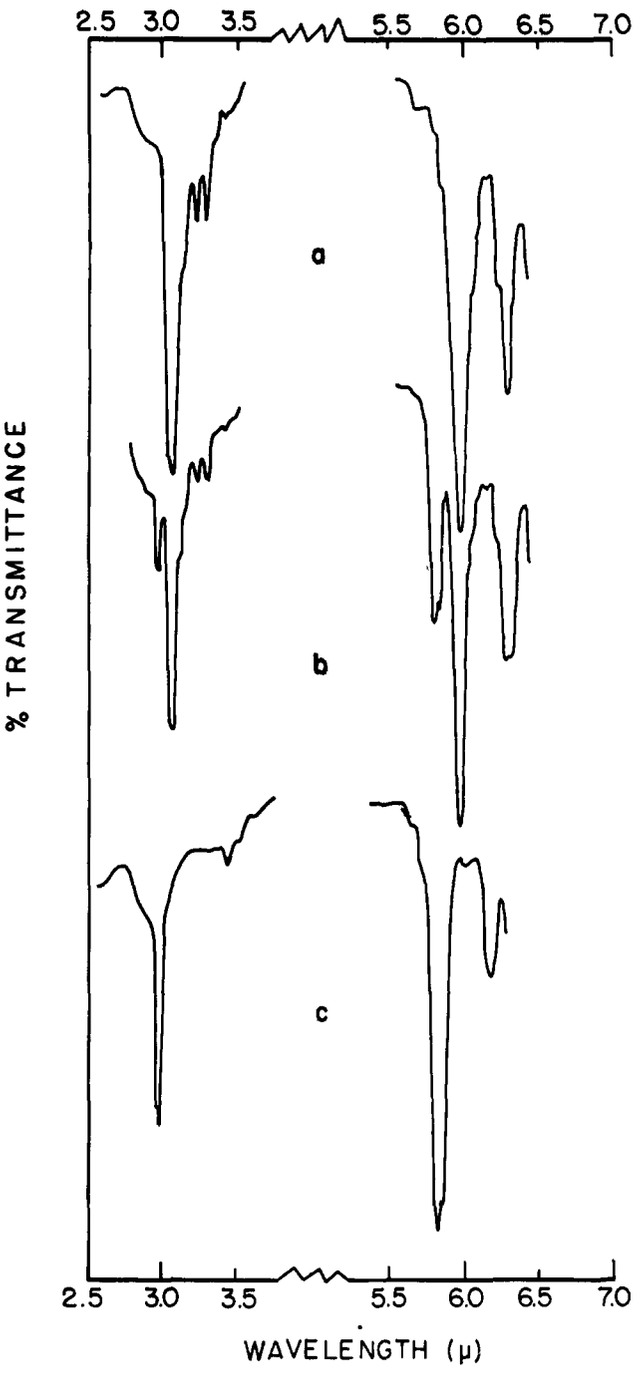

Fig. 6.—Infrared spectra of solid 2-nitro-*p*-acetotoluidide (III) pressed in KBr[11]: a, white form shaken with KBr for 30 sec.; b, yellow form shaken with KBr for 120 sec.; c, yellow form shaken with KBr for 30 sec.

Contrary to this, the white form of III possesses probably the true amide structure stabilized by intermolecular hydrogen bondings. Infrared spectra show that the carbonyl group in the white form is hydrogen bonded, in the yellow form is free. This presents clear evidence for assignment of inter- and intramolecularly hydrogen-bonded structures to the white and yellow crystal forms of III.

Further systematic studies of a number of 2-nitroacetanilides substituted in the 4-position are now in progress. The results of these studies will be published later.

Experimental[13]

o-Nitroacetanilide (I), 1-nitro-2-acetonaphthalide (V), and 2,4-dimethyl-6-nitroacetanilide (VII) are commercially available materials which were recrystallized before use. 2-Nitro-*p*-acetotoluidide (III) was obtained by acetylation of commercially available free amine with acetic anhydride. The low melting yellow form (m.p. 93.5–94°) and the high melting white form (m.p. 95–96°) have been obtained according to Gattermann.[8]

N-Methyl derivatives II, IV, and VI or I, III, and V, respectively, were prepared with a good yield by the method developed by Pachter and Kloetzel.[14] Their structure was confirmed by their melting points, fairly close to those described in the literature, and by the results of microanalyses[15] and infrared spectra.

