antimony chloride was added 20 g. of granulated sodium. The reaction was initiated by heating, after which it became necessary to cool the mixture from time to time. It was filtered while warm, concentrated and mixed with an equal volume of alcohol. The product was dissolved in warm benzene–alcohol mixture. Small glittering plates separated, m. p. 208–209°, yield nearly 33 g.

Anal. Calcd. for $C_{36}H_{27}Sb$: Sb, 21.0. Found: Sb, 20.9.

Tri-*o*-biphenylstibine Dibromide.—Slightly less than the equivalent amount of bromine was mixed with 2 g. of III dissolved in 20 cc. of chloroform. Then petroleum ether was added and the mixture concentrated by distillation until crystallization started. Needle-like clusters appeared, m. p. 152–154°.

Anal. Calcd. for $C_{36}H_{27}SbBr_2 \cdot CHCl_3$: Br, 18.6. Found: Br, 18.8.

The dichloride, prepared in a similar manner, melted at 174–175° but the iodide did not form.

Tri-*o*-biphenylstibine Hydroxide.—Alcoholic ammonia changed the dibromide into a substance separating from alcohol as a powder, m. p. 243–244°.

Anal. Calcd. for $C_{36}H_{29}SbO_2$: Sb, 19.8. Found: Sb, 20.1.

Mono-biphenylstibine Hydroxychloride.[2]—A mixture of 10 g. of tri-biphenylstibine and 8 g. of antimony chloride in 20 cc. of xylene was heated to 220–250° in a sealed tube for one hundred hours. The residue after repeated crystallizations from benzene produced lustrous plates, m. p. 201–202°.

Anal. Calcd. for $C_{12}H_{10}OClSb$: Cl, 10.8; Sb, 37.3. Found: Cl, 10.9; Sb, 37.0.

No traces were found of dibiphenylstibine monochloride.

Mono-biphenylstibine Oxide.—It was obtained in clusters of tiny slender needles by the action of alcoholic ammonia on the hydroxy chloride, m. p. 195–196°.

Anal. Calcd. for $C_{12}H_9OSb$: Sb, 41.9. Found: Sb, 41.5.

Mono-biphenylstibinic Acid.—Chlorination of the basic salt produced a sirupy mixture that was changed into the acid by stirring with water. The resulting white powder was washed thoroughly with cold alcohol, m. p. well above 300°.

Anal. Calcd. for $C_{12}H_{11}SbO_3$: Sb, 37.5. Found: Sb, 37.2.

Summary

Tri-*o*-biphenylphosphine, arsine and stibine have been prepared by the Fittig reaction and their chemical properties investigated.

MEDFORD, MASS. RECEIVED JULY 2, 1940

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[2] Michaelis and Genzken, *Ann.*, **242**, 164 (1887), observed that partial hydrolysis took place in the crystallization of mono-*p*-tolylstibine diiodide from moist chloroform.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BARNARD COLLEGE]

Addition Reactions of Unsaturated *alpha*-Ketonic Acids. VI

BY MARIE REIMER AND ELISE TOBIN

The study of the influence of ring substitution on the reactions of the side-chain of benzalpyruvic acid[1] has been continued with a bromine atom in the *para* position in the benzene ring. As was to have been expected, the influence of the *p*-bromine atom is markedly different from that of the *p*-methoxy[2] and the *p*-methyl[1] groups. Unlike these acids, *p*-bromobenzalpyruvic acid and its esters are sensitive to light, particularly the ethyl ester which polymerizes readily even in the diffused light of the laboratory. In this respect the acid resembles most closely the unsubstituted benzalpyruvic acid. The stability of addition products is greatly increased, the acid forming a stable hydrate so readily that it takes up moisture from the air and a dibromide far less easily decomposed than any other met with in this study of unsaturated α-ketonic acids. There are no brilliant color reactions in sulfuric acid solution as with the methoxy substituted compounds.

The most interesting result of these experiments arises from the unusual stability of the dibromo addition product. The dibromides of the series of six substituted benzalpyruvic acids so far investigated have been unstable, decomposing on standing and losing hydrogen bromide rapidly on contact with moisture. The dibromide here described is not changed after months of exposure to the air and even combines with water to form a hydrate under appropriate conditions. This stability has made it possible to eliminate hydrogen bromide under controlled and reproducible conditions which has led to the preparation of isomeric unsaturated bromo acids. These acids are conspicuously different in properties. The one obtained by heating the dibromide with water has the unusual characteristics of the analogous compounds of the series, prepared in the same way. The compound is pure white in spite of the fact that it has supposedly the same conjugated system as the original bright yellow acid

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[1] Reimer and Chase, THIS JOURNAL, **60**, 2469 (1938).

