Matheson Coleman and Bell ethyl propionate and the Eastman ethyl benzoate were practical grade chemicals.

All melting points are uncorrected and were taken on a Mel-Temp melting point apparatus. Analytical data were obtained at this laboratory. The following procedure is illustrative of the general technique employed.

N-Phenylpropionamide.—A mixture of 20.4 g. (0.2 mole) of ethyl propionate, 18.6 g. (0.2 mole) of aniline, 12.0 g. (0.22 mole) of sodium methoxide powder, and 200 ml. of dry benzene was stirred and refluxed for 7 hr., cooled, and poured carefully into 200 ml. of 10% hydrochloric acid. This mixture was stirred and cooled in an ice bath while 200 ml. of hexane was added. The resulting slurry was filtered on a Büchner funnel, and the filter cake was washed with 100 ml. of cold water, followed by 50 ml. of cold hexane. The resulting crystalline material was air-dried to yield 21 g. (70%) of nearly pure amide which melted between 103 and 105° (lit.[6] m.p. 103–105°).

(6) A. W. Crossley and W. H. Perkin, Jr., *J. Chem. Soc.*, **73**, 33 (1898).

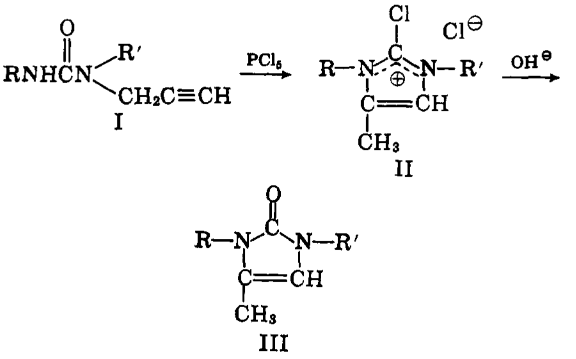
Cyclization of Propynylureas to 2-Imidazolones

P. J. Stoffel and A. J. Speziale

Agricultural Chemicals Division, Monsanto Chemical Company,
St. Louis 66, Missouri

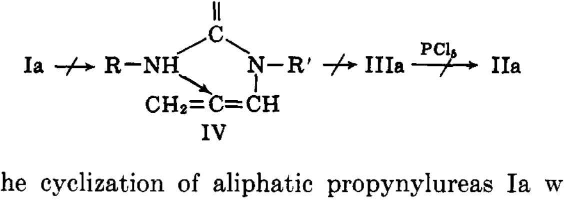
Received April 11, 1963

We have reported[1,2] that propynylureas I undergo intramolecular cyclization on treatment with phosphorus pentachloride to give stable isolable imidazolium chlorides II which were converted by aqueous sodium hydroxide to the imidazolones III.



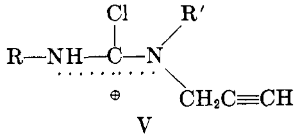
a, R = 3,4-dichlorophenyl; R′ = isopropyl
b, R = butyl; R′ = isopropyl

The possibility of the conversion of I directly to III *via* an allene intermediate IV by isomerization of the propynyl group prior to cyclization was proven to be untenable. Treatment of IIIa with phosphorus pentachloride under the same conditions gave only untractable tars.



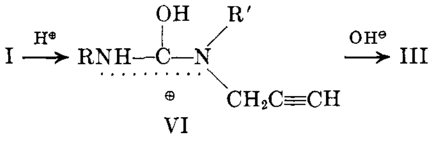
The cyclization of aliphatic propynylureas Ia with phosphorus pentachloride gave extremely hygroscopic intermediate salts, which could not be purified for analysis, but were converted directly with no difficulty to the imidazolones III.

Our proposed mechanism[1] for I → II → III visualized an intermediate carbamido chloride V.



V

Since amides and ureas reportedly[3a,b] undergo O-protonation in the presence of strong acids, we postulated that cyclization I → III could be effected in a similar manner through VI.



VI

Treatment of Ia with concentrated sulfuric acid or *p*-toluenesulfonic acid in benzene gave a sirupy intermediate which could neither by crystallized nor purified, but gave infrared spectra similar to IIa. These sirups, or the aqueous acidic solution directly, gave III on treatment with aqueous sodium hydroxide. Cyclization of Ia could not be induced by anhydrous hydrogen chloride in benzene but cyclized smoothly using a more polar solvent, dioxane.

The acid cyclization of I undoubtedly occurs *via* the O-protonated urea VI following a mechanistic sequence similar to that proposed for phosphorus pentachloride.

When the urea Ia was heated with dilute sodium hydroxide, the imidazolone IIIa was obtained directly. Alkaline cyclization might well involve the allene intermediate IV discussed previously.

