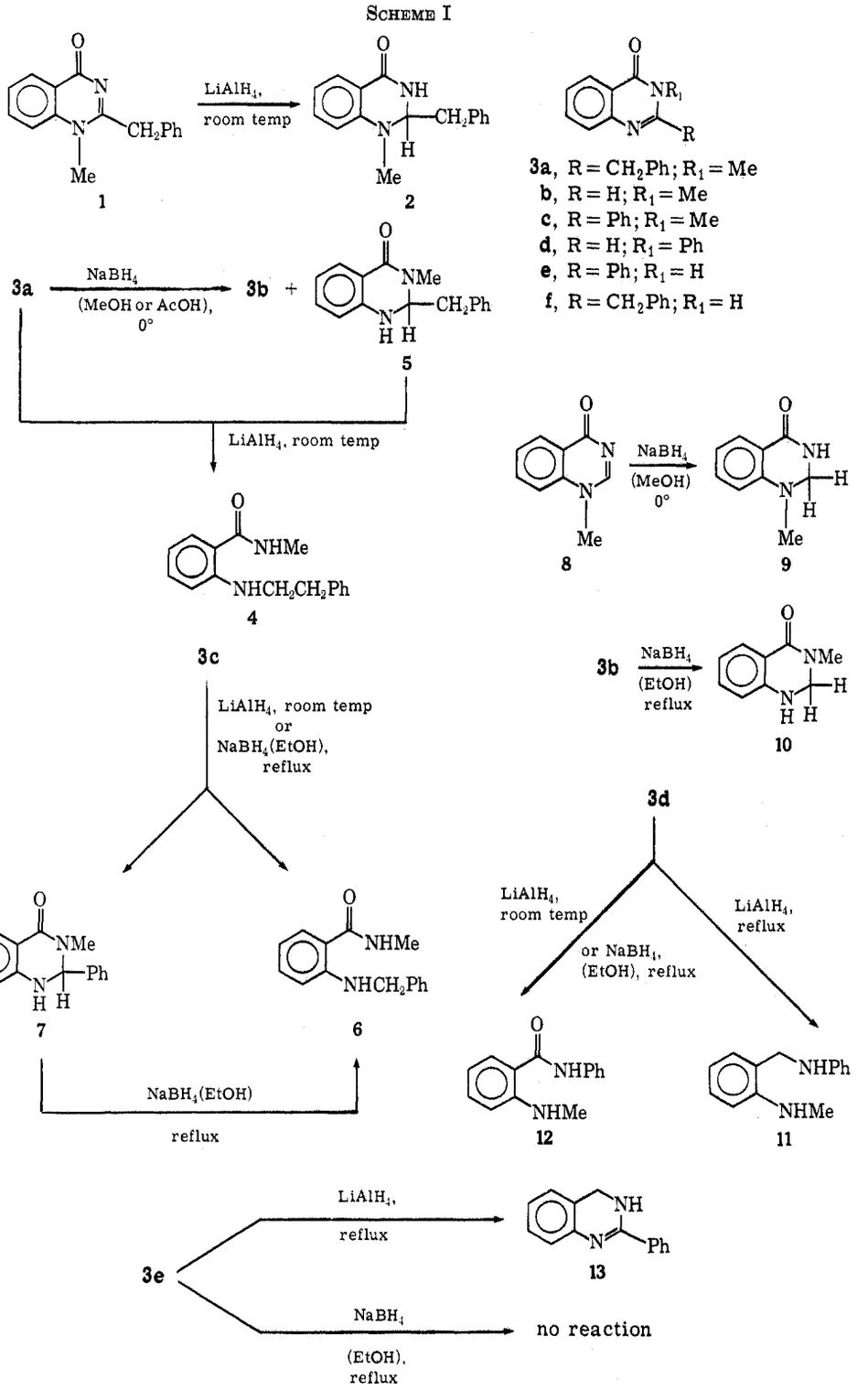
(5) A. Chatterjee and S. Ghosh Mazumdar, *J. Amer. Chem. Soc.*, **76**, 2459 (1954).

