Summary

Schoen's colorimetric method of analyzing *o*-toluidine for its content of the *para* isomer has been shown to be faulty. This was proved by synthesizing *o*-toluidine from phthalic anhydride, thereby avoiding the possibility of any of the *para* isomer being present. However, upon oxidation with potassium dichromate, *o*-toluidine developed a red color indistinguishable from that attributed by Schoen to the *para* isomer only.

The boiling point, density and index of refraction of *para*-free *o*-toluidine were measured.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

THE ADDITION OF METHYL HYPOBROMITE AND METHYL HYPOCHLORITE TO CERTAIN ETHYLENE DERIVATIVES

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In a previous paper[1] it was shown that solutions of cinnamic acid and benzalacetophenone in 85% aqueous methyl alcohol at 0° react with bromine with the resulting addition of methyl hypobromite to the unsaturated compounds. In all probability the reaction proceeds as follows: $Br_2 + CH_3OH \rightleftarrows CH_3OBr + HBr$; $>C=C< + CH_3OBr \longrightarrow >C(OCH_3)CBr<$. As would be expected the addition of bromine takes place simultaneously. Only one other method of adding methyl hypobromite seems to be on record. By the action of bromotrinitromethane with ethylene derivatives in the presence of the appropriate alcohol, E. Schmidt[2] has added methyl hypobromite and certain other alkyl hypobromites to a number of unsaturated compounds.

The present investigation was undertaken with a view to finding the conditions most suitable for the addition of methyl hypobromite by the reaction of bromine and methyl alcohol with ethylene derivatives and to study the reaction with chlorine. If the reaction proceeds as indicated in the above scheme one would not expect the presence of water to be necessary for the addition of methyl hypobromite. In the preliminary paper, on the basis of tests with solutions of cinnamic acid at 0°, it was stated that in 90% or stronger alcohol the reaction is too slow to be practicable. A more extensive investigation of this point, however, has shown that while the reaction is not feasible with solutions of cinnamic acid in absolute methyl alcohol at 0°, the addition of methyl hypobromite in general takes

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[1] Conant and Jackson, THIS JOURNAL, **46**, 1727 (1924).

[2] Schmidt, Bartholomé and Lübke, *Ber.*, **55**, 2099 (1922). Schmidt, Schumacher and Asmus, *Ber.*, **56**, 1239 (1923). Schmidt and Bartholomé, *Ber.*, **57**, 2039 (1924).

place readily in the absence of water. The reaction in absolute methyl alcohol may be carried out either at room temperature or at the boiling point of methyl alcohol. Although the absorption of bromine in some cases was apparently more rapid at the higher temperature, the advantage of carrying out the reaction in boiling methyl alcohol seems to be principally that of increased solubility. The results obtained with the use of absolute methyl alcohol are summarized in Table I.

Table I

Reaction of Ethylene Derivatives with Bromine and Absolute Methyl Alcohol

Substance	Temp., °C.	Product	Yield, %
Benzalacetophenone	25–30	$C_6H_5CH(OCH_3)CHBrCOC_6H_5$	23
		$C_6H_5CHBrCHBrCOC_6H_5$	5
Cinnamic acid	65	$C_6H_5CH(OCH_3)CHBrCOOCH_3$	34
		$C_6H_5CHBrCHBrCOOCH_3$	30
Stilbene	40–50	$C_6H_5CH(OCH_3)CHBrC_6H_5$	64
		$C_6H_5CHBrCHBrC_6H_5$	19

It was not possible to add methyl hypobromite to maleic acid and β-bromostyrene by this method.

The addition of hypobromous acid by means of the reaction of bromine water with ethylene derivatives is limited[1,3] by the insolubility in water of many unsaturated compounds of high molecular weight. It seemed likely that this difficulty might be overcome, at least partially, by the use of methyl alcohol-water mixtures containing a relatively high proportion of water. Accordingly, the reaction of bromine with a solution of cinnamic acid in 50% aqueous methyl alcohol at 0° was tried. The products were α-bromo-β-hydroxyphenylpropionic acid and α-bromo-β-methoxyphenylpropionic acid in approximately equal amounts; the dibromide of cinnamic acid was also formed in smaller quantity.

