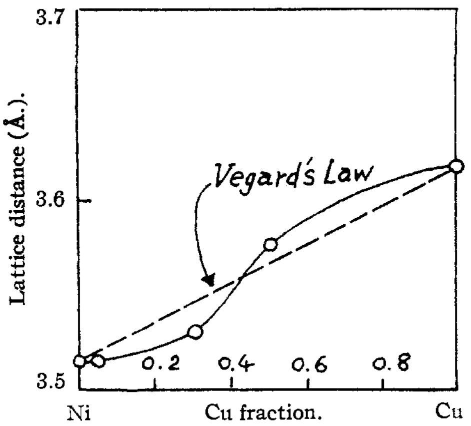

Fig. 1.

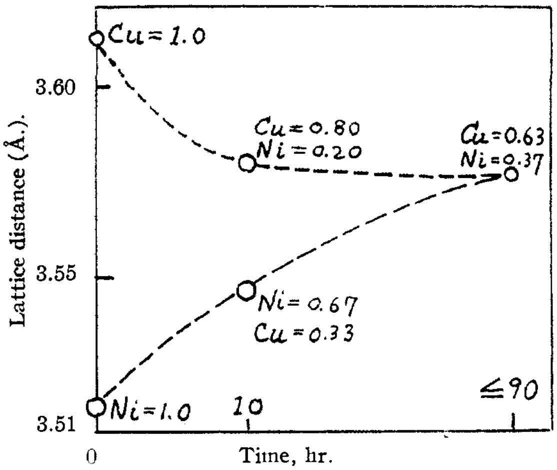

Fig. 2.

clusion that a non-equilibrium state of the alloy phase is formed on the catalyst surface, as stated by Morris and Selwood in their paper. It remains unstable on the surface to an extent depending upon the composition of the catalyst. The authors have come to the same conclusion from an adsorption study of these catalysts.[4]

Acknowledgment.—The interest of Prof. S. Kodama and the effective advice of Prof. S. Tawara in this work are gratefully acknowledged.

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[4] S. Kodama and N. Kadota, unpublished results, 1949.

DEPARTMENT OF FUEL CHEMISTRY
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RECEIVED DECEMBER 11, 1950

The Dehydrogenation of Coumaran

By BODO KLARMANN

Coumaran (2,3-dihydrobenzofuran) is readily available by the elegant synthesis of Bennett and Hafez[1] who effected ring closure by treating the diazotized *o*-amino derivative of *β*-phenylethyl alcohol with base.

The dehydrogenation of coumaran to coumarone (benzofuran) has not been reported, although the reverse reaction has been accomplished by Alexander[2] by reduction with sodium in absolute alcohol and by Weger[3] who employed hydrogenation.

Our experiments have shown that this dehydrogenation can be achieved satisfactorily by the use of sulfur; selenium is less satisfactory. With sulfur, and taking recovered starting material into account, a 45–50% yield was obtained. Since coumarone boils at 169°, and coumaran at 188°, separation by fractional distillation is readily achieved.

Experimental

Three hundred and sixty grams of pure coumaran, m.p. −21.5°, and 96 g. of sulfur are refluxed for 15 hours on an oil-bath (220°) during which time the sulfur dissolves and hydrogen sulfide is evolved. The reaction product was steam distilled, leaving behind a black residue. Addition of sodium chloride to the distillate caused a colorless oil to separate which after drying over calcium chloride was slowly fractionated at 8 mm. through a Widmer column (spiral 70 cm. long). The crude steam distillate (290 g.) yielded as a fore-run approximately 65 g. of pure coumarone boiling constantly at 168–169° (747 mm.), melting at −27°, and resinifying with concd. sulfuric acid in characteristic fashion. Coumarone isolated from high-boiling coal tar fractions by picric acid, purified by recrystallization and regenerated with steam gave an identical melting point.

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[1] Bennett and Hafez, *J. Chem. Soc.*, 287 (1941).

[2] Alexander, *Ber.*, **25**, 2409 (1892).

[3] Weger, *Z. angew. Chem.*, **22**, 391 (1909).

AUGUST BEBEL-STRASSE 11,2
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GERMANY
RECEIVED MAY 14, 1951

The Preparation of Ethylidene Iodide

By R. L. LETSINGER AND C. W. KAMMEYER

Reported methods for the preparation of ethylidene iodide either give poor yields or involve reagents such as aluminum iodide which are not readily available. It has been found that ethylidene iodide can conveniently be prepared in reasonable yields (60%) by the action of aluminum chloride on a mixture of ethylidene chloride and ethyl iodide.

