indicate the presence of a trimolecular compound, but it could be equally well explained by assuming the presence of a dimolecular form having no free carboxyl groups.

Effect of Temperature on the Equilibrium.—An examination of the acid values of I to IV in Table II indicates that the percentage of double molecules in the equilibrium mixtures decreases as the temperature of heating increases. This is to be expected since polymerization is, as a rule, exothermic. We have also noted indications that the percentage of the low-boiling constituent does not change proportionately to that of the double molecule. If it did, the separation of the crotonic acid at 0° would leave a liquid of the same acid value in all instances, but this was found not to be the case.

Summary

The effect of heating crotonic acid has been investigated. It has been proved that the resulting mixture is not a binary mixture, as is stated in the literature, but contains at least three compounds: crotonic acid, a low-boiling constituent (probably isocrotonic acid) and a high-boiling liquid from the properties of which its probable structure has been deduced. It has further been proved that above 110° the system does not show the phenomenon of "false equilibrium" as was previously supposed.

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[Contribution from the Chemical Laboratory of Barnard College]

THE BROMINATION OF 2,4-DIMETHOXYCINNAMIC ACID

By Marie Reimer and Elise Tobin

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In the study, in this Laboratory, of unsaturated α-ketonic acids, certain substituted cinnamic acids have been needed for purposes of identification. This has led to the study of the bromination products of 2,4-dimethoxycinnamic acid which are described in this paper. The acid was prepared by hydrolysis of ethyl 2,4-dimethoxycinnamate made by the Claisen condensation and was the stable form.

We have found that addition of bromine to 2,4-dimethoxycinnamic acid is invariably accompanied by bromination in the ring, the position of the nuclear bromine atom being established by oxidation of the tribromo acid thus formed to 2,4-dimethoxy-5-bromobenzoic acid.[1] The behavior of the dimethoxycinnamic acid on bromination is, therefore, similar to that of the corresponding dimethoxybenzoylacrylic acid.[1] It has not been possible to prepare an unsaturated acid by elimination of hydrogen bromide from the tribromo acid by the usual methods. Invariably saturated alkoxy acids result which are probably formed by direct replacement of bromine by an

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[1] Grace Potter Rice, This Journal, **48**, 3125 (1926).

alkoxyl group rather than by elimination of hydrogen bromide and addition of solvent. This is indicated by the fact that the tribromo acid is stable and does not lose hydrogen bromide below its melting point when heated alone nor when heated in high boiling solvents and that these same alkoxyl products are formed in alcoholic solution in the absence of an alkaline reagent. The ease of replacement of this bromine atom is comparable to that of the chlorine atom in unsaturated compounds containing the grouping $C_6H_5CHClCH{=}CH{-}{-}{-}{-}C_6H_5$. Straus[2] has found this chlorine atom to be increasingly labile with increasing unsaturation of the side chain and particularly with *p*-methoxy substituting groups. As it has been found during the course of previous work that such ease of replacement of bromine is not a characteristic of *p*-methoxy- nor of *o*-methoxycinnamic acid dibromide, with or without a bromine atom in the ring, this great lability of the bromine atom in the compounds under discussion must be ascribed to the presence of both para and ortho methoxyl groups, possibly also to the nuclear bromine atom. It is then, in all probability, the bromine atom adjacent to the ring that is replaced.

Since the usual esterification methods when used with the tribromo acid gave esters of alkoxy acids, the methyl ester of the tribromo acid was prepared by bromination of methyl 2,4-dimethoxycinnamate. Attempts to prepare the ethyl ester of the tribromo acid by bromination of ethyl 2,4-dimethoxycinnamate led to an interesting and unexpected result. Although the bromine and the solvent chloroform were the same as in the previous bromination reactions, the small amount of moisture evidently present hydrolyzed the product almost completely, the substance obtained in practically quantitative yield being 2,4-dimethoxy-5-bromobenzaldehyde. Even with dried reagents it has not as yet been possible to prepare a pure tribromo ethyl ester by this procedure. The crude product of the bromination gives the aldehyde when brought into contact with water. The tribromo acid and its methyl ester yield no trace of the aldehyde even on long boiling with water.

