tion was completed. The sodium salt of the triazole was precipitated by adding ether to the cold mixture. The salt was then dissolved in a minimum amount of water, warming if necessary, and chilled in an ice-bath. The cold salt solution was added dropwise with constant agitation to cold dilute hydrochloric acid. If the addition was too fast or the salt solution too concentrated, a plastic mass was obtained instead of the white powder form of the triazole. But in either case, one recrystallization from hot 95% ethanol yielded the yellow needles of the diazomalonanilide. The product was purified and stored in this form.

Ethyldiazomalon-*p*-aniside was obtained in 55% yield; m.p. 95–96°. *Anal.* Calcd.: C, 54.75; H, 4.98; N, 15.96. Found: C, 55.11; H, 4.85; N, 15.99. Ethyldiazomalon-*p*-toluidide, m.p. 98–99°, and ethyldiazomalon-*p*-bromoanilide,[8] m.p. 138–139°, were prepared in the same way. The corresponding triazoles melt at 91, 88 and 138°. The sample must be put into the bath just below the melting point to obtain a reproducible result.

Solvents.—Commercial acetonitrile was distilled through a helices-packed fractionating column. A middle fraction, b.p. 31–32°, d^{20} 0.7813, n^{20} 1.3450, was collected.

Commercial dimethylformamide was similarly distilled; b.p. 152–153°, d^{20} 0.9392, n^{24} 1.4282.

Kinetics.—Since the triazoles rearrange even in the solid state, they were always freshly prepared before a run. About one gram of the appropriate ethyldiazomalonanilide was dissolved in a minimum amount of hot ethanol and the solution rapidly chilled in an ice-bath. A solution of sodium ethoxide (from 0.1–0.15 g. of sodium in 4 cc. of ethanol) was added to dissolve the malonanilide, then ether was added slowly at 0° to ensure a fine white powdered precipitate of the triazole sodium salt. The salt was removed and dissolved in water, cooled to zero degrees, and added dropwise to cold dilute hydrochloric acid with constant agitation. The combined volume should not exceed 50 cc. and the salt must be added to the acid rather than *vice versa.*

The triazole thus prepared was dried *in vacuo* to constant weight. A typical sample dissolved in ethanol and quenched immediately with excess aqueous potassium iodide and iodate gave 98% or more of the theoretical amount of iodine. For the kinetic runs, a weighed sample of the triazole was dissolved in a known volume of solvent already at the desired temperature. From time to time aliquots of the thermostated solution were withdrawn with an automatic pipet and quickly transferred to a flask containing the potassium iodide–iodate solution, excess distilled water and a magnetic stirrer. The iodine, which appears instantly, was titrated with thiosulfate to a starch end-point. With dimethylformamide and other water-soluble solvents the system is homogeneous. It is doubtful whether the analytical method is fast enough for accurate results with solvents such as toluene in which the rearrangement is extremely fast and the unrearranged acid must be extracted from the hydrocarbon phase.

The runs were quite accurately first order. Rate constants and activation parameters were calculated by the method of least squares.

The salts used in the salt effect experiments were reagent grade, dried at 100–110° overnight or to constant weight and allowed to cool in a desiccator over phosphorus pentoxide.

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TALLAHASSEE, FLORIDA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE RICE INSTITUTE]

The Mustard Oil of *Limnanthes douglasii* Seed, *m*-Methoxybenzyl Isothiocyanate

BY MARTIN G. ETTLINGER AND ALLAN J. LUNDEEN[1]

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The seed of *Limnanthes douglasii* furnished the previously unknown *m*-methoxybenzyl isothiocyanate, obtained also by synthesis.

The meadow foam, *Limnanthes douglasii* R. Br., of the small North American family *Limnanthaceae*, is a herb native to Oregon and California. A century ago, Chatin[2] observed that the plant afforded a pungent, steam-volatile oil that appeared to be an isothiocyanate and gave with ammonia a crystalline thiourea. Guignard[3] demonstrated that the *Limnanthes* oil did not exist in the intact plant but was liberated on maceration of leaf or seed, by an enzyme that could also convert the glucoside sinigrin to allyl isothiocyanate. He noted that the oil in taste and odor resembled that of garden cress, now known to be benzyl isothiocyanate.

