isopropyl malonates in the presence of a morpholine–acetic acid catalyst in a benzene solution. The water formed during the reaction was removed by distillation from the solution.

E. A mixture of crotonaldehyde and 80% isoprene was heated to 170° in a metal bomb. The initial reaction carried the temperature to about 230°. When the temperature began to drop the bomb was cooled, opened and the product distilled under reduced pressure using a helices-packed column with a total condensation partial take-off head. 2,4-Dimethyl-1,2,3,6-tetrahydrobenzaldehyde, b. p. 70–71° (10 mm.), was formed in a 44% yield. An alcoholic solution of 2,4-dimethyl-1,2,3,6-tetrahydrobenzaldehyde and formaldehyde was refluxed four to five hours following the addition of 50% potassium hydroxide solution. 1,1-Dimethylol-2,4-dimethylcyclohexene-4, b. p. 123–124° (1 mm.), was formed in 83% yield. The diacetate of 1,1-dimethylol-2,4-dimethylcyclohexene-4 was prepared by refluxing the diol with acetic anhydride and distilling the acetic acid formed.

F. 2-Acetoxycyclohexanone, b. p. 109–115° (12 mm.), was prepared in 54% yield by refluxing 2-chlorocyclohexanone and anhydrous sodium acetate in acetic acid for eight hours. The Reformatsky reaction was carried out by adding zinc foil to a dry solution of 2-acetoxycyclohexanone and ethyl bromoacetate in benzene.

G. The ketone was refluxed with a 10% excess of the given 2-cyano ester in the presence of an ammonium acetate–acetic acid catalyst.[2] The water formed during the reaction was removed by distillation from benzene solution. The resulting cyclohexylidenecyano ester was hydrogenated in ethyl alcohol over platinum oxide at low pressure.

H. 1,2,3,6-Tetrahydrophthalic anhydride was added to sodium benzyloxyethylate in benzene and the mixture refluxed three hours. Acidification of the alkali-soluble fraction yielded the half ester.

I. Isobutyl chlorocarbonate was added to a cold ether solution of *p*-cresol in the presence of pyridine.

J. The ketone or aldehyde and alcohol were refluxed in the presence of a catalytic amount of *p*-toluenesulfonic acid and of a hydrocarbon solvent of such nature that the water could be removed by distilling the water–hydrocarbon mixture.

K. Styrene oxide and allyl alcohol were warmed together five hours in the presence of a catalytic amount of phosphoric acid.

L. 2,2-Diallylcyclohexanone was reduced by the Meerwein–Ponndorf method.

M. The sodium alcoholate was prepared by adding the given alcohol to a suspension of sodamide in ether–benzene. Allyl bromide was then added and the mixture refluxed twelve hours.

N. bis-β-Hydroxyethyl sulfide was esterified by means of acetic anhydride and then oxidized with 30% hydrogen peroxide in acetic acid–acetic anhydride at 80°. The crude oxidation mixture of di-(2-acetoxyethyl) sulfone was distilled *in vacuo* to yield the pure product.

O. A dilute alcoholic solution of sodium *p*-toluenesulfinate and 2-chlorocyclohexanone was refluxed three hours.

P. Methyl bromoacetate reacted with sodium *n*-octyl mercaptide in absolute ethyl alcohol solution to form *n*-octyl carbomethoxymethyl sulfide. The crude sulfide was oxidized readily at 80° in acetic acid–acetic anhydride solution by means of 30% hydrogen peroxide. Saponification of the *n*-octyl carbomethoxymethyl sulfone using 20% sodium hydroxide gave crude *n*-octyl carboxymethylsulfone in 46% over-all yield. The acid chloride of *n*-octyl carboxymethylsulfone was prepared in the usual manner using thionyl chloride. The acid chloride in benzene was added to a benzene solution of morpholine, thus yielding the desired morpholide.

Q. The Darzens–Claisen reaction was carried out by adding in small quantities 1.5 moles of 95% sodium methylate (Mathieson Alkali Works) to a stirred solution of one mole of ketone and 1.5 moles of chlorester in 400–500 cc. of dry ether. The temperature was maintained at 0–5° for five hours and at room temperature for fifteen hours.

R. An ester interchange was effected by refluxing a methyl or ethyl ester with an excess of a higher boiling alcohol and distilling off the methyl or ethyl alcohol formed. *p*-Toluenesulfonic acid was used as the catalyst.

