t-**Butyl *p*-nitrothiolbenzoate** (**D**) was prepared[10] by the action of *p*-nitrobenzoyl chloride on *t*-butyl mercaptan in benzene–pyridine. It melted after several crystallizations from alcohol–water at 74.5–75° and had a carbonyl band at 1670 cm.$^{-1}$ in the infrared; the ultraviolet absorption in cyclohexane showed λ_{max} 258 mμ (ϵ 19700), shoulder at 286 mμ (ϵ 13900).

Anal. Calcd. for $C_{11}H_{13}NO_3S$: C, 55.40; H, 5.47; N, 5.86; S, 13.40. Found: C, 55.40; H, 5.65; N, 6.04; S, 13.27.

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Unsaturated Six-Membered Ring Lactams[1,2]

ANTHONY J. VERBISCAR[3] AND KENNETH N. CAMPBELL

University of Notre Dame, Notre Dame, Indiana

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The large number of 3,4-unsaturated lactones which have been found physiologically active[4] prompted our reinvestigation of the synthesis of lactams by the well-known reaction[5–7] between sorbic acid and amines under pressure. Using ammonia,[5] the primary product of this reaction is a diamine which on further heating gives 6-methyl-5,6-dihydro-2(1)-pyridone (II, R = H). The position of the C=C double bond was correctly assumed[5] to be 3,4-, although it was not until much later that the identical compound (II, R = H) was prepared[8] by an exchange reaction between ammonia and 6-methyl-5,6-dihydro-2-pyrone. The 3,4-position of the C=C double bond in this hexenolactone was firmly established[9] and was assumed not to have changed during the exchange. Lithium aluminum hydride reductions[7] of the conjugated lactam analogs of II tend to corroborate the 3,4-position assignment. However, data presented elsewhere[6] indicate that some of the lactams were mixtures of the conjugated II and hitherto unreported unconjugated III isomers, as was evident from triplet absorption in the 6-μ region of the infrared and diminished extinction coefficients in the ultraviolet spectra.

In the present work, reaction of straight-chain alkyl amines with sorbic acid gave mixed conjugated II and unconjugated III lactams in close to 70% yields. The yield of lactam from *p*-anisidine was lower and only the conjugated isomer was isolated. Compounds corresponding to structure IV were also isolated, but were unstable and immediately converted to II and III on distillation or heating above 150°. Intermediate IV was isolated in good yield and purified only when dimethylaminopropyl amine was used. Aqueous isopropyl- and *t*-butylamines yielded no 2-pyridones in this reaction, probably for steric reasons.

Separation of the conjugated and unconjugated dihydro-2-pyridones II and III was effected by careful fractionation. The compounds thus prepared in this study are listed in Table I. Both the conjugated (II) and unconjugated (III) dihydro-2-pyridone structures were firmly established by both infrared and ultraviolet spectral evidence through comparison with model compounds.

The ultraviolet spectrum of 6-methyl-5,6-dihydro-2(1)-pyridone (II, R = H) has an absorption peak at 241 mμ (ϵ 1580, previously reported[6] as ϵ 1470). This is comparable to the absorption peak of 1-ethyl-6-methyl-5,6-dihydro-2(1)-pyridone (II, R = C_2H_5) at 250 mμ (ϵ 1570), and that of the model compound, N,N-diethylcrotonamide,[10] λ_{max} 242 mμ (ϵ 6500). The shapes of the absorption curves were also similar. The unconjugated 1-ethyl-6-methyl-1,6-dihydro-2(3)-pyridone (III, R = C_2H_5) showed no absorption peak in the 220–320-mμ region.

Since there is a minimum of strain in the six-membered ring lactams, it was expected that further confirmation of their structures could be gained by comparison with the infrared spectra of model straight-chain amides. N,N-Diethylcrotonamide showed double bond absorption at 6.02 and 6.16 μ, whereas N,N-diethylvinylacetamide showed only one peak in this region, at 6.07 μ. By analogy, the compound assigned structure II showed a doublet at 6.02 and 6.18 μ, whereas the supposed unconjugated structure III showed only one peak at 6.08 μ. Furthermore, N,N-diethylpropionamide, 1-ethyl-6-methyl-2-piperidone, and 6-methyl-2-piperidone all showed a single peak at 6.07–6.08 μ, which is comparable with the absorption of the unconjugated isomer III where the C=C double bond does not interact with the carbonyl group. Identification of the isomers can therefore be made on the basis of either the infrared or ultraviolet spectra.[6] Since the 6.02-μ peak in the conjugated amides was invariably stronger than the 6.18-μ peak, it is reasonable to assume that the 6.02-μ peak was due to carbonyl, since carbonyl absorption is usually stronger than that due to C=C double bonds. The spectra of the saturated pyridones made it clear that the 6.08-μ peak of the unconjugated isomers is at least partly due to the carbonyl group. The unconjugated C=C would not be expected to absorb very strongly and is probably hidden under the 6.08-μ carbonyl peak, which presented a somewhat skew appearance. Upon conjugation the 6.08-μ peak split into the 6.02- and 6.18-μ pair. This unusual shift of the car-