SCHEME I



sulted in the fission of the 2,3 bond with retention of the carbonyl function leading to *o*-(β-phenylethylamino)-*N*-methylbenzamide (**4**) in 55% yield. The same compound was, however, obtained with the same reagent in better yield in a shorter period from the 1,2-dihydro derivative **5** prepared by catalytic hydrogenation of **3a**. The structure of **4** was ascertained from its ir and nmr spectra and confirmed by its synthesis from *o*-amino-*N*-methylbenzamide and β-phenylethyl chloride in the presence of potassium carbonate.

The sodium borohydride reduction of **3a** in methanol at 0°, however, provided an interesting case of C_2-debenzylation leading to 3-methyl-4-quinazolinone (**3b**) in 15% yield. The mechanism of this unusual reaction has already been suggested by us[6] and recently corroborated by Finch and Gschwend.[7]

2-Phenyl-3-methyl-4-quinazolinone (**3c**) on lithium aluminum hydride reduction at room temperature afforded both 2,3-bond cleaved product, *viz.*, *o*-benzylamino-*N*-methylbenzamide (**6**, 60%), and the 1,2-dihydro derivative (**7**, 4%). The structure **6** was confirmed by its synthesis.

(6) S. C. Pakrashi and A. K. Chakravarty, *Chem. Commun.*, 1443 (1969).
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On the other hand, the reduction of **3c** with sodium borohydride in ethanol under reflux afforded both **6** and **7** in 44 and 54% respective yields. The higher yield of compound **6** was, however, obtained when the dihydro derivative **7** itself was treated with sodium borohydride.

It was therefore apparent that the reduction with both the metal hydrides must involve similar mechanisms and that the ring cleavage proceeds *via* the intermediacy of the dihydro derivatives.

The reduction of 1-methyl-4-quinazolinone (**8**) and 3-methyl-4-quinazolinone (**3b**) with lithium aluminum hydride under reflux has been reported[8] to yield the corresponding 1,2,3,4-tetrahydroquinazolines. Sodium borohydride reduction, however, afforded the respective dihydro derivatives (**9** and **10**) even on refluxing in ethanol in the case of **3b**.

3-Phenyl-4-quinazolinone (**3d**) has recently been reported[9] to yield *o*-methylamino-*N*-phenylbenzylamine (**11**) by lithium aluminum hydride treatment under unspecified conditions. In our hands, it suffered very facile reductive cleavage of the 2,3 bond by the same reagent at room temperature, forming *o*-methylaminobenzanilide (**12**) in quantitative yield. Under refluxing condition, **11** was indeed obtained as the major product. Sodium borohydride reduction of **3d** in ethanol under reflux also afforded **12** in *ca.* 70% yield. Thus, we could also confirm the facile reductive ring cleavage of 3-aryl-4-quinazolinones reported by other workers.[9,10]

The results of metal hydride reduction of 4-quinazolinones with no substituent at either of the nitrogen atoms proved to be more interesting. Thus, while 2-phenyl-4-quinazolinone (**3e**) remained unaffected with sodium borohydride, lithium aluminum hydride under reflux led to the reduction of the carbonyl function to give 2-phenyl-3,4-dihydroquinazoline (**13**) in 46% yield rather than effecting ring rupture or reduction of 1,2 double bond. The structure **13** was supported by the nmr signals at δ 4.72 for a CH_2, at δ 5.67 (exchangeable with deuterium) for a NH, and a multiplet at δ 6.75–7.90 for nine aromatic protons and the disappearance of the ir bands at 1665 and 1680 cm^{-1}.

On the other hand, it has already been shown[1] by us that 4-quinazolinone itself and its 2-benzyl derivative (**3f**) remained unaffected under conditions in which 2-benzyl-3-methyl-4-quinazolinone (**3a**) readily yielded its 1,2-dihydro derivative **5** and the ring-cleaved product **4**, while under reflux with lithium aluminum hydride in tetrahydrofuran **3f** underwent an abnormal oxidation at the benzylic methylene group.

