The dipicrate (m. p., 146–147°) showed no depression of m. p. in a mixed m. p. determination with the dipicrate of *m*-N,N-dimethyl-N′,N′-diethylphenylenediamine prepared by the ethylation of *m*-N,N-dimethylaminoaniline.

The orange-red plates of the mono-picrate when treated in 95% ethanol with additional picric acid gave the yellow prisms of the dipicrate (m. p., 145–146°).

In a check experiment the crude initial yield of *m*-N,N-dimethyl-N′,N′-diethylphenylenediamine was 24%; b. p., 102–104° (0.3 mm.), n^{20}_{D} 1.5632; d^{20}_{4} 0.982; *MR* calcd., 63.55; found, 63.7. The picrates of this compound melted at the same points as the picrates prepared from the other experiment.

Ethylation of *m*-N,N-Dimethylaminoaniline.—To a solution of 5 g. (0.037 mole) of *m*-dimethylaminoaniline in 15 cc. of ether was added in an atmosphere of dry nitrogen, 0.04 mole of methyllithium in 25 cc. of ether. After stirring and refluxing for sixteen hours, 6.25 g. (0.04 mole) of ethyl iodide in 10 cc. of ether was added over a fifteen-minute period, and the mixture was then refluxed for one hour. Then 0.05 mole of methyllithium in 30 cc. of ether was added over a period of twenty minutes. The mixture was refluxed for twenty minutes and a heavy tan precipitate formed. Then in succession, by related procedures, there was added 7.8 g. (0.05 mole) of ethyl iodide in 15 cc. of ether; 0.02 mole of methyllithium in 12 cc. of ether; and 3.1 g. (0.02 mole) of ethyl iodide in 15 cc. of ether. Subsequent to hydrolysis by water, and drying of the ether extracts, there was obtained 5 g. (71%) of *m*-N,N-dimethyl-N′,N′-diethylphenylenediamine.

The authors are grateful to Dr. J. B. Dickey for some *m*-nitrodimethylaniline, and they wish to acknowledge the help of Dr. L. A. Woods for the dialkylation procedure using methyllithium and an organic halide.

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The Synthesis of *dl*-Methionine

BY DALE GOLDSMITH AND MAX TISHLER

Recently, Albertson and Tullar reported a synthesis of *dl*-methionine from acetamidocyanoacetic ester and 2-methylmercaptoethyl chloride.[1] We should like to record a similar synthesis of *dl*-methionine consisting of alkylating diethyl acetamidomalonate with the 2-methylmercaptoethyl chloride and of subjecting the resulting compound to hydrolysis and decarboxylation. Our synthesis is an extension of the newly developed route to the α-amino acids from diethyl acetamidomalonic ester.[2] The direct yield of pure *dl*-methionine from the above mentioned reagents is 60% using *t*-butyl alcohol as the solvent for the alkylation step and omitting the isolation of the intermediate diethyl acetamido-(2-methylmercaptoethyl)-malonate. Alkylation in absolute ethanol is almost as satisfactory so far as the yield (56% over-all) is concerned, but the purification of the crude methionine is more difficult. Alkylation in isopropyl alcohol is definitely less satisfactory, and alkylation in either dioxane or xylene leads to poor yields and tarry by-products.

Experimental

Diethyl Acetamido-(2-methylmercaptoethyl)-malonate.—To 1200 cc. of freshly distilled *t*-butyl alcohol was added 14.8 g. of sodium strips and the mixture, protected from air, was refluxed and stirred until the sodium was entirely dissolved. Diethyl acetamidomalonate, 130 g., was added to the warm stirred solution in a few minutes time followed by 82 g. of 2-methylmercaptoethyl chloride. The mixture was stirred and boiled under reflux for six hours, at which time it was neutral to litmus. The completed reaction mixture was concentrated to dryness under reduced pressure and the residue was extracted well with absolute ethanol. The combined extracts and washings were distilled to dryness under reduced pressure and the crude residue (171 g.) was ready for hydrolysis and decarboxylation to *dl*-methionine.

The condensation product can be isolated in a pure form by recrystallizing the residue from a mixture of ether and petroleum ether. After recrystallization, the product melts at 50–52°.

