carboxylate salts (infrared spectrum, KBr) undissolved.[21] Impure perylene (1.4 g., 11.1%) crystallized from the benzene solution. Chromatography of this solution furnished additional perylene (1.1 g., 9%).

Acknowledgment.—We are indebted to Professor J. A. Dixon, Pennsylvania State University, for securing the n.m.r. spectra and for helpful discussions and encouragement. We are obliged to the City University of New York for a research grant permitting continuation of this investigation.

[21] Investigation of the isomer composition of the methyl esters of the perylenecarboxylic acids by chromatography is in progress.

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p-Nitrobenzoic *t*-Butyl Thiolcarbonic Anhydride[1]

D. S. TARBELL AND T. PARASARAN

Department of Chemistry, University of Rochester, Rochester, New York

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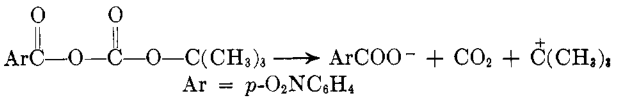
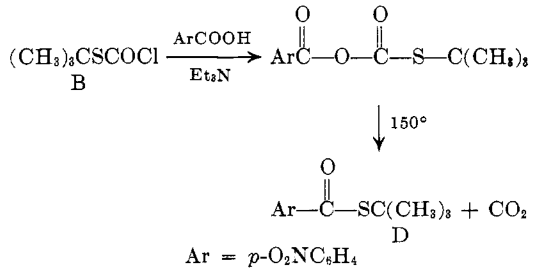
The products formed in the thermal decomposition of *p*-nitrobenzoic *t*-butyl carbonic anhydride[2] (A) indicate that it undergoes alkyl–oxygen cleavage, as shown, rather than the acyl–oxygen cleavage observed with mixed anhydrides with primary or secondary alkyl groups.[3] This note reports the preparation and properties of the sulfur analog of A.



$$\mathrm{Ar\overset{O}{\overset{\|}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}O{-}C(CH_3)_3 \longrightarrow ArCOO^- + CO_2 + \overset{+}{C}(CH_3)_3}$$
$$\mathrm{Ar} = p\text{-}\mathrm{O_2NC_6H_4}$$

t-Butyl thiolchlorocarbonate (B) was prepared, apparently for the first time,[4] by the action of sodium hydride dispersion on *t*-butyl mercaptan in THF, followed by addition of phosgene in THF. *t*-Butyl thiolchlorocarbonate was distilled *in vacuo* and showed carbonyl absorption[5] at 1770 cm.$^{-1}$; it was converted in the usual way into the crystalline mixed anhydride C, m.p. 86.5–87°, which showed bands at 1730 and 1786 cm.$^{-1}$. The mixed anhydride C was converted by heating at 160° to the *p*-nitrothiolbenzoate D (identified by comparison with a synthetic sample) and carbon dioxide; no other products were observed.



The contrast between the behavior of the sulfur compound C and the oxygen analog A is therefore striking; the former gives no apparent alkyl–sulfur cleavage, and gives high yields of products formed by a single mode of decomposition. The oxygen analog A decomposes at a lower temperature and gives a complex mixture of products, some of which are a result of alkyl–oxygen cleavage.

This pair of sulfur–oxygen analogs illustrates the smaller tendency for alkyl–sulfur cleavage as compared to alkyl–oxygen cleavage, which has been observed in numerous other cases.[6]

Experimental

***t*-Butyl Thiolchlorocarbonate (B).**—*t*-Butyl mercaptan (45 g., 0.5 mole) in anhydrous tetrahydrofuran was added slowly with stirring to a slurry of sodium hydride dispersion[7] (50% in mineral oil; 25 g., 0.5 mole) in tetrahydrofuran and the mixture was refluxed with stirring under nitrogen for 2–4 hr. This suspension was then cooled and added with shaking to phosgene (50 g., 0.5 mole) contained in a flask equipped with stirrer and dry ice condenser and cooled in an ice–salt mixture. Air was carefully excluded during the addition to prevent oxidation of the mercaptide. After additional stirring for 2 hr. at room temperature, the mixture was centrifuged and filtered. The filtrate on distillation *in vacuo* yielded fractions boiling at 50–55° (13 mm.). On redistillation, the product boiling at 30–32° (1 mm.) was collected; this formed a thiocarbamate with aniline which had a melting point that was identical with the literature value[8] (147.5–148°).

Anal. Calcd. for C_5H_9ClOS: C, 39.36; H, 5.94; S, 21.02; Cl, 23.23. Found: C, 39.58; H, 6.18; S, 20.74; Cl, 23.05.