The Addition of Methyl Hypochlorite

When solutions of ethylene derivatives in methyl alcohol are treated with chlorine, the addition of methyl hypochlorite to the double linkage of the unsaturated compound takes place. Methyl hypochlorite is doubtless formed by the reaction of chlorine and methyl alcohol in a manner analogous to that described for methyl hypobromite. The reaction was carried out by introducing a stream of chlorine into a vigorously stirred solution of the unsaturated compound in methyl alcohol either at the laboratory temperature or at about 50°. The absorption of chlorine under these conditions was rapid. Table II is a summary of the results.

The mode of addition of methyl hypochlorite to cinnamic acid was shown to be the same as that of methyl hypobromite. By the action of 0.5 *N* sodium hydroxide solution the chloromethoxy ester, which was the prin-

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[3] Goldschmidt, Endres and Dirsch, *Ber.*, **58**, 572 (1925).

TABLE II

REACTION OF ETHYLENE DERIVATIVES WITH CHLORINE AND METHYL ALCOHOL

Substance	Temp., °C.	Product[a]	Yield, %
Benzalacetophenone	25–30	$C_6H_5CH(OCH_3)CHClCOC_6H_5$[b]	56
Cinnamic acid	20–30	$C_6H_5CH(OCH_3)CHClCOOCH_3$	55
		$C_6H_5CH(OCH_3)CHClCOOH$	5
Stilbene	40–60	$C_6H_5CH(OCH_3)CHClC_6H_5$[c]	89

[a] No dichloride was isolated in any of the reactions; however, it was probably present in the oil that was formed with each compound.

[b] Assumed to be the β-methoxy compound by analogy with the corresponding bromomethoxy compound.

[c] Stereoisomers.

cipal product of the reaction with cinnamic acid, was hydrolyzed to the corresponding acid. This is the β-methoxy compound, $C_6H_5CH(OCH_3)$-$CHClCOOH$, since it is identical with the chloromethoxy acid formed by adding mercuric acetate[1] to cinnamic acid and replacing the mercury by chlorine.

Goldschmidt[3,4] has recently shown that solutions of ethyl hypochlorite in carbon tetrachloride are sufficiently stable to be used in reactions with compounds containing aliphatic double bonds. The usual reaction under such conditions is the addition of hypochlorous acid; however, in the case of 1,4-dihydronaphthalene, ethyl hypochlorite was added. On account of the solvent value of carbon tetrachloride, it seemed desirable to try the reaction of chlorine on solutions of an unsaturated compound in carbon tetrachloride-methyl alcohol mixtures. Chlorine was found to react rapidly with cinnamic acid dissolved in carbon tetrachloride and methyl alcohol mixtures containing either 50 or 75% of carbon tetrachloride. α-Chloro-β-methoxy-phenylpropionic acid was obtained in both cases by hydrolysis of the reaction products.

Attempts to add methyl hypo-iodite, by treating solutions of cinnamic acid and anethole in methyl alcohol with iodine, were unsuccessful, no apparent reaction taking place.

The application of this reaction to typical primary, secondary and tertiary alcohols along the lines described in this paper is being investigated. The reaction with certain acetylene derivatives is also under investigation.

Experimental Part

The absolute methyl alcohol used in the work described below was the c. p. grade which had been refluxed over quicklime and distilled through a Glinsky still-head; b. p., 65–66°.

I. Addition of Methyl Hypobromite

The introduction of bromine into the reaction solutions was accomplished by drawing a stream of dry air over the surface of liquid bromine contained

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[4] Taylor, MacMullin and Gammal, THIS JOURNAL, **47**, 395 (1925).

in a small distilling flask, the side arm of which was connected to the reaction flask by means of a delivery tube. The current of air was dried by passage over calcium chloride and was regulated so as to maintain a small excess of bromine in the solution.

Reaction of Benzalacetophenone with Bromine and Absolute Methyl Alcohol at 25-30°.—A solution of 8 g. of benzalacetophenone in 100 cc. of absolute methyl alcohol at 25–30° was treated with 7.5 g. of bromine vapor during two hours. The products were 4.3 g. of crystals melting at 78–92°, 0.6 g. melting at 68–73° and an oil. A fractional crystallization from methyl alcohol yielded 2.8 g. of α-bromo-β-methoxy-β-phenylpropiophenone melting at 75–76°, 0.7 g. of the dibromide of benzalacetophenone and small amounts of intermediate fractions. Mixed-melting-point determinations showed the substance, melting at 75–76°, to be identical with α-bromo-β-methoxy-β-phenylpropiophenone which was prepared by Middleton[5] by the action of mercuric acetate on benzalacetophenone followed by treatment with bromine.

