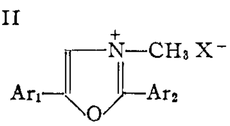
TABLE III

OXAZOLE QUATERNARY SALTS



Ar_1	Ar_2	X	Formula	M.p.,[a] °C.	Nitrogen, % Calcd.	Nitrogen, % Found
C_6H_5	C_6H_5	Perchlorate	$C_{16}H_{14}ClNO_5$	177–188	4.17	4.20
C_6H_5	C_6H_5	*p*-Toluenesulfonate	$C_{23}H_{21}NO_4S$	170–172	3.44	3.25
4-$C_6H_5C_6H_4$	4-$C_6H_5C_6H_4$	*p*-Toluenesulfonate	$C_{35}H_{29}NO_4S$	214–216	2.50	2.52
C_6H_5	1-$C_{10}H_7$	*p*-Toluenesulfonate	$C_{27}H_{23}NO_4S$	144–145	3.06	2.91

[a] Melting points taken on a Fisher–Johns melting point block. Microanalyses by Micro-Tech Laboratories, Skokie, Ill.

Experimental Part

The following procedures are illustrative of the methods used.

N,N′-Diphenacylterephthalamide.—To a stirred solution of 25.0 g. (0.123 mole) of terephthalyl chloride in 300 ml. of dry pyridine, was slowly added 43.0 g. (0.25 mole) of phenacylammonium chloride. The mixture was refluxed for 15 minutes, then allowed to cool and diluted with water. The crude product was filtered, dried and recrystallized from *ca.* 2 l. of pyridine; the yield was 28.5 g. (58%).

1,4-Di-[2-(5-phenyloxazolyl)]-benzene (POPOP).—A mixture of 13.5 g. (0.034 mole) of N,N′-diphenacylterephthalamide in 500 ml. of phosphorus oxychloride was refluxed overnight. Most of the phosphorus oxychloride was distilled from the reaction mixture, and the residue was slowly added to water contained in a 3-l. beaker. The solid was filtered, washed with water, dried and recrystallized from pyridine; the yield was 10.3 g. (84%).

1-Benzoyl-2-(4-phenylbenzoyl)-hydrazine.—Ten grams (0.074 mole) of benzoylhydrazine was added to a stirred solution of 16 g. (0.074 mole) of *p*-phenylbenzoyl chloride in 100 ml. of dry pyridine. The mixture was refluxed for 20 minutes, cooled and treated with water to completely precipitate the crude product. This material was filtered, dried and recrystallized from toluene; the yield was 13.3 g. (57.7%, m.p. 222–224°).

2-Phenyl-5-(4-biphenylyl)-1,3,4-oxadiazole (PBD).—Seventy-six grams (0.24 mole) of 1-benzoyl-2-(4-phenylbenzoyl)-hydrazine in 200 ml. of phosphorus oxychloride was gently refluxed overnight. Most of the phosphorus oxychloride was distilled from the reaction mixture, and the residue was slowly added to water. The oxadiazole was filtered, washed with water, dried and recrystallized from toluene; the yield was 52.0 g. (73%).

2,5-Di-(4-biphenylyl)-3-methyloxazolium *p*-Toluenesulfonate (MBBO).—A mixture of 3.7 g. (0.02 mole) of methyl *p*-toluenesulfonate and 3.7 g. (0.01 mole) of 2,5-di-(4-biphenylyl)-oxazole was heated in an oil-bath at 100° for 1.5 days. The viscous liquid was cooled and dissolved in a small amount of methanol. The addition of dry ether and cooling gave 7.3 g. (99%) of white, crystalline product.

