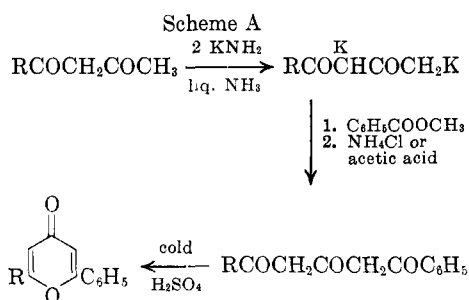# Aroylations of β-Diketones at the Terminal Methyl Group to Form 1,3,5-Triketones. Cyclizations to 4-Pyrones and 4-Pyridones
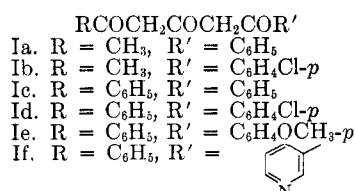
ROBLEY J. LIGHT[1] AND CHARLES R. HAUSER

Several β-diketones were aroylated at the terminal methyl group with aromatic esters by means of two molecular equivalents of potassium amide in liquid ammonia to form 1,3,5-triketones. The triketone from 2-acetylcyclohexanone and methyl benzoate evidently consisted of two isomeric forms which were interconvertible. The triketones were cyclized with acid to form 4-pyrones, and with ammonia or methylamine to give 4-pyridones. These reactions furnish convenient methods of synthesis of such compounds. Mechanisms are considered.

Recently[2] acetyl- and benzoylacetones were benzoylated at the terminal methyl group to form the corresponding 1,3,5-triketones, which were cyclized to give pyrones (Scheme A, R = CH$_3$ or C$_6$H$_5$).[3]

Scheme A

$$\text{RCOCH}_2\text{COCH}_3 \xrightarrow[\text{liq. NH}_3]{\text{2 KNH}_2} \overset{K}{\text{RCOCHCOCH}_2\text{K}}$$

1. C$_6$H$_5$COOCH$_3$
2. NH$_4$Cl or acetic acid

$$\underset{\text{H}_2\text{SO}_4}{\overset{\text{cold}}{\longleftarrow}} \text{RCOCH}_2\text{COCH}_2\text{COC}_6\text{H}_5$$

In the present investigation this novel mode of aroylation of β-diketones and the cyclization of the resulting 1,3,5-triketones were found to be quite general. The triketones were also cyclized with ammonia to form 4-pyridones.

Aroylations of β-diketones to form 1,3,5-triketones. Acetyl- and benzoylacetones were aroylated not only with methyl benzoate but also with other appropriate aromatic esters to form triketones Ia–f. Similarly, 2-acetylcyclohexanone, 2-acetyl-cyclopentanone, and o-hydroxyacetophenone were aroylated with the appropriate esters to give triketones IIa–b, III and IV respectively. The results are summarized in Tables I and II.

RCOCH$_2$COCH$_2$COR'

Ia. R = CH$_3$, R' = C$_6$H$_5$
Ib. R = CH$_3$, R' = C$_6$H$_4$Cl-*p*
Ic. R = C$_6$H$_5$, R' = C$_6$H$_5$
Id. R = C$_6$H$_5$, R' = C$_6$H$_4$Cl-*p*
Ie. R = C$_6$H$_5$, R' = C$_6$H$_4$OCH$_3$-*p*
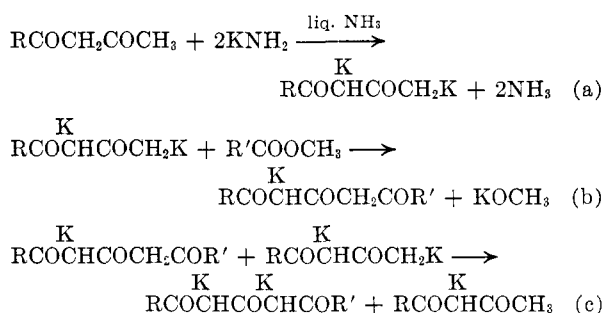If. R = C$_6$H$_5$, R' =

(1) National Science Foundation Predoctoral Fellow, 1958–1960.

(2) C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **80**, 6360 (1958).

(3) For the present purpose only carbanion resonance forms of the potassium salts are considered, although other resonance forms may contribute more to the structure of the molecule.

IIa. R = C$_6$H$_5$
IIb. R = C$_6$H$_4$OCH$_3$-*p*

III

IV
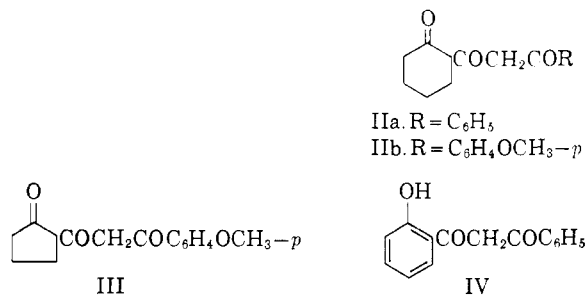
The general procedure for effecting these condensations involved the addition of the β-diketone to two molecular equivalents of potassium amide in liquid ammonia, followed by one-half of an equivalent of the ester. These proportions of the reactants were chosen to comply with the following three-step mechanism, which is an adaptation of that involved in the acylations of ketones with esters by alkali amides to form β-diketones.[4]

$$\text{RCOCH}_2\text{COCH}_3 + 2\text{KNH}_2 \xrightarrow{\text{liq. NH}_3}$$
$$\overset{K}{\text{RCOCHCOCH}_2\text{K}} + 2\text{NH}_3 \quad \text{(a)}$$

$$\overset{K}{\text{RCOCHCOCH}_2\text{K}} + \text{R'COOCH}_3 \longrightarrow$$
$$\overset{K}{\text{RCOCHCOCH}_2\text{COR'}} + \text{KOCH}_3 \quad \text{(b)}$$

$$\overset{K}{\text{RCOCHCOCH}_2\text{COR'}} + \overset{K}{\text{RCOCHCOCH}_2\text{K}} \longrightarrow$$
$$\overset{K}{\text{RCOCHCOCHCOR'}} + \overset{K}{\text{RCOCHCOCH}_3} \quad \text{(c)}$$

Although essentially all of the β-diketone is first converted to its dipotassio salt (step a), only half of this salt may condense with the ester (step b) as the other half effects the conversion of the resulting monopotassio salt of the triketone to its dipotassio salt (step c). Therefore half of the starting β-diketone is regenerated as its monosodio salt in this last step. Actually most of this regenerated β-diketone may be recovered on acidification, a fact that supports the three step mechanism given above.

It can be seen from Table I that the yields of the triketones were fairly good to good (40–62%), ex-

(4) See C. R. Hauser, F. W. Swamer, and J. T. Adams, *Org. Reactions*, **VIII**, 62–63, 114 (1954).