It is thus apparent from the foregoing data that, while its reduction was facile in *N*-methylated 4-quinazolinones, with or without substituents at position 2, C=N was extremely resistant to reducing agents in those with free NH. It therefore appeared likely that the reduction to dihydro derivative proceeds *via* a quinazolinium cation[11,12] (Scheme II) in analogy[13,14] to the reduction of *N*-alkylpyridinium salts by metal hydride to 1,2-dihydropyridines. In any case, however, the carbonyl group at position 4 could be reduced only by lithium aluminum hydride treatment under forcing conditions with or without concomitant cleavage of the hetero ring, depending on the substitution pattern. Thus, our results show that, with the exception of 3-phenyl compound **3d**, the other monosubstituted 4-quinazolinones (**3b**, **8**, or **3e**) did not suffer ring rupture, contrary to the claim by Gelling, *et al.*,[9] for the compound **3e**. On the other hand, the reductive cleavage of 2,3-disubstituted and 3-phenyl derivatives occurred at the bond between C_2 and the tertiary nitrogen atom. A similar observation was made by Larizza, *et al.*,[15] with secondary tertiary diamines.

Though the mechanism has already been suggested,[9] using different metal hydrides and by variation of reaction conditions, we could clearly show that the ring rupture (retaining the carbonyl function) of 2,3-disubstituted 4-quinazolinones requires the intermediacy of the dihydro derivative[16] by either lithium aluminum hydride at room temperature or sodium borohydride in ethanol under reflux. Nevertheless, the reason for difference in ring opening between mono- or disubstituted or 2-phenyl substituted derivatives is not clear. However, primary reduction of C=N and adequate stabilization of the anion at N-3, apparently necessary for the cleavage of the 2,3 bond of 2,3-disubstituted 4-quinazolinones, would also explain why only 3-phenyl-4-quinazolinone (**3d**) among the monosubstituted derivatives studied undergoes facile cleavage.

On the other hand, the formation of quinazolinium cation being not favored in compounds with a free NH group, the preferred site for hydride attack would be the amide carbonyl function leading to 3,4-dihydroquinazoline derivatives.

Experimental Section[17]

General Procedure for Lithium Aluminum Hydride Reductions.—Unless otherwise mentioned, solutions of 4-quinazolinones in dry and freshly distilled tetrahydrofuran (100 ml/g of quinazolinone) were added dropwise to a magnetically stirred slurry of powdered lithium aluminum hydride in the same solvent (100 ml/g of hydride). The reaction mixture was then stirred at room temperature or refluxed, as the case may be, for a specified period. The complex was decomposed with water and worked up in the usual way.

Reduction of 2-Benzyl-3-methyl-4-quinazolinone (3a). A. With Lithium Aluminum Hydride.—The compound **3a** (0.25 g) was treated with lithium aluminum hydride (0.5 g) at room temperature for 3 hr. The oily product (0.25 g) was chromatographed. The fractions eluted with benzene (200 ml) on crystallization yielded *o*-(β-phenylethylamino)-*N*-methylbenz-

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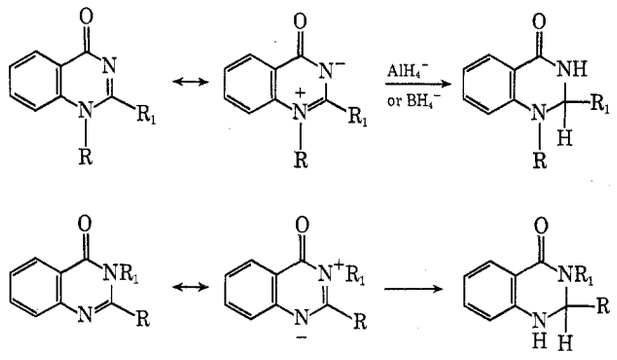
(16) The intermediacy of the dihydro derivative was also shown by Okumura, *et al.*,[10] who observed that the reductive cleavage of the 2,3 bond of 2-methyl-3-phenyl-4-quinazolinone by sodium borohydride is more facile in its 1,2-dihydro form.