Anal. Calcd. for $C_{12}H_{21}O_5NS$: C, 49.47; H, 7.27; N, 4.81. Found: C, 49.51; H, 7.31; N, 4.66.

***dl*-Methionine.**—A mixture of the crude diethyl acetamido-(2-methylmercaptoethyl)-malonate (above residue), 478 cc. of water and 122 cc. of concentrated hydrochloric acid was boiled under reflux for six hours during which time the ester dissolved. At this time an additional quantity of dilute hydrochloric acid (478 cc. of water and 122 cc. of conc. hydrochloric acid) was added and the mixture was boiled three hours longer. The mixture was concentrated to dryness under reduced pressure; about 150 cc. water was added to the residue and the concentration was repeated. The residue was dissolved in about 800 cc. of absolute ethanol and clarified with a small amount of charcoal. To the resulting solution was added 125 cc. of pyridine and after twenty-four hours storage at 5° the product was collected; wt. 59.3 g. (66.4% yield).

The crude product was purified by dissolving in 450 cc. of water, clarifying the solution with charcoal, concentrating the filtrate to 350 cc. and allowing the resulting solution to crystallize. After four hours an equal volume of ethanol was added and the mixture was stored at 0–5° for twelve hours. The weight of pure *dl*-methionine was 54.1 g.; yield 60.5%.

Anal. Calcd. for $C_5H_{11}NO_2S$: N, 9.39. Found: N, 9.46.

When the *t*-butyl alcohol in the alkylation step was replaced by 280 cc. of absolute ethanol, the yield of crude *dl*-methionine was 63% and of pure product 56%.

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[1] Albertson and Tuller, THIS JOURNAL, **67**, 502 (1945).

[2] Albertson and Archer, *ibid.*, **67**, 308 (1945); Snyder, Shekleton and Lewis, *ibid.*, **67**, 310 (1945).

The Quantum Yield in the Photo-reaction between Methyl Iodide and Nitric Oxide

BY T. IREDALE AND E. R. MCCARTNEY

Because of its continuous absorption spectrum, and because the products of its photodecomposition are mainly iodine, methane, with small amounts of other hydrocarbons, methyl iodide is presumed to dissociate by light absorption in the near ultraviolet into $CH_3 + I$. The quantum yield is very low because of the high probabilities of the reverse reactions $CH_3 + I = CH_3I$ and $CH_3 + I_2 = CH_3I + I$. These matters are fully discussed in recent textbooks and papers.[1,2,3,4]

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[1] Noyes and Leighton, "Photochemistry of Gases," p. 334.

[2] Spence and Wild, *Proc. Leeds Phil. Lit. Soc. Sci.*, **3**, 141 (1936).

[3] Iredale and Stephan, *Trans. Faraday Soc.*, **33**, 800 (1937).

[4] Iredale, *ibid.*, **35**, 458 (1939).

In the last communication[4] was described how the quantum yield may be increased by the addition of NO to the photodecomposing CH_3I, the NO reacting with the CH_3 radical and so preventing the reverse reactions. The quantum yield (1.6) was obtained by comparing the velocity of photodecomposition with that of the photooxidation of CH_3I studied by Bates and Spence,[5] where they obtained a quantum yield of about two. With nitric oxide a kinetic equation was obtained which seemed to account for the results pretty well, except that the quantum yield, 1.6, was too large, and should actually have been about unity. This discrepancy was too great to be accounted for by experimental errors. Blaedel, Ogg and Leighton[6] have recently considered these discrepancies, and have indicated that the quantum yield of Bates and Spence should be 1.0 instead of 2.3, when account is taken of the temperature coefficient of the chloroacetic acid actinometer which Bates and Spence used.

The present writers have now carried out a more direct measurement of the quantum yield of the process $CH_3I + NO + h\nu = I + CH_3NO$.