TABLE I

YIELDS OF 1,3,5-TRIKETONES FROM β-DIKETONES AND ESTERS BY MEANS OF POTASSIUM AMIDE

β-Diketone	Ester	Triketone	M.P. °[a]	Yield, %[b]
Acetylacetone	Methyl benzoate	1-Phenyl-1,3,5-hexanetrione (Ia)	105–109[c,d]	53[e]
Acetylacetone	Methyl p-chlorobenzoate	1-(p-Chlorophenyl)-1,3,5-hexanetrione (Ib)	97–98[f]	52
Benzoylacetone	Methyl benzoate	1,5-Diphenyl-1,3,5-pentanetrione (Ic)	106–110[g,h]	57–62[i,j]
Benzoylacetone	Methyl p-chlorobenzoate	1-(p-Chlorophenyl)-5-phenyl-1,3,5-pentanetrione (Id)	106–107.5[h]	47
Benzoylacetone	Methyl anisate	1-(p-Methoxyphenyl)-5-phenyl-1,3,5-pentanetrione (Ie)	121–122[k]	61[l]
Benzoylacetone	Ethyl nicotinate	1-Phenyl-3-pyridyl-1,3,5-pentanetrione (If)	90–91[m]	40
2-Acetylcyclohexanone	Methyl benzoate	1-(2-Oxocyclohexyl)-3-phenyl-1,3-propanedione (IIa)	83–86[n,h] 100–110[q,m]	37–44[o,p]
2-Acetylcyclohexanone	Methyl anisate	1-(p-Methoxyphenyl)-3-(2-oxocyclohexyl)-1,3-propanedione (IIb)	86–90[r,s]	45[t]
2-Acetylcyclopentanone	Methyl anisate	1-(p-Methoxyphenyl)-3-(2-oxocyclopentyl)-1,3-propanedione (III)	91–95[u]	42[t]
o-Hydroxyacetophenone	Methyl benzoate	o-Hydroxydibenzoylmethane (IV)	117–122[v,f]	14[t]

[a] Melting points given are for analytical samples in the cases of new compounds. [b] Yields are based on the ester. The melting point range for the product from which the yield was determined was usually slightly greater than that given in the table. [c] Reported m.p.[2] 107–108° and 106–107°.[16] [d] Recrystallized from methanol or 95% ethanol. [e] Reported[2] yield, 60%. [f] Recrystallized from methanol. [g] Reported[2, 15] m.p. 107–108°. The melting point was changed to 110–115° by recrystallizing from acidic ethanol. See experimental and note g., Table II. [h] Recrystallized from 95% ethanol. [i] Reported[2] yield, 58%. [j] A 96% crude yield of the theoretically regenerated benzoylacetone was recovered. [k] Recrystallized from benzene. [l] An 86% crude yield of the theoretically regenerated benzoylacetone was recovered. [m] Recrystallized from a mixture of ethanol and water. [n] α-Form, the purest fraction isolated. [o] Yield includes both α- and β-forms. [p] A 92% yield of the theoretically regenerated 2-acetylcyclohexanone was recovered. [q] β-Form, the purest fraction isolated. [r] A small amount of crystals, m.p. 80–105°, was also obtained. [s] Recrystallized from methanol or n-hexane. [t] Crude yield. [u] Recrystallized from a mixture of benzene and petroleum ether (b.p. 30–60°). [v] Crude. Reported[19] m.p. 117–120° for crude material.

TABLE II

INFRARED DATA, ENOL TESTS, AND ANALYSES FOR 1,3,5-TRIKETONES

Triketone	Color of Crystals	Infrared Spectra[a,b] μ μ	Enol Test[c]	Empirical Formula	Analyses,[a] % Carbon Calcd.	Found	Hydrogen Calcd.	Found
Ia[d]	Straw yellow	6.24, 6.37	Green	—	—	—	—	—
Ib	Pale green	6.19, 6.37	Green	$C_{12}H_{11}O_3Cl$[e]	60.39	60.64	4.64	4.83
Ic[f]	Brown[g]	6.24, 6.37	Green	—	—	—	—	—
Id	Yellow	6.24, 6.40	Green	$C_{17}H_{13}O_3Cl$[h]	67.9	67.78	4.36	4.35
Ie	Bright yellow	6.24, 6.37	Green	$C_{18}H_{16}O_4$	72.96	73.26	5.44	5.61
If[i]	Yellow	6.26, 6.40	Green	$C_{16}H_{13}O_3N$[j]	71.90	72.09	4.90	5.07
IIa α-form[k]	Brown	6.24, 6.35[l]	Green[m]	$C_{15}H_{16}O_3$	73.75	73.70	6.60	6.78
β-form[k]	Pale yellow	6.14, 6.28, 6.39[n]	Reddish-brown	$C_{15}H_{16}O_3$	73.75	73.79	6.60	6.58
IIb	Brownish-yellow	6.24,[o] 6.30, 6.40	Green	$C_{16}H_{18}O_4$	70.05	70.29	6.61	6.51
III	Pale green	6.13[o] 6.30	Green	$C_{15}H_{16}O_4$	69.21	69.02	6.20	6.11
IV	Yellow	6.24, 6.37	Reddish-brown	—	—	—	—	—

[a] Reference 33. [b] Absorption bands found in the enol-chelate region from 5.5 μ to 6.5 μ. All bands are strong unless noted otherwise. [c] Color produced with ethanolic ferric chloride. [d] Ultraviolet spectrum:[33] λ_{max} = 246 mμ, 337 mμ; log ε = 3.80 (8 × 10⁻⁵M solution), 4.16. [e] Anal. Calcd. for $C_{12}H_{11}O_2Cl$: Cl, 14.96. Found: 14.71. [f] Ultraviolet spectrum:[33] λ_{max} = 247 mμ, 374 mμ; log ε = 4.04, 4.50. [g] Yellow crystals were obtained when Ic was recrystallized from acidic ethanol. See experimental and note g. Table I. [h] Anal. Calcd. for $C_{17}H_{13}O_3Cl$: Cl, 11.79. Found: 11.95. [i] Amphoteric. See experimental. [j] Anal. Calcd. for $C_{16}H_{13}O_3N$: N, 5.24. Found: 5.20. [k] The purest fraction isolated. [l] The same infrared spectrum was obtained in carbon tetrachloride solution as in the potassium bromide pellet. [m] Changed to reddish-brown on standing. [n] Showed a strong hydroxyl band at 3.00 μ. The infrared spectrum of a carbon tetrachloride solution, however, was identical with that of the α-form. [o] Shoulder.

cept that (14%) for compound IV. Although these yields were based on the ester, at least certain of them would not be much less if based on the β-diketone used minus that recovered (see notes j, l, and p of Table I).

As the conversion yield of a ketone to a β-diketone may often be improved by the use of an extra equivalent of alkali amide,[4] it seemed possible

that the conversion yield of a β-diketone to a triketone might be improved similarly. In this procedure step c in the above mechanism would be effected by an extra equivalent of alkali amide, thereby avoiding the regeneration of half of the β-diketone. Accordingly, benzoylacetone was added to three molecular equivalents of potassium amide in liquid ammonia, followed by two equivalents of

methyl benzoate.[5] Triketone Ic was obtained in 37% yield based on the diketone. Although this conversion yield is a little higher than that (about 30% based on the diketone) obtained in the general procedure, only 21% of the crude diketone was recovered as compared to 48% recovered in the general procedure (see note j, Table I). The general procedure seems to provide a slightly cleaner reaction, but this second method may prove more satisfactory in cases where the diketone is very expensive and difficult to recover.

