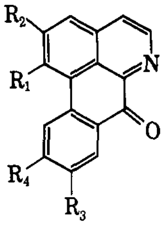
plished by Clemmensen reduction[6,11] of either liriodenine itself to *dl*-anonaine or its methiodide to *dl*-roemerine.

In our studies on the reduction of this type of substituted heterocycle, we have observed that catalytic hydrogenation of 1,2,9,10-tetramethoxydibenz[*de,g*]-quinolin-7-one (II) in acetic acid using Adam's catalyst resulted in the uptake of about 3 mole equivalents of hydrogen, but upon working up, we found the only isolable product to be an excellent yield of the demethoxylated derivative III. Undoubtedly, reoxidation of the primary hydrogenated product must have occurred, but we have not been able to characterize it or any of the possible intermediates. Although the removal of an aromatic methoxyl group as a result of catalytic hydrogenation and work-up is unusual, it may be a characteristic of the heterocycle which was examined. In any event, since the tetramethoxy compound II is readily available from papaverine, the preceding reductive procedure is the method of choice for the synthesis of III, which we have also prepared by the unambiguous method developed earlier.[1]



I, R_1R_2 = OCH_2O; R_3 = R_4 = H
II, R_1 = R_2 = R_3 = R_4 = OCH_3
III, R_1 = H; R_2 = R_3 = R_4 = OCH_3

Experimental

All melting points are uncorrected.

Catalytic Reduction of 1,2,9,10-Tetramethoxydibenz[*de,g*]-**quinolin-7-one.**—The yellow alkaloid (5.5 g.) in acetic acid (30 ml.) containing platinum oxide (300 mg.) was shaken in a hydrogen atmosphere for 1 hr., after which the uptake (*ca.* 1200 ml.) of hydrogen ceased. The colorless solution was filtered, concentrated to dryness, and taken up in methylene chloride. The solution, which was now dark green, was washed with dilute sodium hydroxide, dried, passed down a column of alumina (Woelm activity III), and eluted with methylene chloride, which removed a trace of a yellow substance not further investigated. Further elution of the column with chloroform containing a trace of ethanol gave a yellow substance (4.5 g.). This compound crystallized from chloroform, gave pure 2,9,10-trimethoxydibenz[*de,g*]quinolin-7-one (III, 4.1 g.), m.p. 264° dec.; $\nu_{C=O}$ 1640 cm.$^{-1}$; λ_{max}^{EtOH} mμ (ϵ), 238 (31,400), 270 (3,800), 292 (25,200) 359 (10,100), and 430 (4,100).

Anal. Calcd. for $C_{19}H_{15}NO_4$: C, 71.04; H, 4.71; N, 4.36; $3OCH_3$, 29.00. Found: C, 71.05; H, 4.84; N, 4.76; OCH_3, 28.75.

The oxime prepared by heating the base in pyridine with hydroxylamine hydrochloride had m.p. 220–221°.

Anal. Calcd. for $C_{19}H_{16}N_2O_4$: C, 67.85; H, 4.80; N, 8.33. Found: C, 67.98; H, 4.93; N, 8.59.

1,2'-Dinitro-4',5'-dimethoxybenzoyl-6-methoxyisoquinoline.—1,2'-Dinitro-4',5'-dimethoxybenzyl-6-methoxy-3,4-dihydroisoquinoline[12] (0.2 g.) dissolved in acetic acid (2 ml.) was warmed to 70° in the presence of sodium dichromate (0.3 g.) when a vigorous exothermic reaction set in. After the reaction was complete, it was diluted with water (15 ml.) and extracted into methylene chloride which was washed with alkali, dried, and concentrated to a foam. Upon addition of methanol and warming, a crystalline product (120 mg.), the nitrobenzoyl-3,4-dihydroisoquinoline, was obtained, m.p. 195–196° dec.; $\nu_{C=O}^{Nujol}$ 1690 cm.$^{-1}$; λ_{max}^{EtOH} mμ (ϵ), 244 (25,720) and 200–204 (12,980).

Anal. Calcd. for $C_{19}H_{18}N_2O_6$: C, 61.61; H, 4.90. Found: C, 61.57; H, 5.07.

The preceding amine (100 mg.) was dissolved in boiling alcohol (5 ml.), a few drops of 2 *N* potassium hydroxide was added, and a red color was produced which slowly became yellow as the reflux was continued. Upon cooling, crystals were obtained which were filtered off and recrystallized from acetic acid to furnish the nitrobenzoylisoquinoline (85 mg.), m.p. 202°; $\nu_{C=O}^{Nujol}$ 1678 cm.$^{-1}$; λ_{max}^{EtOH} mμ (ϵ), 220 (33,060), 254 (44,110), and 317–322 (12,890).

Anal. Calcd. for $C_{19}H_{16}N_2O_6$: C, 61.95; H, 4.38. Found: C, 61.88; H, 4.51.