It seems reasonable to ascribe this difference in the behavior of the bromination product of the ethyl ester, on the one hand, and of the tribromo acid and its methyl ester on the other to a difference in space configuration. To test this assumption it would be necessary to prepare a tribromo ethyl ester, the diastereoisomer of the unstable one above postulated, which would be expected to have the characteristics of the tribromo acid and its methyl ester. It has been possible to prepare such an isomeric compound. Since the tribromo acid on treatment with diazomethane gave a tribromo methyl ester which, like the acid, was not hydrolyzed to the aldehyde, the tribromo acid was treated with diazoethane. As was expected, a tribromo ethyl ester resulted which behaved in all respects like the tribromo acid and

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[2] Straus and Dützmann, *J. prakt. Chem.*, [2] **103**, 1 (1921).

its methyl ester. This ester has then undoubtedly the same space configuration as that of the tribromo acid. It may be considered to be derived from an ethyl-dimethoxycinnamate geometrically isomeric with the one from which the acid used in this study was prepared, which was made by the Claisen condensation, is pale yellow, melts at 68–69° and is hydrolyzed on bromination. When this ester was distilled under diminished pressure, a colorless solid melting at 61° was obtained. This is the isomeric ester. It does give on bromination the same tribromo ethyl ester that was obtained by action of diazoethane on the tribromo acid. The space relations of these esters are now under investigation.

Experimental Part

2,4-Dimethoxycinnamic acid was prepared from its ethyl ester obtained by Claisen condensation of 2,4-dimethoxybenzaldehyde and ethyl acetate according to the method of Perkin and Schiess,[3] which gives much better yields of the acid than the Perkin synthesis described by the same authors. 2,4-Dimethoxybenzaldehyde was prepared by the method used by Freudenberg[4] for veratric aldehyde. It was obtained in 85% yield and used without further purification. The resorcyl aldehyde needed in its preparation was obtained in good yield by the Gatterman method as modified by Johnson and Lane.[5]

The ethyl ester of 2,4-dimethoxycinnamic acid, melting at 68–69°, obtained in a yield of 70% was saponified by boiling for an hour with an excess of 10% sodium hydroxide. The cooled solution on acidification deposited an 85–90% yield of the stable form of the corresponding acid. It was purified by crystallization from glacial acetic acid, which proved to give the purest product, although there was considerable loss of substance with this solvent.

Reaction of Bromine on 2,4-Dimethoxycinnamic Acid

Since it was not found possible to prepare a dibromo addition product of the acid, as bromination in the ring invariably accompanied the addition reaction, the following brominations were carried out with two molecular proportions of bromine.

2,4-Dimethoxy-5-bromocinnamic Acid Dibromide, $(CH_3O)_2BrC_6H_2CHBrCHBrCOOH$ (I).—Fifteen grams of 2,4-dimethoxycinnamic acid was suspended in 250 cc. of chloroform, the mixture cooled and 8.2 cc. of bromine added slowly; the acid dissolved readily and, toward the end of the reaction, the bromo compound separated out. The mixture was shaken for a few minutes, the solid product then filtered and washed repeatedly with small amounts of cooled chloroform until it was practically colorless. By evaporation of the mother liquor in a current of dry air, further small amounts separated. The substance, obtained in practically quantitative yield, is a granular solid melting at 228–229° with vigorous decomposition. It is readily soluble in acetone and glacial acetic acid, very slightly soluble in chloroform, benzene and ether. As it was not found possible to purify it further by crystallization from any solvent, the carefully washed crude product was analyzed.

Anal. Subs., 0.1944: CO_2, 0.2110; H_2O, 0.0437. Calcd. for $C_{11}H_{11}O_4Br_3$: C, 29.54; H, 2.48. Found: C, 29.60; H, 2.52.

To determine the position of the nuclear bromine atom, the acid was oxidized with potassium permanganate. The product of the oxidation was proved to be 2,4-dimeth-

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[3] Perkin and Schiess, *J. Chem. Soc.*, **85**, 164 (1904).