***p*-Nitrobenzoic *t*-Butyl Thiolcarbonic Anhydride (C).**—Dry ether (300 ml.) was chilled to −5° by an ice–salt bath, then *p*-nitrobenzoic acid (1.67 g., 0.01 mole) and *t*-butyl thiolchlorocarbonate (1.53 g., 0.01 mole) were added. The mixture was stirred and 1.01 g. (0.01 mole) of triethylamine in ether was added dropwise. The stirring was continued for 2 hr. more and the resulting mixture was filtered, washed with very dilute acid, with sodium bicarbonate solution and water, and was dried. The ether was evaporated at room temperature at reduced pressure leaving a material which was contaminated with *p*-nitrobenzoic acid; this was removed by extracting the material with carbon tetrachloride in the cold, leaving the mixed anhydride in 80–90% yield. The product was recrystallized twice or thrice from a mixture of carbon tetrachloride and petroleum ether, avoiding strong and prolonged heating. After three crystallizations, the pale yellow needles melted at 86.5–87°. The infrared spectrum contained peaks at 1730 and 1785 cm.$^{-1}$ which are characteristic of mixed carboxylic–carbonic anhydrides.[9] Ultraviolet absorption in cyclohexane showed λ_{max} 254 mμ (ϵ 26,900).

Anal. Calcd. for $C_{12}H_{13}NO_5S$: C, 50.86; H, 4.62; N, 4.94; S, 11.32. Found: C, 50.92; H, 4.58; N, 4.97; S, 11.24.

Decomposition of the Mixed Anhydride.—In a typical run designed to determine the yield of carbon dioxide, *p*-nitrobenzoic *t*-butyl thiolcarbonic anhydride (0.363 g., 0.00128 mole) was placed in a 10-ml. two-necked flask; through one neck a stream of prepurified nitrogen (free from oxygen and carbon dioxide) was led and the other neck carried an outlet tube and a condenser with an outlet tube. The outlet tube was connected to two microascarite tubes. The sample was heated at 160° for 2 hr. and 0.0595 g. of carbon dioxide was collected (106% of theory). The pot residue was recrystallized from ethanol–water, melted at 75.0°, and did not depress the melting point of an authentic sample of *t*-butyl *p*-nitrothiolbenzoate prepared as below. The infrared spectra of the two were identical.

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[1] Aided by Grant G-11240 from the National Science Foundation.

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[3] E. J. Longosz and D. S. Tarbell, *ibid.*, **26**, 2161 (1961); C. J. Michejda, D. S. Tarbell, and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **84**, 4113 (1962).

[4] *t*-Butoxycarbonyl derivatives have been studied extensively by L. A. Carpino [*e.g.*, *ibid.*, **79**, 98 (1957); **82**, 2725 (1960)] and have been used as protecting groups in peptide syntheses.

[5] A. W. Baker and G. H. Harris [*ibid.*, **82**, 1923 (1960)] report that CH_3SCOCl absorbs at 1766 cm.$^{-1}$.

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***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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[10] *Cf.* R. Adams, E. K. Rideal, W. B. Burnett, R. L. Jenkins, and E. E. Dreger, *J. Am. Chem. Soc.*, **48**, 1758 (1926).

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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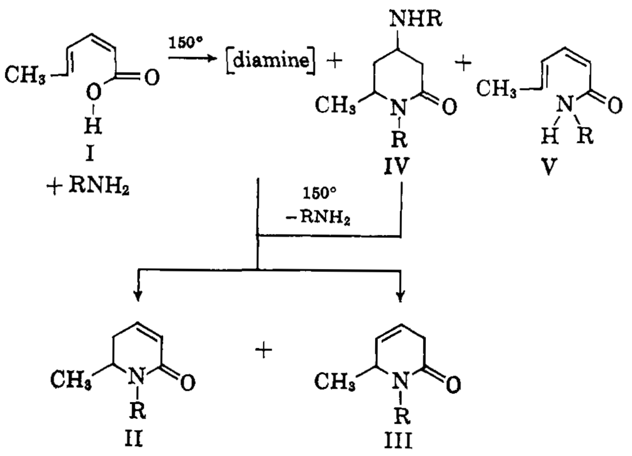
The large number of 3,4-unsaturated lactones which have been found physiologically active[4] prompted our reinvestigation of the synthesis of lactams by the well-known reaction[5–7] between sorbic acid and amines under pressure. Using ammonia,[5] the primary product of this reaction is a diamine which 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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