Dr. Joe E. Hodgkins found at Rice that the thiourea in ammoniated distillates of *Limnanthes douglasii* seed, chromatographed on paper,[4] appeared to be a single substance with R_{Ph} 1.02 ± 0.02 and was consequently distinct from all thioureas of volatile natural mustard oils of known structure.[5] In our further work, the *Limnanthes* isothiocyanate, formed in approximate amount of 0.5% of seed, was isolated and characterized as the thiourea, m.p. 101–101.5°, and the N′-phenylthiourea, m.p. 86–87°. The phenylthiourea was originally obtained from a benzene solvate as a metastable dimorph, m.p. 76.5–77°, which changed to the higher-melting form. The infrared spectra of the solid modifications differed markedly between 7.5 and 15 μ.[6]

Analyses of the mustard oil and derivatives showed that the isothiocyanate had the empirical formula C_9H_9ONS and contained one methoxyl group. The thiourea in ethanol had an ultraviolet absorption maximum at 244 mμ (log ε 4.15), comparable to that shown by monosubstituted thioureas with a saturated carbon atom adjacent to the chromophore,[7,8] whereas the absorption band[7,9]

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(1) National Science Foundation Predoctoral Fellow.

(2) A. Chatin, *Compt. rend.*, **38**, 772 (1854); *Ann. sci. nat., Botan.*, [4] **6**, 247 (1856).

(3) L. Guignard, *Compt. rend.*, **117**, 751 (1893); *J. botanique*, **7**, 417 (1893).

(4) A. Kjaer and K. Rubinstein, *Acta Chem. Scand.*, **7**, 528 (1953).

(5) A thiourea with R_{Ph} 1.02 ± 0.01 has been derived in small amounts from turnip and rape, of the mustard family (K. A. Jensen, J. Conti and A. Kjaer, *ibid.*, **7**, 1267, 1271 (1953)), but has not been further characterized. Compare benzylthiourea, R_{Ph} 0.9; β-phenylethylthiourea, 1.1; 4-methylthiobutylthiourea, 0.97 (A. Kjaer and R. Gmelin, *ibid.*, **9**, 542 (1955)).

(6) *Cf.* infrared spectra of dimorphs of allylthiourea (A. A. Ebert, Jr., and H. B. Gottlieb, THIS JOURNAL, **74**, 2806 (1952)).

(7) A. Clow and N. L. Helmrich, *Trans. Faraday Soc.*, **36**, 685 (1940).

(8) A. Kjaer, J. Conti and I. Larsen, *Acta Chem. Scand.*, **7**, 1276 (1953).

(9) A. Kjaer, K. Rubinstein and K. A. Jensen, *ibid.*, **7**, 518 (1953). The statement that a N-methallyl (alkyl) group exerts a hypsochromic effect in a N′-phenylthiourea is formally true, but as the figure in the reference might suggest, the effect appears to be caused not by displacement of the phenylthiourea band, but by appearance of intense absorption at short wave lengths by the N-alkylthioamide group acting as a partial chromophore.

of phenylthiourea lay at 267 mμ. However, the *Limnanthes* thiourea absorbed very strongly at short wave lengths (log ε 4.17 at 220 mμ, greater than that of benzylthiourea,[8] 4.00) and had a subsidiary band at 273 mμ (3.41). The nature of the second chromophore was clearly implied by the spectrum of the mustard oil in ethanol, which exhibited an isothiocyanate[9,10] band at 250 mμ (3.20), intense absorption at short wave lengths (log ε *ca.* 3.85 at 220 mμ) and maxima at 274 (3.38) and 280 mμ (3.33) corresponding to the known bands of anisole[11] (in methanol 272 (3.35) and 278 mμ (3.27)) and methyl tolyl ethers.[12] The conjugated phenyl isothiocyanate absorbed at similarly long wave lengths but with much greater intensity[13] (log ε *ca.* 4.45 at 220 mμ; maxima in ethanol at 267 (4.06) and 278 mμ (4.06)).