(17) All melting points were recorded in open capillaries and are uncorrected. Silica gel was employed throughout for column chromatography and benzene–petroleum ether (bp 60–80°) was mostly used for crystallization. The nmr spectra were recorded on a 60-MHz Varian instrument in $CDCl_3$ and the chemical shifts are expressed in parts per million from TMS as internal standard. The infrared spectra were determined in Nujol mull on a Perkin-Elmer Infracord Model 137. The homogeneity of the compounds was ascertained by tlc on 0.3-mm silica gel G plates using chloroform–ethyl acetate–formic acid (5:4:1) and benzene–ethyl acetate–petroleum ether (5:3:2) as the solvent systems. The spots were located by exposing the dried plates to iodine vapor. Unless otherwise stated, the products were identified by direct comparison with authentic specimens.

SCHEME II



amide (4) as long needles (0.14 g, 55%): mp 113°; ir 3330 (NH), 1645, and 1635 cm^{-1} (C=O); nmr δ 2.9 (d, 3, $-NHCH_3$, J = 5 Hz), 2.93 and 3.38 (m, 2 H each, $-CH_2CH_2-$), 6.13 (br, 1, $-NHCH_2-$), 6.4–7.45 (m, 9, ArH).

Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.56; H, 7.14; N, 11.03. Found: C, 75.55; H, 7.20; N, 11.06.

Hydrogenation of 3a to 5.—The compound **3a** (0.2 g) in absolute alcohol (15 ml) was stirred in an atmosphere of hydrogen in the presence of Pd/C (10%) for 15 hr. The oily product on crystallization afforded 1,2-dihydro-2-benzyl-3-methyl-4-quinazolinone (**5**, 0.13 g), mp 140–141° in 65% yield: ir 3265 (NH), 1630 (C=O), 1610 cm^{-1}; nmr δ 2.98 (d, 2, $-CHCH_2-$, J = 7 Hz), 3.08 (s, 3, NCH_3), 4.63 (t, 1, $-CHCH_2-$, J = 7 Hz), 4.42 (br, 1, -NH), 7.87 (dd, 1, C_5 H, J = 8, 2 Hz), 6.4–7.4 (m, 8, ArH).

Anal. Calcd for $C_{16}H_{16}N_2O$: C, 76.16; H, 6.40; N, 11.12. Found: C, 76.41; H, 6.65; N, 11.03.

Lithium Aluminum Hydride Reduction of 5 to 4.—The dihydro derivative **5** (75 mg) was reduced with lithium aluminum hydride (0.15 g) at room temperature for 0.5 hr. The oily product on crystallization afforded **4** in 73% yield.

Preparation of *o*-(β-Phenylethylamino)-*N*-methylbenzamide (4).—*o*-Amino-*N*-methylbenzamide (0.75 g) was refluxed with β-phenyl ethyl chloride (1.5 ml) in 5% aqueous alcoholic potassium carbonate (20 ml) for 16 hr. The reaction mixture was cooled, diluted with water (50 ml), and extracted with chloroform. The chloroform extract was evaporated and the residue was taken up in ether (20 ml) and extracted with 2 *N* HCl (4 × 30 ml). The acid extract was basified (Na_2CO_3) and again extracted with chloroform. The crude product could not be induced to crystallize and purification by chromatography over silica gel yielded **4** (0.15 g, 12%), mp 112–113°, besides the starting material.

Reduction of 2-Phenyl-3-methyl-4-quinazolinone (3c). A. With Lithium Aluminum Hydride.—Compound **3c** (0.3 g) was treated with lithium aluminum hydride (0.6 g) at room temperature for 1.5 hr. The product (0.28 g) on crystallization yielded *o*-benzylamino-*N*-methylbenzamide (**6**) in shining flakes (0.1 g): mp 125–126°; ir 3305 (NH), 1632 (C=O), 1600 cm^{-1}; nmr δ 2.92 (d, 3, $-NHCH_3$, J = 5.2 Hz), 4.38 (s, 2, $-CH_2-$), 5.97 (br, 1, $-NHCH_2-$), 7.93 (br, 1, -CONH-), 6.35–7.4 (m, 9, ArH).