LOS ALAMOS, N. M.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

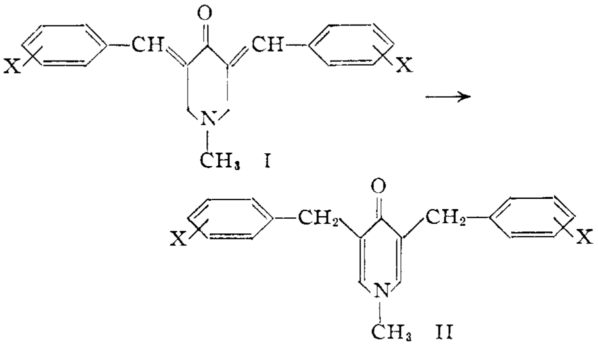
γ-Pyridones by Isomerization. Substituted 1-Methyl-3,5-dibenzyl-4-pyridones

BY NELSON J. LEONARD AND DAVID M. LOCKE[1,2]

RECEIVED SEPTEMBER 20, 1954

The isomerization of substituted 1-methyl-3,5-dibenzylidene-4-piperidones to the correspondingly substituted 1-methyl-3,5-dibenzyl-4-pyridones has been effected in boiling ethylene glycol solution using palladium-on-charcoal. The general method extends the range of this type of aromatization reaction to heterocyclic compounds and marks the introduction of ethylene glycol as a useful solvent for this conversion.

The efficacy of the aromatization reaction in converting 2,6-dibenzylidenecyclohexanone to 2,6-dibenzylphenol[3–5] and substituted 3,7-dibenzylidene-1,2-cycloheptanediones to the correspondingly substituted 3,7-dibenzyltropolones[6,4] suggested that this reaction might be of equal value in the analogous heterocyclic systems. Accordingly, we have studied, as a first example of heterocyclic aromatizations of this type, the isomerization of a series of substituted 1-methyl-3,5-dibenzylidene-4-piperidones (I) to the corresponding 1-methyl-3,5-dibenzyl-4-pyridones (II).



	X		X		X
a	H	e	*m*-NO_2	i	*p*-*i*-C_3H_7
b	*p*-CH_3	f	*p*-Cl	j	*p*-$(CH_3)_2N$
c	*o*-CH_3	g	*o*-Cl	k	*p*-C_6H_5
d	*p*-NO_2	h	*p*-CH_3O		

We were encouraged in our belief that the isomerization of I to II would in general occur readily because of the aromatic character—and hence comparatively greater stability—of the 4-pyridone nucleus, as suggested by Arndt[7] and amply con-

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[1] Sinclair Refining Company Fellow in Organic Chemistry, 1952–1953. Work done under the sponsorship of the Sinclair Research Laboratories, Inc.

[2] National Science Foundation Fellow, 1953–1954.

[3] R. Weiss and J. Ebert, *Monatsh.*, **65**, 399 (1935).

[4] N. J. Leonard and G. C. Robinson, THIS JOURNAL, **75**, 2143 (1953).

[5] E. C. Horning, *J. Org. Chem.*, **10**, 263 (1945).

[6] N. J. Leonard and J. W. Berry, THIS JOURNAL, **75**, 4989 (1953).

[7] (a) F. Arndt and A. Kalischek, *Ber.*, **63**, 587 (1930); (b) F. Arndt, *ibid.*, **63**, 2963 (1930); (c) F. Arndt, P. Nachtwey and J. Pusch, *ibid.*, **58**, 1633 (1925).