Experimental

A mixture of 39.6 g. (0.4 mole) of ethylidene chloride and 187 g. (1.2 moles) of ethyl iodide was heated with 2.0 g. of aluminum chloride on a steam-bath for three hours. During this time ethyl chloride, which was formed in the reaction, bubbled out of the solution. The mixture was then poured into water, washed with a sodium bisulfite solution, and dried over magnesium sulfate. On distillation 67.3 g. (60%) of ethylidene iodide was obtained; b.p. 75–76° (25 mm.); d^{25}_4 2.794.

In a similar reaction where the mole ratio of ethyl iodide to ethylidene chloride was two to one, the yield of the iodide was 42%.

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RECEIVED JUNE 6, 1951

The Hydrogenolysis of Sulfilimines and its Application to the Purification of Sulfides

By M. A. MCCALL, D. S. TARBELL AND MARY ANN HAVILL

Several types of solid derivatives have been proposed for the characterization of liquid sulfides,[1]

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[1] (a) Faragher, Morrell and Comay, THIS JOURNAL, **51**, 2774 (1929); (b) Ipatieff, Pines and Friedman, *ibid.*, **60**, 2731 (1938); (c) Ipatieff and Friedman, *ibid.*, **61**, 684 (1939); (d) Mann and Pope, *J. Chem. Soc.*, **121**, 1052 (1922). Other types of derivatives, including sulfonium salts, are discussed by Connor in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 858–861, 867–868.

TABLE I

SULFILIMINES, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NS}\langle^{R'}_{R}$

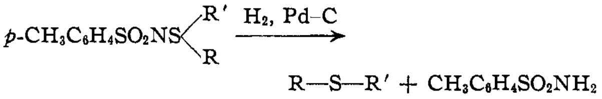
R	R	M.p., °C.	Yield,[a] %	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
iso-C_3H_7	C_6H_5	116.5–117 dec.	89	$C_{16}H_{19}O_2NS_2$	59.78	59.93	5.96	6.21
CH_3	n-C_4H_9	89–90.5	70	$C_{12}H_{19}O_2NS_2$	52.71	52.97	7.00	6.97
$C_6H_5CH_2$	C_6H_5	146–147	76	$C_{19}H_{17}O_2NS_2$	65.01	65.25	5.18	5.20
t-C_4H_9	C_6H_5	98–100 dec.	50	$C_{17}H_{21}O_2NS_2$	60.86	60.74	6.31	6.32

[a] Yields are for analytically pure material.

of which the sulfilimines[1d,2] appear to be the most useful. There has not been a very satisfactory procedure for the preparation of crystalline derivatives from liquid sulfides, from which the purified sulfides could be readily regenerated.[3] The present note indicates a useful process for this purpose.

During a study of some allyl and propenyl aryl sulfides[4] we observed that treatment of the sulfilimines of these sulfides with hydrogen and palladium–charcoal led to a very rapid hydrogenolysis of the sulfur–nitrogen bond in the sulfilimines, with formation of the sulfide (in which partial saturation of the double bond had occurred) and p-toluenesulfonamide, both in high yield.

This reaction, the equation for which is



$$p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NS}\langle^{R'}_{R} \xrightarrow{\text{H}_2,\ \text{Pd-C}} \text{R—S—R}' + \text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$$

was investigated for a number of sulfilimines derived from sulfides of different types, and was found to be a general reaction. The sulfilimines examined included ones derived from diaryl, dialkyl and aralkyl aryl sulfides.[5] The sulfilimines are easily prepared from the sulfides, and can be purified readily by crystallization or chromatography; the ease of regeneration of the sulfides from the purified sulfilimines by catalytic hydrogenation indicates that this process may be useful in work with liquid sulfides.

The new sulfilimines prepared in this work are listed in Table I, and the yields obtained on hydrogenolysis are shown in Table II.