Anal. Calcd for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.72; N, 11.67. Found: C, 74.60; H, 6.82; N, 11.16.

The mother liquor on chromatography afforded more of **6** (80 mg, total yield 60%) along with 1,2-dihydro derivative **7** (12 mg, 4%), mp 165–166°.

B. With Sodium Borohydride.—The metal hydride (1 g) was added to an ethanolic solution (15 ml) of **3c** (0.3 g) and refluxed for 5 hr. The oily product (0.3 g) was chromatographed. The fraction eluted with 50% benzene in petroleum ether (500 ml) on crystallization furnished **6** (44%), mp 125–126°.

Further elution (400 ml) with benzene–chloroform (1:1) afforded **7** crystallizing in needles (0.16 g, 54%): mp 165–166°; ir 3250 (NH), 1630 (C=O), 1610 cm^{-1} (sh); nmr δ 2.85 (s, 3, $-NCH_3$), 4.8 (br, 1, -NH), 5.67 (s, 1, C_2 H), 7.88 (dd, 1, C_5 H, J = 8, 2 Hz), 6.4–7.4 (m, 8, ArH).

Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.93; N, 11.77. Found: C, 75.97; H, 6.25; N, 11.63.

Sodium Borohydride Reduction of 7 to 6.—The dihydro derivative **7** (50 mg) was treated with sodium borohydride (0.1 g) in ethanol (5 ml) under reflux for 3 hr. Usual work-up, chromatography, and crystallization of the product afforded **6** (30 mg) in 60% yield.

Preparation of *o*-Benzylamino-*N*-methylbenzamide (6).—*o*-Amino-*N*-methylbenzamide (0.65 g) was refluxed in 5% aqueous alcoholic KOH (20 ml) with benzyl chloride (1.5 ml) for 20 hr. It was cooled, diluted with water (50 ml), and extracted with chloroform, and the organic extract was evaporated. From the crude mixture, the amine was separated by extraction of ethereal solution with 2 *N* HCl. The base on regeneration was extracted with chloroform. The crude product on crystallization yielded **6** (0.45 g, 45%) in shining flakes, mp 125–126°, identical in all respects with the reduction product.

Sodium Borohydride Reduction of 1-Methyl-4-quinazolinone (8).—Reduction of **8** (0.1 g) with sodium borohydride (0.5 g) in dry methanol (5 ml) was carried out at 0° and the oily product (60 mg) was converted to its picrate, crystallizing out of alcohol in golden yellow flakes, mp 245° dec. The base, regenerated through IRA-400 ion-exchange resin, on repeated crystallizations afforded the 2,3-dihydro derivative **9** in prisms (40 mg, 40%): mp 112°; ir ($CHCl_3$) 3415 and 3200 (NH), 1680–1640 cm^{-1} (broad, C=O); nmr δ 2.83 (s, 3, $-NCH_3$), 4.41 (d, 2, $-CH_2-$, J = 3 Hz), 6.68 (d, 1, C_8 H, J = 8 Hz), 6.88 (dt, 1, C_6 H, J = 7, 1 Hz), 7.41 (octet, 1, C_7 H, J = 8, 7, 2 Hz), 7.93 (dd, 1, C_5 H, J = 8, 2 Hz), 8.15 (br, 1, -CONH-).

Anal. Calcd for $C_9H_{10}N_2O$: C, 66.64; H, 6.22; N, 17.29. Found: C, 66.34; H, 6.01; N, 17.40.

Sodium Borohydride Reduction of 3-Methyl-4-quinazolinone (3b).—The compound **3b** (0.2 g) was reduced in ethanol (15 ml) with sodium borohydride (0.5 g) under reflux for 3 hr. The oily product (0.185 g) on repeated crystallizations furnished 1,2-dihydro derivative **10** in long needles (0.156 g, 78%): mp 115° (lit.[18] mp 115°); ir 3230 (NH), 1660–1610 cm^{-1} (broad, C=O); nmr δ 3.03 (s, 3, $-NCH_3$), 4.57 (s, 2, $-CH_2-$), 4.77 (br, 1, NH), 7.85 (dd, 1, C_5 H, J = 7.5, 2 Hz), 6.5–7.4 (m, 3, ArH).