The structures of the triketones were established by cyclization to 4-pyrones and 4-pyridones as described in the next two sections. These results showed that the triketones did not have such a structure as V, which could not have been converted to these cyclic products. Neither could the triketones from 2-acetylcyclohexanone and 2-acetylcyclopentanone have been the ring-methylene aroylation products, for example, VI, which should not be expected to cyclize readily to give a 4-pyrone
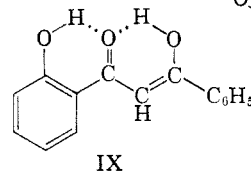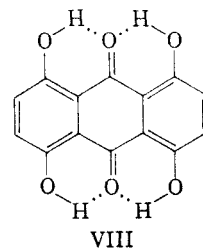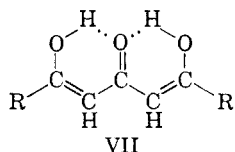

V

VI
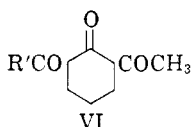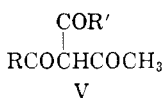
or a 4-pyridone for steric reasons. This is in agreement with the previous alkylations of 2-acetylcyclohexanone and 2-acetylcyclopentanone with benzyl chloride, in which the terminal methyl group and not the ring-methylene group was involved in the condensation.[6]

It can be seen from Table II that for all of the triketones studied the infrared bands in the carbonyl and enol-chelate region from 5.5μ to 6.5μ were above 6μ, indicating a considerable shift in the carbonyl absorption. Except for a weak band at 2.9μ in all the spectra run in potassium bromide pellets (attributed to moisture in the potassium bromide), only the β-form of triketone IIa gave a strong band at 3μ showing the presence of a free hydroxyl group. That no hydroxyl band was being masked by the potassium bromide was demonstrated in the case of triketones Ia and Ic, which showed no bands near 3μ when their spectra were determined in mineral oil mulls. These spectra suggest an enol-chelate structure such as VII for the triketones. This structure is similar to those proposed for 1,4,5,8-tetrahydroxyanthraquinone (VIII)[7] and for o-hydroxydibenzoylmethane (IX),[8] the keto form of which would be IV.

VII

IX

VIII

The enol-chelate absorption of VIII was reported as 1592 cm.$^{-1}$ (6.27μ) and 1577 cm.$^{-1}$ (6.34μ)[7] which is comparable with the bands given in this region for the triketones listed in Table II. The spectra in this region are complicated by the absorption of the phenyl group, and the correct assignment of the individual bands is difficult.[9] Ultraviolet spectra for triketones Ia and Ic are given in notes d and f of Table II.

It can further be seen from Table II that the triketones produced green enol tests with ethanolic ferric chloride, except the β-form of triketone IIa and compound IV, which gave reddish-brown enol tests. β-Diketones of the type $RCOCH_2COR'$ generally give cherry red enol tests.[10] The metal chelating properties of the triketones should be interesting.[11]

Triketone IIa was obtained in two forms, designated α and β, which differed in their melting points, solubilities, colors, infrared spectra, and enol tests (see Tables I and II). Although neither form was isolated as a sharply melting solid, the infrared spectrum of the samples of each prepared for analysis indicated that they were not contaminated appreciably with one another. Yet each could be converted to the other (see experimental).

From its properties, the α-form appears to have the enol-chelate type of structure X similar to that (VII) represented above for other triketones.

X

(5) While only one equivalent of this ester would theoretically be required, an extra equivalent was employed in accordance with the corresponding procedure for the acylation of ketones; see ref. 4, page 114.

(6) T. M. Harris and C. R. Hauser, *J. Am. Chem. Soc.*, **81**, 1160 (1959).

(7) H. Bloom, L. H. Briggs, and B. Cleverley, *J. Chem. Soc.*, 178 (1959). See also ref. 9, pp. 142–144.
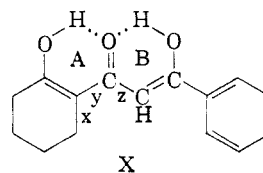
(8) E. H. Holst, Ph.D. thesis, 1955, Pennsylvania State University. Private communication from W. C. Fernelius, Department of Chemistry, Pennsylvania State University. See also ref. 9, p. 143.

(9) See L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2d. ed., John Wiley and Sons, New York, N. Y., 1958, p. 64.

(10) See G. T. Morgan, H. D. K. Drew, and C. R. Porter, *Ber.*, **58**, 333 (1925); C. R. Hauser and J. T. Adams, *J. Am. Chem. Soc.*, **66**, 345 (1944).

(11) Samples of triketones Ia and Ic have been sent to W. C. Fernelius of Pennsylvania State University, who is studying the metal derivatives of these triketones.

It is the least polar form judging from solubilities in ethanol and carbon tetrachloride, and its infrared spectrum more nearly resembles those of the other triketones. The more polar β-form could possibly be a conformational isomer in which the planarity of enol-chelate ring A in formula X is disrupted by rotation about bond y, thus freeing the hydroxyl group and accounting for the 3.00 μ band in the infrared spectrum. The eclipsed interaction between bonds x and z would be expected to oppose the stabilizing effect of the hydrogen bonding in ring A. A similar eclipsed interaction has been suggested to occur in 3-methylacetylacetone, the enol form of which shows an hydroxyl band at 2.94μ, whereas the enol form of acetylacetone shows only a weak band at that frequency.[12,13] The possibility that the β-form of IIa was a cyclic hemiacetal analogous to the intermediate shown in equation 2 has not been ruled out. However, such a structure would be expected to absorb at a shorter wave length than that observed in the carbonyl region (see Table II), and it would not be expected to give a positive enol test.

Triketone Ic was obtained both as brown and as bright yellow crystals (see note g, Table I), but the two samples gave identical infrared spectra.
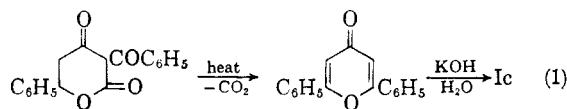
It should be mentioned that two isomeric forms of the triketone 3,5,7-nonanetrione have been reported by Deshapande.[14] One form was converted to the other having a different color and a different molar refractive index.

In contrast to the β-diketones listed in Table I, no triketone was isolated when trifluoroacetylacetone or dimedone (1,1-dimethylcyclohexane-3,5-dione) was treated with methyl benzoate under similar conditions. The dimedone was largely recovered.

