cedure to provide monolithioferrocene in the absence of dilithioferrocene. While the work for which this lithiation procedure was needed is still incomplete, we wish to report our monolithiation technique at this time because of its potential general utility.

It was found that treatment of ferrocene in diethyl ether solution with an equimolar amount of *n*-butyllithium—instead of the usual large excess[3,4,6]—at room temperature during 5–6 hours gives rise to a reaction mixture containing monolithioferrocene in the absence of the dilithiated species. We have found the 5–6 hour reaction period to be optimum, and that the desired material is produced under these conditions in 25–26% yield. The convenience of this procedure is enhanced by the fact that commercially-available *n*-butyllithium[8] works equally as well as the freshly prepared material.

Recently, Seyferth, and co-workers[9] reported procedures which also provide only monolithioferrocene. Treatment of chloromercuriferrocene with ethyllithium, *n*-butyllithium or phenyllithium gives rise to monolithioferrocene in yields of 64, 50, and 58%, respectively. Monolithioferrocene is also generated in 43% yield by reaction between *n*-butyllithium and diferrocenylmercury[9]; with the use of a large excess of *n*-butyllithium, yields in the neighborhood of 75% have been reported.[10] While these procedures give rise to high yields when calculated on the basis of the reacting mercury compounds, the over-all yields from ferrocene are, however, low. Chloromercuriferrocene is obtained in yields of about 50%[4,11] from ferrocene, and diferrocenylmercury is obtained in only about 35% yield[11] from ferrocene. Conversion of ferrocene to monolithioferrocene *via* these mercury compounds, therefore, gives the latter in about 25–28% yield. Thus, the presently described procedure provides the over-all conversion in comparable yield, but it does so with a great deal more experimental ease and economy.

Experimental

In an oven-dried flask fitted with stirrer, condenser, and gas-inlet tube was placed a solution of ferrocene (10.0 g.; 0.054 mole) in 150 ml. of anhydrous ether. After the system was thoroughly flushed with dry nitrogen—and while it was kept in an atmosphere of nitrogen—*n*-butyllithium[8] (0.056 mole, from 35 ml. of a 1.59 M[12] hexane solution) was added from a hypodermic syringe. While maintained under a slight head of nitrogen, the reaction mixture was stirred at room temperature during 6 hr. At that time a 5.00-ml. aliquot was withdrawn and added jet-wise to a slush of absolute ether and Dry Ice. After the excess Dry Ice had been allowed to evaporate and the basic ethereal residue washed with several portions of water, the combined aqueous extracts were acidified with 6 N hydrochloric acid. The mass of yellow precipitate was collected, washed with water, and dried. This material was found to be totally soluble in ether, giving no indication of the presence of the ether-insoluble ferrocenedicarboxylic acid. The ethereal solution was dried and evaporated, yielding 103 mg. (25% yield) of ferrocenecarboxylic acid which was identified by means of its infrared spectrum. In other runs, carbonation was carried out after 4, 5, and 8 hr. of lithiation. In each case only monoferrocenecarboxylic acid was obtained in yields of, 20, 26, and 21%, respectively.

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[8] *n*-Butyllithium in hexane solution, obtained from the Foote Mineral Co., West Chester, Pa., was used.

[9] D. Seyferth, H. P. Hofmann, R. Burton, and J. F. Helling, *Inorg. Chem.*, **1**, 227 (1962).

[10] M. D. Rausch, *ibid.*, **1**, 414 (1962).

[11] M. Rausch, M. Vogel, and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957).

[12] Determined according to the procedure described by R. G. Jones and H. Gilman [*Org. Reactions*, **VI**, 353 (1951)].

An Improved Synthesis of Phenyl(trichloromethyl)mercury from Sodium Methoxide and Ethyl Trichloroacetate

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Recently, Seyferth[2] and co-workers have reported a novel synthesis of dihalocarbon adducts under neutral conditions. The dichlorocarbon intermediate was phenyl(trichloromethyl)mercury prepared from phenylmercuric chloride (or bromide), with potassium *tert*-butylate and chloroform as the trichloromethyl anion precursor. However, our attempts to prepare the dichlorocarbon precursor, phenyl(trichloromethyl)mercury, from commercial grade potassium *tert*-butylate, using the method first described by Russian workers,[3] was quite unsuccessful. In order to avoid the tedious preparation of pure potassium *tert*-butylate, ethyl trichloroacetate and commercial sodium methoxide[4] were employed as the source of the needed trichloromethyl anion to give high yields (62%) of phenyl(trichloromethyl)mercury.

