into τ values given above, assuming τ values of 2.73 for internal (solvent) chloroform peak, 5.35 for external water reference, and 8.77 for external cyclohexane reference, for the sake of convenience in comparing shift values.

4-Methylene-5,5-pentamethylene-3-phenyl-2-oxazolidinone (IVB) from 1-Ethynylcyclohexanol (IB).—To a solution of 3.5 g. of IB[6] in 40 ml. of toluene, 3.7 g. of phenyl isocyanate was added and the mixture was heated under reflux for 4 hr. and then the solvent was removed under reduced pressure. The residue was diluted with about 40 ml. of petroleum ether (b.p. 30–60°) and this solution was extracted with 5% methanolic potassium hydroxide solution. The methanol layer was separated, neutralized with dilute hydrochloric acid, and extracted again with petroleum ether (b.p. 30–60°). Concentrating this petroleum ether solution, followed by two recrystallizations of the residue from petroleum ether (b.p. 30–60°), gave 6.4 g. (88%) of the oxazolidinone, m.p. 167–167.5°.

Anal. Calcd. for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.12; N, 5.76. Found: C, 74.05; H, 7.04; N, 5.83.

Infrared absorptions (Nujol): 1750 (—O—CO—N<), 1643 (>C=C<), 954, 946, 838, 772, 767, 705 cm.$^{-1}$.

5-Methyl-4-methylene-3-phenyl-5-[2-(2,6,6-trimethyl-1-cyclohexenyl)-ethyl]-2-oxazolidinone (IVC).—A mixture of 1.8 g. of the ethynylcarbinol of dihydro-β-ionone,[7] 30 ml. of toluene, and 0.9 g. of phenyl isocyanate was heated under reflux for 4 hr. and the reaction mixture was treated similarly as above. Two recrystallizations of the product from petroleum ether (b.p. 30–60°) afforded the oxazolidinone, m.p. 129–130°.

Anal. Calcd. for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13. Found: C, 77.50; H, 8.72; N, 4.08.

Infrared absorptions (Nujol): 1750 (—O—CO—N<), 1643 (>C=C<), 981, 834, 765, 757, 702 cm.$^{-1}$.

5,5-Pentamethylene-3-phenyl-2,4-oxazolidinedione (VI) from IVB by Ozonolysis.—A solution of 200 mg. of IVB in 40 ml. of methylene chloride was saturated with ozonized oxygen at −75° during 20 min. and the reaction mixture was added dropwise into a suspension of 8 g. of zinc powder in 25 ml. of glacial acetic acid with vigorous stirring. The mixture was stirred for 3 hr. at room temperature, refluxed for 1 hr., and then concentrated. No formaldehyde could be isolated from the lower-boiling products. The concentration residue was diluted with water, filtered, and the filter cake was washed with ether. The filtrate was extracted with ether and all ether washings and extracts were combined, washed with water, dried, and concentrated to afford a crystalline residue, m.p. 133–136°. Recrystallizations from methanol gave colorless needles, m.p. 138–139°.

Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16. Found: C, 68.36; H, 6.14.

Infrared absorptions (Nujol): 1810, 1750, and 1730 (—O—CO—N—CO—C), 764, 722, 687 cm.$^{-1}$.

***N*-Phenylcarbamate (VIII) of Ethyl 1-Hydroxycyclohexane Carboxylate (VII).**—To a solution of 2.2 g. of VII[8] in 10 ml. of toluene, 1.5 g. of phenyl isocyanate was added and the mixture was refluxed for 3 hr. and then concentrated. The yellow residue crystallized upon standing overnight. Recrystallization from methanol gave colorless needles, m.p. 109.5–110.5°.

Anal. Calcd. for $C_{16}H_{21}NO_4$: C, 65.95; H, 7.27. Found: C, 65.91; H, 7.41.

Infrared absorptions (Nujol): 3230 (N—H), 1735 (ester carbonyl), 1690, and 1550 (urethane) cm.$^{-1}$.

5,5-Pentamethylene-3-phenyl-2,4-oxazolidinedione (VI) from VIII.—In a small test tube 1 g. of the carbamate (VIII) was heated at 200–210° under 15 mm. for 30 min., then was recrystallized from ethanol to afford colorless needles, m.p. 139.5–140°. Analyses for carbon and hydrogen gave correct values, and the identity with the ozonolysis product of IVB above described was established beyond doubt by a mixed m.p. and by comparison of infrared spectra, which were completely superimposable.