Whereas methyl benzoate and the other aromatic esters listed in Table I served as satisfactory aroylating agents, an attempt to effect the propionylation of the dipotassio salt of benzoylacetone with phenyl propionate was unsuccessful. As the starting β-diketone was mainly recovered, its dipotassio salt appears to have merely ionized an α-hydrogen of the ester, thereby rendering both reactants ineffective.
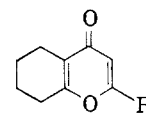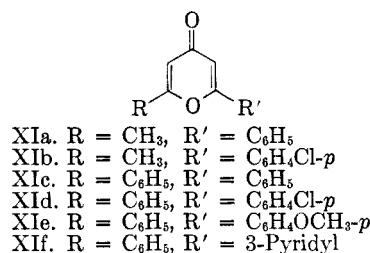
The present method of synthesis of 1,3,5-triketones is considered more convenient than that described previously involving the base catalyzed ring - opening of a 4 - pyrone.[15-18] The latter method may be illustrated for the symmetrical triketone Ic

starting with dehydrobenzoyl acetic acid (Equation 1).

$$C_6H_5 \overset{O}{\underset{O}{\bigcirc}}\!\!\overset{COC_6H_5}{\underset{O}{\Big|}} \xrightarrow[-CO_2]{heat} C_6H_5 \overset{O}{\underset{O}{\bigcirc}} C_6H_5 \xrightarrow[H_2O]{KOH} Ic \quad (1)$$
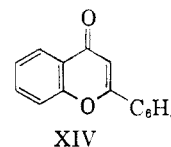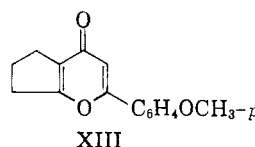
However, for the special case of compound IV, our method appears not to be as satisfactory as that involving the base catalyzed rearrangement of the O-benzoyl derivative of o-hydroxyacetophenone.[19]

Cyclization of 1,3,5-triketones to form 4-pyrones. Triketones Ia–f were cyclized by means of cold sulfuric acid[20] to form 4-pyrones XIa–f. Similarly triketones IIa–b, III and IV gave pyrones XIIa–b, XIII and flavone XIV respectively. The results are summarized in Tables III and IV.

XIa. R = CH$_3$, R' = C$_6$H$_5$
XIb. R = CH$_3$, R' = C$_6$H$_4$Cl-p
XIc. R = C$_6$H$_5$, R' = C$_6$H$_5$
XId. R = C$_6$H$_5$, R' = C$_6$H$_4$Cl-p
XIe. R = C$_6$H$_5$, R' = C$_6$H$_4$OCH$_3$-p
XIf. R = C$_6$H$_5$, R' = 3-Pyridyl

XIIa. R = C$_6$H$_5$
XIIb. R = C$_6$H$_4$OCH$_3$-p

XIII

XIV

The mechanism of the reaction presumably involves the cyclization of an enol form of the triketone to give a hemiacetal type of structure, which undergoes dehydration. This may be illustrated with the symmetrical triketone Ic (Equation 2). For the other triketones, which are unsymmetrical, the reaction may follow two paths leading to the same pyrone, depending upon whether the 1- or 3-keto group is involved in the enolization.

(12) See G. S. Hammond, *Steric Effects in Organic Chemistry*, M. S. Newman, ed., John Wiley and Sons, New York, N. Y., 1956, p. 446–447.

(13) Molecular models show that the interference of the eclipsing groups is greater in triketones IIa and IIb than in triketones III and IV. While IIb may have a β-form (see note r, Table I), III and IV give no such indication.

(14) S. S. Deshapande, Y. V. Dingankar, and D. N. Kopil, *J. Ind. Chem. Soc.*, 11, 595 (1934).

(15) K. Balenović and R. Munk, *Archiv. Kem.*, 18, 41 (1946); *Chem. Abstr.* 42, 2926a (1948).

(16) S. Ruhemann, *J. Chem. Soc.*, 93, 1281 (1908).

(17) G. Soliman and I. E. El-Kholy, *J. Chem. Soc.*, 1755 (1954).

(18) In this laboratory 2-methyl-6-phenyl-4H-pyran-4-one (XIa) was opened with barium hydroxide according to Ruhemann's procedure[16] to form triketone Ia in 46% yield.

(19) T. S. Wheeler, *Org. Synthesis*, 32, 72 (1952).

(20) Triketone Ic was first cyclized in this manner by Balenović; see ref. 15.

TABLE III

CYCLIZATION OF 1,3,5-TRIKETONES TO FORM 4-PYRONES

Triketone	Pyrone	Recrystallization Solvent	M.P. °^{a}	Yield, %^{b}
Ia	2-Methyl-6-phenyl-4H-pyran-4-one (XIa)	n-Hexane	85–87^{c,d}	60
Ib	2-(p-Chlorophenyll)-6-methyl-4H-pyran-4-one (XIb)	Methanol-water, or ethanol-pet. ether^e	111–112.5	90
Ic	2,6-Diphenyl-4H-pyran-4-one (XIc)	Ethanol-water	138.5–141.5^f	91^g
Id	2-(p-Chlorophenyl)-6-phenyl-4H-pyran-4-one (XId)	Ethanol-water	159–160^h	90
Ie	2-(p-Methoxyphenyl)-6-phenyl-4H-pyran-4-one (XIe)	Ethanol-water, or ethanol-benzene	162.5–164^i	88
If	2-Phenyl-6-(3-pyridyl)-4H-pyran-4-one (XIf)	Ethanol-water	157–158	91
IIa^j	5,6,7,8-Tetrahydroflavone (XIIa)	Ethanol-water	121–123	70–76
IIb	4'-Methoxy-5,6,7,8-tetrahydroflavone (XIIb)	Ethanol-water	148–150^k	70
III	Cyclopenteno[b]-6-(p-methoxyphenyl)-4H-pyran-4-one (XIII)	Ethanol-water	160–162	59^l
IV	Flavone (XIV)	Ethanol-water	96–98^m	63

^{a} Melting points given are for analytical samples in the cases of new compounds. ^{b} The melting point range for the product from which the yield was determined was usually greater than that given in the table. ^{c} Reported[36] m.p. 87–88°. ^{d} Isolated first as a low melting solid, (see Experimental). ^{e} B.p. 30–60°. ^{f} Reported m.p.[2] 138.5–141.5° and 139–141°.[15] ^{g} Reported yield,[2] 94%. ^{h} Reported[17] m.p. 160°. ^{i} Reported[17] m.p. 160–161°. ^{j} Both the α- and β-forms of IIa gave the same pyrone. ^{k} Isolated first as a high melting salt (see experimental). ^{l} Crude yield was 86%. ^{m} Reported m.p. 97°; H. Simonis, Z. Angew. Chem., **39**, 1461 (1926).