Reaction of Benzalacetophenone with Bromine and Absolute Methyl Alcohol at 65°.—Seven g. of bromine vapor was introduced into a solution of 8 g. of benzalacetophenone in 100 cc. of absolute methyl alcohol which was boiled under a reflux condenser. About 35 minutes was required to complete the reaction. The yield was 6 g. of substance melting at 64–73° and an oil. Several recrystallizations from methyl alcohol gave pure α-bromo-β-methoxy-β-phenylpropiophenone; m. p., 75–76°.

Reaction of Cinnamic Acid with Bromine and Absolute Methyl Alcohol.—The reaction of cinnamic acid with bromine and absolute methyl alcohol at 0–5° was found to be so slow that it was abandoned. The reaction was tried, therefore, at the boiling point of methyl alcohol. Fifteen g. of cinnamic acid was dissolved in 100 cc. of absolute methyl alcohol. The solution was boiled under a reflux condenser and bromine vapor was introduced until 18 g. had reacted. The absorption of bromine was slow, several hours being required to complete the reaction. On cooling the solution to room temperature it deposited 9.4 g. of crystals; m. p., 114–115°. The substance is insoluble in sodium carbonate solution. It is probably impure methyl ester of cinnamic acid dibromide, the melting point of which is given in the literature as 117°. By concentration of the solution and recrystallization of the resulting solid material from methyl alcohol, there was obtained 9.5 g. of colorless crystals melting at 65–67°, 0.4 g. of impure dibromide and some oil. The substance melting at 65–67° is insoluble in sodium carbonate solution. It was shown to be methyl α-bromo-β-methoxy-phenylpropionate by its hydrolysis to the corresponding acid and by its preparation from methyl cinnamate, methyl alcohol and bromine.

For its hydrolysis 1.0 g. of substance was heated at about 90° with 0.5 *N* sodium hydroxide solution for 30 minutes. The product was 0.6 g. of crystals contaminated with a small amount of oil. After recrystallization from chloroform it melted at 182–183°; mixtures of the substance with known α-bromo-β-methoxy-phenylpropionic acid melted at the same temperature. The ester was also hydrolyzed by the action of 0.5 *N* sodium hydroxide solution at room temperature for about 24 hours. In this case the product must be purified by boiling with sodium carbonate solution for a few minutes to decompose the dibromide of cinnamic acid which is mixed with the bromomethoxy acid.

Reaction with Methyl Cinnamate.—Schrauth[6] has recently shown that the addition of mercuric acetate to cinnamic acid followed by replacement of the mercury by bromine gives the high-melting isomer of α-bromo-β-methoxy-phenylpropionic acid. A

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[5] Middleton, This Journal, **45**, 2763 (1923).

[6] Schrauth and Geller, *Ber.*, **55**, 2783 (1922).

similar reaction with methyl cinnamate yields the low-melting stereoisomer of this acid. Inasmuch as there was this difference in the products of the reaction of the mercury compound with cinnamic acid and its ester, the reaction of bromine and methyl alcohol with methyl cinnamate was tried. By treating a solution of 10 g. of methyl cinnamate in 100 cc. of methyl alcohol at room temperature with 11 g. of bromine, there were obtained 7.1 g. of methyl α-bromo-β-methoxy-phenylpropionate (m. p., 66–67°) and 6.3 g. of the methyl ester of cinnamic acid dibromide (m. p., 115–116°). A mixture of the bromomethoxy ester thus obtained with the product of the reaction with cinnamic acid (m. p., 65–67°) melted at 65.5–66.5°. Upon hydrolysis with hot 0.5 *N* sodium hydroxide solution the bromomethoxy ester gave the high-melting isomer of α-bromo-β-methoxy-phenylpropionic acid; m. p., 182–183°.