Anal. Calcd for $C_9H_{10}N_2O$: C, 66.64; H, 6.22; N, 17.29. Found C, 66.70; H, 6.26; N, 16.95.

Reduction of 3-Phenyl-4-quinazolinone (3d). A. With Lithium Aluminum Hydride.—Compound **3d** (0.25 g) was reduced with lithium aluminum hydride (0.5 g) at room temperature for 1 hr. The oily product (0.25 g) on crystallization afforded long needles (0.20 g, 80%) of *o*-methylaminobenzanilide (**12**): mp 125–126°; ir 3375 and 3200 (NH), 1640 (sh) and 1630 cm^{-1} (C=O); nmr δ 2.82 (s, 4, $-NHCH_3$), 7.82 (br, 1, -CONH-), 6.4–7.65 (m, 9, ArH).

Anal. Calcd for $C_{14}H_{14}N_2O$: C, 74.40; H, 6.24; N, 12.40. Found: C, 74.80; H, 6.28; N, 12.19.

Compound **3d** (0.3 g) was treated with the same reagent (1 g) under reflux for 6 hr. The oily product (0.29 g) on repeated chromatography yielded, besides **12** (0.05 g, 13%), a homogeneous oil (0.19 g, 63%) characterized as *o*-methylamino-*N*-phenylbenzylamine (**11**): ir (thin film) 3325 and 3000 (NH), 1595 cm^{-1}; nmr δ 2.85 (s, 3, $-NHCH_3$), 3.92 (br, 2, two NH–), 4.2 (s, 2, $-CH_2-$), 6.5–7.5 (m, 9, ArH); mass spectrum *m/e* (rel intensity) 212 (M^+, 100), 211 (14), 197 (21), 195 (36), 121 (73), 120 (95), 119 (77), 106 (50), 105 (21), 104 (45), 93 (71), 92 (57), 91 (60), 78 (50), 77 (54).

B. With Sodium Borohydride.—Reduction of **3d** (35 mg) was carried out with sodium borohydride (70 mg) in ethanol under reflux for 2.5 hr. Usual work-up and repeated crystallizations yielded **12** (27 mg) in 77% yield.

Reduction of 2-phenyl-4-quinazolinone (3e).—Compound **3e** (0.5 g) was reduced with lithium aluminum hydride (1.5 g) under reflux for 6 hr. The solid product (0.43 g) was boiled with benzene and filtered. The residue (0.1 g) was the unconverted starting material. The filtrate on chromatographic resolution afforded a further amount (25 mg) of **3e** and 0.23 g (46%) of 2-phenyl-3,4-dihydroquinazoline (**13**) crystallizing in fine needles: mp 139° (lit.[19] mp 142–143°); ir 3180 (NH), 1580 cm^{-1}; nmr δ 4.72 (s, 2, $-CH_2-$), 5.67 (s, 1, -NH), 6.75–7.9 (m, 9, ArH).

Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.84; H, 5.82; N, 13.47. Found: C, 81.25; H, 6.08; N, 13.20.

Registry No.—**4**, 35042-12-7; **5**, 26750-20-9; **6**, 35042-14-9; **7**, 16285-32-8; **9**, 35042-16-1; **10**, 16353-

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02-9; **11**, 35042-18-3; **12**, 21258-59-3; **13**, 1904-73-0.

Acknowledgment.—The authors are indebted to Dr. Nitya Nand, Central Drug Research Institute, Lucknow, and to Dr. J. Chakravarty, formerly in Brookhaven National Laboratory, New York, for the nmr spectra and to Dr. R. D. Macdonald, Microanalytical Laboratory, University of Melbourne, Australia, for microanalyses.