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(2) Taken in part from the Doctoral Thesis of A. J. V., University of Notre Dame, 1954.

(3) To whom correspondence should be at the Institute of Drug Design, 770 S. Arroyo Parkway, Pasadena, Calif.

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TABLE I

LACTAMS AND MODEL AMIDES

Compound	B.p. (mm.) or m.p., °C.	$n^{20}D$	Formula	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found	N, % Calcd.	N, % Found	Ultraviolet, λ_{max}, mμ (ϵ_{max})	Infrared,[a] λ_{max}, μ
6-Methyl-5,6-dihydro-2(1)-pyridone	108–109[b]									241[c,d] (1580)	2.94,[e] 3.13, 5.98, 6.17
6-Methyl-2-piperidone	89–90[f]										2.94,[e] 3.13, 6.07
1,6-Dimethyl-5,6-dihydro-2(1)-pyridone	109–110[c,g] (13)	1.4984									6.02, 6.18
1,6-Dimethyl-1,6-dihydro-2(3)-pyridone	104 (13)	1.4958	$C_7H_{11}NO$	67.15	67.46	8.86	8.88	11.19	11.02		6.07
1-Ethyl-6-methyl-5,6-dihydro-2(1)-pyridone	111–112 (13)	1.4914	$C_8H_{13}NO$	69.02	69.15	9.41	9.44	10.06	10.10	250[h] (1570)	6.02, 6.18
1-Ethyl-6-methyl-1,6-dihydro-2(3)-pyridone	106–107 (13)	1.4985	$C_8H_{13}NO$	69.02	68.87	9.41	9.65	10.06	9.80	252[h] (331)	6.08
1-Ethyl-6-methyl-2-piperidone	105–106 (13)	1.4766	$C_8H_{15}NO$	68.05	67.41	10.71	10.87	9.92	9.80		6.07
1-Propyl-6-methyl-5,6-dihydro-2(1)-pyridone	121–122 (15)	1.4875	$C_9H_{15}NO$	70.56	70.10	9.87	9.82	9.14	9.22		6.02, 6.18
1-Phenyl-6-methyl-5,6-dihydro-2(1)-pyridone	93 (0.05)[g]	1.5728									6.02, 6.16, 6.23
1-(*p*-Anisyl)-6-methyl-5,6-dihydro-2(1)-pyridone	65–66 155–162 (0.2)		$C_{13}H_{15}NO$	71.85	71.66	6.95	6.96	6.45	6.20		5.98,[e] 6.13, 6.19
1-(3′-Dimethylaminopropyl)-6-methyl-5,6-dihydro-2(1)-pyridone	92–95 (0.25)	1.4922	$C_{11}H_{20}N_2O$	67.29	67.47	10.24	10.07	14.27	13.94		6.02, 6.18
1-(3′-Dimethylaminopropyl)-4-(3′-dimethylaminopropylamino)-6-methyl-2-piperidone	167–168 (0.35)	1.4892	$C_{16}H_{34}N_4O$	64.38	64.40	11.48	11.09	18.77	18.51		3.08, 6.10
N,N-Diethylcrotonamide	111 (19)[i]	1.4750								242[h] (6500)	6.02, 6.16
N,N-Diethylvinylacetamide	95 (15)	1.4594	$C_8H_{15}NO$	68.04	68.39	10.71	10.18	9.92	9.96		6.07

[a] Taken in a sandwich cell unless otherwise noted. [b] Reported in ref. 5. [c] Reported in ref. 6. [d] Absolute ethyl alcohol solvent. [e] Nujol mull. [f] Reported in ref. 8. [g] Reported in ref. 7. [h] Isopentane solvent. [i] Reported in ref. 10.

bonyl absorption to lower wave lengths upon conjugation to a C=C double bond is not clearly understood and interference with normal amide absorption[11] seems to be involved.