The *Limnanthes* mustard oil, apparently containing methoxyl, phenyl ether, and unconjugated[14] isothiocyanate groups, was therefore *o*-, *m*- or *p*-methoxybenzyl isothiocyanate. The *p*-isomer was excluded by the known[15] melting point (135°) of *p*-methoxybenzylthiourea and the absence in the infrared spectrum of the *Limnanthes* isothiocyanate of any band between 11.7 and 12.7 μ.[16] Permanganate oxidations of the mustard oil and thiourea gave *m*-methoxybenzoic acid, m.p. 105–106°, identified with authentic material. Hence, the *Limnanthes* mustard oil was *m*-methoxybenzyl isothiocyanate.

m-Methoxybenzaldehyde was transformed to *m*-methoxybenzylamine[17,18] in a single step by the Leuckart reaction[19] in 53% yield, greater than the yields reported with the *o*- and *p*-isomers (30–23%) and nearly as much as those obtained with benzaldehyde and *p*-tolualdehyde (60–62%). Reaction of the amine with phenyl isothiocyanate furnished N-*m*-methoxybenzyl-N′-phenylthiourea, m.p. 88.5–90° (77–78°). *m*-Methoxybenzyl isothiocyanate was prepared from the amine in 82% yield by the Kaluza–Hodgkins[20] synthesis and converted to *m*-methoxybenzylthiourea, m.p. 101–103°. The natural and synthetic mustard oils were identical.

m-Methoxybenzyl isothiocyanate belongs to the rare class of natural products that contain a benzene ring substituted as in *m*-cresol. Formal derivatives of *o*- and *p*-cresol are far more common, and indeed *p*-hydroxybenzyl isothiocyanate, though its known botanical distribution is restricted, has long been recognized as the product of white mustard. The only natural *m*-substituted analog of the *Limnanthes* mustard oil or its precursor appears to be zierin,[21] from *Zieria laevigata* (*Rutaceae*), a glucoside of *m*-hydroxybenzaldehyde cyanohydrin.[22,23]

Experimental

Isolation of Thioureas.—Twenty-five grams of *Limnanthes douglasii* seed[24] was milled[25] in 150 cc. of petroleum ether, and the dry residue was macerated in 100 cc. of water at 60° during an hour and steam distilled. The distillate (*ca.* 200 cc.), treated with ammonia and partly evaporated next day, contained 0.136 g. of the thiourea by ultraviolet spectrophotometric assay, corresponding to a yield of 5 g./kg. of isothiocyanate from seed. Values from other assays ranged downward to 3.4 g./kg. The solution was evaporated *in vacuo* and the residue crystallized from benzene to furnish 0.12 g. of *m*-**methoxybenzylthiourea**, m.p. 100°. The analytical sample, crystallized from benzene–petroleum ether, melted at 101–101.3°.

Anal.[26] Calcd. for $C_9H_{12}ON_2S$: C, 55.07; H, 6.16; N, 14.27; S, 16.34; CH_3O, 15.81. Found: C, 55.01; H, 6.04; N, 14.30; S, 16.00; CH_3O, 15.57.

The ultraviolet absorption spectrum of an aqueous solution had maxima at 238 (log ε 4.14) and 272 mμ (3.35), minima at 228 (4.09) and 265 mμ (3.32). The respective extinctions at 220, 240 and 260 mμ were 14800, 13600 and 2350 in water, 14700, 12600 and 4000 in ethanol. The infrared spectrum of the solid mulled in oil had conspicuous bands beyond 7.5 μ at 7.91, 8.55, 9.08, 9.69, 10.14, 10.80, 11.57, 12.21, 12.66, 13.67 and 14.37 μ.

A distillate of 25 g. of seed was extracted with ether, which was evaporated and the residue warmed a few minutes on the steam-bath with *ca.* 0.1 cc. of aniline. The product, crystallized from benzene and from benzene–petroleum ether, melted solvated at 68–68.5° and at 72.3–72.8°. The analytical sample of **N-*m*-methoxybenzyl-N′-phenylthiourea** after a stay *in vacuo* melted at 76.5–77°.

Anal. Calcd. for $C_{15}H_{16}ON_2S$: C, 66.14; H, 5.92; N, 10.29. Found: C, 65.87; H, 5.84; N, 9.88.

The melting point of one sample rose to 86–87° after 3.5 months, whereas that of the analyzed material kept in a desiccator remained at 76–77° after six months.

