chloropyrrolidine.[9] This solution was refluxed for 3.5 hr., cooled, and acidified with aqueous hydrochloric acid. The volume of solution was reduced to *ca.* 100 ml. by reduced pressure distillation. The solution was then extracted with three 100-ml. portions of benzene. The benzene extract was washed with three 30-ml. portions of water saturated with sodium chloride. The washings were discarded and the benzene solution dried over sodium sulfate. After the benzene was removed, 15.7 g. (64.0%) of crude solid I was obtained. The solid was dissolved in warm benzene and charcoal was added. This solution was warmed on a steam bath for 10–15 min.; Filter-Cel was added and the solution filtered. After removal of the benzene, the solid was recrystallized from ethyl ether-purified petroleum ether (b.p. 90–100°). The recrystallized white solid was sublimed, m.p. 123–125°.

Anal. Calcd. for $C_{10}H_{13}O_4N$: C, 56.86; H, 6.20; N, 6.63. Found: C, 56.92; H, 6.33; N, 6.71.

1-Carboethoxy-2-hydroxy-3-oxopyrrolizidine (IV).—Six grams (0.0285 mole) of sublimed I was dissolved in 50 ml. of 95% ethanol and placed in a hydrogenation bomb, and 3 g. of W-2 Raney nickel was added. At 100° and 2000 p.s.i. the theoretical amount of hydrogen was taken up in 4 hr. The solution was allowed to cool to room temperature and brought to atmospheric pressure. The solution was then filtered. After removal of the solvent the solid was recrystallized from ethyl acetate-purified petroleum ether (b.p. 60–68°) and sublimed, m.p. 128.2–132.1°.

Anal. Calcd. for $C_{10}H_{15}O_4N$: C, 56.32; H, 7.09; N, 6.57. Found: C, 56.24; H, 7.01; N, 6.54.

1-Carboethoxy-2-hydroxy-3-oxopyrrolizidine Tosylate (V).—A 0.153-g. (2.31 mmoles) sample of IV was dissolved in 10 ml. of anhydrous pyridine, and 1.11 g. (5.71 mmoles) of recrystallized *p*-toluenesulfonyl chloride was added. The solution was stored at 0° for 17 hr. and then poured onto crushed ice. Within 0.5 hr., a copious white precipitate formed. This was filtered, washed with water, and after being dried, 0.634 g. (67.8%) of V was obtained, recrystallized from ethyl acetate, m.p. 123.1–124.2°.

The infrared spectrum of V in 10% chloroform solution had no absorption bands in the 3.0-μ region and had peaks at 5.80 and 6.24 μ. The ultraviolet spectrum in 95% ethanol had one peak at 226 mμ (ϵ 12,500).

Anal. Calcd. for $C_{17}H_{21}O_6NS$: C, 55.72; H, 5.50; Found: C, 55.63; H, 5.97.

1-Carboethoxy-3-oxopyrrolizid-1,8-ene (VI).—A 0.529-g. (1.43 mmoles) sample of V was placed in a flask and 50 ml. of anhydrous *t*-butyl alcohol was added. The solution was warmed on a steam bath for 5–10 min., and most of the tosylate dissolved. To this warmed stirred solution, 7.49 ml. of 0.193 *N* (1.43 mmole) of potassium *t*-butoxide in *t*-butyl alcohol was added. The solution became bright red as each drop of base was added, but the color then disappeared and only persisted after *all* the base had been addded. The solution was acidified with dilute hydrochloric acid and then extracted with benzene. The benzene was removed by reduced pressure distillation. The residue was chromatographed on a column packed with Florosil (60/100 mesh, Floridian Co., Tallahassee, Florida). The chromatographed material (over 90%) was sublimed, m.p. 88.9–90.0°.

Anal. Calcd. for $C_{10}H_{13}O_3N$: C, 61.52; H, 6.71; N, 7.18. Found: C, 61.61; H, 6.66; N, 6.55.

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Formylation of *t*-Butylamine and *t*-Octylamine[1,2]

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During studies on isocyanides in these laboratories we have had occasion to prepare large quantities of formo-*t*-butylamide. Neither the formylation of *t*-butylamine by formic acid nor the Ritter reaction on isobutylene or *t*-butyl alcohol[3] is appealing as a routine preparation, the former because mixing the very volatile *t*-butylamine with formic acid is a troublesome and tedious procedure, and the latter because of the obvious hazards of working with hydrogen cyanide. We have found that *t*-butylamine can be formylated conveniently by refluxing and then distilling an equimolar mixture of ethyl formate and *t*-butylamine. The high rate of this reaction is in striking contrast with the negligible rate of acetylation of *t*-butylamine by methyl acetate[4] at 25°. Similarly *t*-octylamine (2,4,4-trimethyl-2-pentylamine) is formylated at approximately the same rate.

Experimental[5]

Equimolar quantities of ethyl formate and *t*-butylamine were refluxed in tared flasks, the excess reagents and ethanol were distilled on the water bath, and the residual formo-*t*-butylamide was weighed. The procedure was checked by distilling several batches. Typical yields for 4,16,32, and 48 hr. of reflux were 29.4, 66.8, 79.2, and 84.0%, respectively. Similarly, a mixture of 120 g. (1.0 mole) of *t*-octylamine and 150 g. (2.0 moles) of ethyl formate was refluxed 12 hr. and then distilled. The *formo-t-octylamide* was obtained in a yield of 98 g. (62%), b.p. 245–248°. This material is slightly amber in color and may be better purified by vacuum distillation.

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[1] Abstracted from the M.S. theses of Marvin K. Newton and Gerald J. Papenmeier, University of Kansas City, 1960.

[2] The authors gratefully acknowledge support of this work by the National Science Foundation under Grant No. G10031.

[3] J. J. Ritter and J. Kalish, *J. Am. Chem. Soc.*, **70**, 4048 (1948).

[4] E. McC. Arnett, J. G. Miller, and A. R. Day, *ibid.*, **72**, 5635 (1950).

[5] A gift of *t*-octylamine from the Rohm & Haas Corporation is gratefully acknowledged. The other chemicals were purchased.

Bridged Polycyclic Compounds. XVIII. Addition of Dialkyl Azodicarboxylates to Norbornadiene[1]

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Recent reports have established that norbornadiene (I) exhibits unusual chemical reactivity as