4-Methyl-3-phenyl-4-oxazolin-2-one (IX).—To a solution of 5 g. of propargyl *N*-phenylcarbamate (IIIA)[9] in 200 ml. of ether was added several drops of 10% methanolic potassium hydroxide solution and the mixture was stirred for 10 min. at room temperature. After the reaction mixture was washed and dried, the solvent was removed by distillation and the residue was recrystallized from methanol to afford 2 g. of colorless needles, m.p. 97.5–98°.

Anal. Calcd. for $C_{10}H_9NO_2$: C, 68.61; H, 5.18; N, 8.00. Found: C, 68.56; H, 5.18; N, 8.08.

Infrared absorptions (Nujol): 1760 (—O—CO—N<), 1683, 1635 (>C=C<), 773, 740, 712 cm.$^{-1}$.

4-Methyl-3-phenyl-2-oxazilidinone (X).—A mixture of 2 g. of the oxazolinone (IX), 100 ml. of ethanol, and 1.2 g. of 30% palladium-charcoal[10] was shaken in an atmosphere of hydrogen at ordinary pressure and at room temperature. The calculated amount of hydrogen was absorbed during 8 hr. The catalyst was filtered and the solvent was removed. Recrystallization of the residue, which solidified on cooling, from ether afforded colorless needles, m.p. 52–52.5°.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26. Found: C, 67.98; H, 6.39.

Infrared absorptions (Nujol): 1728 (>C=O), 755, 733, 690 cm.$^{-1}$.

Acknowledgment.—The authors are indebted to Mr. S. Satoh, Osaka University, to Mr. N. Hayakawa, Japan Atomic Energy Institute, and to the Electronics Co. of Japan for NMR measurements. The assistance of these people is gratefully acknowledged.

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Reaction of Some Organic Compounds with Cupric Bromide

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Cupric bromide in methanol does not react with chalcones or 7-hydroxycoumarins either in the cold or hot. However, when dioxane is used in place of methanol, the reaction does take place to brominate the hydroxycoumarins and the chalcones.

Kochi[1] has reported the use of cupric chloride for the chlorination of acetophenone and diethyl ketone. Fort,[2] considering the usefulness of the applicability of this reaction, brominated isophorone, 3,4,5-trimethylanisole, β-naphthol, and 5,5-dimethylcyclohexane-1,3-dione by using cupric bromide in methanol or methanol–water at room

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temperature. Oxidation of steroids with cupric bromide in alcohol has been recently studied by Sollman.[3] As bromination by pyridine–bromine complex[4] had already been studied in our laboratory where nuclear halogenation has been found to occur in the 2′-hydroxychalcones, it was interesting to see whether cupric bromide in alcohol could be successfully used to bring about halogenation as reported on other compounds.[5]

2′ - Hydroxy - 5′ - methyl - 4 - methoxychalcone and cupric bromide in two molar proportions were taken in methanol (or methanol–water) and kept overnight. It was found that no halogenation took place and the chalcone remained unchanged. In another experiment, a solution of the chalcone and cupric bromide in methanol was refluxed for two hours. Again it was found that there was no halogenation and the chalcone remained unchanged.

In parallel experiments on β-methylumbelliferone it was found that either in cold or on refluxing there was no bromination by cupric bromide in methanol and β-methylumbelliferone remained unchanged.

These results were in keeping with the reported results, as the chalcone and the β-methylumbelliferone are not active hydrogen compounds (*cf*, compounds brominated by Fort[2]).

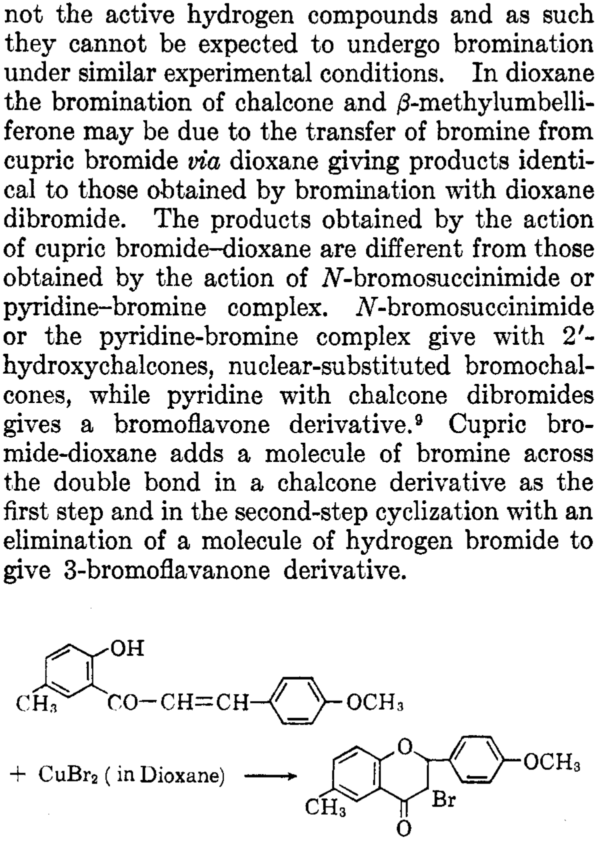
Dioxane is an active hydrogen compound and it very readily gives dioxane dibromide with bromine.[6] Dioxane dibromide has been reported to be used as a brominating agent.[6] Dioxane dibromide in the cold with chalcones give chalcone dibromides (unpublished work). However, in hot solutions 2′-hydroxychalcones give the 3-bromoflavanone derivatives.