Isolation of Mustard Oil.—One half pound of ground *L. douglasii* seed and 5 g. of white mustard flour[27] were digested in 1 l. of water at 60° for 1.5 hours, and two such macerates were combined and steam distilled until 3 l. was collected. Assay of the first 2 l. of distillate by treatment of an aliquot with ammonia and spectrophotometry indicated the presence of 1.9 g. of isothiocyanate, whereas the third liter contained only 0.18 g. The distillate was saturated with salt and ex-

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[10] M. Pestemer and B. Litschauer, *Monatsh.*, **65**, 239 (1935); *cf.* M. G. Ettlinger and J. E. Hodgkins, *J. Org. Chem.*, **21**, 204 (1956).

[11] K. L. Wolf and W. Herold, *Z. physik. Chem.*, **B13**, 201 (1931); *cf.* H. E. Ungnade, THIS JOURNAL, **75**, 432 (1953).

[12] E. A. Braude, E. R. H. Jones and E. S. Stern, *J. Chem. Soc.*, 1087 (1947); A. Burawoy and J. T. Chamberlain, *ibid.*, 2310 (1952).

[13] *Cf.* S.-C. Woo and T. C. Chu, *J. Chinese Chem. Soc.*, **5**, 162 (1937).

[14] 2-Methoxy-6-methylphenyl isothiocyanate was perhaps not excluded.

[15] F. Hueter, *Chem. Ber.*, **80**, 273 (1947); S. Saijo, *J. Pharm. Soc. Japan*, **72**, 1009 (1952); [*C. A.*, **47**, 3298 (1953)].

[16] *Cf.* L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1954, Ch. 5.

[17] W. H. Carothers, C. F. Bickford and G. J. Hurwitz, THIS JOURNAL, **49**, 2908 (1927).

[18] C. W. Shoppee, *J. Chem. Soc.*, 696 (1932).

[19] K. G. Lewis, *ibid.*, 2249 (1950).

[20] J. E. Hodgkins and M. G. Ettlinger, *J. Org. Chem.*, in press.

[21] H. Finnemore and J. M. Cooper, *J. Proc. Roy. Soc. N. S. Wales*, **70**, 175 (1936).

[22] The parallelism of natural mustard oils and cyanogenetic glycosides, and amino acids also, is evident if the series of isopropyl (A. Kjaer and J. Conti, *Acta Chem. Scand.*, **7**, 1011 (1953)), *sec*-butyl, benzyl and *p*-hydroxybenzyl isothiocyanates is compared with that of the cyanohydrin glycosides of acetone, methyl ethyl ketone (H. Finnemore, J. M. Cooper and M. B. Stanley, *J. Soc. Chem. Ind.*, **57**, 162 (1938); T. A. Henry, *ibid.*, **57**, 248 (1938)), benzaldehyde and *p*-hydroxybenzaldehyde, or with that of valine, isoleucine, phenylalanine and tyrosine. ADDED IN PROOF.—A. Kjaer, R. Gmelin and R. B. Jensen (*Acta Chem. Scand.*, in press) have found *p*-methoxybenzyl isothiocyanate in *Aubrieta* (*CruciFerae*).

[23] Synthetic derivatives of *m*-hydroxy*phenyl* isothiocyanate, substituted on the oxygen atom by a three- or four-carbon alkyl or alkenyl group, have recently been commended as anthelmintics (H. Spiegelberg and G. Rey-Bellet, U. S. Patent 2,595,723 [*C. A.*, **47**, 3343 (1953)]; F. Hoffmann-La Roche and Co., British Patents 673,798 and 678,125; Swiss Patents 279,109 and 283,652 [*C. A.*, **47**, 6441, 8092 (1953); **48**, 7635, 8822 (1954)]).

[24] Obtained as *Floerkea douglasii* from Theodore Payne, 2969–2999 Los Feliz Blvd., Los Angeles 39, Calif.

[25] With a Sargent Centrifugal Wet Mill, Size 1 (E. H. Sargent and Co., Chicago, Ill.).

[26] Microanalyses by Dr. A. Elek, 4763 W. Adams Blvd., Los Angeles 16, Calif.

[27] *Sinapis alba* seed is known[8] not to contain appreciable amounts of volatile isothiocyanates, but the flour did seem to raise the background absorption[8] of the distillate.

tracted continuously with ether during 48 hours. The extract (600 cc.) obtained from 3 lb. of seed in succession was dried on sodium sulfate and concentrated, and the residue was distilled *in vacuo* to furnish 2.5 g. of mustard oil, b.p. 87–106° at 0.45 mm. Redistillation afforded **m-methoxybenzyl isothiocyanate**, b.p. 105–106° at 0.45 mm., $n^{28.4}_{\mathrm{D}}$ 1.5867, d^{30} 1.145 g./cc. The refractive index was slightly less than that of synthetic material, and percentages of nitrogen and sulfur were 0.9–1.2 unit smaller than theoretical.