Experimental

Infrared spectra were determined on a Baird Model AB-1 spectrophotometer. Ultraviolet spectra were measured on a Beckman Model DU quartz photoelectric spectrophotometer. Autoclave reactions were carried out in (a) a 100-ml. capacity stainless steel bomb with an electrically heated jacket, and (b) in a 1-l. capacity stainless steel rocking-type bomb made by the American Instrument Company. Fractionations were carried out in a 0.8 × 30 cm. Podbielniak column with Hasteloy "B" packing. This column was equipped with a Flexopulse timer made by Eagle Signal Corporation, and a Leeds and Northrup iron *vs.* constantan thermocouple. Elemental analysis are by W. Beazley, Micro-Teck Laboratories, Skokie, Ill. Melting and boiling points are uncorrected.

Reaction of Sorbic Acid with Amines.—The method used in this work is essentially that as reported elsewhere[5,7] with only minor variations.

A higher yield of product IV was obtained when relatively anhydrous amines were used. Only in the case of dimethylaminopropylamine was this product (IV) completely identified, since in this case it was relatively stable. Heating the products of structure IV at about 150° split out the amine to give the mixed dihydro-2-pyridones.

Aqueous methanol was used in the autoclave reaction with aniline in order to give a homogeneous reaction mixture. Only sorbic acid anilide[12] (V, R = C_6H_5) was obtained when no methanol was added. The yields of 2-pyridones from the aromatic amines were much lower than from the alkyl amines. Aniline gave only a 6.5% yield of pure 1-phenyl-6-methyl-5,6-dihydro-2(1)-pyridone, and *p*-anisidine a 2.3% yield of pure 1-(*p*-anisyl)-6-methyl-5,6-dihydro-2(1)-pyridone (recrystallized from carbon tetrachloride and hexane).

The conjugated isomer predominated in every case where fractional distillation was used. For R = ethyl, the yield of crude mixed isomers was 70%, which upon fractionation gave II (conjugated) and III (unconjugated) in a ratio of about 3:1.

6-Methyl-2-piperidone.—The reduction of 3 g. (0.027 mole) of 6-methyl-5,6-dihydro-2(1)-pyridone (II, R = H) was carried out in 25 ml. of 95% ethanol using 0.1 g. of 10% palladium-on-charcoal catalyst and an initial hydrogen pressure of 40 p.s.i. The theoretical amount of hydrogen was taken up in 7 min. The product was isolated and crystallized from ethyl acetate to give a

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nearly quantitative yield of 6-methyl-2-piperidone, m.p. 89–90°. Kuhn and Jerchel[8] prepared this compound using a platinum oxide catalyst and report m.p. 84–85°.

1-Ethyl-6-methyl-2-piperidone.—Three grams (0.022 mole) of 1-ethyl-6-methyl-5,6-dihydro-2(1)-pyridone (II, R = C_2H_5) was hydrogenated as above in 15 min. The crude product (2.6 g., 85%) was fractionated on the Podbielniak column to give pure 1-ethyl-6-methyl-2-piperidone (Table I).

This compound was also prepared accidentally in an attempt to N-alkylate 6-methyl-5,6-dihydro-2(1)-pyridone (II, R = H). In this experiment metallic sodium was powdered in the usual manner in toluene. After cooling, an equimolar portion of the lactam (II, R = H) was added; an immediate reaction took place and all of the sodium was used up. Ethyl iodide was added; the mixture was refluxed for 7 hr. and distilled to give a 39% yield of the alkylated and reduced product, 1-ethyl-6-methyl-2-piperidone, as indicated by an identical infrared spectrum, index of refraction, and boiling point.

1-Ethyl-6-methyl-5,6-dihydro-2(1)-pyridone.—Sodamide was prepared in the usual manner using 300 ml. of liquid ammonia, a crystal of ferric nitrate, and 1.3 g. (0.056 g.-atom) of sodium. After addition of 5.6 g. (0.050 mole) of 6-methyl-5,6-dihydro-2(1)-pyridone with stirring the ammonia was allowed to evaporate. Fifty milliliters of dry benzene and 11 g. (0.070 mole) of ethyl iodide were added, and the mixture was refluxed for 3 hr. Distillation yielded 3.4 g. (50%) of a product whose infrared spectrum and boiling point were identical with those of 1-ethyl-6-methyl-5,6-dihydro-2(1)-pyridone which had the correct elementary composition (Table I).