2,9,10-Trimethoxydibenz[*de,g*]**quinolin-7-one** (III).—The preceding nitrobenzoylisoquinoline (350 mg.) was hydrogenated in acetic acid using palladium (5%) on charcoal as the catalyst. After filtration and concentration to dryness, the crude product was dissolved in *N* sulfuric acid (12 ml.), cooled to 0°, and diazotized by the dropwise addition of 0.1 *N* sodium nitrite (7.5 ml.). The reddish solution gradually changed to a tan color as it was allowed to warm up to room temperature; 3 drops of sulfuric acid was added and the solution was warmed on the steam bath for 30 min. Upon cooling, addition of base (sodium hydroxide), and extraction into methylene chloride, a crystalline residue (205 mg.) was obtained. This was placed on a column of alumina (Woelm, activity III). The methylene chloride eluate was discarded and further elution with chloroform containing a trace of ethanol gave the pure product (110 mg.), m.p. 268° dec.

Anal. Calcd. for $C_{19}H_{15}NO_4$: C, 71.04; H, 4.71. Found: C, 71.08; H, 4.77.

It was identical in all respects with the sample prepared from 1,2,9,10-tetramethoxydibenz[*de,g*]quinolin-7-one.

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A New Synthesis of 2-Aryl-4,6-diphenyl-*s*-triazines

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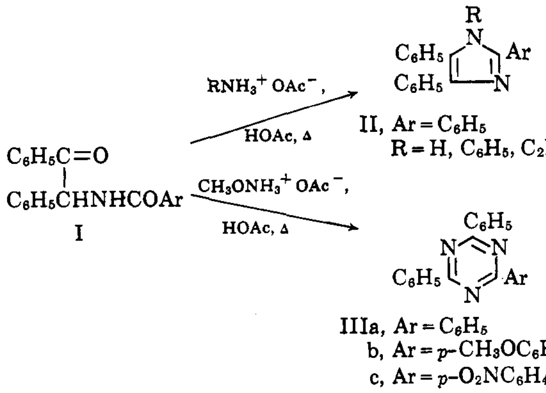
Received June 19, 1963

Since N-desylbenzamide (I, Ar = C_6H_5) reacts with ammonium,[1] anilinium,[1] or ethylammonium acetate in boiling acetic acid to give the corresponding 2,4,5-triphenylimidazole (II), it was anticipated that the reaction of I with methoxyammonium acetate would lead to 1-methoxy-2-aryl-4,5-diphenylimidazoles. Surprisingly, 2-aryl-4,6-diphenyl-*s*-triazines (III) crystal-



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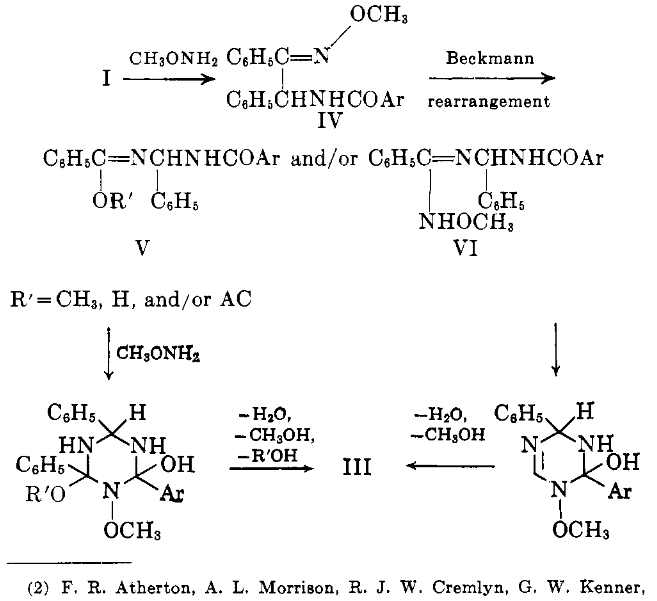
lized from the cooled reaction mixtures in yields of 12–26%. The methoxyammonium acetate is necessary for the formation of III; N-desyl-*p*-methoxybenzamide (I, Ar = *p*-$CH_3OC_6H_4$) is recovered unchanged when this reagent is omitted.

The formation of III poses an interesting mechanistic problem. Somehow a nitrogen atom must be inserted between the keto and saturated carbons of I; we feel that this most probably occurs *via* a Beckmann rearrangement of the O-methyloxime IV. Intermediate V (R′ = CH_3) would be involved if the rearrangement were intramolecular. However, nucleophilic displacement during[2] and following[3] Beckmann rearrangements have been reported, so that routes involving V (R′ = H or Ac) and VI, corresponding to displacement by water (from formation of IV), acetic acid, or methoxyamine, must also be considered. If R′ in structure V is H, tautomerization to nitrogen would probably occur.[4] Conversion of ketone and methoxyamine to the O-methyloxime[5] and Beckmann rearrangements of O-alkyloximes[5,6] have been reported, but conditions considerably more vigorous than refluxing acetic acid must usually be used to bring about rearrangement of oximes or their ethers.[7] Perhaps the nearest analogy is a reported Beckmann rearrangement in formic acid on the water bath.[8] The facile rearrangement of IV may be due to steric factors. Molecular models show that the C=N group cannot be coplanar with the phenyl group attached to it. It has been reported that such noncoplanarity can accelerate the Beckmann rearrangement considerably.[9]

If III is to form, the N-methoxy group of IV must be *anti* to the migrating -CH(C_6H_5)NHCOAr group.[10]



The formation of some of the *syn* isomer may account for our low yields; the apparent formation of two isomeric oximes from I (Ar = C_6H_5) has been reported.[1] The low yields are not due to incompleteness of the reactions; doubling the reaction times did not increase the yields of IIIb or IIIc and increased the yield of IIIa only from 26% to 28%.