This new synthesis affords a convenient, rapid method for the preparation of the unique, neutral dichlorocarbon precursor and it may be used to prepare small or moderately large quantities (10 to 60 g.) with equal ease.

Experimental

Materials.—The powdered sodium methoxide, obtained from the Matheson Co., Inc., was always transferred in a drybox under an atmosphere of dry nitrogen to a dry erlenmeyer flask.

The phenylmercuric bromide, obtained from Wood Ridge Chemical Corporation, was pulverized prior to weighing.

The ethyl trichloroacetate, obtained from Eastman Kodak Co., was distilled prior to use.

Phenyl(trichloromethyl)mercury.—In a 500-ml. three-necked, round bottom flask equipped with a reflux condenser and an efficient mechanical stirrer were placed 200 ml. of anhydrous, thiophene-free benzene, 24 g. (0.18 mole) of ethyl trichloroacetate and 13.2 g. (0.037 mole) of phenylmercuric bromide. The mixture was stirred and cooled in an ice–water bath for 15 min. Sodium methoxide (8.4 g., 0.154 mole) was added all at once from an erlenmeyer flask attached to the round bottomed flask by a flexible tube. The mixture was stirred for 1.5 hr. with cooling then quenched with an equal volume of water. After thorough mixing, the benzene layer was decanted and filtered. The aqueous mixture was extracted with three 100-ml. portions of benzene. The organic layers were combined and evaporated to dryness under a stream of air. Phenyl(trichloromethyl)mercury (10.5 g., 71% yield), a white solid, m.p. 110–112°,

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[1] This work was supported by a grant from the University of Delaware Research Fund.

[2] D. Seyferth, J. M. Burlitch and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962); D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **84**, 1757 (1962).

[3] O. A. Reutov and A. N. Lovtsova, *Dokl. Akad. Nauk SSSR*, **139**, 622 (1961); *Chem. Abstr.*, **56**, 1469 (1962).

[4] W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

was obtained. Washing of this residue once with 20 ml. of cold ethanol gave 9.0 g. (62% yield) of the desired product, m.p. 114–115° (reported[2] m.p. 116.5–118°, reported[3] 114°).

N-Alkyl Cleavage in Acid Hydrolysis of Norbornane γ-Lactams

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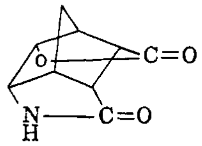
When the lactone-lactam I previously described by Worrall,[2] was refluxed in 5% hydrochloric acid, N-alkyl cleavage occurred and the product, isolated in 85% yield, was found to be identical with an authentic sample of the nortricyclenic acid lactone II.[3,4] In a similar manner III was found to give IV which was converted into II by reduction with sodium borohydride followed by heating. The ketone IV had been previously prepared by oxidation of II.[4] The amino acid lactone V,[5] is converted into its hydrochloride under the conditions mentioned above, indicating that the N-alkyl cleavages observed occur in the lactams instead of the amino acids. The unusual N-alkyl cleavages observed are considered to proceed *via* an intermediate bridged carbonium ion such as VI. In a similar manner N-*t*-butylisobutyramide, VII, evolved isobutylene when refluxed in 20% hydrochloric acid.



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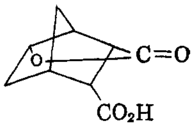

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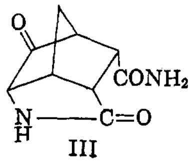

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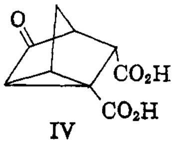

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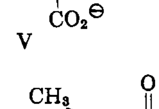

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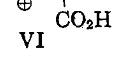

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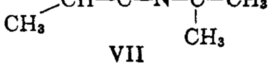

$$(CH_3)_2CH-\overset{O}{\overset{\|}{C}}-\overset{H}{N}-C(CH_3)_3$$

VII

Experimental[6]