[4] Freudenberg, *Ber.*, **53**, 1416 (1920).

[5] Johnson and Lane, THIS JOURNAL, **43**, 348 (1921).

oxy-5-bromobenzoic acid by a mixed melting point with a sample of that acid obtained from another source.

Esterification of the tribromo acid was at first attempted in alcoholic solution but in all such reactions one bromine atom was replaced by an alkoxyl group. The methyl ester of 2,4-dimethoxy-5-bromocinnamic acid dibromide (II) was obtained by the reaction of the acid in ethereal solution with a slight excess of diazomethane. The ester crystallizes from the ether and can be purified from benzene or from ether, from which it separates in large firm crystals melting, with decomposition, at 142°.

Anal. Subs., 5.605 mg.: CO_2, 6.47 mg.; H_2O, 1.59 mg. Calcd. for $C_{12}H_{13}O_4Br_3$: C, 31.25; H, 2.84. Found: C, 31.48; H, 3.17.

Methyl Ester of α-Bromo-β-methoxy-2,4-dimethoxy-5-bromohydrocinnamic Acid, $(CH_3O)_2BrC_6H_2CH(OCH_3)CHBrCOOCH_3$ (III).—This ester crystallized out from solution when the tribromo acid was allowed to stand overnight in methyl alcohol saturated with hydrogen chloride. It separates in compact, colorless crystals melting, without decomposition, at 149°.

Anal. Subs., 0.1695: CO_2, 0.2359; H_2O, 0.0628. Calcd. for $C_{13}H_{16}O_5Br_2$: C, 37.87; H, 3.91. Found: C, 37.95; H, 4.15.

This ester was also formed by recrystallization of the tribromo methyl ester (II) from boiling methyl alcohol and from the tribromo acid by allowing the acid to stand for several hours in contact with methyl alcohol. In the latter case the corresponding acid was also obtained.

α-Bromo-β-methoxy-2,4-dimethoxy-5-bromohydrocinnamic Acid (IV).—The methyl alcoholic solution of the tribromo acid on standing overnight deposited a considerable quantity of the methyl ester (III) just described. The alcoholic solution was poured into aqueous sodium carbonate, this extracted with ether and the alkaline solution acidified. The heavy white precipitate was crystallized from benzene from which the acid separates in tiny shining hard crystals melting at 171° with effervescence and charring. From 1.0 g. of tribromo acid 0.6 g. of acid and 0.3 g. of methyl ester were obtained. This acid readily gives the ester (III) by action of diazomethane.

Anal. Subs., 5.069 mg.: CO_2, 6.77 mg.; H_2O, 1.77 mg. Calcd. for $C_{12}H_{14}O_5Br_2$: C, 36.19; H, 3.55. Found: C, 36.42; H, 3.91.

The ethyl ester (V) of the methoxy acid (IV) was obtained by the reaction of the acid in ethereal solution with diazoethane. The substance crystallizes from ethyl alcohol or from absolute ether in characteristic bunches of hexagonal plates. It melts at 109°.

Anal. Subs., 5.125 mg.: CO_2, 7.37 mg.; H_2O, 2.00 mg. Calcd. for $C_{14}H_{18}O_5Br_2$: C, 39.44; H, 4.23. Found: C, 39.22; H, 4.37.

The Ethyl Ester of 2,4-Dimethoxy-5-bromocinnamic Acid Dibromide (VI).—Five grams of freshly prepared tribromo acid was moistened with ether and a slight excess of freshly prepared diazoethane in ethereal solution added slowly. The acid dissolved readily and the ester began almost at once to separate from the solution as a pure white granular solid. It was filtered and washed with dry ether. The substance melts with vigorous effervescence at 158°. It is soluble in boiling benzene, very slightly soluble in ether and methyl and ethyl alcohols. With the latter solvents it reacts readily. It is very slightly soluble in boiling water and does not appear to react with it.