TABLE II

REGENERATION OF SULFIDES FROM HYDROGENOLYSIS OF SULFILIMINES, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NS}\langle^{R'}_{R}$

Sulfilimine R	Sulfilimine R'	Yield of sulfilimine,[a] %
iso-C_3H_7	C_6H_5	59
CH_3	n-C_4H_9	55
n-C_4H_9	n-C_4H_9[b]	51
C_6H_5	C_6H_5[c]	71
$C_6H_5CH_2$	C_6H_5[d]	[d]
t-C_4H_9	C_6H_5	[e]

[a] Yield of analytically pure crystalline sulfilimine prepared from the regenerated sulfide. [b] Todd, Fletcher and Tarbell, THIS JOURNAL, **65**, 350 (1943). [c] Tarbell and Weaver, *ibid.*, **63**, 2939 (1941). [d] Yield was 75% of isolated sulfide. [e] See footnote 5.

Experimental[6]

General Procedure for Preparation of Sulfilimines.—The sulfide (0.02 mole) was dissolved at room temperature in a small quantity of ethyl or methyl alcohol or other water-miscible solvent (approx. 50 cc.). Chloramine-T (0.03 mole) was dissolved in an approximately 50% water solution of the same solvent used for the sulfide. The two solutions were then mixed with stirring. If the sulfide separated from the solution on mixing, more of the organic solvent was added until the final solution was complete. The reaction mixture was then warmed to 60–70° for a few minutes on a steam-bath, usually in an open beaker, with the escape of some of the volatile solvent. The treated reaction mixture was then allowed to stand overnight. If crystals did not form on standing, more water was added to the warmed solution until it began to cloud; then it was allowed to cool slowly, or more solvent was removed by evaporation. The crystals were filtered by suction, washed with water to remove the excess unreacted chloramine-T, and then with a little ethyl ether to remove any p-toluenesulfonamide, dried, and crystallized from suitable solvents, such as methyl or ethyl alcohol, alcohol–water mixtures, benzene, benzene–hexane or benzene–heptane mixtures.

General Procedure for Hydrogenolysis of Sulfilimines.—Three to four grams of 5% palladium-on-Norite catalyst[7] was suspended in 50 cc. of ethyl or methyl alcohol and activated by reducing in hydrogen at atmospheric pressure in a low-pressure reduction apparatus. After the absorption of hydrogen had stopped, the solvent was removed and the catalyst was washed with more alcohol until the washings were free of hydrochloric acid. The catalyst was returned to the reduction flask with 50 cc. of fresh alcohol and again reduced until absorption stopped. The apparatus was then opened and the sulfilimine (0.01 M) was added directly to the alcohol suspension of activated catalyst. It was then stirred with a magnetic stirrer in an atmosphere of hydrogen until one mole equivalent of hydrogen had been absorbed. If there was no danger of reducing the sulfide further, the hydrogenolysis could be continued until the absorption of hydrogen stopped.

The catalyst was removed by suction and washed freely with peroxide-free ethyl ether. If the sulfide was volatile, it was found better to filter by conventional gravity filtration.[8] The ether–alcohol solution was then washed with three 100–150-cc. portions of 5% sodium hydroxide solution to remove the p-toluenesulfonamide. The combined basic wash solution was then washed with a small amount of peroxide-free ethyl ether which was combined with the other ether solution. The ether was removed by distilling slowly from a small, 7 in. Vigreux column or modified Claisen flask.[9] The remaining liquid sulfide may be flash-distilled or used directly. Solid sulfides crystallized after most of the solvent was removed. Mixed melting points of the sulfilimines de-

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(2) Further references on sulfilimines are given by Tarbell and Weaver, THIS JOURNAL, **63**, 2939 (1941).

(3) The mercuric chloride complexes of sulfides can be decomposed by hydrogen sulfide (Mabery, *Am. Chem. J.*, **13**, 232 (1891)) but the properties of the complexes do not appear very favorable for purification purposes.

(4) Tarbell and McCall, THIS JOURNAL, **73**, in press.

(5) The sulfilimine of t-butyl phenyl sulfide did not behave normally on hydrogenation; no sulfilimine could be obtained by treatment of the hydrogenation solution with chloramine-T in the usual way, and there appeared to be some thiophenol formed in the reduction.

(6) The authors wish to thank Miss Claire King for the microanalyses.

(7) "Catalyst C," *Org. Syntheses*, **26**, 78 (1946).

(8) Some of the sulfides seemed to be easily lost by volatility when suction filtration was used.

(9) Some of the sulfides were found to distil over with the solvent (especially alcohol) when removed under vacuum.

rived from liquid sulfides or mixed melting points of the solid sulfides were taken in all cases.

DEPARTMENT OF CHEMISTRY
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The Synthesis of New β-Diketones

BY ROBERT LEVINE AND JAMES K. SNEED

For other work, which is now in progress in this Laboratory, the following four β-diketones were required.