Reaction of Cinnamic Acid with Bromine and 50% Aqueous Methyl Alcohol.—A mixture of 300 cc. of absolute methyl alcohol and 300 cc. of water was saturated with cinnamic acid at 0°. This required 2.7 g. of cinnamic acid. Bromine vapor was passed into the solution, which was kept at 0–5°, until the yellow color of unreacted bromine persisted. Approximately 3 g. of bromine reacted. The colorless precipitate was filtered off and dried. It weighed 0.3 g.; m. p., 179–180°. The filtrate was concentrated to a volume of about 300 cc. and after cooling deposited 1.7 g. of crystals which melted at 175–177°. The remainder of the material was recovered from the solution by extraction with ether. It was a light yellow oil which weighed 2.2 g. The oil soon solidified; recrystallization from benzene gave 1.5 g. of somewhat impure α-bromo-β-hydroxy-phenylpropionic acid melting at 117–123°. Further recrystallization from benzene yielded the pure bromohydroxy acid; m. p., 124–124.5°. Its identity with the product obtained by the reaction of bromine water with cinnamic acid, according to the procedure of Read and Andrews,[7] was established by mixed-melting-point determinations. The 2.0 g. of high-melting material obtained as described above was dissolved in saturated sodium carbonate solution and boiled for a few minutes. The separation of an oil resembling bromostyrene indicated the decomposition of the dibromide of cinnamic acid. The oil was extracted with ether, and acidification of the sodium carbonate solution yielded 1.2 g. of substance melting at 180–181°. After recrystallization it melted at 182–183°; mixed-melting-point determinations showed it to be α-bromo-β-methoxyphenylpropionic acid.

Reaction of Stilbene with Bromine and Absolute Methyl Alcohol.—Five g. of stilbene was dissolved in 250 cc. of hot absolute methyl alcohol into which was passed about 4.5 g. of bromine vapor. The temperature was maintained at 40–50° in order to keep the stilbene in solution. A rapid absorption of bromine resulted and the reaction was complete in about two hours. During the reaction a colorless solid which is principally the dibromide of stilbene separated. At the end of the reaction the solution was heated to the boiling point and filtered. The solid thus obtained melted at 220–230° and is doubtless impure dibromostilbene which has a melting point of 237° when pure. After the separation of the remainder of the material from the filtrate and a fractional crystallization from methyl alcohol the yield was 0.9 g. melting at 220–230°, 0.9 g. melting at 155–175°, 4.8 g. melting at 115–116°, 0.4 g. melting at 112–115° and a small amount of oil. The preparation of an analytically pure sample of the low-melting material proved to be difficult. After several recrystallizations from methyl alcohol it melted at 115–116°, but methoxyl determinations by the Zeisel method gave methoxyl values slightly higher than that calculated for α,β-diphenyl-α-bromo-β-methoxy-ethane ($C_6H_6CH(OCH_3)CHBrC_6H_6$). Since the bromine content was found to be somewhat low, the impurity is not the dibromide. By recrystallizing the subtance melting at 115–116° from benzene or chloroform the separation of some higher-melting substance

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[7] Read and Andrews, *J. Chem. Soc.*, **119,** 1774 (1921).

was effected. Material with an unchanging melting point upon recrystallization, however, could not be obtained by this means. The best results were obtained by repeatedly recrystallizing the substance melting at 115–116° from benzene followed by a final recrystallization from methyl alcohol; the melting point was then 115.5–116.5°.

Anal. Calcd. for $C_{16}H_{15}OBr$: C, 61.9; H, 5.2; OCH_3, 10.7; Br, 27.5. Found: C, 61.3; H, 5.8; OCH_3, 11.6, 11.5; Br, 26.3, 26.4.

II. Addition of Methyl Hypochlorite

Reaction of Benzalacetophenone with Chlorine and Absolute Methyl Alcohol.—Fifteen g. of benzalacetophenone was dissolved in 150 cc. of absolute methyl alcohol. The solution was stirred vigorously while chlorine, dried by passing through concd. sulfuric acid, was introduced at the rate of about two bubbles per second. Occasional tests with moist starch-potassium iodide paper showed the rapid absorption of the chlorine. The reaction temperature was that of the room. When approximately 1.8 liters of chlorine had been passed into the solution its absorption ceased. After distillation of part of the solvent, 11 g. of colorless needles melting at 68–69° was separated. One recrystallization from methyl alcohol gave the pure chloromethoxy derivative of benzalacetophenone; m. p., 69–70°. The remainder of the material consisted of a small amount of the impure chloromethoxy compound and a non-crystalline oil.