Hydrolysis of Lactone-lactam of *endo-cis*-2,3-Dicarboxy-*endo*-5-amino-*endo*-6-hydroxynorbornane (I).—The lactone-lactam I (0.75 g., m.p. 191–192.5°) prepared as previously described[2] was refluxed in 20 ml. of 5% hydrochloric acid for 12 hr. The product was isolated as long white needles by concentrating the solution to a small volume and cooling. Recrystallization from water gave 0.61 g. (81%), m.p. 207–207.5°, alone and on admixture with an authentic sample of II.[7] Its infrared spectrum was identical with that of the authentic sample.

Anal. Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.47. Found: C, 59.90; H, 4.75.

The aqueous solution remaining after the removal of II was made basic and steam distilled. The ammonia liberated was titrated with standard acid using a modified micro-Kjeldahl procedure[8] and 99% of the theoretical nitrogen content resulting from N-alkyl cleavage was detected.

Acid Hydrolysis of III.—The keto-lactam, III (0.10 g., m.p. 234–236°) prepared as previously described[2] was refluxed for 6 hr. in 20 ml. of 10% hydrochloric acid. After work-up as described above, a 70% yield of pure IV was obtained, m.p. 238–238.5° (reported[3] 239°), $\nu_{\max}^{\mathrm{KBr}}$ 1780, 1710, 1690 cm.$^{-1}$. Nitrogen analysis, as described above, indicated quantitative N-alkyl cleavage.

Conversion of IV into II.—The ketone, IV (0.048 g.), was added to a solution of 0.056 g. of sodium borohydride in 1 ml. of 50% ethanol. After standing at room temperature for 2 hr. the solution was made acidic with dilute hydrochloric acid and continuously extracted with ether for 10 hr. Evaporation of the ether left a solid which was heated in a sublimation tube at 170° and 40 mm. for 3 hr. The unszblimed residue (0.010 g.) was identical in melting point and infrared spectrum with an authentic sample of II.

Hydrolysis of N-*t*-butylisobutyramide.—N-*t*-Butylisobutyramide[9] (0.800 g., m.p. 115–117°) was added to a refluxing solution of 20 ml. of 20% hydrochloric acid in a closed system containing a gas burette. After 1 hr. 94 ml. (75% yield) of gas was evolved. The gas was identical in its infrared spectrum (10-cm. gas cell) with isobutylene.

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[1] National Defense Education Act Fellow, 1959–1962.

[2] W. S. Worrall, *J. Am. Chem. Soc.*, **82**, 5707 (1960).

[3] K. Alder and F. Brockhagen, *Ber.*, **87**, 167 (1954).

[4] A. Winston and P. Wilder, Jr., *J. Am. Chem. Soc.*, **76**, 3045 (1954).

[5] L. H. Zalkow and C. D. Kennedy, the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., September 9–14, 1962, Abstracts, 94Q.

[6] All melting points were taken on a Fisher–Johns melting point apparatus and are uncorrected. Analyses were done by Dr. A. Bernhardt (Mulheim, Germany). Infrared spectra were recorded on a Beckman IR-5 spectrophotometer.

[7] The authors thank Dr. P. Wilder, Jr., for an authentic sample of II.

[8] L. Miller and J. A. Houghton, *J. Biol. Chem.*, **159**, 373 (1945).

[9] Kindly supplied by Dr. R. C. Freeman, Monsanto Chemical Co., St. Louis, Mo.

The Effect of Coördination on the Reactivity of Aromatic Ligands. VII. Specific Ion Effects on Diazo Coupling Rates[1]

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The effect of coördination to zinc ion on the rate of coupling of a phenolic chelating agent with a diazonium salt has been reported in a previous paper in this series.[2] The present work was undertaken to extend these rate studies to complexes of a number of other metal ions. The metal ions selected for this work were restricted to those which exhibit only one oxidation state in aqueous solution. In this way, side reactions of the metal ions with the diazonium salt were minimized.

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[1] We wish to acknowledge, with thanks, the financial assistance of the U. S. Army Research Office (Durham).

[2] K. D. Maguire and M. M. Jones, *J. Am. Chem. Soc.*, in press.