Anal. Calcd. for C_9H_9ONS: C, 60.31; H, 5.06; CH_3O, 17.31. Found: C, 60.21; H, 5.31; CH_3O, 16.74.

The ultraviolet absorption spectrum of a solution in 2,2,4-trimethylpentane had a plateau at 252–262 mμ (log ε 3.20), maxima at 274 (3.38) and 281 (3.34), and minima at 241 (3.09) and 278 mμ (3.30). In ethanol minima appeared at 242 (3.18), 258 (3.18) and 278 mμ (3.32). The infrared spectrum of the neat liquid had bands of the methyl and methylene groups at 3.41, 3.50, 6.86 and 6.97 μ, the isothiocyanate group at 4.81 μ, the benzene ring at 6.24, 6.71, 12.80 and 14.2 μ, the aryl ether group at 7.91 μ, and other conspicuous peaks at 7.49, 8.67, 9.52 and 13.53 μ.

Comparison of Ultraviolet Spectra.—Phenylthiourea in ethanol absorbed maximally at 267 mμ (log ε 4.14), with an inflection at 245 (3.97) and minimum at 227 mμ (3.92). N-Ethyl-N′-phenylthiourea in ethanol had a maximum at 248 (4.21) and inflections at 244 (4.20) and 260 (4.18), with a minimum at 226 mμ (4.04). The logarithmic extinction was 4.17–4.18 throughout the range 256–268 mμ.

Phenyl isothiocyanate in 2,2,4-trimethylpentane had maxima at 269 (4.04) and 280 (4.04), minima at 237 (3.44) and 275 mμ (4.01).

Oxidations.—A mixture of 0.5 g. of *Limnanthes* mustard oil and a solution of 1 g. of potassium permanganate in 60 cc. of water was boiled under reflux three hours and filtered, and the solution was acidified and extracted with ether. The ether was evaporated and the residue crystallized from water to afford 0.22 g. of *m*-methoxybenzoic acid, m.p. 105–106°. The melting point of a mixture with authentic *m*-methoxybenzoic acid[28] (m.p. 106–108°) was undepressed, whereas a mixture with *o*-methoxybenzoic acid[29] (m.p. 100.5–102.5°) began to melt at 77°.

A similar oxidation of 0.2 g. of the *Limnanthes* thiourea furnished 0.04 g. of *m*-methoxybenzoic acid.

Synthesis.—*m*-Hydroxybenzaldehyde, m.p. 103–104°, purified by sublimation at 100° and 3 mm. and crystallization from benzene,[30] was converted[31] to *m*-methoxybenzaldehyde by dimethyl sulfate and alkali in 87–91% yield. Treatment with hot ammonium formate, followed by acid hydrolysis, according to Lewis' procedure[19] furnished in 48–53% yield[32] *m*-methoxybenzylamine, b.p. 81° at 0.8 mm., 110° at 7 mm., 141° at 30 mm. (lit.[17,18] 103–104° at 6 mm., 131° at 26 mm.), n^{28}_{D} 1.5438. The amine hydrochloride formed platelets from benzene–ether; m.p. 165.5–166.5° (lit.[33] 160°). N-*m*-Methoxybenzylacetamide melted at 58–60° (lit.[17] 58.5–59°), N-*m*-methoxybenzyl-*p*-nitrobenzamide at 125–126° (lit.[18] 124°). **N-*m*-Methoxybenzylbenzamide,** prepared with benzoyl chloride and 10% sodium carbonate and crystallized from chloroform–ligroin or aqueous ethanol, melted at 67.8–68.2°.

Anal. Calcd. for $C_{15}H_{15}O_2N$: C, 74.66; H, 6.27. Found: C, 74.92; H, 6.22.