TABLE IV

INFRARED AND ULTRAVIOLET SPECTRA AND ANALYSES FOR 4-PYRONES

Pyrone	Infrared Spectra^{a,b,c} μ	μ	μ	Ultraviolet Spectra^a λ_{max}, mμ	log ε	Empirical Formula	Analyses,^{a} % Carbon Calcd.	Found	Hydrogen Calcd.	Found
XIa	6.00s, 6.19s			272^d	4.31^d	—	—	—	—	—
XIb	6.03s, 6.18m, 6.26m			278	4.31	$C_{12}H_9O_2Cl^e$	65.32	65.06	4.11	4.02
XIc	6.05 s, 6.17 m–w,	6.28 m–w, 6.36 m–w		254, 281^f	4.31, 4.36^f	—	—	—	—	—
XId	6.03 s, 6.25 s, 6.37 w			260, 283	4.35, 4.39	—	—	—	—	—
XIe	6.09 s, 6.26 s, 6.39 m			268, 313	4.41, 4.32	—	—	—	—	—
XIf^g	6.09 s, 6.29 m			250, 282	4.22, 4.31	—	—	—	—	—
XIIa	6.05 s, 6.20 s			272	4.35	$C_{15}H_{14}O_2$	79.62	79.58	6.24	6.17
XIIb	6.05 s, 6.21 s			301	4.35	$C_{16}H_{16}O_3$	74.98	74.77	6.29	6.39
XIII	6.04 s, 6.23 s, 6.37 m			302	4.37	$C_{15}H_{14}O_3$	74.36	74.45	5.83	6.05
XIV	6.07 s, 6.27 w, 6.36 w			250, 293	4.32, 4.40	—	—	—	—	—

^{a} Reference 33. ^{b} s = strong, m = medium, w = weak. ^{c} Absorption bands found in the region from 5.5 μ to 6.5 μ. ^{d} Reported[21] ultraviolet spectrum: λ_{max} = 274 mμ; log ε = 4.32. ^{e} Anal. Calcd. for $C_{12}H_9O_2Cl$: Cl, 16.07. Found: 16.13. ^{f} Reported[21] ultraviolet spectrum: λ_{max} = 257 mμ, 283 mμ; log ε = 4.36, 4.41. ^{g} Satisfactory analysis was obtained only for a picrate (see Experimental).
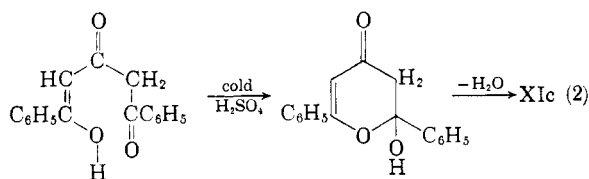

It can be seen from Table III that the yields of the 4-pyrones were good to excellent (59–91%). Both the α- and β-forms of triketone IIa gave the same pyrone XIIa in equally good yields.

It can be seen from Table IV that the carbonyl absorption of all the 4-pyrones was at 6μ or above, which is to be expected for the doubly conjugated carbonyl group. Moreover, the 4-pyrones all gave similar ultraviolet spectra which were in agreement with those reported earlier[21] for XIa and XIc (see notes d and f, Table IV) and which

seemed to be characteristic of the 4-pyrone structure. The pyrone structure of XIIa was further supported by aromatization of the cyclohexane ring to form flavone (XIV).

The present method of synthesis of 4-pyrones through the triketones compares favorably with earlier methods in most cases and is an improvement in some. One of the better previous methods involved the Claisen type of acylation of ketones with ethyl phenylpropiolate accompanied by cyclization (Equation 3).[17]
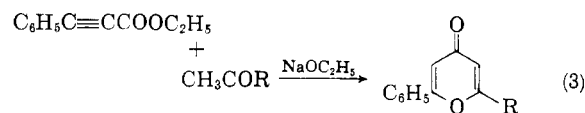
(21) P. Franzosini, G. Traverso, and M. Sanesi, Ann. Chim. (Rome), **45**, 128–140 (1955).

TABLE V

CYCLIZATION OF 1,3,5-TRIKETONES TO FORM 4-PYRIDONES

Triketone	Pyridone	Recryst. Solvent	M.P.°[a]	Yield,[b] %
Ia	2-Methyl-6-phenyl-4-(1H)-pyridone (XVa)	Water[c]	175–177[d]	quant.
Ib	2-(p-Chlorophenyl)-6-methyl-4(1H)-pyridone (XVb)	Methanol	236–237[e]	70
Ic	2,6-Diphenyl-4(1H)-pyridone (XVc)	Benzene	175–179[f]	45[g]
Id	2-(p-Chlorophenyl)-6-phenyl-4(1H)-pyridone (XVd)	Ethanol	208–212	30[g,h]
Ie	2-(p-Methoxyphenyl)-6-phenyl-4(1H)-pyridone (XVe)	Ethanol	219–222	16[g]
IIa[i]	2-Phenyl-5,6,7,8-tetrahydro-4(1H)-quinolone (XVIa)	Ethanol	266–269[j]	76
IIb	2-(p-Methoxyphenyl)-5,6,7,8-tetrahydro-4(1H)-quinoline (XVIb)	Propanol-water	289–291[e]	75
III	Cyclopenteno[b]-6-(p-methoxyphenyl)-4(1H)-pyridone (XVII)	—[k]	>300[e]	70[h]

[a] Melting points given are for analytical samples in the cases of new compounds. [b] The melting point range for the product from which the yield was determined was usually greater than that given in the table. [c] Water solution formed a gell when cooled (see experimental). [d] Crude residue. Reported[16] m.p. 177–178°. Part of the recrystallized material melted at 176–180° and the remainder at 189–191° (see experimental). [e] This melting point was obtained after sublimation *in vacuo.* [f] Reported[27] m.p. 178°. [g] Most of the unchanged triketone was recovered from the reaction mixture. [h] Crude yield. [i] α-Form was used. [j] Decomposes. [k] Attempts to recrystallize XVII from various solvents were unsuccessful.

TABLE VI

INFRARED AND ULTRAVIOLET SPECTRA AND ANALYSES FOR 4-PYRIDONES

| Pyridone	Infrared Spectra[a,b,c] μ μ μ	Ultraviolet Spectra[a] λmax, mμ log ε	Empirical Formula	Analyses,[a] % Carbon Calcd.	Found	Hydrogen Calcd.	Found	Nitrogen Calcd.	Found
XVa	6.16 s, 6.34 s, 6.55 b	238 4.40	—	—	—	—	—	—	—
XVb	6.16 s, 6.36 m–s, 6.52 s	243 4.47	$C_{12}H_{10}ONCl$	65.61	65.51	4.59	4.74	6.38	6.49
XVc	6.18 s, 6.35 s, 6.54 s	246 4.48	—	—	—	—	—	—	—
XVd	6.19 s, 6.38 s, 6.56 s	251 4.41	$C_{17}H_{12}ONCl$	72.47	72.32	4.30	4.34	4.97	5.10
XVe	6.17 s, 6.34 m, 6.49 s	256 4.41	$C_{18}H_{15}O_2N$	77.96	77.90	5.45	5.26	5.05	5.13
XVIa	6.15 s, 6.30 w, 6.54 s	241, 4.45, 268 4.21	$C_{15}H_{15}ON$	79.97	79.70	6.71	6.59	6.22	6.13
XVIb	6.15 s, 6.31 w, 6.57 s	251, 4.40, 272 4.30	$C_{16}H_{17}O_2N$	75.27	75.22	6.71	6.86	5.49	5.48
XVII	6.19 s, 6.36 w, 6.52 s, 6.59 s	251, 4.38, 275 4.26	$C_{15}H_{15}O_2N$	74.66	74.84	6.27	6.04	5.81	6.04

[a] Reference 33. [b] s = strong, m = medium, w = weak, b = broad. [c] Absorption bands found in the region from 5.5μ to 6.6μ.

