The infrared spectra of the products were run on a Perkin-Elmer model 21 spectrophotometer.

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Reactivity Ratios of 2-Methyl-5-cinnamoylpyridine, 3-Cinnamoylpyridine, and 3-Pyridalacetophenone with Styrene

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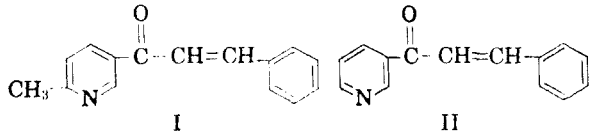
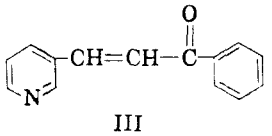
Received June 18, 1956

To find the effect of structure on the reactivity of three similar monomers, the reactivity ratios of 2-methyl-5-cinnamoylpyridine (I), 3-cinnamoylpyridine (II), and 3-pyridalacetophenone (III) with styrene were determined as suggested by Mayo and Lewis.[1] Polymerization was achieved in benzene solution and the composition of the resulting polymers was determined by nitrogen analysis. The results are summarized in Table I. The error in the "r" values was estimated by assuming a 0.1 per cent error in the nitrogen analysis.



I

II



III

TABLE I

REACTIVITY RATIOS

M_1	r_1	M_2	r_2
Styrene	0.92 ± 0.08	2-Methyl-5-cinnamoylpyridine	-0.15 ± 0.2
Styrene	0.85 ± 0.05	3-Cinnamoylpyridine	0.09 ± 0.1
Styrene	0.50 ± 0.1	3-Pyridalacetophenone	0.00 ± 0.25

The very low "r" values of these ketones are in agreement with previous experience[2] that pyridine analogs of chalcone do not homopolymerize. It is of interest that the r_1 values of styrene vary from about 1.0 to 0.5. Since the reactivity ratio is a measure of the tendency of one monomer to add to itself or to the comonomer, the results show that the styrene radical is less reactive toward 2-methyl-5-cinnamoylpyridine and 3-cinnamoylpyridine than toward 3-pyridalacetophenone. This seems to indicate that a double bond adjacent to the pyridine ring is more active than one next to the benzene ring.

We were unsuccessful in attempts to determine reactivity ratios with butadiene because of failure to achieve copolymerization in a bulk recipe.

EXPERIMENTAL

3-Pyridalacetophenone. The method described before[2] was followed using one-molar quantities. There was obtained 50 g. of 3-pyridalacetophenone, m.p. 102–103°.

2-Methyl-5-cinnamoylpyridine. The synthesis of 2-methyl-5-cinnamoylpyridine[2] was improved. The compound was prepared by adding 44 g. (0.41 mole) of redistilled benzaldehyde to a pre-cooled solution of 18 g. of sodium hydroxide in 165 ml. of water and 50 ml. of methanol. Then 55 g. (0.41 mole) of redistilled 2-methyl-5-acetylpyridine was added slowly keeping the temperature below 5°. After three hours of stirring below 15° the mother liquor was decanted and the yellow oil was dissolved in 1500 ml. of 10% by volume sulfuric acid. This solution was heated on the steam-bath for one hour, diluted with 4000 ml. of water, cooled, and carefully neutralized with a 10% solution of sodium hydroxide until a heavy precipitate was formed. The solid was collected, and the filtrate was treated twice more in the same manner. After drying, the crude product was recrystallized twice from cyclohexane yielding 40.3 g. (47%) of a light green crystalline solid, m.p. 79°.

3-Cinnamoylpyridine. This ketone was prepared by adding 20.6 g. (0.2 mole) of redistilled benzaldehyde and 23.6 g. (0.2 mole) of redistilled 3-acetylpyridine to a solution of 2.5 ml. of piperidine in 250 ml. of pyridine. The mixture was heated on the steam-bath for one hour and for an additional 15 minutes under reflux. It was poured into 1500 ml. of cold water and left standing overnight. Dehydration with sulfuric acid (225 ml. in 850 ml. of water) and neutralization were carried out as reported above for 2-methyl-5-cinnamoylpyridine. After drying, the resulting crude product was recrystallized twice from cyclohexane yielding 9.3 g. (22.3%) of a light yellow crystalline product, m.p. 84.5–85°.

The molecular weight of the product was determined by the Rast method.[3]

Anal. Calc'd for $C_{14}H_{11}NO$: C, 80.38; H, 5.26; N, 6.98; M.W., 209. Found: C, 80.46; H, 5.42; N, 6.71; M.W., 204.

The infrared absorption spectrum showed characteristic bands at 1665, 1645, 1610, 1607, 1500, 985, and 695 cm.$^{-1}$ in agreement with the proposed structure.*

The ultraviolet absorption spectrum showed maxima at 240 mμ, log ϵ 6.38, and at 312 mμ, log ϵ 6.49.**

Reactivity ratio determinations. Polymerization was carried out in benzene solution at 50° using 0.4000 g. of azobisisobutyronitrile initiator. The polymer was precipitated in low-boiling petroleum ether and unreacted monomer was extracted by the same solvent in a Soxhlet extractor for four hours. For further purification the polymer was twice reprecipitated from benzene. The conversions in these reactivity ratio studies were of the order of 5 to 10% and never more than 10%. The experimental data are summarized in Table II.

(1) Mayo and Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

(2) Marvel, Coleman, and Scott, *J. Org. Chem.*, **20**, 1785 (1955).

