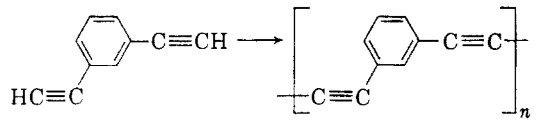
cal solution of copper(I) chloride.[1] Excellent yields are generally obtained. Recently Eglinton and Galbraith[2] found that copper(II) acetate in methanolic pyridine was a superior oxidant since reactions can be carried out in homogeneous media. Sondheimer and co-workers[3] have utilized this procedure for the preparation of some unusual large ring polyacetylenes.

We have found that acetylenes can be coupled in a matter of minutes at room temperature with oxygen or air using a catalytic amount of an amine complex of a copper(I) salt in an organic solvent. Pyridine can serve as both ligand and solvent. The copper(II) carboxylates are the only copper(II) salts that are catalysts for the reaction but they are far inferior in catalytic activity to copper(I) salts.

As an example: To a 500-ml. Erlenmeyer flask there was added 250 ml. of pyridine, 2 g. of copper(I) chloride, and 50 g. (0.49 mole) of phenylacetylene. Oxygen was bubbled through the vigorously stirred reaction mixture (Fisher "Vibromixer") which was kept in a bath at 30°. A vigorous reaction ensued and the temperature rapidly rose to 40°. After 40 min. the reaction had subsided and there was isolated 42.7 g. (0.21 mole, 86% yield) of diphenyldiacetylene, colorless needles, m.p. 88° (lit., m.p. 88°).



When *m*-diethynylbenzene[4,5] is oxidized in the same manner a pale yellow polymer separates out at the end of the reaction in essentially quantitative yield. *Anal.* for $C_{10}H_4$: C, 96.8; H, 3.2. Found C, 96.4; H, 3.5. The polymer is soluble in solvents such as chlorobenzene and nitrobenzene above 100°. Evaporation of a nitrobenzene solution at 170° yields transparent, flexible films. Infrared analysis of end groups ($\equiv$CH stretching, 3290 cm.$^{-1}$) indicates a molecular weight of at least 7000[6] and intrinsic viscosities (nitrobenzene, 150°) as high as 0.25 decil./g.[6] have been obtained. This material appears to be quite stable at room temperature. When rapidly heated *in vacuo* it abruptly decomposes at about 180°, evolving hydrogen and a small amount of methane[6] and leaving a residue of carbon. When ignited at room temperature in air an explosive reaction takes place; however, the net result is the loss of most of the hydrogen and some carbon, presumably as carbon dioxide, for a total weight loss of only 5–6%.

Oxidation of *p*-diethynylbenzene[5] gives a bright yellow product that is completely insoluble in all solvents we have tried and decomposes rapidly at about 100°.

Aliphatic ethynyl compounds are also oxidized with catalysts of this type. Further work will be reported in the near future.

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Volatile Methyl Ketone Formed in Rubber Oxidation

Sir:

Tobolsky and Mercurio[1] have suggested that the volatile methyl ketone produced in high yield during the oxidation of rubber is 2,5-hexanedione rather than levulinaldehyde; no experimental support for this suggestion was offered.

The original identification of levulinaldehyde as an oxidation product was made by Whitby,[2] who gave no details in his report. We wish to report the following observations in confirmation of Whitby's identification. Treatment of the liquid condensed[3] from the reaction of 200 ml. of oxygen and 2-3 g. of rubber at 120° and 1 atm. with 2,4-dinitrophenylhydrazine reagent[4] yields a crude bis-dinitrophenylhydrazone whose X-ray diffraction pattern is indistinguishable from that of authentic levulinaldehyde bis-2,4-dinitrophenylhydrazone,[5]

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and differs from that of the 2,5-hexanedione derivative. (Infrared spectra will not distinguish unequivocally between these two alternatives.)

Fractionation of a similar condensate on silica, without pretreatment, by the method of Bulen, Varner, and Burrell[6] yields a chromatogram with two major peaks (acetic and formic acids) and three minor peaks (two unidentified, one occurring at the position expected for levulinic acid). After passage of the crude reaction product over a silver oxide column[7] before fractionation, a new major peak appears at the position expected for levulinic acid. Its identification has been confirmed by comparison of the X-ray diffraction patterns of the silver salt and of the dinitrophenylhydrazone with those from authentic material.

Efforts to find 2,5-hexanedione in the neutral fraction after silver oxide treatment have not been successful. Control experiments showed that hexanedione was not oxidized to an acid by silver oxide at room temperature following the procedures used for oxidation of levulinaldehyde, or acid fractionation.

Gas-liquid chromatography on cyanoethylated glycerol, Apiezon L, or dioctyl sebacate–sebacic acid yields a large peak corresponding to levulinaldehyde. It gives evidence of only traces of material boiling higher. Hexanedione is readily separated from the aldehyde; if present at all as an oxidation product, it is formed in less than 5% of the yield of levulinaldehyde.[8]

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Solvolysis of *S*-Benzoyl-8-mercaptoquinoline and the Spectrum of 8-Mercaptoquinoline

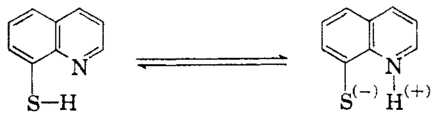
Sir:

The preparation 8-mercaptoquinoline *via* Edinger's method[1] involves the isolation of its *S*-benzoate. Although the ester when recrystallized from ethanol appears to be a reddish crystalline solid, the use of chloroform for recrystallization results in the formation of colorless crystals. The pure, colorless ester will slowly solvolyze in hydroxylic solvents as Banfield surmised.[2] We have found the solvolysis to follow pseudo first order kinetics in anhydrous methanol and ethanol. The specific reaction rate constant of the ester methanolysis at 20° is approximately 1.4×10^{-5} sec^{-1} whereas the rate of the corresponding ethanolysis is at least one order of magnitude slower. We are now engaged in a detailed study of the kinetics of the *S*-benzoate solvolysis in various hydroxylic solvents and in the presence of various metal cations to probe the effect of chelate formation on the reaction rate.

In connection with the reactions of 8-mercaptoquinoline and its derivatives it is interesting to note the dramatic solvent effect upon the long wave-length absorption of 8-mercaptoquinoline itself. Pure anhydrous 8-mercaptoquinoline is a mobile hygroscopic blue liquid which takes on a purplish hue as it becomes wet. The completely hydrated compound ($+2H_2O$) is a red crystalline solid. The color of the anhydrous material varies from red violet in *t*-butyl alcohol to orange in aqueous solutions. In acidic or basic aqueous media the solutions appear yellow. Measurements of the visible absorption spectra yield the following results:

Solvent	λ_{max}, mμ	ε (l./mole cm.)
H_2O	448	2032
CH_3OH	490	133
C_2H_5OH	503	43
n-C_4H_9OH	509	27
$(CH_3)_3COH$	528	17

The dramatic increase of the molar extinction with dielectric constant and the disappearance of the band in both acidic and basic aqueous solutions indicate that the species responsible is the dipolar ion (Ib). The dipolar ion would be formed in increasing concentration as a result of the shift of the equilibrium to the right with dielectric constant. The blue shift of the absorption band would seem to indicate an *n*-π transition of the dipolar form. If so, the unusually large molar extinction


Ia Ib

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