It should be mentioned that long ago Feist[22] prepared the symmetrical 4-pyrone XIc by the decarboxylation of dehydrobenzoylacetic acid (see Equation 1). Recently, Neelakantan[23] reported that this 4-pyrone can be prepared in excellent yield by condensing ethyl benzoate with acetone in the presence of sodium ethoxide, but no details were given.
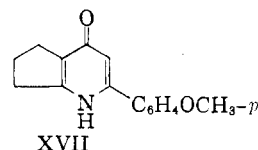
It should be pointed out that 4-pyrones such as XIIa-b apparently can not be prepared by the reduction of flavones, as the direct reduction of flavone will occur first in the oxide ring.[24]

Cyclizations of 1,3,5-triketones with ammonia to form 4-pyridones. Triketones Ia-e were converted to pyridones XVa-e by treatment with ethanolic ammonia.[25] Similarly triketones IIa-b and III

gave pyridones XVIa-b and XVII respectively. The results are summarized in Tables V and VI.
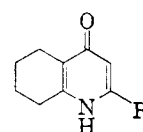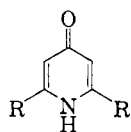
XVa. R = CH₃, R' = C₆H₅   XVIa. R = C₆H₅
XVb. R = CH₃, R' = C₆H₅Cl-p   XVIb. R = C₆H₄OCH₃-p
XVc. R = C₆H₅, R' = C₆H₅
XVd. R = C₆H₅, R' = C₆H₄Cl-p
XVe. R = C₆H₅, R' = C₆H₄OCH₃-p

XVII

These reactions appear to be initiated by the addition of the ammonia to the 1- or 3-carbonyl group of the triketone to form a ketone-ammonia type of intermediate,[26] which undergoes cyclization and dehydration to produce the 4-pyridone.

(22) F. Feist, *Ber.,* 23, 3726 (1890).
(23) L. Neelakantan, *J. Org. Chem.,* 22, 1584 (1957).
(24) See S. Wawzonek, *Heterocyclic Compounds,* Vol. 2, R. C. Elderfield, ed., John Wiley and Sons, New York, 1951, pp. 256–57.
(25) Apparently this method has not previously been employed with triketones, although triketone Ia has been cyclized with aqueous ammonia to form XVa in unreported yield.[16]

(26) This intermediate might also arise from the conjugate addition of ammonia to an enol form of the triketone.

This may be represented with the symmetrical triketone Ic (Equation 4).

$$\text{XVc} \quad (4)$$
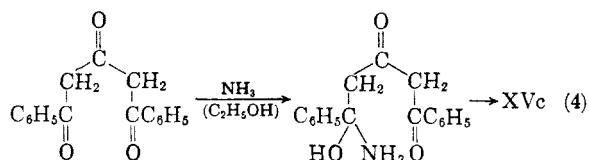
Although the 4-pyridone XVc has previously been prepared from 4-pyrone XIc and ethanolic ammonia,[27] the pyrone was apparently not an intermediate in the present reaction, as the conditions employed by us failed to effect the conversion of this pyrone or of pyrone XIe to the corresponding 4-pyridones.

It can be seen from Table V that the yields were good to excellent for most of the 4-pyridones. The low yield (16%) obtained from triketone Ie could probably be improved, as most of the unchanged triketone was recovered. The present method appears more convenient than the earlier methods which proceed through 4-pyrones.[22,27-30]

It can be seen from Table VI that the 4-pyridones give slightly larger extinction coefficients than the 4-pyrones in the ultraviolet region. This may indicate that the 4-pyridones have the quinoid nucleus (tautomer XVIII) rather than the benzenoid nucleus (tautomer XIX). In line with this the extinction coefficient of 1,2,6-trimethyl-4-(1H)-pyridone has been reported[31] as about 14,000, which is close to that for 2,6-dimethyl-4H-pyran-4-one, whereas that for the benzenoid structure in 2,6-dimethyl-4-methoxypyridine is less than 1500.[31]
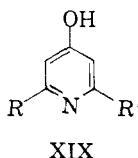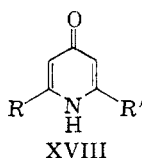
Finally triketone Ic was cyclized with methylamine to form the N-methyl-4-pyridone XX in 42% yield. This compound has previously been prepared by the reaction of methylamine with the unsaturated ketone XXI, but no yield was reported.[32]
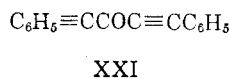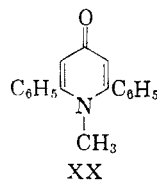
At least certain of the other 1,3,5-triketones prepared in this work could presumably also be cyclized with primary amines to form corresponding N-alkyl or N-aryl derivatives.

The N-methyl pyridone XX reacted with an equivalent of methyl iodide to form an ether insoluble salt, but the site of the alkylation (nitrogen or oxygen) was not determined.

EXPERIMENTAL[33]

β-Diketones and esters. 2-Acetylcyclohexanone and 2-acetylcyclopentanone were prepared by the boron fluoride catalyzed acetylation of cyclohexanone and cyclopentanone respectively.[34] Methyl p-chlorobenzoate was prepared by the esterification of p-chlorobenzoic acid and methanol by means of sulfuric acid. The other β-diketones and esters were obtained from commercial sources and usually redistilled or recrystallized.

Preparation of the dipotassio salts of β-diketones. To a stirred solution of 0.4 mole of potassium amide in 500–600 ml. of commercial anhydrous liquid ammonia[2] was added 0.2 mole of the β-diketone. Solids were added through a powder funnel, and liquids as a solution in about 50 ml. of anhydrous ether. Acetylacetone was first converted into its ammonium salt by carefully pouring some liquid ammonia into an ether solution of this diketone. A vigorous reaction occurred to precipitate a voluminous white solid. This slurry was then poured into the potassium amide solution through a powder funnel, rinsing the last bit in with some dry ether. Care should be taken to exclude moisture during this operation. Other β-diketones showed little or no reactivity towards the liquid ammonia and could be added directly to the potassium amide solution.

The solution was stirred for 20–60 min. and then considered to contain 0.2 mole of the dipotassio β-diketone. Benzoylacetone formed a yellowish green solution, 2-acetylcyclopentanone a green solution, and acetylacetone and 2-acetylcyclohexanone greyish white suspensions. o-Hydroxyacetophenone formed a white precipitate unless the solution was more dilute.