Anal. Subs., 4.766 mg.: CO_2, 5.77 mg.; H_2O, 1.26 mg. Calcd. for $C_{13}H_{15}O_4Br_3$: C, 32.85; H, 3.18. Found: C, 33.02; H, 2.96.

When this tribromo ethyl ester was boiled with methyl alcohol, the ethyl ester (V) of the methoxy acid (IV) was obtained. From ethyl alcohol the ethyl ester (VII) of the ethoxy acid (VIII) crystallized. The substance has, therefore, undoubtedly, the same configuration as the tribromo acid and its methyl ester.

The ethyl ester of α-bromo-β-ethoxy-2,4-dimethoxy-5-bromohydrocinnamic acid, $(CH_3O)_2BrC_6H_2CH(OC_2H_5)CHBrCOOC_2H_5$ (VII), was formed when the tribromo acid was treated with ethyl alcohol saturated with hydrogen chloride. It separates from ethyl alcohol in fine needles melting at 105–107°.

Anal. Subs., 0.1588: CO_2, 0.2384; H_2O, 0.0722. Calcd. for $C_{15}H_{20}O_5Br_2$: C, 40.91; H, 4.58. Found: C, 40.94; H, 4.96.

This ester was also obtained in small quantity when the tribromo acid was allowed to stand overnight with ethyl alcohol. As in the parallel reaction with methyl alcohol, the corresponding acid was also formed and was separated in the way there described.

α-Bromo-β-ethoxy-2,4-dimethoxy-5-bromohydrocinnamic Acid (VIII) crystallizes from benzene in small thick prisms melting at 161–162° with decomposition. By action of diazoethane on this acid, the ethyl ester (VII) is readily formed.

Anal. Subs., 6.140 mg.: CO_2, 8.49 mg.; H_2O, 2.16 mg. Calcd. for $C_{13}H_{16}O_5Br_2$: C, 37.87; H, 3.91. Found: C, 37.70; H, 3.94.

The methyl ester (IX) of the ethoxy acid (VIII) was obtained by the action of diazomethane on that acid and by crystallization of the methyl ester of the tribromo acid (II) from ethyl alcohol. It crystallizes readily from methyl alcohol or ether in rosets of firm needles melting at 138° with preliminary softening at 134°.

Anal. Subs., 6.167 mg.: CO_2, 8.98 mg.; H_2O, 2.29 mg. Calcd. for $C_{14}H_{18}O_5Br_2$: C, 39.44; H, 4.23. Found: C, 39.71; H, 4.15.

In marked contrast to the behavior of the dibromides of unsaturatated α-ketonic acids, which readily lose hydrogen bromide on heating or even spontaneously,[6] the tribromo acid above described did not lose hydrogen bromide to form an unsaturated acid under the usual conditions. It was recovered unchanged after heating at 100° and also after long heating in high-boiling solvents such as toluene, xylene and cymene. Action of potassium hydroxide in methyl alcoholic solution gave two products, a styrene derivative, as was to have been expected, and a small quantity of an acid, not however the corresponding unsaturated acid but the methoxy acid (IV). This same acid was formed by reaction of potassium acetate in methyl alcoholic solution.

1-Bromo-2-(2,4-dimethoxy-5-bromophenyl)-ethylene, $(CH_3O)_2BrC_6H_2CH{=}CHBr$ **(X).**—Five grams of the tribromo acid was stirred rapidly into 15 cc. of a saturated solution of potassium hydroxide in methyl alcohol. There was vigorous effervescence and a pasty solid separated. This was filtered, washed with a trace of alcohol and then repeatedly with water. The substance is readily soluble in the usual organic solvents. It separates from diluted methyl alcohol in clumps of fine white crystals melting at 67–68°. The yield was 80%.

Anal. Subs., 5.096 mg.: CO_2, 6.98 mg.; H_2O, 1.51 mg. Calcd. for $C_{10}H_{10}O_2Br_2$: C, 37.26; H, 3.10. Found: C, 37.35; H, 3.32.