The initial synthetic sample of N-*m*-methoxybenzyl-N′-phenylthiourea, crystallized from benzene–petroleum ether, melted solvated at 66°, undepressed by mixture with *Limnanthes* phenylthiourea of similar m.p. The material was crystallized from aqueous ethanol to afford the metastable form, melting constantly at 77–78°. A month later, the sample melted at 88.5–89.5° and did not depress the m.p. of the similarly transformed *Limnanthes* specimen on admixture. Subsequently a solution of 1 g. each of *m*-methoxybenzylamine and phenyl isothiocyanate in 10 cc. of ethanol, allowed to crystallize spontaneously and chilled, afforded 1.72 g. of the high-melting form. The analytical sample formed prisms from aqueous ethanol; m.p. 88.5–90°.

Anal. Calcd. for $C_{15}H_{16}ON_2S$: C, 66.14; H, 5.92. Found: C, 66.17; H, 6.05.

When the stable form of N-*m*-methoxybenzyl-N′-phenylthiourea was dissolved in benzene, evaporation furnished platelets, m.p. 67–69°, containing benzene in a molar ratio to the phenylthiourea of *ca.* 0.9. The solvate lost benzene at a slow and irregular rate at 30°, whether under atmospheric pressure or 0.3 mm., to give on occasion material melting at 75–77°. Aged samples tended to resolidify on fusion and melt at 89°. Once the stable form had appeared, it was invariably obtained on attempted crystallization of the low-melting modification from aqueous ethanol. Mixtures of the stable dimorph with the lower melting one (analytical specimen from *Limnanthes*) or solvate melted at 87.5° and above.

Infrared spectra of the solid solvate and the form melting at 76° mulled in oil were indistinguishable. The spectra of the stable and unstable dimorphs were nearly identical between 2.5 and 7.3 μ, save that the 6.3-μ band of the high-melting modification was broader. The N–H stretching peaks at 3.01 and 3.12 (stronger) μ were unaltered. Conspicuous maxima beyond 9 μ of the low-melting form lay at 9.49, 10.51, 12.46, 12.82, 13.41 and 14.4 μ, of the high-melting form at 9.54, 10.27, 11.44, 12.95, 13.39, 14.38 and 14.50 μ.

A solution of 3.8 g. of *m*-methoxybenzylamine in 10 cc. of water was added dropwise to an ice-cold mixture of 2 cc. of carbon disulfide and a solution of 2 g. of potassium hydroxide in 25 cc. of water. The solution was warmed to room temperature, chilled and treated with 4 cc. of ethyl chlorocarbonate, let warm again and treated with 2 g. of potassium hydroxide dissolved in 10 cc. of water.[34] The mixture was stirred 20 minutes and extracted with ether, which was dried and distilled to furnish 3.3 g. (66%) of *m*-methoxybenzyl isothiocyanate, b.p. 128° at 3 mm., n^{26}_{D} 1.5912. The infrared spectra of the natural and synthetic mustard oils were identical.

Anal. Calcd. for C_9H_9ONS: N, 7.82; S, 17.89. Found: N, 7.71; S, 18.03.

The fore- and after-runs, treated with aqueous alcoholic ammonia at 5° overnight, afforded on recrystallization 0.85 g. (16%) of *m*-methoxybenzylthiourea, m.p. 102°, undepressed on mixture with a sample from *Limnanthes*.

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(28) Obtained by permanganate oxidation of *m*-methoxybenzaldehyde (S. N. Chakravarti and W. H. Perkin, Jr., *J. Chem. Soc.*, 196 (1929)).

(29) Obtained from salicylic acid, dimethyl sulfate and alkali (C. Graebe, *Ann.*, **340**, 204 (1905)), precipitated by acetic acid and crystallized from an acetate buffer (E. Cattelain, *Bull. soc. chim.*, [4] **41**, 114 (1927)).

(30) R. B. Woodward, *Org. Syntheses*, **25**, 55 (1945).

(31) R. N. Icke, C. E. Redemann, B. B. Wisegarver and G. A. Alles, *ibid.*, **29**, 63 (1949).

(32) The result suffered considerably if the reaction with the formate was interrupted.

(33) T. Curtius and L. F. Potter, *J. prakt. Chem.*, [2] **85**, 422 (1912).

(34) The net concentration of base was less than that used to decompose carboethoxy *n*-butyldithiocarbamate.[20] *Cf.* O. E. Schultz and E. Barthold, *Arch. Pharm.*, **285**, 267 (1952).