Aroylation of dipotassio β-diketones to form 1,3,5-triketones (Tables I and II). To a stirred solution or suspension of 0.2 mole of a dipotassio β-diketone in 500 ml. of liquid ammonia was added, during 1 or 2 min., 0.1 mole of an ester dissolved in about 50 ml. of anhydrous ether. After stirring for 30–90 min. longer, the reaction mixture was neutralized and worked up by one of the procedures described below.

In the preparations of triketones Ia–b, IIa–b, III, and IV, the liquid ammonia of the reaction mixture was evaporated as an equal volume of ether was added. The resulting ethereal suspension was then poured with stirring into a slight excess of cold, dilute acetic acid. After shaking thoroughly, the two layers were separated, care being taken that the aqueous layer was weakly acidic. The ethereal layer was washed with water, followed by sodium bicarbonate solution, and dried over Drierite. The solvent was removed and the residue was recrystallized directly to give the triketone, or the β-diketone was first removed by distillation in vacuo and the residue then recrystallized.

(27) L. Neelakantan, J. Org. Chem., 23, 741 (1958).

(28) See H. S. Mosher, Heterocyclic Compounds, Vol. 1, R. C. Elderfied, ed., John Wiley and Sons, New York, N. Y., 1950, pp. 472–474.

(29) W. Borsche and W. Peter, Ann., 453, 148 (1927).

(30) S. S. Deshapande, J. Ind. Chem. Soc., 9, 303 (1932).

(31) R. C. Gibbs, J. R. Johnson, and E. C. Hughes, J. Am. Chem. Soc., 52, 4895 (1930).

(32) J. Chauvelier, Bull. Soc. Chim. France, 21, 734 (1954).

(33) Melting points were taken on a Fisher-Johns melting point apparatus which had been calibrated with melting point standards. Infrared spectra were determined with a Perkin-Elmer Infracord by the potassium bromide pellet method unless stated otherwise. Ultraviolet spectra were determined with a Warren Spectracord spectrophotometer using $2 \times 10^{-5} M$ solutions in 95% ethanol with a 1 cm. sample cell. Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

(34) See ref. 4, p. 131.

In the preparations of triketones Ic-d, the liquid ammonia reaction mixture was neutralized by adding an excess (25 g.) of solid ammonium chloride.[35] The liquid ammonia was then evaporated as an equal volume of ether was added. The resulting ethereal suspension was shaken with water, and the two layers were separated. The ethereal layer was dried over Drierite, and the solvent removed under reduced pressure. The residue was recrystallized directly to give the triketone. When triketone Ic was recrystallized from ethanol, dark brown crystals were obtained having a melting point of 106–110°. If a small amount of concentrated hydrochloric acid were added to the hot, dark ethanol solution, the solution became clearer and, upon cooling, bright yellow crystals formed, m.p. 110–115°. Both solids had the same crystalline form and identical infrared spectra both in potassium bromide pellets and in mineral oil mulls.

In the preparation of triketone Ie, the reaction mixture was neutralized similarly with ammonium chloride, and the liquid ammonia was replaced by ether. The resulting ethereal suspension was shaken with water to dissolve the inorganic salts. The remaining suspension of the triketone, which was only slightly soluble in the ether, was filtered and recrystallized from benzene.

In the preparation of triketone If the reaction mixture was neutralized with ammonium chloride, the liquid ammonia replaced by ether, and the ethereal suspension shaken with dilute hydrochloric acid (30 ml. of conc. hydrochloric acid diluted). A yellow insoluble salt was formed which was filtered from the ether and water layers. The salt was neutralized by shaking in a separatory funnel with ether and aqueous sodium bicarbonate. These two layers were separated, and the ethereal layer was dried over Drierite. The solvent was removed under reduced pressure, and the residue was recrystallized from an ethanol water mixture to give triketone If. The triketone was amphoteric, being soluble in aqueous sodium carbonate or sodium hydroxide, and forming an insoluble salt with hydrochloric acid.

Isolation of α and β forms of triketone IIa. The two forms of IIa were obtained relatively free of each other (as shown by their infrared spectra) only with difficulty, and neither gave a very sharp melting point. The general procedure was followed up to the point of removing the solvent and distilling out the excess 2-acetylcyclohexanone, except that the reaction mixture was stirred in ether for an hour before neutralizing it with aqueous acetic acid. The residue from the distillation was taken up in hot 95% ethanol, and on cooling the α-form crystallized in brown crystals, m.p. 83–86° in the purest sample obtained. The β-form was fractionally precipitated from the filtrate of the α-form by the gradual addition of water. The best fraction obtained was a white solid, m.p. 100–110°.

The α-form softened after standing several months. It gave a green color with ethanolic ferric chloride, which on standing changed to the reddish brown color given by the β-form. By dissolving the α-form in hot ethanol, some of the β-form could be obtained upon the addition of water. The infrared spectrum of the α-form in the carbonyl and enol-chelate region, determined both in carbon tetrachloride solution and in potassium bromide pellets, showed strong bands at 6.24 μ and 6.35 μ (see Table II). Neither spectrum showed a band in the hydroxyl region around 3 μ (except for the weak absorption at 2.9 μ arising from moisture in the potassium bromide, which was present in all spectra made by the potassium bromide pellet method).

The β-form gave a reddish brown color with ethanolic ferric chloride. The infrared spectrum determined in potassium bromide showed strong bands at 6.14 μ, 6.28 μ, and 6.39 μ in the carbonyl and enol-chelate region (see Table II),

and a strong hydroxyl band was present at 3.00 μ. The spectrum of a carbon tetrachloride solution, however, was identical with that of the α-form. The residue left after evaporation of the solvent from a carbon tetrachloride solution of the β-form gave a green color with ethanolic ferric chloride, characteristic of the α-form. The analytical data are given in Table II. Both forms were cyclized to the same pyrone XIIa.

Cyclizations of 1,3,5-triketones to form 4-pyrones (Tables III and IV). A 1-g. sample of the triketone was dissolved in 10 ml. of conc. sulfuric acid at 0°C. After 10 min. at this temperature, the solution was poured into ice water. The resulting precipitate was collected on a funnel, washed with water, and recrystallized from an appropriate solvent to give the 4-pyrone.

In the cyclization of triketone Ia, there was first obtained a solid, m.p. 50–53°, which was apparently a hydrate of the pyrone XIa. This solid was dissolved in hot benzene, and the solvent evaporated to dryness on the steam bath. The residue was recrystallized from n-hexane to give the pyrone XIa, m.p. 85–87° (reported[36] m.p. 87–88°). The picrate prepared from either the hydrate or the free pyrone melted at 155–158°, and the melting point was not depressed on mixing the two samples.

The product from the cyclization of triketone If gave analyses between those calculated for pyrone XIf and its monohydrate even after several recrystallizations from ethanol-water. It was converted to a picrate, which melted at 217–223° dec., after three recrystallizations from methyl cellosolve.

Anal. Calcd. for $C_{22}H_{14}O_9N_4$ (picrate): N, 11.71. Found: 11.88.