Apparatus and Procedure.—The photochemical set-up was similar to that previously described.[4] The reaction cell was of clear quartz, about 4 cm. in diameter, and 7 cm. long, and connected to the rest of the glass apparatus by a quartz-glass seal. The nearest greased tap was 80 cm. from the cell. The source of radiation was a Hanovia mercury arc (medium pressure). Great difficulty was experienced in getting sufficient intensity of the 2537 Å. resonance radiation, even with the cooled arc. Filters were used to isolate the whole region 2500–2700 Å.,[7] which gave more readable results. This, however, involved the use of an *average* or *weighted mean* quantum, which we obtained by using the radiation in the uranyl oxalate actinometer described by Leighton and Forbes[8]; the quantum yield of the decomposition being 0.6 in this region. The Moll large surface thermopile which was used in conjunction with a Moll galvanometer, was calibrated with the aid of a Hefner lamp as previously described.[9] One centimeter deflection on the galvanometer scale corresponded to 1.014×10^{-6} cal./sec. The diameter of the light beam was adjusted so that the whole area of it (π sq. cm.) fell on the thermopile elements. Corrections were applied for the non-uniformity of the beam, and for relection at the rear window of the photo-cell.

TABLE I

Temperature, 15–20° C. Mean galvanometer deflections corresponding to absorbed light: ∽ 0.2–0.6 cm. Thiosulfate titrations: ∽ 0.2–2 cc.

Pressure, mm. CH_3I	Pressure, mm. NO	Time of irradiation, min.	Quantum yield
78.5	20.5	1158	0.5
105.0	52.0	1367	0.84
109	85.0	931	1.2
119	87	3324	0.91
122	90	1101	1.1
102	95	4184	1.14
122	100	948	1.2
101	154	917	0.9

Results and Discussion.—The results are shown in Table I.

When the pressure of the NO is > 50 mm., the quantum yield reaches a value ∽ 1. The variations (0.9 → 1.2) are some indication of the order of accuracy of the experimental results.[10] They permit, however, of the earlier interpretation of the photo-reaction being adopted, namely

$$\begin{array}{lr} CH_3I \longrightarrow CH_3 + I & (1) \\ CH_3 + NO \longrightarrow CH_3NO & (2) \\ I + I \longrightarrow I_2 & (3) \end{array}$$

Only when the NO pressure is low, do the back reactions $CH_3 + I_2 = CH_3I + I$ and $CH_3 + I = CH_3I$ begin to lower the quantum yield. Blaedel, Ogg and Leighton[6] consider that the second of these reactions (recombination) is negligible compared with the first. The present measurements, of course, give no indication of this, but West[11] has shown that addition of carbon dioxide raises the quantum yield of the photodecomposition of methyl iodide presumably because of the more ready recombination of iodine atoms by three body collisions with the carbon dioxide and also, perhaps, the more ready recombination of methyl radicals to give ethane. This matter has, as yet, not been explored very fully. The iodine formed was frozen out, and titrated with approx. 0.005 *N* sodium thiosulfate. The other product of the reaction CH_3NO, or its decomposition product, was not identifiable.

No reaction occurred between methyl iodide and nitric oxide at room temperature in the dark.

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[5] Bates and Spence, *Trans. Faraday Soc.*, **27**, 468 (1931).

[6] Blaedel, Ogg and Leighton, THIS JOURNAL, **64**, 2500 (1942).

[7] Bowen, *J. Chem. Soc.*, 76 (1935).

[8] Leighton and Forbes, THIS JOURNAL, **52**, 3139 (1930).

[9] Gibson and Iredale, *Trans. Farad. Soc.*, **32**, 571 (1936).

[10] The re-adjusted value (0.8) of the previous quantum yield (1.6) obtained[4] by comparison with Bates and Spence's results,[5] points to a rather inaccurate extrapolation.

[11] West and Schlessinger, THIS JOURNAL, **60**, 961 (1938).

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A Dimorphic Form of *d*-Catechin

BY O. KELLER AND L. BERGER

Extraction of *water washed* gum gambir with acetone (one part) and ether (nine parts) according to Freudenberg,[1] or with acetone (ten parts), yields *d*-catechin, m. p. 174.5–175.5° cor.; $[\alpha]^{26}_{578}$ +16.3°; $[\alpha]^{26}_{D}$ +15.3°; $C = 5\%$ in 50% acetone in agreement with Freudenberg and Purrmann[2] who report m. p. 174–175°; $[\alpha]_{578}$ +17.1°; $C = 9\%$ in 50% acetone for *d*-catechin.

We now find that extraction of *unwashed* gum

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[1] Freudenberg, *Ber.*, **54**, 1204 (1921).

[2] Freudenberg and Purrmann, *Ann.*, **437**, 277 (1924).