Experimental

3′-(3,4-Dichlorophenyl)-1-isopropyl-4-methyl-2-imidazolone (IIIa) A. **Sulfuric Acid.**—A solution of urea Ia (28.3 g., 0.1 mole) and concentrated sulfuric acid (10.5 g., 0.12 mole) in 100 ml. of benzene was refluxed for 6 hr. A dark blue acid layer separated from the benzene. The acid layer was stirred into 500 ml. of water and made alkaline with 50% aqueous sodium hydroxide. The product separated and was recrystallized from methanol in colorless prisms, m.p. 112.1–112.8°, 25.0 g., 87.5% yield.

B. *p*-**Toluenesulfonic Acid.**—The reaction was run exactly as in method A using toluenesulfonic acid (20.0 g., 0.11 mole). The product was obtained as colorless prisms, m.p. 111.5–112.2°, 19.0 g., 66.7% yield.

C. **Hydrochloric Acid.**—With the same charge as A, and passing in anhydrous hydrogen chloride for 8 hr. at 80°, gave unchanged urea Ia. The same charge using 100 ml. of dioxane at 80° for 8 hr. gave the cyclized urea IIIa by quenching the reaction in 500 ml. of water, adding 50% aqueous sodium hyroxide until alkaline, and extracting IIIa with three 100-ml. portions of ether. Large white prisms were obtained from ethyl acetate, m.p. 111.1–112.1°, 19.7 g., 69.0% yield.

D. **Sodium Hydroxide.**—A slurry of urea Ia (14.4 g., 0.05 mole) in 20 ml. of 20% aqueous sodium hydroxide and 100 ml. of water was held at 80° for 8 hr. On cooling, a tan oil separated. The remaining liquid was extracted with three 50-ml. portions of ether and combined with the oil. Ether was evaporated, giving the solid product. Small prisms were obtained from ethyl acetate, m.p. 110.8–111.6°, 9.0 g., 62.0% yield.

---

(1) P. J. Stoffel and A. J. Speziale, *J. Am. Chem. Soc.*, **84**, 501 (1962).

(2) P. J. Stoffel and A. J. Speziale, *J. Org. Chem.*, **27**, 3079 (1962).

(3) (a) W. D. Kumler, *J. Am. Chem. Soc.*, **84**, 4983 (1962); (b) A. R. Katritzky and R. A. Y. Jones, *Chem. Ind.* (London), 722 (1961).

The products from A, B, C, and D were identical in complete elemental analyses, mixture melting points, infrared and nuclear magnetic resonance spectra.

3-Butyl-4-methyl-1-isopropyl-2-imidazolone (IIIb).—A solution of 3-butyl-1-isopropyl-1-(2-propynyl)urea (19.6 g., 0.1 mole) and phosphorus pentachloride (20.8 g., 0.1 mole) in 150 ml. of benzene was gradually heated and held at reflux for 4 hr. until hydrogen chloride was no longer evolved. On cooling, a brown oil separated. The oil was taken up in 100 ml. of water, and made alkaline with 20% sodium hydroxide. The product separated as an oil. Distillation gave a colorless oil, b.p. 115–119° (2.0 mm.), $n^{25}\text{D}$ 1.4780, 14.2 g., 72.7% yield.

Anal. Calcd. for $C_{11}H_{20}N_2O$: C, 67.45; H, 10.20; N, 14.30. Found: C, 67.15; H, 10.02; N, 14.24.

Direct Reduction of Carboxylic Acids to Aldehydes by Lithium in Ethylamine[1]

ALBERT W. BURGSTAHLER, LEONARD R. WORDEN, AND
TOM B. LEWIS

Department of Chemistry, University of Kansas, Lawrence, Kansas

Received May 27, 1963

The synthesis of an aldehyde from a carboxylic acid ordinarily involves transformation of the acid into a derivative which subsequently is reduced.[2] In recent work in this laboratory we observed the direct reduction of a carboxylic acid to an aldehyde when dehydroabietic acid was treated with lithium in ethylamine over a prolonged period in the absence of an added proton source.[3] This interesting result, all the more remarkable because an excess of reducing agent was present throughout the reaction, prompted an investigation of the action of lithium in ethylamine on a number of other carboxylic acids.

In the present study we found that primary and secondary carboxylic acids, as well as tertiary carboxylic acids such as dehydroabietic acid, are reduced to aldehydes by lithium in ethylamine. Although yields as high as 80% were observed, generally they were much lower (see Table I). Efforts to find optimum conditions for the reduction by variation of the temperature, time, and method of quenching were of only limited success. Best results were obtained at the boiling point of anhydrous ethylamine (17°), which was satisfactory for use without a cosolvent except in the case of stearic acid, which was reduced in considerably higher yield in the presence of an equal volume of ether. Generally a reaction time of four to six hours proved to be most effective. Quenching the reaction with ammonium chloride gave higher yields than quenching with water, alcohol, or ammonium acetate.