S. Benzaldehyde and levulinic acid were condensed in the presence of sodium hydroxide.[3] The crude acid was esterified as described in Method C.

T. Esterification was accomplished by adding the acid chloride to an ice-cold solution of alcohol and pyridine in benzene.

U. Esterification as in Method T except that no attempt was made to keep the solution cold.

V. Propylene oxide was added to an ethereal solution of *o*-tolylmagnesium bromide. The ether was replaced with benzene and the reaction mixture refluxed overnight.

W. Isobutyrophenone and formalin were refluxed three hours in the presence of potassium hydroxide. A large amount of ketone was recovered.

X. Ethyl bromoacetate reacted with sodium *n*-decyl mercaptide in absolute alcohol to give *n*-decyl carboethoxymethyl sulfide. The crude sulfide was oxidized at 80° with 30% hydrogen peroxide in acetic acid–acetic anhydride solution.

Y. Equivalent amounts of 1,2,3,6-tetrahydrophthalic anhydride and diethylamine were allowed to react together. The crude product was taken up in benzene and converted to the acid chloride by the use of thionyl chloride. The acid chloride was esterified as described in Method T.

Z. Undecylenyl chloride was added to a large excess of diethylamine at 0°.

AA. The phthalimides were prepared by the strong heating of the properly substituted phthalic anhydride with an excess of primary amine, followed by vacuum distillation.

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(2) Cope, This Journal, **63**, 3452 (1941).

(3) Rapson and Shuttleworth, *J. Chem. Soc.*, 33 (1942).

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Alkyl Selenocyanates

The new selenocyanates listed in Table I have been prepared according to the method of Wheeler and Merriam.[1]

Procedure.—A solution of 0.25 mole of the alkyl bromide (Columbia Organic Chemicals Co., Inc.) and 0.3 mole of potassium selenocyanate (prepared from elemental selenium and potassium cyanide in water[2] or absolute alcohol,[3] the latter method being preferable for laboratory use) in 250 cc. of hot 95% ethanol was refluxed for six hours during which time crystals of potassium bromide separated. Most of the alcohol was then distilled off, water added, and the mixture extracted with ether–benzene. The solution was distilled after drying over anhydrous sodium sulfate.

The resulting selenocyanates are more toxic to fungi than the corresponding thiocyanates, but their disgusting odor forbids their use. In the case of the decyl compound this odor may be ascribable to the small quantity of volatile forerun obtained in the distillate. The yellow *n*-

Table I

Selenocyanates	B. p., °C.	mm.	Yield, %	Formula	% Nitrogen Calcd.	Found
n-Butyl	88–90	13	44	C_5H_9NSe	8.64	8.71
n-Hexyl	114	13	69	$C_7H_{13}NSe$	7.37	7.24
n-Decyl	97–98	0.2	67	$C_{11}H_{21}NSe$	5.69	5.44

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(1) Wheeler and Merriam, This Journal, **23**, 299 (1901).

(2) Schiellerup, *Ann.*, **109**, 125 (1859).

(3) Birckenbach and Kellermann, *Ber.*, **58**, 790 (1925).

butyl selenocyanate, although sealed in ampules and kept in the dark, turned black after a month; the yellow *n*-hexyl compound slowly turned pink but got no darker; the colorless *n*-decyl compound remained colorless although exposed to light and air.

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1,5-Endomethylene-3,7-di-*p*-toluenesulfonyl-1,3,5,7-tetrazacycloöctane

A variation in reaction conditions has produced this new compound instead of the 1,3,5-tri-*p*-toluenesulfonylcyclotrimethylenetriamine reported by McMaster.[1] To 0.05 mole (7 g.) of hexamethylenetetramine in 80 cc. of water was added 0.199 mole (37.8 g.) of *p*-toluenesulfonyl chloride. To this stirred solution, covered with 60 cc. ether, was added 53 cc. of a 15% aqueous sodium hydroxide solution (0.199 mole, 7.95 g. sodium hydroxide) at such a rate that the alkalinity was held at *p*H 8.5–10. The product was a sticky mass which was filtered after trituration with ethanol to weigh 10 g. and melt about 220°. Two crystallizations from nitromethane increased this melting point to 236°. Yield of crude product is 46% of theoretical, and is almost insoluble in acetone, benzene, chloroform, ether and water but dissolves in pyridine.