TABLE I

SUBSTITUTED 1-METHYL-3,5-DIBENZYLIDENE-4-PIPERIDONES

1-Methyl-4-piperidones, 3,5-Di-	I	Yield, %	M.p., °C.	Color and crystal form	Infrared absorption maxima, cm.$^{-1}$ [f] Conj. C=O	Conj. C=C and phenyl			Formula	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Nitrogen, % Calcd.	Found
Benzylidene-	a[9]	51	115–117	Y. plate.[a,b]	1672	1620	1592	1494	$C_{20}H_{19}NO$						
(*p*-Methyl)-	b	63	192–195	Y. ndls.[c,d]	1670	1606	1584		$C_{22}H_{23}NO$	83.23	82.98	7.30	7.36	4.41	4.40
(*o*-Methyl)-	c	69	117–118	Y. ndls.[c]	1675	1623	1593		$C_{22}H_{23}NO$	83.23	83.47	7.30	7.28	4.41	4.48
(*p*-Nitro)-	d	100	229–231	O. prisms[e]	1673	1615	1595		$C_{20}H_{17}N_3O_5$	63.31	62.93	4.53	4.60	11.08	10.89
(*m*-Nitro)-	e	82	189.5–190.5	Y. ndls.[d]	1676	1620	1598		$C_{20}H_{17}N_3O_5$	63.31	63.37	4.53	4.67	11.08	10.96
(*p*-Chloro)-	f	89	174–176	Y. ndls.[d]	1674	1617	1584	1495	$C_{20}H_{17}Cl_2NO$	67.04	67.01	4.78	4.95	3.91	4.01[g]
(*o*-Chloro)-	g[9]	80	150–151	Y. ndls.[c,d]	1677	1626	1602	1565	$C_{20}H_{17}Cl_2NO$						
(*p*-Methoxy)-	h	66	199–202	Y. ndls.[c,d]	1672	1620	1603	1515	$C_{22}H_{23}NO_3$	75.62	75.41	6.63	6.72	4.01	4.23
(*p*-Isopropyl)-	i	36	115–117	Y. ndls.[b]	1670	1618	1607	1512	$C_{26}H_{31}NO$	83.60	83.47	8.37	8.21	3.75	3.76
(*p*-Dimethylamino)-	j	58	223–225	O. ndls.[b]	1655	1620	1587	1530	$C_{24}H_{29}N_3O$	76.76	76.89	7.78	7.47	11.19	11.38
(*p*-Phenyl)-	k	72	199–202	Y. ndls.[d]	1672	1618	1590	1494	$C_{32}H_{27}NO$	87.04	86.60	6.16	6.13	3.17	3.16

[a] Y. = yellow, O. = orange, ndls. = needles, plate. = platelets. Solvent: [b] Aqueous ethanol. [c] Ethanol. [d] Acetone. [e] Chloroform. [f] Infrared spectra were determined in Nujol mull. [g] Calcd.: Cl, 19.79. Found: Cl, 19.46.

firmed by chemical and physical evidence.[7,8] Moreover, examples of aromatization by catalytic isomerization at high temperatures can be cited which lead to the formation of substituted pyridines.[9] The closest analogy to the isomerizations discussed in the present paper lies in the finding of Robinson and his co-workers[10] that the product isolated from the reaction of benzaldehyde with isodihydrostrychnine, which contains an unsaturated α-piperidone III-ring, was not the benzylidene derivative but the isomeric substituted β-benzyl-α-pyridone.

The condensation of various aldehydes with 1-methyl-4-piperidone and 1-benzoyl-4-piperidone has been studied by McElvain, Rorig and McMahon,[11,12] and the conditions which they employed, aqueous ethanolic potassium hydroxide or anhydrous hydrogen chloride in ethanol, were effective for the preparation of I but were not without drawbacks. Piperidine (or piperidine acetate) in ethanol[4,6,13–15] also was effective in promoting condensation of various substituted benzaldehydes with 1-methyl-4-piperidone and permitted ready isolation of the products I. Since 1-methyl-4-piperidone itself is commensurate in basicity with piperidine, it was felt that this reactant would serve as sufficient catalyst for the condensation. Although most of the reactions were run with added piperidine (and acetic acid), several were investigated omitting such addition and the yields were found to be entirely comparable to the cases employing an added catalyst. Using the conditions developed in this study, a number of aldehydes were caused to react with 1-methyl-4-piperidone to give the desired discondensation products. A summary of the results is contained in Table I. In general the reaction proceeded smoothly, and good yields could be obtained by adjusting the time of reaction in individual cases. Electron-withdrawing groups in the substituted benzaldehyde appeared to aid the condensation slightly, but yields were apparently dependent primarily on solubility factors. In fact, the principal difficulty encountered was the solubility of some of the dibenzylidene derivatives in the reaction medium. In several cases (Ic, i, j) separation of the product was induced by adding seed crystals of the product as obtained by other methods.[11,12]