As bromination by cupric bromide in methyl alcohol failed in the case of the chalcones and β-methylumbelliferone, it was thought interesting to use dioxane as a medium in place of methanol. 2′-Hydroxy-5′-methyl-4-methoxychalcone was dissolved in dioxane and cupric bromide was added to it. It was kept overnight. Similarly β-methylumbelliferone was dissolved in dioxane and to it was added cupric bromide and the mixture was kept overnight. In neither case was bromination effected and the chalcone and β-methylumbelliferone remained unchanged. In the next series of experiments the reaction conditions were changed. The chalcone with cupric bromide in dioxane and similarly β-methylumbelliferone with cupric bromide in dioxane were dissolved and refluxed for two hours. Solutions were diluted and the solids separated were crystallized from ethanol to which acetic acid was added. As expected, bromo products were obtained in both the cases. The bromo compound obtained from the chalcone was identified as 3-bromo-6-methyl-5′-methoxyflavanone by (a) taking a mixed melting point with an authentic sample of 3-bromo-6-methyl-4′-methoxyflavanone (prepared after the method of Limaye[7]) which showed no depression) and (b) converting it to 6-methyl-4′-methoxyflavone by treatment with ethanolic sodium hydroxide solution.[8]

The bromo product obtained in the case of β-methylumbelliferone was found to be the mixture of 3,6- and 3,8-dibromo-β-methylumbelliferone.

Discussion

Comparing the results so far studied by different workers, it is evident that a cupric halide in methanol (or methanol–water) reacts with active hydrogen compounds. Compounds with reactive methylene groups suffer halogenation readily with cupric bromide in methanol. As already stated, the chalcone and the coumarin derivative in question are not the active hydrogen compounds and as such they cannot be expected to undergo bromination under similar experimental conditions. In dioxane the bromination of chalcone and β-methylumbelliferone may be due to the transfer of bromine from cupric bromide *via* dioxane giving products identical to those obtained by bromination with dioxane dibromide. The products obtained by the action of cupric bromide–dioxane are different from those obtained by the action of *N*-bromosuccinimide or pyridine–bromine complex. *N*-bromosuccinimide or the pyridine-bromine complex give with 2′-hydroxychalcones, nuclear-substituted bromochalcones, while pyridine with chalcone dibromides gives a bromoflavone derivative.[9] Cupric bromide-dioxane adds a molecule of bromine across the double bond in a chalcone derivative as the first step and in the second-step cyclization with an elimination of a molecule of hydrogen bromide to give 3-bromoflavanone derivative.



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Experimental

Cupric Bromide with Chalcone in Methanol.—2′-Hydroxide-5′-methyl-4-methoxychalcone, m.p. 98° (0.5 g.), and cupric bromide (1.2 g.) were taken in methanol (40 ml.). In one experiment it was kept overnight. In another experiment it was refluxed for 2 hr. After dilution with water the solid which separated was crystallized from ethanol–acetic acid. It was unchanged chalcone.

Cupric Bromide with β-Methylumbelliferone in Methanol. β-Methylumbelliferone, m.p. 184° (1 g.), cupric bromide (2.5 g.) were taken in methanol (50 ml.) and kept overnight. In another experiment it was refluxed for 2 hr. After dilution with water the solid which separated was crystallized from ethanol–acetic acid. It was unconverted β-methylumbelliferone.

Cupric Bromide with Chalcone in Dioxane. (a) In Cold.—The chalcone (0.5 g.) and cupric bromide (1.2 g.) in dioxane (30 ml.) were kept overnight. On dilution with water and crystallization from ethanol–acetic acid original chalcone was obtained.