In the cyclization of triketone IIb, there was first obtained a solid, m.p. 250–260° dec., which was apparently the salt of pyrone XIIb. This solid was refluxed with ethanol for several minutes, cooled, and water then added to precipitate the free pyrone XIIb, m.p. 148–150°. The addition of two drops of conc. sulfuric acid to an acetone solution of 0.3 g. of the pyrone precipitated the salt, m.p. 254–258° dec.

Dehydrogenation of 4-pyrone XIIa to form flavone (XIV). A 1-g. sample of pyrone XIIa was mixed with 1 g. of 5% palladium on charcoal in a small round bottomed flask equipped with a condenser, and the mixture was heated at 200° for 2 hr. The residue was cooled, taken up in ether, and the catalyst was removed by filtration. The ether was evaporated and the residue was then taken up in a small amount of benzene and placed on an alumina column. Elution successively with 200–300 ml. of petroleum ether (b.p. 30–60°), benzene, and finally ethanol produced sufficient fractionation so that an early fraction contained 0.05 g. (5% yield) of flavone (XIV), m.p. 95–97° after recrystallization from n-hexane. A mixed melting point with an authentic sample of flavone prepared from IV was not depressed, and the infrared spectra of the two samples were identical.

Cyclization of 1,3,5-triketones with ammonia to form 4-pyridones (Tables V and VI). To 1 g. of the triketone dissolved in 50 ml. of absolute ethanol was slowly added commercial, anhydrous liquid ammonia until the flask was cold. The solution was evaporated to dryness by heating in an open beaker over a steam bath, and the process was then repeated with the residue. In the preparation of XVe, n-propyl alcohol was used as a solvent instead of ethanol. The pyridone was isolated from the residue by recrystallization from an appropriate solvent (See Table V). In some cases purification was effected by vacuum sublimation.

In the preparation of 4-pyridone XVa, the crude residue melted at 175–177° (reported[16] m.p. 177–178°). The pyridone could be recrystallized from hot water, but if the water solution were allowed to cool, it formed a gell from which no crystals could be obtained. This behavior was also

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(35) When triketone Ia was neutralized in liquid ammonia using this procedure, Hauser and Harris[2] obtained a 38% yield of triketone Ia and a 16% yield of 2-methyl-6-phenyl-4-(1H)-pyridone (XVa). By neutralizing in ether with acetic acid they obtained a 60% yield of triketone and no pyridone.

(36) S. Ruhemann, *J. Chem. Soc.*, **93**, 431 (1908).

observed by Ruhemann.[16] However, only part of the recrystallized pyridone melted at 176–180°, the rest melting at 189–190°.

Cyclization of triketone Ic with methylamine to form 4-pyridone XX. Methylamine was bubbled into an ethanolic solution of 9.3 g. of triketone Ic, and the solvent was then removed on the steam bath. The oily residue was recrystallized from a mixture of benzene and hexane to give 3.9 g. (42%) of 2,6-diphenyl-1-methyl-4(1H)-pyridone (XX), m.p. 185–188° (reported[32] m.p. 187°). The infrared spectrum in the region 5.5–6.5 u showed a strong band at 6.16 μ, a medium band at 6.47 u, and a weak band at 6.37 μ. Ultraviolet spectrum: λmax = 237 mμ, 270 mμ; log ε = 4.39, 4.26.

A 1.8-g. sample of this compound was added to 7 ml. of acetonitrile, and a few drops of methanol were added to dissolve all the solid. An excess (2 ml.) of methyl iodide was added, and the solution was allowed to stand overnight at room temperature. Ether was added to precipitate 1.7 g. (61%) of the methiodide of 4-pyridone XX (white crystals), m.p. 123–129° dec. The product was recrystallized by dissolving it in methanol and adding ether. Three recrystallizations changed the melting point to 129–137° dec. The infrared spectrum in the region 5.5–6.5 u showed a strong band at 6.15 μ, and a medium band at 6.36 μ. Ultraviolet spectrum: λmax = 279 mμ; log ε = 4.06; broad shoulder at 232–239 mμ; log ε = 4.40.

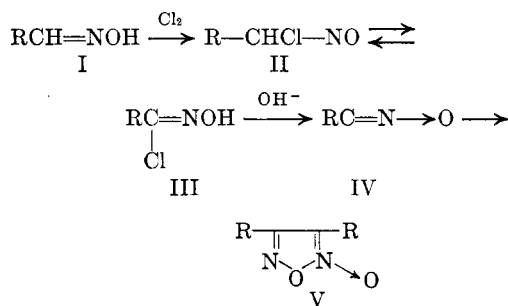*Anal.* Calcd. for $C_{19}H_{18}ONI$: C, 56.59; H, 4.50; N, 3.47. Found: C, 56.32; H, 4.77; N, 3.40.

Durham, N. C.

Infrared Spectra of the Nitrile N-Oxides: Some New Furoxans

RICHARD H. WILEY AND B. J. WAKEFIELD

A number of arylnitrile N-oxides have been prepared in carbon tetrachloride solution and their infrared spectra studied. Absorption bands at 2295 cm.$^{-1}$ and 1370 cm.$^{-1}$ characteristic of the triple bond and N-oxide linkages of the nitrile oxide group have been identified. Several new diaryl furoxans have been obtained by dimerization of these nitrile N-oxides and two new aliphatic nitrile oxides have been obtained in solution.

The nitrile N-oxides (IV) are somewhat unstable compounds formed by the action of dilute alkali on hydroxamic chlorides as indicated in the reaction scheme:[1–9] and the assignment of a proper

$$RCH{=}NOH \xrightarrow{Cl_2} R{-}CHCl{-}NO \rightleftharpoons$$

I II

$$RC{=}NOH \xrightarrow{OH^-} RC{\equiv}N{\rightarrow}O \longrightarrow$$

(with Cl below)

III IV

structure has received considerable attention.[6,10–12] They are highly reactive toward olefinic linkages

to form isoxazoles[13] and they dimerize readily to furoxans[5] (V). Because of the ease with which they dimerize very little is known about their physical properties. A few appropriately substituted types; e.g., p-chlorobenzonitrile N-oxide, dimerize slowly and the physical properties of these compounds have been studied.[12,14,15] Others, such as benzonitrile N-oxide, dimerize rapidly during isolation and are difficult to characterize. The lowest molecular weight recorded[6,7] for benzonitrile N-oxide is 134, whereas theory requires 119, indicating that partial dimerization occurs before the molecular weight can be determined.

We have now devised a procedure for recording the spectra of the less stable nitrile N-oxides in carbon tetrachloride solution. The nitrile N-oxides were prepared from the hydroxamic chlorides obtained by the route given above. The oximes were prepared by standard methods[16] and were chlorinated at 0° in 8N hydrochloric acid[17] or in organic solvents. The hydroxamic chlorides were not purified as the melting points of the crude products agreed well with recorded values. The hydroxamic chlorides were dissolved or suspended in carbon

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