That these compounds possess the assigned dibenzylidenepiperidone structure I was indicated not only by their yellow color and by their intense color reactions with sulfuric acid (*cf.* 2,6-dibenzylidenecyclohexanone[16]) but by their absorption spectra. Each of the compounds exhibited two absorption maxima in the 6μ region, in addition to the characteristic phenyl bands near 1600 and 1500 cm.$^{-1}$. The two maxima, which in the representative case of the unsubstituted 1-methyl-3,5-dibenzylidene-4-piperidone (Ia) were found at 1672 and 1620 cm.$^{-1}$, can be attributed to the doubly conjugated ketone[17–19] and to the conjugated carbon–carbon double bond, respectively. These are comparable with the bands having the same assignments in 2,6-dibenzylidenecyclohexanone (1663 and 1610 cm.$^{-1}$) and 2,7-dibenzylidenecyclo-

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(8) (a) K. von Auwers, *Ber.*, **63**, 2111 (1930); (b) E. Hückel, *Z. Elektrochem.*, **43**, 752 (1937); (c) D. G. Leis and B. C. Curran, THIS JOURNAL, **67**, 79 (1945); (d) E. R. Riegel and M. C. Reinhard, *ibid.*, **48**, 1334 (1926); (e) H. Specker and H. Gawrosch, *Ber.*, **75**, 1338 (1942); (f) I. G. Ross, *J. Chem. Soc.*, 1374 (1951).

(9) (a) H. S. Mosher in "Heterocyclic Compounds," Volume I, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1950, p. 456; (b) E. Späth, F. Kuffner and F. Kittel, *Ber.*, **72**, 1109 (1939).

(10) (a) Sir Robert Robinson in "Progress in Organic Chemistry," Volume I, J. W. Cook, Ed., Academic Press, Inc., New York, N. Y., 1952, p. 12; (b) A. M. Stephen, D. Phil. Thesis, Oxford University, 1948; (c) L. H. Briggs, H. T. Openshaw and Sir Robert Robinson, *J. Chem. Soc.*, 903 (1946).

(11) S. M. McElvain and K. Rorig, THIS JOURNAL, **70**, 1820 (1948).

(12) S. M. McElvain and R. E. McMahon, *ibid.*, **71**, 901 (1949).

(13) P. Karrer and C. Cochand, *Helv. Chim. Acta*, **28**, 1181 (1945).

(14) H. Schlenk, *Ber.*, **81**, 175 (1948).

(15) H. Schlenk, *ibid.*, **85**, 901 (1952).

(16) D. Vorländer and K. Hobohm, *ibid.*, **29**, 1836 (1896).

(17) R. B. Barnes, R. C. Gore, U. Liddel and V. Z. Williams, "Infrared Spectroscopy," Reinhold Publishing Corp., New York, N. Y., 1944, p. 21.

(18) H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945).

(19) The C=O stretching frequency observed for 1-methyl-3,5-di-(*p*-dimethylaminobenzylidene)-4-piperidone (Ij) was about 15 cm.$^{-1}$ lower than those of the other substituted 1-methyl-3,5-dibenzylidene-4-piperidones, a fact which may be related to the finding of N. H. Cromwell, F. A. Miller, A. R. Robinson, R. L. Frank and D. J. Wallace, THIS JOURNAL, **71**, 3337 (1949), that the spectral contribution of a tertiary amine group, acting through a carbon–carbon double bond conjugated with a ketone carbonyl, $>N-\overset{|}{C}=CH-\overset{|}{C}=O$, is to lower the C=O stretching frequency in the infrared. In the case of Ij, the action of the tertiary amine group could be transmitted through the additional interposed benzene ring.