(3) R. L. Shriner and R. C. Fuson, *The Systematic Identification of Organic Compounds*, 3rd edition, John Wiley and Sons, Inc., New York, 1947, p. 50.

* Mr. J. Brader determined the infrared spectrum and made the interpretation.

** The ultraviolet analysis was determined by Miss G. Meerman.

TABLE II

REACTIVITY RATIO DETERMINATIONS WITH STYRENE

Sample Number	Charge/ Weight Ratio[a]	Benzene, ml.	Time, hours	Nitrogen, %
	2-METHYL-5-CINNAMOYLPYRIDINE			
24-A	85/15	7	3	0.98
24-D	72/25	12	3	1.40
24-C	50/50	22	5	2.64
r_2 (2-methyl-5-cinnamoylpyridine) = -0.15 ± 0.2				
r_1 (styrene) = 0.92 ± 0.08				
	3-CINNAMOYLPYRIDINE			
23-2	75/25	13	3	1.84
23-3	60/40	20	3	2.44
23-4	40/60	35	5.3	3.39
r_2 (3-cinnamoylpyridine) = 0.09 ± 0.1				
r_1 (styrene) = 0.85 ± 0.05				
	3-PYRIDALACETOPHENONE			
23-III	85/15	20	3	1.52
23-II	75/25	25	3	2.08
23-IV	60/40	44	3	2.97
r_2 (3-pyridalacetophenone) = 0.00 ± 0.25				
r_1 (styrene) = 0.50 ± 0.1				

[a] Styrene/Ketone.

Acknowledgment. The work discussed herein was performed as a part of the synthetic rubber research project sponsored by the National Science Foundation.

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3-Dehydro Derivatives of Some Indole Alkaloids

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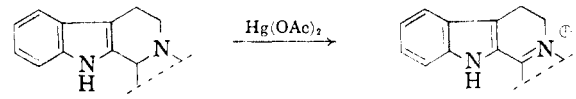
Received June 21, 1956

As part of an extensive study of dehydrogenation of indole alkaloids it was of interest to investigate the action of mercuric acetate on these natural products. In view of a recent publication[1] on the same subject, this phase of the study is presented at this time.

While much experimentation, especially in recent years,[2] on model compounds as well as alkaloids has shown that tertiary amines can be oxidized to immonium salts by mercuric acetate, there has been only one report on this reaction in the field of yohimbé or rauwolfia alkaloids, *i.e.* the dehydrogenation of yohimbine to an uncharacterized, colored substance.[3]

When yohimbane, *d,l*-alloyohimbane, and ajmalicine were subjected to mercuric acetate oxidation, yellow 3-dehydro products (I) were obtained.[4] Their spectra distinguish them readily from their precursors as well as from tetradehydro products. The infrared spectra exhibit characteristic 1625, 1570, and 1540 cm.$^{-1}$ peaks, while the ultraviolet spectra show maximum absorption at 248 mμ (log ϵ 4.10) and 353 mμ (log ϵ 4.41) (*cf.* Figure 1). Because of its additional chromophore in ring E ajmalicine showed slight deviations in its ultraviolet absorption curve (*cf.* Figure 1).



I

d,l-Epialloyohimbane yielded no appreciable dehydro product, even under forcing conditions. The reason for this inertness is obscure, although it must be intimately connected with the steric requirements of the transition complex of the mercuric acetate reaction. In their dehydrogenation studies Weisenborn and Diassi[1] discovered that *normal*[5] and *allo* compounds undergo the oxidation, while *pseudo* and *epiallo* systems do not, and ascribed this phenonomenon to the necessary availability of an axial C_3-H bond in order to accommodate a coplanar transition state in the reaction mechanism originally proposed by Leonard.[2] While this argument satisfies the behavior of the conformationally unequivocal *normal* and *pseudo* compounds, it appears ambiguous for the *allo* and *epiallo* substances, one of whose two all-chair, C/D trans conformations always possesses an axial C_3 hydrogen atom.[6] Whereas admittedly in such unreactive compounds as reserpine, methyl reserpate, and deserpidine[1] this conformation is the less favorable one,[6,7] the opposite is the case with the essentially inert *d,l*-epialloyohimbane.[6] In short, the mechanism of the mercuric acetate oxidation of amines will require much refinement before its steric course will become clear.

All Δ^3 products reverted to their dehydro precursors on sodium borohydride reduction as well as catalytic hydrogenation. Three previous examples of reductions of 3-dehydro compounds concur with

(1) F. L. Weisenborn and P. A. Diassi, *J. Am. Chem. Soc.*, **78**, 2022 (1956).

(2) *Cf.* N. J. Leonard, W. J. Middleton, P. D. Thomas, and D. Chaudhury, *J. Org. Chem.*, **21**, 344 (1956) and preceding papers.

(3) A. Schomer, *Archiv. Pharm.*, **265**, 509 (1927).

(4) Both yohimbine and yohimbone have been converted to their 3-dehydro derivatives. However, the former will not be treated here in deference to the prior communication by Weisenborn and Diassi,[1] and discussion of the latter will be postponed until a later date.

(5) The term *normal* is applied to those substances having the stereochemistry of yohimbine at carbons 3, 15, and 20.

(6) E. Wenkert and L. H. Liu, *Experientia*, **11**, 302 (1955).

(7) C. F. Huebner, H. B. MacPhillamy, E. Schlittler, and A. F. St. André, *Experientia*, **11**, 303 (1955).