The compound is very readily affected by the light. It rapidly takes on a rose pink color in diffused light and becomes black in a short time in bright sunlight. The aqueous washings from this substance on acidification yielded a small amount of the methoxy acid (IV). The styrene derivative (X) readily reacted further with bromine.

1,1-Dibromo-2-bromo-2-(2,4-dimethoxy-5-bromophenyl)-ethane, $(CH_3O)_2BrC_6H_2$-$CHBrCHBr_2$ **(XI).**—The substance separated from chloroform in quantitative yield as a slightly yellow powder, which after washing repeatedly with small amounts of cold methyl alcohol was colorless. It melts at 146° with slight effervescence.

Anal. Subs., 4.825 mg.: CO_2, 4.45 mg.; H_2O, 0.98 mg. Calcd. for $C_{10}H_{10}O_2Br_4$: C, 24.91; H, 2.09. Found: C, 25.15; H, 2.27.

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[6] Reimer, THIS JOURNAL, **48**, 2454 (1926); Reimer and Howard, *ibid.*, **50**, 2506 (1928).

This tetrabromo compound is perfectly stable when pure and does not change color on long standing. One of the four bromine atoms, presumably the one nearest the benzene ring, is very easily replaced by alkoxyl groups as in the case of the tribromo acid. On boiling the substance with methyl alcohol, in which it is only slightly soluble, a methoxy tribromo compound is formed.

1,1-Dibromo-2-methoxy-2-(2,4-dimethoxy-5-bromophenyl)-ethane, $(CH_3O)_2BrC_6H_2CH(OCH_5)CHBr_2$ **(XII)**.—The substance crystallizes from methyl alcohol or from ligroin in stiff prisms melting at 138–139°. The same substance was obtained by the action of potassium hydroxide in methyl alcoholic solution on the tetrabromo compound.

Anal. Subs., 4.965 mg.: CO_2, 5.55 mg.; H_2O, 1.27 mg. Calcd. for $C_{11}H_{13}O_3Br_3$: C, 30.48; H, 3.00. Found: C, 30.48; H, 2.86.

1,1-Dibromo-2-ethoxy-2-(2,4-dimethoxy-5-bromophenyl)-ethane, $(CH_3O)_2BrC_6H_2CH(OC_2H_5)CHBr_2$ **(XIII)**.—This substance is formed when the tetrabromo compound is boiled with ethyl alcohol. The product left after evaporation of the solvent was recrystallized from ligroin; melting point 117–120°.

Anal. Subs., 5.314 mg.: CO_2, 6.35 mg.; H_2O, 1.79 mg. Calcd. for $C_{12}H_{15}O_3Br_3$: C, 32.21; H, 3.36. Found: C, 32.59; H, 3.77.

Action of Bromine on the Esters of 2,4-Dimethoxycinnamic Acid.—Methyl 2,4-dimethoxycinnamate was prepared by Claisen condensation by the same procedure as for the ethyl ester, and by the action of diazomethane on the acid. Either of these methods is simpler than that of Tiemann and Will.[7] It is most conveniently purified by distillation under diminished pressure. The pale yellow oil which distils at 216° (20 mm.) solidifies on cooling and, after one crystallization from methyl alcohol, is obtained in stiff colorless needles melting at 87°. Reaction of bromine on this ester gave, in quantitative yield, the tribromo ester (II) already described.

The ethyl ester of 2,4-dimethoxycinnamic acid behaved in an entirely different manner on treatment with bromine. The bromine was rapidly decolorized and on evaporation of the chloroform used as solvent, a yellow granular solid was left. This, after washing with benzene, was found to melt at 110–132°, showing it to be a mixture, and preliminary analysis gave 43.4% of carbon instead of 32.9% calculated for the expected tribromide. After purification, the product gave analytical results agreeing with those of an aldehyde, $(CH_3O)_2BrC_6H_2CHO$. That the product has this formula was proved by its ready oxidation with ammoniacal silver nitrate solution to 2,4-dimethoxy-5-bromobenzoic acid and by the preparation of its semicarbazone.