Anal. Calcd. for $C_{19}H_{24}O_4N_4S_2$: C, 52.3; H, 5.42; N, 12.8; S, 14.6. Found: C, 52.5; H, 5.50; N, 12.6; S, 15.4.

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[1] McMaster, THIS JOURNAL, **56**, 204 (1934).

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1-(1-Diethylamino-3-propyl)-6-methoxy-3-methyl-1,2-dihydro-2-keto-quinoxaline

Twenty-three grams (0.091 mole) of 3-amino-4-(1-diethylamino-3-propylamino)-anisole[1] and 9.7 g. (0.11 mole) of pyruvic acid were allowed to react in 200 cc. of *p*-cymene according to the procedure of Kipnis, Weiner and Spoerri.[2] After refluxing for two hours, the solution was allowed to cool and the base removed from the cymene by extraction with dilute hydrochloric acid. The aqueous layer was made alkaline (ammonium hydroxide), extracted with carbon tetrachloride, and the organic layer was steam-distilled until about 3 liters of distillate were collected. The residual oil was again taken up in carbon tetrachloride, dried over potassium carbonate and distilled. The first distillation took place with much decomposition, the product being collected at 210–230° (4 mm.); however, on redistillation in a 15-cc. Claisen flask with a heated Vigreux column, the product boiled without decomposition at 195–197° (3 mm.), giving 9.5 g. (34.5% of the theoretical) of the product, a light yellow oil.

Anal. Calcd. for $C_{17}H_{25}N_3O_2$: N, 13.85. Found: 14.00.

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[1] Prepared by the method of Izmail'skiĭ and Simonov, *J. Gen. Chem. U. S. S. R.*, **10**, 1588 (1940); through *C. A.*, **35**, 2870 (1941). A substantial increase in yield (93%) was obtained by reducing the corresponding 3-nitro compound with hydrogen and Raney nickel at room temperature and an initial pressure of 2 atmospheres.

[2] Kipnis, Weiner and Spoerri, THIS JOURNAL, **66**, 1989 (1944).

[3] The Wm. S. Merrell Co., Postdoctoral Fellow.

A New Derivative of Kojic Acid

Four and twenty-five hundredths grams (0.03 mole) of kojic acid (assay better than 90%[1]) was dissolved in 50 ml. of ethanol. To this mixture was added 1.2 g. of sodium hydroxide dissolved in 5 ml. of water, and after thoroughly mixing the two solutions 5.97 g. (0.03 mole) phenacyl bromide was added. The resulting solution was shaken in a stoppered 125-ml. Erlenmeyer flask for fifteen minutes, during which time the phenacyl derivative had begun to precipitate out. The flask was then heated, under reflux, over a steam-bath for thirty minutes. The material was cooled and filtered, and repeatedly washed with water; the yield was 7.7 g. The compound was recrystallized twice from 90% alcohol producing long white needles, m. p. 156–157°.

Elementary analysis at this point gave inconclusive results. The compound was recrystallized twice from absolute ethanol, dried in the oven at 110° for twenty-four hours, and finally allowed to cool in the vacuum desiccator over sulfuric acid; m. p. 157.5–158°. The compound gave no test with ferric chloride and reduced Fehling solution only on prolonged heating.

Anal.[2] Calcd. for $C_{14}H_{12}O_6$: C, 60.88; H, 4.35. Found: C, 60.78; H, 4.40.

The analysis has shown that the expected 2-hydroxymethyl-5-phenacyl oxy-α-pyrone was not formed.

A small amount of the compound was acetylated in the usual way[3] recrystallized once from absolute ethanol and dried in the vacuum desiccator over sulfuric acid; m. p. 129–130°.

Anal. Calcd. for $C_{16}H_{14}O_7$: C, 60.38; H, 4.43. Found: C, 60.5; H, 4.6.

No attempt is made in this note to postulate the complete structure of these derivatives of kojic acid.

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RECEIVED MARCH 29, 1946

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[1] H. N. Barham, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 31 (1939).

[2] Analyses by Dr. Carl Tiedcke.

[3] Shriner and Fuson, "Identification of Organic Compounds," 2nd ed. John Wiley and Sons, New York, N. Y., p. 137.