Anal. Calcd. for $C_9H_{10}N_2O_3$ (II), m.p. 70–71.5° (lit.[16] m.p. 70°): C, 55.67; H, 5.19; N, 14.43. Found: C, 55.67; H, 5.10; N, 14.55.

Calcd. for $C_{10}H_{12}N_2O_3$ (IV), m.p. 65–66° (lit.[17] m.p. 64°): C, 57.68; H, 5.81; N, 13.46. Found: C, 57.88; H, 5.83; N, 13.37.

Calcd. for $C_{13}H_{12}N_2O_3$ (VI), m.p. 114–115° (lit.[18] m.p. 112–113°): C, 63.92; H, 4.96; N, 11.47. Found: C, 64.16; H, 4.98; N, 11.55.

Acknowledgment.—The author wishes to thank Professor Melvin Calvin for many helpful discussions during the course of this work, and to acknowledge the valuable comments of the referees.

(13) All melting points are uncorrected.
(14) I. J. Pachter and M. C. Kloetzel, *J. Am. Chem. Soc.*, **74**, 1321 (1952).
(15) All microanalyses were performed by the Microanalytical Laboratory, Department of Chemistry, University of California.
(16) M. A. Philips, *J. Chem. Soc.*, 2820 (1029).
(17) St. Niementowski, *Ber.*, **20**, 1874 (1887).
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The Removal of the 1-Methoxyl Group from 1,2,9,10-Tetramethoxydibenz[*de*,*g*]quinolin-7-one by Catalytic Hydrogenation

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We recently have recognized and proven by synthesis[1] the structures of liriodenine (I) and 1,2,9,10-tetramethoxydibenz[*de*,*g*]quinolin-7-one (II), the two yellow alkaloids[2] of *Liriodendron tulipifera* L. Since then a number of groups have identified their alkaloids with liriodenine, *viz.*, oxoushinsunine from *L. tulipifera* L.,[3] *Michelia compressa* Maxim.,[4] *M. compressa* Maxim. var. *formosana Kanchira*,[5,6] *M. Alba* DC.,[7] and *Magnolia coco* (Lour.) DC.[8]; and spermatheridine from *Atherosperma moschatum* Labill.[9] Liriodenine has since been prepared from the aporphines, roemerine, or ushinsunine by chromic acid or manganese oxide oxidations,[10,6] and the reverse reaction has been accom-

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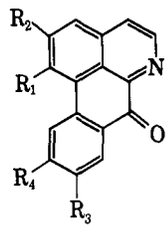
(3) M. Tomita and H. Furukawa, *J. Pharm. Soc. Japan*, **82**, 1199 (1962).
(4) M. Tomita and H. Furukawa, *ibid.*, **82**, 925 (1962).
(5) T.-H. Yang, *ibid.*, **82**, 794 (1962).
(6) S.-S. Yang, W.-Y. Huang, L. C. Lin, and P.-Y. Yeh, *Chemistry* (Taipei), 144 (1961). In this reference the alkaloid also is called micheline.
(7) T.-H. Yang, *J. Pharm. Soc. Japan*, **82**, 811 (1962).
(8) T.-H. Yang, S. Lu, and C. Hsiao, *ibid.*, **82**, 816 (1962).
(9) I. R. C. Bick, P. S. Clezy, and W. D. Crow, *Australian J. Chem.*, **9**, 111 (1956). Identity was established by direct comparison: I. R. C. Bick, personal communication.

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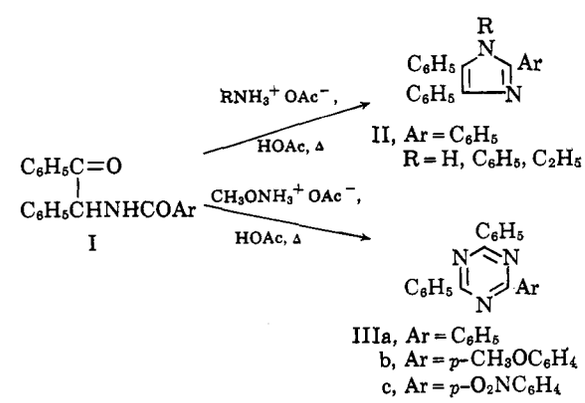
Since N-desylbenzamide (I, Ar = C_6H_5) reacts with ammonium,[1] anilinium,[1] or ethylammonium acetate in boiling acetic acid to give the corresponding 2,4,5-triphenylimidazole (II), it was anticipated that the reaction of I with methoxyammonium acetate would lead to 1-methoxy-2-aryl-4,5-diphenylimidazoles.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



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