Nicotinoyltrifluoroacetone.—Commercial sodium methoxide (0.2 mole, 11.4 g. of commercial 95% material[1]) was placed in a 1000-ml. three-neck, round-bottom flask, equipped with ground glass joints and carrying a mercury-sealed stirrer, a reflux condenser and dropping funnel (drying tubes). The sodium methoxide was suspended in 250 ml. of anhydrous ether and to the rapidly stirred mixture, cooled in an ice-bath, 0.2 mole (28.4 g.) of ethyl trifluoroacetate, diluted to 125 ml. with anhydrous ether, was added. The ice-bath was removed and then 0.2 mole (24.2 g.) of 3-acetylpyridine, diluted to 125 ml. with anhydrous ether, was added dropwise. After the addition of the ketone was complete, the mixture was stirred and refluxed for two hours on a water-bath. The water bath was removed and water (*ca.* 100 ml., exothermic reaction) was added slowly to dissolve the solid which was present and the mixture extracted with several 100-ml. portions of ether to remove unreacted ester and ketone. The aqueous phase was acidified with 0.2 mole of glacial acetic acid and extracted with ether until the extracts no longer gave a positive test with alcoholic iron(III) chloride solution. The combined extracts were dried over Drierite, the solvent distilled and the residue crystallized to give 38.2 g. (88.0%) of nicotinoyltrifluoroacetone, m.p. 173.5–174°. *Anal.* Calcd. for $C_9H_6O_2NF_3$: C, 49.78; H, 2.79. Found: C, 49.87; H, 2.86. The β-diketone gave a green copper chelate, m.p. 262–262.5°. *Anal.* Calcd. for $C_{18}H_{10}O_4N_2F_6Cu$: C, 43.60; H, 2.02. Found: C, 43.34; H, 1.91.

Isonicotinoyltrifluoroacetone.—Using the apparatus described above, a mixture of 0.345 mole (47.3 g.) of 4-acetylpyridine, 0.345 mole (19.6 g.) of 95% sodium methoxide and 0.345 mole (49.0 g.) of ethyl trifluoroacetate was refluxed for six hours. Then, the addition of 0.345 mole (20.5 g.) of glacial acetic acid caused the precipitation of a mixture of sodium acetate and condensation product. Water (*ca.* 250 ml.) was added to the vigorously stirred reaction mixture to dissolve the sodium acetate and the mixture filtered. The precipitate was washed with several portions of water and dried in a vacuum desiccator. In this manner, there was obtained 71.4 g. (95.2%) of isonicotinoyltrifluoroacetone, m.p. 213–214.5° (sealed tube). *Anal.* Calcd. for $C_9H_6O_2NF_3$: C, 49.78; H, 2.79. Found: C, 49.81; H, 2.75. The β-diketone gave a green copper chelate, which decomposed without melting when heated above 280°. *Anal.* Calcd. for $C_{18}H_{10}O_4N_2F_6Cu$: C, 43.60; H, 2.02. Found: C, 43.40; H, 1.77.

Nicotinoyl-2-thenoylmethane.—When 0.25 mole (31.5 g.) of 2-acetylthiophene, 0.3 mole (41.1 g.) of methyl nicotinate and 0.50 mole of sodium amide[2] (prepared from 11.5 g. of sodium) were allowed to react for two hours, as described previously for other heterocyclic β-diketones,[2] and the mixture worked up as described above for the preparation of nicotinoyltrifluoroacetone, there was obtained 34.1 g. (59%) of nicotinoyl-2-thenoylmethane, m.p. 133–134°. *Anal.* Calcd. for $C_{12}H_9O_2NS$: C, 62.32; H, 3.92. Found: C, 62.46; H, 3.68. The β-diketone formed a picrate, m.p. 208–209°. *Anal.* Calcd. for $C_{18}H_{12}O_9N_4S$: N, 12.17. Found: N, 12.29.