N,N-Diethylvinylacetamide.—In a reaction flask with reflux condenser and gas absorption attachment were placed 25.8 g. (0.30 mole) of vinylacetic acid[13,14] and 41.7 g. (0.35 mole) of thionyl chloride. The reaction started immediately and was allowed to continue overnight. The mixture was refluxed for 0.5 hr. and a solution of 58 g. (0.80 mole) of diethylamine in 100 ml. of dry ether was added slowly with stirring. The precipitate was filtered; the solution was dried over magnesium sulfate and distilled. The crude N,N-diethylvinylacetamide was fractionated through the Podbielniak column to yield 22.7 g. (54%) of high purity material (Table I).

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Dinitrocarbazoles

HENRY M. GROTTA, CHARLES J. RIGGLE, AND ARTHUR E. BEARSE

Battelle Memorial Institute, Columbus, Ohio

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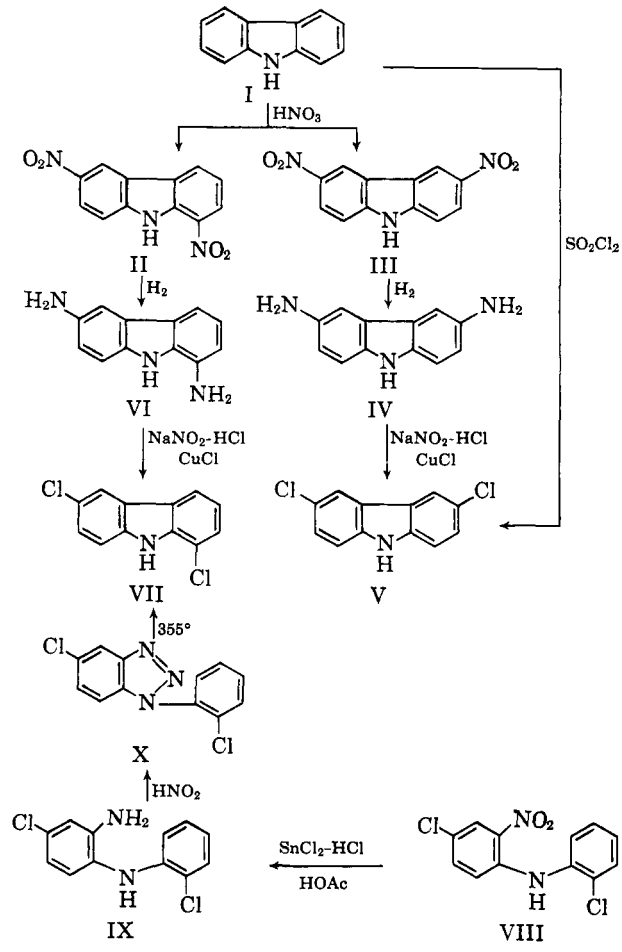
Although it has been recognized that attempts to dinitrate carbazole lead to mixed products,[1] only 3,6-dinitrocarbazole (III) appears to have been isolated from these mixtures. Its melting point has been variously reported as 365–367°,[1] about 360°,[2] 357°,[3] and even as low as 320°.[4] Its structure was assigned by Täuber[5] on the basis of the similarity of its reduction product (IV) with 3,6-diaminocarbazole unambiguously prepared from 2,2′,5,5′-tetraminodiphenyl. Crystal form, solubilities of its salts, and darkening temperatures of the two materials agreed. The isomeric 1,6-dinitrocarbazole (II) appears in the literature only as a speculative structure for a material charring between 300 and 360°.[6] We have found that both 1,6-dinitrocarbazole and 3,6-dinitrocarbazole are present in major amounts in the crude dinitrocarbazole mixture.



Carbazole (I) was nitrated in acetic acid at 75° with 3 equiv. of 70% nitric acid, and, alternatively, by treatment in acetic acid first with 1 equiv. of sodium nitrite and then with 2 equiv. of nitric acid at temperatures up to 100°. Extraction of the crude product from either nitration procedure with alcoholic potassium hydroxide produced two fractions: a red solid residue and a deep red solution. Acidification of the latter precipitated a yellow solid which recrystallized from nitrobenzene as fine yellow needles, m.p. 386–387°. Its reduction and conversion to the dichloride (V) by the Sandmeyer procedure provided a material identical with 3,6-dichlorocarbazole (m.p. 202–203°) prepared from carbazole and sulfuryl chloride,[7] the structure of which has been established by Plant.[8]

Digestion of the alcoholic alkali-insoluble residue with acid and recrystallization from nitrobenzene produced a dinitrocarbazole in glistening golden

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