Anal. Calcd. for $C_{16}H_{15}O_2Cl$: OCH_3, 11.29; Cl, 12.90. Found: OCH_3, 10.94; Cl, 13.18.

The usual product of the reaction was the chloromethoxy compound melting at 69–70°. In one experiment, however, there was obtained in addition to the compound melting at 69–70° a small amount of material which melted at 98–99° after several recrystallizations from methyl alcohol or toluene. This is probably the other racemate of the chloromethoxy derivative of benzalacetophenone.

Anal. Calcd. for $C_{16}H_{15}O_2Cl$: OCH_3, 11.29. Found: 10.28, 10.09.

The structure of the chloromethoxy compound was not established. However, since the addition of methyl hypobromite to benzalacetophenone yields α-bromo-β-methoxy-β-phenylpropiophenone the substance is probably the β-methoxy compound, $C_6H_5CH(OCH_3)CHClCOC_6H_5$.

Reaction with Cinnamic Acid.—A thoroughly stirred solution of 20 g. of cinnamic acid in 250 cc. of methyl alcohol (b. p., 64–65°) was treated with chlorine in the manner described for benzalacetophenone. The reaction was started at 20° but the temperature soon rose to 30°; the solution was then cooled so that the temperature was maintained at 20–30°. The chlorine was rapidly absorbed and the reaction was complete at the end of one and one-half hours. Distillation of the methyl alcohol yielded a colorless oil. This was dissolved in ether and thoroughly extracted with sodium carbonate solution. From the ethereal solution which contained the material insoluble in sodium carbonate there was obtained 28 g. of oil which soon crystallized; m. p., 46–50°. By recrystallization from methyl alcohol 17 g. of colorless crystals melting at 50–54° was obtained. The residue from the crystallization was an oil containing some crystals. Another crystallization from methyl alcohol of the substance melting at 50–54° gave the pure methyl ester of α-chloro-β-methoxy-phenylpropionic acid; m. p., 54–55°.

Anal. Calcd. for $C_{11}H_{13}O_3Cl$: Cl, 15.51. Found: 15.70.

Mixed-melting-point determinations showed the substance to be identical with the product obtained in the reaction of chlorine and methyl alcohol with methyl cinnamate. Hydrolysis with dil. sodium hydroxide solution gave α-chloro-β-methoxy-phenylpropionic acid.

The acid material resulting from the reaction of cinnamic acid with chlorine and methyl alcohol was recovered by acidification of the sodium carbonate solution obtained in the extraction described above. It was an oil weighing 1.4 g. The oil soon crystallized; m. p., 120–140°. After three recrystallizations from chloroform, colorless crystals melting at 163–164° resulted. A mixture of this substance with about an equal amount of cinnamic acid dichloride (m. p., 163–164°) melted at 148–154°. A mixed-melting-point determination showed the substance to be identical with the product of hydrolysis of the compound melting at 54–55°. It is, therefore, the chloromethoxy derivative of cinnamic acid.

Hydrolysis of the Methyl Ester.—Five g. of the compound melting at 54–55° was hydrolyzed by the action of 0.5 *N* sodium hydroxide solution at room temperature for ten hours. The product weighed 3.1 g. and melted at 135–147°. By recrystallization from methyl alcohol or chloroform the pure chloromethoxy derivative of cinnamic acid was obtained; m. p., 163–164°.

Anal. Calcd. for $C_{10}H_{11}O_3Cl$: C, 55.94; H, 5.16; Cl, 16.52. Found: C, 55.50; H, 5.47; Cl, 16.73.

The chloromethoxy acid undergoes no apparent change when boiled with 0.5 *N* sodium hydroxide solution for about ten minutes. Since this treatment decomposes cinnamic acid dichloride to give chlorostyrene, heating with dilute alkali may be used to purify the chloromethoxy acid which is mixed with the dichloride.