Isonicotinoyl-2-thenoylmethane.—A mixture of 0.50 mole (63.0 g.) of 2-acetylthiophene, 0.25 mole (34.3 g.) of methyl isonicotinate and 0.25 mole (14.5 g.) of 95% sodium methoxide was refluxed for six hours and the reaction stopped by the addition of glacial acetic acid and water as described above in the preparation of isonicotinoyltrifluoroacetone. The mixture was extracted with ether until a negative test was obtained with alcoholic iron(III) chloride solution, the extracts dried over Drierite and the solvent and unreacted reactants distilled. The residue was recrystallized from 95% ethanol to give 37.6 g. (64.8%) of isonicotinoyl-2-thenoylmethane; m.p. 152–152.5°. *Anal.* Calcd. for $C_{12}H_9O_2NS$: C, 62.32; H, 3.92. Found: C, 62.25; H, 3.68. The β-diketone gave a picrate, m.p. 211–212.5°. *Anal.* Calcd. for $C_{18}H_{12}O_9N_4S$: N, 12.17. Found: N, 12.42.

CONTRIBUTION NO. 818
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH 13, PENNSYLVANIA

RECEIVED APRIL 16, 1951

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[1] Purchased from the Mathieson Chemical Corporation, Niagara Falls, N. Y.

[2] Harris and Levine, THIS JOURNAL, **70**, 3360 (1948).

Preparation and Microbiological Activity of an Homolog of Lysine

BY A. D. MCLAREN AND C. A. KNIGHT

Considerable attention has been directed recently to the investigation of compounds which are structurally similar to metabolically important substances.[1] In the present communication we are reporting the synthesis of a lysine homolog, ε-C-methyllysine (2,6-diaminoheptanoic acid), and some effects of this compound on the growth of 2 lactobacilli, *Leuconostoc mesenteroides* P-60 and *Streptococcus faecalis*, American Type Culture Collection No. 9790.

Experimental

The 2,6-diaminoheptanoic acid dihydrochloride was prepared by a several step synthesis according to the procedures of Eck and Marvel[2] from 2-methylcyclohexanone oxime.[3] The intermediates, 2-keto-7-methylhexamethylenimine and 6-aminoheptanoic acid, have been reported elsewhere.[3]

6-Benzoylaminoheptanoic Acid.—2-Methylcyclohexanone oxime, 630 g., was converted to the benzoylamino acid.[2] The product, m.p.[4] 87–89°, weighed 749 g.

Anal. Calcd. for $C_{14}H_{19}O_3N$: C, 67.42; H, 7.70. Found: C, 67.24; H, 7.70.

6-Benzoylamino-2-bromoheptanoic Acid.—6-Benzoylaminoheptanoic acid, 720 g., was brominated in the usual way.[2] The 2-bromo acid, m.p. 152–153.5°, crystallizes very slowly from acetone or chloroform over a period of months. Consequently some of the product was withdrawn and recrystallized for analyses and further syntheses.

Anal. Calcd. for $C_{14}H_{18}O_3NBr$: C, 51.23; H, 5.53; N, 4.27. Found: C, 51.57; H, 5.55; N, 4.51.

6-Benzoylamino-2-aminoheptanoic Acid.—The bromo-acid, 16 g., was allowed to react with ammonia according to the procedures of Eck and Marvel.[2] The product, m.p. 247–250°, weighed 9 g.

Anal. Calcd. for $C_{14}H_{20}O_3N_2$: C, 63.60; H, 7.62; N, 10.62. Found: C, 63.40; H, 7.72; N, 10.70.

2,6-Diaminoheptanoic Acid Dihydrochloride.—6-Benzoylamino-2-aminoheptanoic acid, 1 g., was hydrolyzed[2] to give 0.42 g. of ε-C-methyllysine dihydrochloride. The product, m.p. 190.5–192°, sinters at *ca.* 185° and releases bubbles at *ca.* 206°.

Anal. Calcd. for $C_7H_{18}O_2N_2Cl_2$: C, 36.02; H, 7.78; N, 12.02. Found: C, 36.21; H, 7.58; N, 11.89.

Tests for Lysine Activity and Lysine Inhibition.—Tests were set up for the microbiological assay of lysine using either *Streptococcus faecalis* or *Leuconostoc mesenteroides* and employing the conditions previously described[5] with the exceptions that the tests were run in a total volume of 2 ml.

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[1] D. W. Woolley, *Physiol. Rev.*, **27**, 308 (1947).

[2] J. C. Eck and C. S. Marvel, "Organic Syntheses," Coll. Vol. 2, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 74, 76, 374.

[3] H. E. Ungnade and A. D. McLaren, *J. Org. Chem.*, **10**, 29 (1945).

[4] All melting points are corrected.

[5] C. A. Knight, *J. Biol. Chem.*, **171**, 297 (1947).