TABLE I

LITHIUM–ETHYLAMINE REDUCTION OF CARBOXYLIC ACIDS

Acid	Tepm., °C.	% yield aldehyde[a]	% recovered acid[b]
Trimethylacetic acid	−78	0	0
	0	14	0
Cyclohexanecarboxylic acid	−78	0	0
	0	27	0
	17	20	20
	17[c]	18	0
1-Methylcyclohexanecarboxylic acid	17	26	60
Octanoic acid	17	26	5
Undecanoic acid	17	30	5
Lauric acid	0	21	3
	17	64	8
Stearic acid	17	40	0
	17[c]	72	0
Dehydroabietic acid	17	80[d]	0
Podocarpic acid methyl ether	17	0[d]	100

[a] Yields of aldehyde were determined by isolation of the 2,4-dinitrophenylhydrazones, whose melting points were compared with standard values (*cf.* ref. 11). [b] See Experimental. [c] Ether was employed as a cosolvent. [d] The aromatic ring also was reduced (*cf.* ref. 3).

Although the yields of aldehyde generally were better from acids of higher molecular weight than from those of lower molecular weight, the reaction does not appear to be affected appreciably by steric factors, since the yields of aldehyde from lauric acid and dehydroabietic acid[3] (primary and tertiary acids, respectively) were approximately equal. On the other hand, the highly hindered axial carboxyl group in podocarpic acid methyl ether was not reduced.

With respect to the mechanism of the reduction, the action of lithium in ethylamine on the preformed lithium salt of lauric acid gave only an 11% yield of aldehyde as opposed to a 64% yield obtained when lithium was added to a solution of the free acid in ethylamine. This suggests that these reductions occur preferentially *via* the ethylamine salt of the acid. Moreover, since isolation of the aldehyde did not require treatment of the reaction mixture with strong acid, it appears likely that a simple hydride addition product rather than a dihydroamidine[2e] or similar base-stable intermediate is formed during the reduction. In any event, the reduction was shown *not* to occur *via* dehydrogenation of an intermediate alcohol, as in the work of Smith and coworkers,[4] since 1-octanol was unaffected when treated with lithium in ethylamine under conditions which led to the reduction of octanoic acid. In contrast to the nonreducing nature of the medium employed by Smith, *et al.*, our system contains reducing species (blue solution of lithium in ethylamine) throughout the entire reaction period.

Since only fair yields of aldehydes were obtained in most of these reductions, a more extensive investigation of applications of this procedure has not been undertaken. Furthermore, since aromatic,[5] olefinic,[6] and other centers of unsaturation[6,7] also are reduced by

---

(1) Presented before the Division of Organic Chemistry, 145th National Meeting of the American Chemical Society, New York, N. Y., September, 1963.

(2) (a) E. Mosettig and R. Mozingo, *Org. Reactions*, **4**, 362 (1948); (b) A. J. Birch, *Quart Rev.* (London), **4**, 69 (1950); (c) V. M. Micovic and M. Lj. Mihailvic, *J. Org. Chem.*, **18**, 1190 (1953); (d) E. Mosettig, *Org. Reactions*, **8**, 218 (1954); (e) A. J. Birch, J. Cymerman-Craig, and M. Slaytor, *Chem. Ind.* (London), 1559 (1954); (f) *Australian J. Chem.*, **8**, 512 (1955); (g) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **80**, 5377 (1958); (h) L. I. Zakharkin and I. M. Khorlina, *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (Eng. Transl.), **12**, 2046 (1959); *Tetrahedron Letters*, No. **14**, 619 (1962); (i) H. A. Staab and H. Bräunting, *Ann.*, **654**, 119 (1962).

(3) A. W. Burgstahler and L. R. Worden, *J. Am. Chem. Soc.*, **83**, 2581 (1961). The reduction of simple esters to mixtures of acyloins and aldehydes by sodium in liquid ammonia has been reported by M. S. Karasch, E. Sternfeld, and F. R. Mayo, *J. Org. Chem.*, **5**, 362 (1940).

(4) S. Smith, R. Thompson, and E. O. Woolfolk, *ibid.* **27**, 2662 (1962).

(5) R. A. Benkeser, M. L. Burrous, J. J. Hazdra, and E. M. Kaiser, *ibid.*, **28**, 1094 (1963), and earlier papers.

(6) R. A. Benkeser, C. Arnold, Jr., R. F. Lambert, and O. H. Thomas, *J. Am. Chem. Soc.*, **77**, 6042 (1955).

(7) R. A. Benkeser, R. F. Lambert, P. W. Ryan, and D. G. Stoffey, *J. Org. Chem.*, **24**, 854 (1959).