Experimental

1-Ethyl-2,4,5-triphenylimidazole (II, R = C_2H_5).—A mixture of 0.95 g. of N-desylbenzamide,[1] 7.2 g. of ethylammonium acetate, and 30 ml. of acetic acid was heated at reflux for 18.5 hr., cooled, and stirred with 300 ml. of 6.6% sodium hydroxide. Recrystallization of the resulting solid from hexane gave 0.67 g. (69%) white crystals, m.p. 126.5–127.5°.

Anal. Calcd. for $C_{23}H_{20}N_2$: C, 85.2; H, 6.2; N, 8.6. Found: C, 85.6, 85.6; H, 6.6, 6.6; N, 8.6, 8.5.

Kulisch[11] reports m.p. 234° for this compound. We repeated Kulisch's procedure and obtained a product, m.p. 112–114°, with an infrared spectrum identical to that of the 126.5–127.5° material. The melting point of 234° is apparently in error.

2,4,6-Triphenyl-*s*-triazine (IIIa).—A mixture of 0.70 g. of N-desylbenzamide, 1.7 g. of methoxyamine (prepared from its hydrochloride[12]), and 17 ml. of acetic acid was heated at reflux for 7 hr., cooled in ice, and filtered to give 0.18 g. (26%) of IIIa, m.p. 232–234° (lit.[13] m.p. 232–233°), m.m.p. 232–235°.

2-(*p*-Methoxyphenyl)-4,6-diphenyl-*s*-triazine (IIIb).—N-Desyl-*p*-methoxybenzamide was prepared from the $SnCl_2$–HCl salt of desylamine and *p*-anisoyl chloride by the method used to prepare N-desylbenzamide.[1] Recrystallization from ethanol gave 86% of white crystals, m.p. 121–123°.

Anal. Calcd. for $C_{22}H_{19}NO_3$: C, 76.5; H, 5.5; N, 4.1. Found: C, 76.1, 76.1; H, 5.6, 5.6; N, 4.1, 4.2.

This material (0.70 g.), 1.7 g. of methoxyamine, and 17 ml. of acetic acid were heated under reflux for 7 hr., cooled in ice, and filtered to give 0.17 g. (25%) of IIIb, m.p. 157.5–158.5°. An authentic sample of IIIb was prepared by the method used by Cook and Jones[14] to prepare IIIc, using *p*-anisoyl chloride instead of *p*-nitrobenzoyl chloride. The crude product was crystallized from acetic acid and stirred with carbon tetrachloride. The mixture was filtered, the solvent was removed *in vacuo*, and the residue was recrystallized from ethanol yielding 10% IIIb, m.p. 156–158°.

Anal. Calcd. for $C_{22}H_{17}N_3O$: C, 77.9; H, 5.0; N, 12.4. Found: C, 77.8, 78.1; H, 5.1, 5.3; N, 12.3, 12.3.

The products prepared by the two methods had identical infrared spectra and a mixture melted at 157–159°.

When N-desyl-*p*-methoxybenzamide was boiled with acetic acid alone for 7 hr., nothing crystallized on cooling. Dilution with water and neutralization with ammonia gave 94% starting material, m.p. 115–119°. Recrystallization from ethanol raised the melting point to 120–122°.

2-(*p*-Nitrophenyl)-4,6-diphenyl-*s*-triazine (IIIc).—N-Desyl-*p*-nitrobenzamide was prepared from the $SnCl_2$–HCl salt of desylamine and *p*-nitrobenzoyl chloride[1] and recrystallized from ethanol; a 47% yield of pale yellow needles, m.p. 171–173°, was obtained.

Anal. Calcd. for $C_{21}H_{16}N_2O_4$: C, 70.0; H, 4.5; N, 7.8. Found: C, 70.3, 70.5; H, 4.5, 4.5; N, 7.8, 7.7.

A mixture of 0.70 g. of this product, 1.7 g. of methoxyamine, and 17 ml. of acetic acid was heated at reflux for 7 hr., cooled, and filtered to give 0.083 g. (12%) of IIIc, m.p. 217.5–218.5° (lit.[14] m.p. 218°), m.m.p. 219–221°.

Acknowledgment.—The author is indebted to W. Z. Heldt for stimulating discussions and to R. L. Alderson, B. F. Burgess, and C. A. Roeper for technical assistance.

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