Isomeric Diacetal and Dimethoxime Derivatives of Acenaphthenequinone

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Received March 6, 1972

The reactions of acenaphthenequinone (**1**) with ethylene glycol and methoxyamine were investigated. The acetalization reaction afforded the monoacetal (**2**), the normal diacetal (**3**), and the bisdioxane (**4**). The use of mass spectrometry to differentiate between structures **3** and **4** is outlined. The loss of $C_2H_4O_2$ from the molecular ion of **4** is diagnostic for the bisdioxane structure. The two isomeric methoximes were determined by nmr spectroscopy to have the symmetrical (**6**, *E,E*) and unsymmetrical (**8**, *E,Z*) structures.

In the course of some studies that required the protection of one or both carbonyl groups of acenaphthenequinone (**1**), we investigated the reaction of **1** with both ethylene glycol and methoxyamine, respectively. In each case, we were able to isolate and identify isomeric addition products, and these are the subject of this paper.

Ethylene Glycol Adducts.[1]—The condensation of an α diketone with ethylene glycol in the presence of acid, when investigated about 40 years ago, was found to give a mixture of two isomers. The structure of the products obtained with glyoxal sulfate[2] or *cis*- or *trans*-2,3-dichlorodioxane[3] and ethylene glycol was a matter of controversy until quite recently.[4,5] Of late, a renaissance of activity has taken place in this general area, both in the synthesis and the differentiation of the isomeric acetals.[6-10] We have directed our attention to the use of mass spectrometry[11] as a means of structural assignment.

The acid-catalyzed reaction of acenaphthenequinone (**1**) with an excess of ethylene glycol in benzene gave a tricomponent mixture that was separated by silica gel plate chromatography. The least polar component was identified as the monoacetal (**2**), on the basis of its ir spectrum (>C=O at 5.78 μ), elemental analysis, and mass spectrum. The low-resolution mass spectrum of **2** is shown in Figure 1. The composition of the M^+ at *m/e* 226 was confirmed by high-resolution techniques as $C_{14}H_{10}O_3$. The odd-electron ion at *m/e* 198, arising from the loss of the ketonic carbonyl as carbon monoxide, was ten times as abundant as the ion at *m/e* 198 resulting from the elimination of ethylene. The *m/e* 170 ion had the molecular composition $C_{11}H_6O_2$. The *m/e* 198 ion eliminated C_2H_4O to form the *m/e* 154 ion. Metastable-ion defocusing experiments[12,13] confirmed that the *m/e* 182 ion was also a precursor of the *m/e* 154 ion, although the precursor ion was present in only very small abundance. However, doubly charged ions at *m/e* 182, 154, and 126 were present. Although the elimination of carbon dioxide from the *m/e* 170 ion was expected, the double decarbonylation to form the *m/e* 142 and 114 ions was unexpected, especially since the loss of a nuclear carbon was involved. To explain this finding, we postulate that the ion resulting from the elimination of ethylene from the *m/e* 198 ion rearranged, in part, to 1,8-naphtholactone, which in turn decarbonylated in two steps to form the *m/e* 114 ion. Recently, Seibl described the fragmentation of 1,8-naphtholactone by a double decarbonylation in a similar manner.[14]

The material of intermediate polarity (mp 213.5-214°) and the most polar product (mp 147.5-148°) both analyzed satisfactorily for $C_{16}H_{14}O_4$. The mass spectrum of the low-melting isomer (**3**) is shown in Figure 2. Below *m/e* 200, the mass spectrum is very similar to that of the ketonic product (**2**). The doubly charged ions at *m/e* 182, 154, and 126 are, however, more prominent in the spectrum of **3**. As in **2**, it is believed that the *m/e* 170 ion exists as the 1,8-naphtholactone ion, from which two CO groups are eliminated successively. The *m/e* 198 ion may be formed in three different ways: (1) by loss of ethylene, followed by the elimination of carbon dioxide; (2) by loss of $C_3H_4O_2$;[15] and (3) by ring cleavage, with successive losses of $C_2H_3O\cdot$ and $CHO\cdot$. The chemical-ionization spectrum of the low-melting isomer (**3**) is shown in Figure 3. The base ion at *m/e* 183 was probably protonated acenaphthenequinone, which had been formed through the consecutive elimination of two C_2H_4O moieties from the protonated molecular ion (MH^+) at *m/e* 271. These data for the low-melting

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