(b) In Hot.—The chalcone (0.5 g.) and cupric bromide (1.2 g.) in dioxane (30 ml.) were refluxed for 2 hr. The mixture as diluted with water and the solid which separated was crystallized from ethanol–acetic acid, m.p. 165°. Mixed melting point of the bromo compound m.p. 165° with 3-bromo-6-methyl-4′-methoxyflavanone, gave no depression. Compound m.p. 165° on treatment with ethanolic sodium hydroxide solution gave a flavone derivative identical with 6-methyl-4′-methoxyflavone, m.p. 168°.

Cupric Bromide with β-Methylumbelliferone in Dioxane. (a) In Cold.—β-Methylumbelliferone (1 g.) and cupric bromide (2.5 g.) were kept overnight in dioxane (50 ml.). The mixture was diluted with water and the solid separated was crystallized from ethanol–acetic acid. It was unconverted β-methylumbelliferone.

(b) In Hot.—β-Methylumbelliferone (1 g.) and cupric bromide (2.5 g.) in dioxane (50 ml.) were refluxed for 2 hr. The mixture was diluted with water and the solid obtained was fractionally crystallized from acetic acid. 3,6-Dibromo-, m.p. 274°, and 3,8-dibromo-4-methylumbelliferone, m.p. 248°, were the products. Identity was shown by a mixed melting point with the authentic samples.

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Organic Fluorine Compounds. XXVIII. Reaction of Sulfonic- and Mixed Sulfonic-Carboxylic Acid Anhydrides with Anhydrous Hydrogen Fluoride

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The generalization of the method of Colson and Fredenhagen provides an easy preparation of acyl fluorides from the corresponding acid anhydrides or acyl chlorides and anhydrous hydrogen fluoride.[1]

The method has now been extended to the preparation of sulfonyl fluorides. Sulfonyl chlorides generally do not react with anhydrous hydrogen fluoride at or below room temperature to give the corresponding sulfonyl fluorides. At elevated temperatures and under pressure, however, the reaction probably takes place.

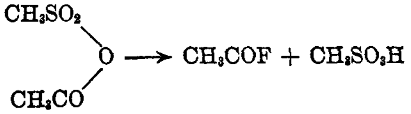
Sulfonic acid anhydrides react with anhydrous hydrogen fluoride to give the corresponding sulfonyl fluorides

$$(RSO_2)_2O + HF \longrightarrow RSO_2F + RSO_3H$$

Both aliphatic and aromatic sulfonic acid anhydrides react with equal ease. The separation of the sulfonyl fluorides from the by-product sulfonic acids can be achieved by water washing and subsequent vacuum distillation. The following sulfonyl fluorides (all known from literature) have been prepared.

Boiling points and infrared spectra are identical with compounds described in literature.[2,3]

Mixed anhydrides of carboxylic and sulfonic acid, as acetic methanesulfonic anhydride, gave in reactions with anhydrous hydrogen fluoride only acyl fluorides and sulfonic acids (Table II).

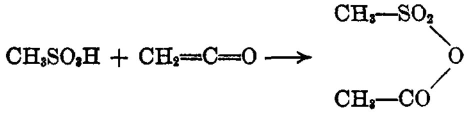


$$CH_3SO_2{-}O{-}COCH_3 \longrightarrow CH_3COF + CH_3SO_3H$$

When the mixed acetic sulfonic anhydrides are treated with aromatic hydrocarbons in the presence of anhydrous hydrogen fluoride, acid-catalyzed Friedel-Crafts acylation only takes place.

$$C_6H_6 + CH_3CO{-}O{-}SO_2CH_3 \xrightarrow{HF} C_6H_5COCH_3 + CH_3SO_3H$$

Acetic sulfonic anhydrides were prepared according to Baroni[4] by the interaction of the corresponding sulfonyl halides with silver acetate. The reaction of ketene with the appropriate sulfonic acids gives only low yields of mixed anhydrides.



$$CH_3SO_3H + CH_2{=}C{=}O \longrightarrow CH_3{-}SO_2{-}O{-}CO{-}CH_3$$

Experimental

Sulfonic acid anhydrides were prepared according to methods of Khorona[5] and Field,[6] acetic sulfonic anhydrides according to Baroni.[4]

Preparation of Acetic Sulfonic Anhydrides with Ketene.—Alkylsulfonic acid (1 mole) in liquid sulfur dioxide solution was placed into a 250-ml. flask and 1 mole of ketene gener-

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