TABLE II

SUBSTITUTED 1-METHYL-3,5-DIBENZYL-4-PYRIDONES

					Infrared absorption maxima, cm.$^{-1f}$										
1-Methyl-4-pyridones,[a] 3,5-Di-	II	Yield, %	M.p., °C.	Crystal form[b]	Pyridone C=O	Phenyl and pyridone arom.			Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Benzyl-	a	100	167–168	Ndls.[c]	1648	1600	1550	1496	$C_{20}H_{19}NO$	83.00	83.19	6.62	6.85	4.84	4.76
(*p*-Methyl)-	b	92	231–234	Ndls.[d]	1652		1556	1515	$C_{22}H_{23}NO$	83.23	83.27	7.30	7.45	4.41	4.32
(*m*-Nitro)-	e	85	251–252	Prisms[e]	1650		1561		$C_{20}H_{17}N_3O_5$	63.31	63.05	4.53	4.32	11.08	10.97
(*p*-Methoxy)-	h	85	201.5–202	Prisms[e]	1650	1612	1550	1513	$C_{22}H_{23}NO_3$	75.62	75.33	6.63	6.49	4.01	4.07
(*p*-Isopropyl)-	i	79	215.5–217	Ndls.[c]	1650		1558	1515	$C_{26}H_{31}NO$	83.60	83.57	8.37	8.51	3.75	3.75
(*p*-Dimethylamino)-	j	84	215–217	Ndls.[c]	1652	1607	1556	1495	$C_{24}H_{29}N_3O$	76.76	76.66	7.78	7.68	11.19	11.16
(*p*-Phenyl)-	k	77	242.5–243	Ndls.[d,e]	1649	1615	1555	1524	$C_{32}H_{27}NO$	87.04	86.89	6.16	6.03	3.17	3.14

[a] IIc, obtained as a faintly yellowish glass and not analytically pure, had infrared maxima at 1651, 1608, 1575 and 1498 cm.$^{-1}$; IId separated as colorless needles from dimethylformamide, m.p. 300–301° dec., also off 0.6% in carbon and contaminated with Id, as indicated by the infrared band at 1674 cm.$^{-1}$ in addition to bands at 1650, 1607 and 1565 cm.$^{-1}$; IIf, m.p. 189.5–190°. *Anal.* Calcd. for $C_{20}H_{17}Cl_2NO$: Cl, 19.79. Found: Cl, 15.80; infrared maxima at 1648, 1600, 1556, 1494 cm.$^{-1}$; IIg, yellowish glass; analysis high in carbon; infrared maxima at 1652, 1575 and 1500 cm.$^{-1}$ (smear). [b] All colorless. Solvent: [c] Aqueous ethanol. [d] Ethanol. [e] Acetone. [f] Infrared spectra were determined in Nujol mull.

heptanone (1672 and 1623 cm.$^{-1}$).[20] The ultraviolet absorption spectrum of Ia in 95% ethanol exhibited maxima at 231 mμ (log ϵ 4.23) and at 327 mμ (log ϵ 4.42). The spectrum is practically identical with that of 2,6-dibenzylidenecyclohexanone in the same solvent,[20–22] thus supplying further evidence for the assigned structure (Ia).

With a series of substituted dibenzylidenepiperidones of verified structure thus made available, the feasibility of their aromatization to the corresponding pyridones was investigated. Unlike the case of 2,6-dibenzylidenecyclohexanone,[3] hydrogen bromide in acetic acid (with or without the addition of peroxides) was found to be ineffective. The only isolable product was the hydrobromide of Ia when isomerization of this compound was attempted. It was found, however, that the isomerization proceeded smoothly in the presence of palladium-on-charcoal[5,6] under a wide variety of conditions, both with and without solvent, to give good yields (90–100%) of the desired 1-methyl-3,5-dibenzyl-4-pyridone (IIa). The use of a solvent was found desirable since it permitted uniform temperature control and facilitated separation of the reaction product from the catalyst. Ethylene glycol was discovered to be an ideal solvent, and its boiling point provided a favorable temperature for reaction, while that of ethanol was too low and that of triethylene glycol[6] unnecessarily high. Solution of the substituted dibenzylidenepiperidones (I) was effected readily at the boiling point, the catalyst was separated by filtration of the hot solution, and cooling of the filtrate and/or dilution with water caused the separation of the product. These results indicate that the heterocyclic isomerization can be accomplished under conditions much milder than those required for the corresponding carbocyclic example.[23] While 2,6-dibenzylidenecyclohexanone required heating at 255–265° with palladium-on-carbon for 5 hours to produce 2,6-dibenzylphenol in 91% yield,[5] the aromatization of 1-methyl-2,6-dibenzylidene-4-piperidone was found to occur quantitatively at 195° during one-half hour.

The reaction conditions developed for the conversion of Ia to IIa were applied to the substituted dibenzylidenepiperidones with the results summarized in Table II.