Structure of the Chloromethoxy Acid.—That the compound is α-chloro-β-methoxy-phenylpropionic acid was established by showing its identity with the product of the reaction of chlorine with α-acetoxymercuri-β-methoxy-phenylpropionic acid. The mercury compound was prepared by the reaction of mercuric acetate with cinnamic acid in methyl alcohol solution according to the procedure described in a previous paper.[1] A suspension of 2.2 g. of the mercury compound in 15 cc. of methyl alcohol was treated with chlorine as long as absorption took place. After introducing a small excess of chlorine, it was allowed to stand at room temperature until the presence of free chlorine could no longer be detected by means of moist starch-potassium iodide paper. This process was repeated until all of the solid material had dissolved. The methyl alcohol was distilled, the residue dissolved in ether and the solution thoroughly extracted with concd. aqueous potassium chloride and finally with water. Distillation of the ether gave 1.0 g. of colorless crystals melting at 150–154°. After two recrystallizations from chloroform the substance melted at 163–164°. A mixed-melting-point determination showed the compound to be identical with the product of hydrolysis of the methyl ester obtained in the reaction of chlorine and methyl alcohol with cinnamic acid as described above.

Reaction with Methyl Cinnamate.—By the reaction of chlorine with a solution of 10 g. of methyl cinnamate in 125 cc. of methyl alcohol at 25–30° there was obtained 8 g. of solid melting at 50–55° and an oil. After recrystallization from methyl alcohol the substance melted at 54–55°. A mixture of the compound with the product from the reaction of chlorine and methyl alcohol with cinnamic acid melted at the same temperature. Hydrolysis with 0.5 *N* sodium hydroxide solution gave α-chloro-β-methoxy-phenylpropionic acid; m. p., 163–164°.

Reaction with Cinnamic Acid in Carbon Tetrachloride-Methyl Alcohol Mixtures.—Fifteen g. of cinnamic acid was dissolved in 75 cc. of carbon tetrachloride and to this solution was added 75 cc. of methyl alcohol (b. p., 64–65°). Chlorine was passed into the vigorously stirred solution in the usual manner, a rapid absorption resulting. When about 3 liters of chlorine had been introduced, tests showed the presence of free chlorine. The product was an oil, insoluble in dil. aqueous sodium hydroxide, being probably a mixture of acid esters. Since the oil did not crystallize readily, it was boiled with 0.5 *N* sodium hydroxide solution for about 30 minutes. The small amount of insoluble oil, which is probably chlorostyrene, was extracted with ether. From the aqueous solution was obtained 11 g. of colorless oil which soon crystallized; m. p., 80–140°. Recrystallization from chloroform gave 4 g. of the slightly impure chloromethoxy derivative of cinnamic acid melting at 157–160° and 2 g. of substance melting at 115–130°. The residue from the crystallization was a mass of crystals containing some oil. It undoubtedly contained a considerable amount of the chloromethoxy acid. The material melting at 157–160° after recrystallization melted at 163–164°. A mixture of the substance with known α-chloro-β-methoxy-phenylpropionic acid melted at the same temperature.

The reaction was carried out also in mixtures which contained 75% of carbon tetrachloride and 25% of methyl alcohol by volume. In this case α-chloro-β-methoxy-phenylpropionic acid was obtained by hydrolysis of the reaction product. Its purification, however, was more difficult than when the reaction was carried out in 50% mixtures. A solution of 15 g. of cinnamic acid in a mixture of 120 cc. of carbon tetrachloride and 40 cc. of methyl alcohol was treated with chlorine and the product hydrolyzed as described above. This gave 9 g. of crystals melting at 70–125° and an oil. From the substance melting at 70–125° was obtained by recrystallization 1.5 g. of pure α-chloro-β-methoxy-phenylpropionic acid. The greater portion of the remaining material was a solid melting at 80–105° and was obviously impure. Although the fractional crystallization was not completed, this low-melting material doubtless contained a considerable amount of the chloromethoxy derivative of cinnamic acid.