2,4-Dimethoxy-5-bromobenzaldehyde (XIV).—The substance is most readily obtained in pure condition by boiling the crude product of the bromination reaction with water. It separates from aqueous solution in a mass of very fine shining needles, from alcohol in sturdy needles or from benzene in branching clumps of fine thread-like crystals resembling a fungus growth. These after standing for some time crumble to small rhombic crystals. The substance melts without decomposition, 134–138°.

Anal. Subs., 5.468 mg.: CO_2, 8.90 mg.; H_2O, 1.74 mg. Calcd. for $C_9H_9O_3Br$: C, 44.08; H, 3.67. Found: C, 44.38; H, 3.56.

The semicarbazone is a fine white granular solid, very slightly soluble in methyl alcohol. It decomposes at about 275°.

Anal. Subs., 5.04 mg.: CO_2, 7.43 mg.; H_2O, 1.77 mg. Calcd. for $C_{10}H_{12}O_3N_3Br$: C, 39.74; H, 3.97. Found: C, 40.20; H, 3.93.

Since the preliminary analysis of the bromination product of ethyl 2,4-dimethoxycinnamate showed the product to be almost exclusively made up of the aldehyde, the

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[7] Tiemann and Will, *Ber.*, **15**, 2079 (1882).

presence of the latter was attributed to water in the reagents which had presumably hydrolyzed the tribromo ethyl ester first formed in the reaction. The experiment was, therefore, repeated with carefully dried chloroform and bromine which had been distilled from phosphorus pentoxide. The product melted with decomposition over a long range, showing it to be probably a bromo addition compound but very impure. Repeated trials have not as yet given a pure substance. When this crude product was treated with water, a copious yield of the aldehyde was obtained.

When ethyl 2,4-dimethoxycinnamate (68–69°), prepared by the Claisen condensation, was distilled under diminished pressure, a yellow oil boiling at 219° (22 mm.) was obtained. This distillate solidified on cooling and, on crystallization from low boiling petroleum ether, separated in perfectly colorless needles melting at 61°. A mixture of this ester and the one previously used (68–69°) melted from 45–55°. Analysis proved it to be an isomeric form.

Anal. Subs., 0.1148: CO_2, 0.2777; H_2O, 0.0730. Calcd. for $C_{13}H_{16}O_4$: C, 66.10; H, 6.78. Found: C, 65.97; H, 7.05.

This isomeric ester on bromination with the usual laboratory reagents or with those that had been carefully dried gave, in quantitative yield, the ethyl ester of 2,4-dimethoxy-5-bromocinnamic acid dibromide (VI) previously described.

Summary

The bromination of 2,4-dimethoxycinnamic acid and its methyl and ethyl esters has been described. The acid differs from *p*-methoxycinnamic acid and from *o*-methoxycinnamic acid in the fact that addition of bromine is invariably accompanied by bromination in the ring and in the extraordinary ease of replacement of the β-bromine atom in the bromination products by alkoxyl groups. The two isomeric ethyl esters of the acid give different products on bromination.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE HALL LABORATORY OF CHEMISTRY, WESLEYAN UNIVERSITY]

BENZYLPINACOLONES AND THEIR REDUCTION PRODUCTS. I

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Sodamide syntheses,[1] in ether, with pinacolone and benzyl chloride yielded mono- and dibenzylpinacolones, $C_6H_5CH_2CH_2COC(CH_3)_3$, $(C_6H_5CH_2)_2CHCOC(CH_3)_3$. Benzylpinacolone has been described by one of us[2] but an improved method of preparation is reported here.

Dibenzylpinacolone in toluene reacted with sodamide and benzyl chloride producing tribenzylpinacolone, $(C_6H_5CH_2)_3CCOC(CH_3)_3$. Good yields resulted in this synthesis only when the original ketone, a readily purified crystalline solid, was distilled just prior to the runs. Possibly this is due to a higher proportion of an enolic modification in the freshly distilled material.

[1] Haller and Bauer, *Ann. chim.*, [8] **29**, 313 (1913).

[2] Hill, Spear and Lachowicz, THIS JOURNAL, **45**, 1557 (1923).