The desired substituted 3,5-dibenzyl-4-pyridones (II) were obtained pure in seven of the eleven conversions attempted (alkyl, aryl, alkoxy and dimethylamino substituents), and in good yield. The two products with benzyl groups possessing *ortho* substituents (IIc, g) failed to crystallize and were not obtained analytically pure; however, their infrared spectra indicated that aromatization had, in fact, occurred. The product from the isomerization of 1-methyl-3,5-di-(*p*-chlorobenzylidene)-4-piperidone (If) was obtained in crystalline form and possessed a sharp melting point and a distinctive spectrum, but microanalysis pointed to the partial stripping of chlorine from the molecule in the process. 1-Methyl-3,5-di-(*p*-nitrobenzylidene)-4-piperidone (Id) was partially isomerized, but the solubility relationships of the isomers made purification of IId difficult, a feature not encountered with the *m*-nitro-substituted compounds (Ie → IIe).

The products resulting from the treatment of compounds I with palladium-on-charcoal in boiling ethylene glycol have been established as substituted 1-methyl-3,5-dibenzyl-4-pyridones (II) by an accumulation of evidence. Analyses indicated that the products are isomeric with their respective precursors, and the loss of visible color was suggestive both of aromaticity and of structural disturbance of the dibenzylidene ketone chromophore. The failure of the products to give color reactions with sulfuric acid[16] also was indicative of the latter. In the infrared spectra (Table II), a new maximum appeared in the region 1648–1652 cm.$^{-1}$, which is attributable to the pyridone carbonyl function,[24–26a] also one at 1550–1561 cm.$^{-1}$, which is associated

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(20) N. J. Leonard and G. C. Robinson, THIS JOURNAL, **75**, 2714 (1953).

(21) H. S. French and L. Wiley, *ibid.*, **71**, 3702 (1949).

(22) J. W. Berry, Ph.D. thesis, University of Illinois, 1953.

(23) This is analogous to the finding of H. Adkins and L. G. Lundsted, THIS JOURNAL, **71**, 2964 (1949), that in the dehydrogenation of heterocycles over nickel catalysts, "the temperatures and time intervals required for reaction are less for the heterocyclic compounds than for the carbocyclic compounds."

(24) R. Adams and V. V. Jones, THIS JOURNAL, **71**, 3826 (1949), observed a maximum at 1649 cm.$^{-1}$ for β-(N-2-pyridone)-propionic acid and one at 1660 cm.$^{-1}$ for N-*n*-propyl-2-pyridone, both in the mull.

(25) W. F. Cockburn and L. Marion, *Can. J. Chem.*, **29**,13 (1951), reported maxima at 1652–1653 cm.$^{-1}$ for a series of alkaloids containing the 1,6-alkylene-2-pyridone moiety, in chloroform solution.

(26) R. Adams, V. V. Jones and J. L. Johnson, THIS JOURNAL, **69**, 1810 (1947), found in the infrared absorption spectrum of 1-methyl-3-hydroxy-4-pyridone, as determined in the mull, maxima at (a) 1650 and (b) 1570 cm.$^{-1}$.

with the pyridone aromatic system.[26b,27] There was also a distinct change in ultraviolet absorption in going from 1-methyl-3,5-dibenzylidene-4-piperidone (Ia) to its isomer. The absorption maximum of the 1-methyl-3,5-dibenzyl-4-pyridone (IIa) in 95% ethanol at 276 mμ (log ε 4.31) may be compared with the maximum of 1-methyl-4-pyridone at 260 mμ (log ε 4.3).[8d–f] The synthetic utility of the general aromatization procedure lies in the fact that the intermediates (I) can be synthesized by reactions applicable to non-aromatic systems, and a conjunct to aromatic substitutions and transformations thus is afforded.

Experimental[28]

Absorption Spectra.—The infrared spectra were obtained with a Perkin–Elmer automatic recording spectrometer, model 21. The ultraviolet absorption spectra were determined using a Cary recording spectrophotometer, model 11.