Reaction of Stilbene with Chlorine and Methyl Alcohol.—Six g. of stilbene was dissolved in 225 cc. of methyl alcohol (b. p., 64–65°). The thoroughly stirred solution was treated at 40–60° with chlorine in the usual manner. A rapid reaction resulted. When the solution had ceased to absorb chlorine the methyl alcohol was distilled until the volume was about 50 cc. Colorless crystals soon separated. These weighed 4 g.; m. p., 80–89°. By concentrating the filtrate 3.3 g. of substance melting at 54–57° and 0.3 g. melting at 42–48° were obtained. The remainder of the material was an oil containing some crystals. After several recrystallizations from methyl alcohol of the substance melting at 80–89° the chloromethoxy derivative of stilbene with a melting point of 96–97° was obtained.

Anal. Calcd. for $C_{15}H_{15}OCl$: OCH_3, 12.57; Cl, 14.38. Found: OCH_3, 12.10, 11.88; Cl, 14.72.

It has not been found possible so far to purify completely the low-melting substance. By recrystallization from methyl alcohol of the substance melting at 54–57° some of the high-melting chloromethoxy compound was separated. After repeating the recrystallization several times, material with a melting point of 55–57° was obtained. A methoxyl determination showed that this substance consisted for the most part of a methoxyl compound. Since the chlorine analyses were high and the methoxyl value was low it seems likely that the material was a mixture of a chloromethoxy derivative of stilbene and the dichloride of stilbene. The chloromethoxy compound is probably a stereoisomer of the compound which melts at 96–97°.

Anal. Calcd. for 85% $C_{15}H_{15}OCl$ + 15% $C_{14}H_{12}Cl_2$: OCH_3, 10.7; Cl, 16.5. Found: OCH_3, 10.4; Cl, 16.4, 16.2.

III. Attempted Addition of Methyl Hypo-iodite

Solutions of iodine in methyl alcohol gave no apparent reaction with cinnamic acid and anethole. Thus, after a solution of 10 g. of cinnamic acid and 1 g. of iodine in 100 cc. of methyl alcohol had stood for 12 months, the color due to the iodine still remained. Likewise, a solution of 1 g. of iodine in 75 cc. of methyl alcohol was not decolorized by 5 g. of anethole after standing for the same period of time.

Summary

1. The presence of water is unnecessary for the addition of methyl hypobromite by the reaction of bromine and methyl alcohol with ethylene derivatives. By the reaction of bromine and absolute methyl alcohol either at 25° or 65° methyl hypobromite was added to benzalacetophenone, cinnamic acid and stilbene. With cinnamic acid, esterification also takes place.

2. A solution of cinnamic acid in 50% aqueous methyl alcohol at 0° reacts with bromine with the simultaneous addition of hypobromous acid, methyl hypobromite and bromine.

3. The action of chlorine on solutions of benzalacetophenone, cinnamic acid and stilbene in methyl alcohol either at 25° or 50° results in the addition of methyl hypochlorite to the double linkage of the unsaturated compound. The product with cinnamic acid was the methyl ester of α-chloro-β-methoxy-phenylpropionic acid. The reaction with cinnamic acid was also carried out with solutions in carbon tetrachloride-methyl alcohol mixtures containing either 50 or 75% of carbon tetrachloride.

4. Attempts to add methyl hypo-iodite to cinnamic acid and anethole with the use of iodine and methyl alcohol were unsuccessful.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE RICE INSTITUTE]

SUBSTITUTED AMIDES. I. THE PREPARATION OF SUBSTITUTED ACETAMIDES AND THE CORRESPONDING PRIMARY AMINES[1]

BY H. O. NICHOLAS AND J. L. E. ERICKSON

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In 1879 Rudolph[2] showed that a reaction takes place between acetamide and benzyl chloride with the formation of benzylacetamide. On repeating his work for the purpose of ascertaining the general applicability of this reaction in organic synthesis, we noted that the yield of benzylacetamide was very small. Also, a large amount of ammonium chloride was formed in the reaction, a fact which he did not mention. After carefully purifying and drying the alkyl halide and the acetamide, it was found that during the course of the reaction ammonium halide was still formed, and that no halogen acid was evolved. The source of the ammonium halide was determined by passing dry hydrogen bromide through anhydrous acetamide

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[1] Constructed from a thesis submitted by J. L. E. Erickson in partial fulfilment of the requirements for the degree of Master of Science at the Rice Institute.

[2] Rudolph, *Ber.*, **12**, 1297 (1879).