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 photo-oxidation 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.

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

$$CH_3I \longrightarrow CH_3 + I \tag{1}$$

$$CH_3 + NO \longrightarrow CH_3NO \tag{2}$$

$$I + I \longrightarrow I_2 \tag{3}$$

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.

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

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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).

gambir by either of the above methods or by the original method of Perkin and Yoshitake[3] using hot ethyl acetate gives a catechin of m. p. 210–213° cor.; $[\alpha]^{26}D$ +14.7°; $C = 5\%$ in 50% acetone. The tetramethyl ether and the pentaacetyl ester of this high-melting catechin, however, correspond exactly with those reported by Freudenberg and Purrmann prepared from *d*-catechin, m. p. 174–175°.[2] The rotation and the properties of the derivatives indicate that the catechin thus obtained is chiefly *d*-catechin. Its high melting point indicates that it is either a dimorphic form of *d*-catechin or a mixture of *d*-catechin with small amounts of *dl*-catechin (m. p. 212–214°) or *dl*-*epi*catechin (m. p. 224–226°). Perkin and Yoshitake[3] obtained a so-called "acacatechin" from acacia or Bengal catechin which melted at 204–205°, and which on careful fractional crystallization by Freudenberg and Purrmann proved to consist chiefly of *l* and *dl*-catechin with small amounts of *l* and *dl*-*epi*catechin. However, recrystallization of the high melting catechin from *ten* to *twelve* volumes of hot water gives, in almost quantitative yield, the low melting *d*-catechin, m. p. 174–175°, indicating that it is a dimorphic form.

Freudenberg notes that *d*-catechin crystallizes with four molecules of water and melts at 93–95°. The anhydrous product melts at 174–175°. We have found that many samples of *d*-catechin melting at 174–175° and also 210–213° contain water of crystallization (0.1 to 1 mole) depending upon the method of crystallization and the duration and type of drying.

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[3] Perkin and Yoshitake, *J. Chem. Soc.*, **81**, 1162 (1902).

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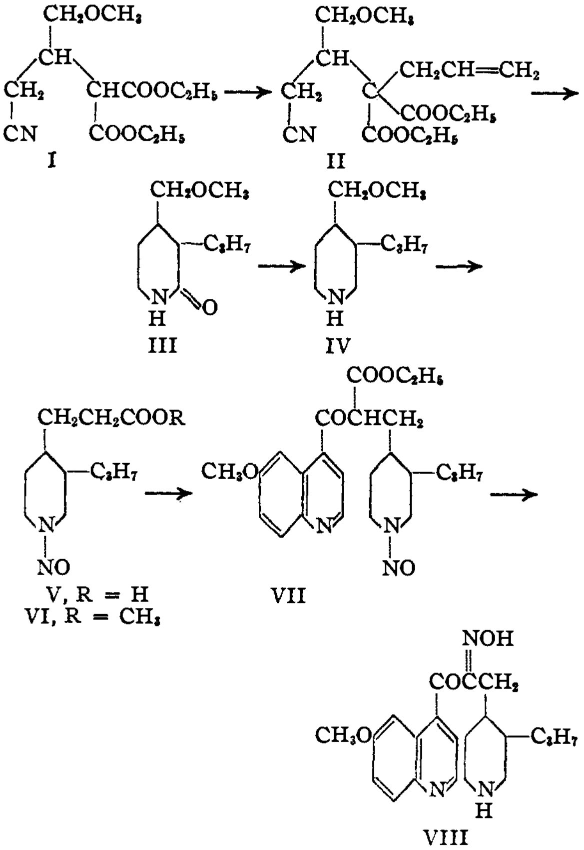
RECEIVED OCTOBER 23, 1945

6'-Methoxy-8-oximino-3-propylrubatoxanone

By C. F. KOELSCH

The experiments described in the present paper were carried out as models for part of a projected synthesis of quinine. Key substances in the series of reactions used[1] are formulated in the accompanying chart. It is indicated that condensation of VI with ethyl quininate yielded VII, but this compound could not be purified. When the condensation product was boiled with hydrochloric acid, it was converted into a crystalline substance which appears to be the dihydrochloride of VIII, a compound whose reduction should yield interesting results. The research, however, was interrupted in 1942, before the reduction could be studied, and in view of the recent synthesis of quinine in another laboratory,[2] no further work on the subject is contemplated.



Experimental

4,4-Dicarbethoxy-3-methoxymethyl-Δ⁶-heptenonitrile (II).—To a solution of 46 g. of sodium in 550 ml. of dry alcohol were added 320 g. of ethyl malonate and 190 g. of γ-methoxycrotononitrile. The mixture was heated under reflux for ninety minutes, then treated with 25 g. of sodium iodide (dried at 300°) and 160 g. of allyl chloride. Heating was continued for an additional ninety minutes,[3] then most of the alcohol was removed, and water and ether were added. Fractional distillation gave 407 g. (70%), b. p. 192–195° at 19 mm.

Anal. Calcd. for $C_{15}H_{23}NO_5$: C, 60.6; H, 7.7. Found: C, 60.7; H, 7.8.

4-Methoxymethyl-3-propylpiperidone-2 (III).—When a solution of 420 g. of II in 100 ml. of alcohol was reduced with hydrogen at 2200 lb. and 150° using Raney nickel, the calculated amount of hydrogen was absorbed in three and one-half hours. The sirupy product, freed of alcohol, was boiled and stirred for twenty hours with 180 g. of potassium hydroxide in 3500 ml. of water, and the unsaponified part (65 g.) was then removed with ether. The aqueous solution was distilled to about 750 ml., acidified strongly with sulfuric acid, filtered from potassium sulfate, and extracted with five 100-ml. portions of ether. The product, a thick sirup (188 g.) was heated at 185°, giving 158 g. of crude lactam; an additional 22 g. was obtained by distilling the extracted aqueous solution to dryness, combining the residue with the potassium sulfate, and extracting the whole with alcohol. Several fractionations of the crude lactam gave 95 g., b. p. 175–180° at 6 mm.

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[1] *Cf.*, Koelsch, THIS JOURNAL, **65**, 2458, 2460 (1943); **66**, 1611 (1944).

[2] Woodward and Doering, *ibid.*, **66**, 849 (1944); **67**, 860 (1945).

[3] Orienting experiments indicated that the alkylation was nearly complete after seventy minutes of boiling. When allyl chloride was used without sodium iodide, the alkylation required eight hours. When allyl bromide was used, the reaction mixture required external cooling, and the reaction was complete after less than fifteen minutes. Approximately the same yield of alkylation product was obtained in each of these experiments.