Substituted 1-Methyl-3,5-dibenzylidene-4-piperidones (I).—The condensations were effected according to the following general directions. To 5 ml. of absolute ethanol were added 0.57 g. (5 millimoles) of 1-methyl-4-piperidone[11] and 10 millimoles of the appropriate aldehyde. After the solution had been heated under reflux for three days, it was cooled, and the solid was removed by filtration and recrystallized from an appropriate solvent. In several instances (see Table I) product failed to separate until the solution was seeded with crystals obtained from condensations in the presence of ethanolic hydrogen chloride or aqueous ethanolic potassium hydroxide.[11] Although some variation of optimum reaction time was observed with the different aldehydes, three days appeared in general to be most satisfactory. The addition of 5 drops of piperidine and 2 drops of acetic acid to the reaction mixture appeared to have little effect on the yields obtained in the condensation. In addition, use of a large excess of aldehyde was found to be unnecessary.

Each of the dibenzylidenepiperidones gave an intense color reaction with concentrated sulfuric acid, varying with the individual compounds from red to blue.

Attempting Aromatization with Hydrogen Bromide–Acetic Acid.—Under the conditions described for the conversion of 3,7-dibenzylidene-1,2-cycloheptanedione to 3,7-dibenzyltropolone,[4] 1-methyl-3,5-dibenzylidene-4-piperidone gave a 75% yield of 1-methyl-3,5-dibenzylidene-4-piperidone hydrobromide, yellow needles, m.p. 235–239° dec. (bath temperature rising at 2° per minute, capillary inserted at 225°).

Anal. Calcd. for $C_{20}H_{20}BrNO$: C, 64.87; H, 5.44; N, 3.78. Found: C, 65.04; H, 5.57; N, 3.74.

The free base obtained from this hydrobromide by neutralization with sodium bicarbonate in aqueous ethanol separated in the form of yellow platelets, melting point and mixed melting point with 1-methyl-3,5-dibenzylidene-4-piperidone identical.

Aromatization with Palladium-on-carbon.—A mixture of 0.5 g. of 1-methyl-3,5-dibenzylidene-4-piperidone and 0.05 g. of 10% palladium-on-carbon catalyst[29] was heated at 175–185° for one hour at 26 mm. pressure. The cooled reaction mixture was taken up in absolute ethanol and filtered to remove catalyst. Dilution with water caused the separation of 0.46 g. (92%) of colorless needles, m.p. 165–166.5°. Similar results could be obtained by sublimation of the reaction mixture at 215–225° and 1 mm. pressure. In either case, one recrystallization from aqueous ethanol gave colorless needles, m.p. 167–168° (also used with Ie and h).

Aromatization with Palladium-on-carbon in Ethylene Glycol. 1-Methyl-3,5-dibenzyl-4-pyridones (II).—The aromatizations were accomplished according to the following general directions. To 5 ml. of ethylene glycol were added 0.5 g. of substituted or unsubstituted 1-methyl-3,5-dibenzylidene-4-piperidone and 0.05 g. of palladium-on-carbon catalyst. This mixture was heated at the reflux temperature (194–195°, thermometer in solution) for one-half hour. The hot solution was filtered to remove catalyst, and the catalyst was washed with several milliliters of hot ethylene glycol. Subsequent cooling and, in some cases, dilution with water to the cloud point, caused the separation of the product, which was filtered, washed with water to remove ethylene glycol, dried, and recrystallized from an appropriate solvent. The results of the aromatizations accomplished according to these directions are included in Table II.

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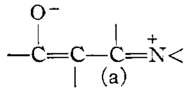
[27] A very strong band in the infrared region 1536–1561 cm.$^{-1}$ ("near 1540 cm.$^{-1}$") has been attributed[19] to a lowered C=C or enhanced C—N frequency due possibly to the form (a) contributing



$$-\overset{\overset{\displaystyle O^-}{|}}{C}=C-\overset{|}{\underset{|}{C}}=\overset{+}{N}<$$

appreciably to the ground state of certain β-amino-α,β-unsaturated ketones.

[28] All melting points are corrected. The authors are indebted to Mrs. Lucy Chang, Mrs. Esther Fett and Mr. Joseph Nemeth for the microanalyses, to Miss Helen Miklas and Mr. James Brader for determination of the infrared spectra, and to Miss Gerardine Meerman for determination of the ultraviolet absorption spectra.

[29] R. Mozingo, *Org. Syntheses*, **26**, 78 (1946).