[2] Reimer, *ibid.*, **48**, 2454 (1926).

$$\underset{\text{yellow}}{\text{4-BrC}_6\text{H}_4\text{CH=CHCOCOOH}} \longrightarrow \text{4-BrC}_6\text{H}_4\text{CHBrCHBrCOCOOH} \longrightarrow \underset{\text{white}}{\text{4-BrC}_6\text{H}_4\text{CH=CBrCOCOOH}}$$

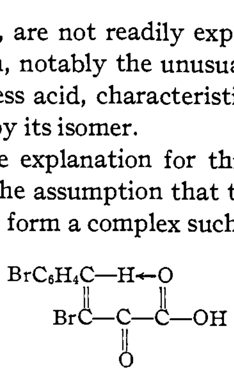
It does not react with methyl alcohol, saturated with hydrogen chloride, although no such hindrance is to be expected; it is readily methylated, however, by diazomethane. Its colorless benzene solution changes in diffused light to a brilliant greenish-yellow, the colored product polymerizing in direct sunlight.

The isomeric acid is obtained from the dibromide by slow elimination of hydrogen bromide in dilute alkaline solution. The acid is pale yellow; it gives in a few moments a quantitative yield of ester when treated with cold methanol saturated with hydrogen chloride; its solution in benzene at room temperature shows no change in color after many weeks of exposure to diffused light nor has any polymerization in direct sunlight been detected.

The melting points of these two isomeric compounds lie very close together but the crystal forms are so different that the two readily can be distinguished in minute quantity as shown by the accompanying micro drawings. The colorless acid is so much more soluble in benzene than its isomer that the two can be separated by making use of this difference.

Having obtained these two isomeric compounds in pure condition it was found that practically quantitative transformation of one to the other readily could be accomplished. The change of the colorless to the pale yellow acid is brought about by shaking the colorless acid with a dilute solution of sodium carbonate. The white sodium derivative of the colorless acid formed dissolves slowly to give a clear, pale yellow solution which, on acidification, deposits the yellow acid. The reverse change is accomplished by heating the yellow acid at its melting point for a few minutes. This ease of transformation in one direction or the other at will, and particularly the practically quantitative nature of the change in either direction, is certainly not what one would expect of *cis–trans* forms nor do these compounds undergo the transformation which would be expected if this were a case of geometrical isomerism: there is no change from one acid to the other when benzene solutions are exposed to light with or without the presence of iodine. Differences between the isomers, also, are not readily explained by a *cis–trans* relation, notably the unusual characteristics of the colorless acid, characteristics not shared in any respect by its isomer.

A plausible explanation for this behavior may be found in the assumption that the colorless acid is chelated to form a complex such as



the hydrogen attached to ethylenic carbon forming a hydrogen bond. With a sufficiently stable chelate ring such a structure would account for the loss of color, since the original conjugation is broken. Esterification with alcohol would not be expected as the carbonyl oxygen of the carboxyl group, which should take part in such a reaction, is otherwise engaged; this would not, however, interfere with the reaction of diazomethane. The brilliant, greenish-yellow color assumed by benzene solutions in diffused light is like that of many free radicals and may be due to a drift of electrons in the direction of the unsaturated carbon, concentrating there loosely bound electrons readily activated by light, a condition which could lead to polymerization in direct sunlight. The yellow acid, which behaves normally, would have the normal, open-chain formula and isomerization of the colorless to the pale yellow acid would be, then, simply the slow opening of the chelate ring in alkaline solution to the open chain acid; the reverse change, which is rapid, the closing to the stable, chelate ring at increased temperature. Having such a relation in mind other differences between the acids can be accounted for readily: that the colorless acid is ten times as soluble in benzene but only one-eighth as soluble in water as the yellow acid; that its sodium derivative is more soluble in alcohol than in water; that, whereas the yellow acid is rapidly oxidized in alcoholic solution with hydrogen peroxide to the corresponding cinnamic acid, the colorless acid is not affected at all under the same conditions, showing again that the α-ketocarboxyl group is different in the two compounds, being unreactive in the stable, chelate form. That the chelate ring suggested would be a stable one is assured by the fact that it has a ring of six valence angles, two between single valences, four between a single and a double link, giving a ring entirely without strain, as pointed out by Sidgwick[3] in another connection. As the existence of the colorless compound is conditioned by the bromine atom of the side chain, no such compound existing when the side chain is unbrominated, its stability must also be attributed, in part at least, to the presence of bromine attached to unsaturated carbon.

Until recently,[4] in the majority of cases of hydrogen bonding described in the literature, the bonded hydrogen has been that of an hydroxyl group[5] and the criteria used to establish this condition have been changes in properties, particularly physical properties, due to the loss of the hydroxyl group as such. Such criteria are of course useless here. The ultraviolet absorption spectra[6] of the two acids, however, show differences unlike those to be expected of *cis–trans* isomers in which the graphs are similar but shifted in position.[7] The accompanying graphs of the ultraviolet absorption of the two isomeric acids under discussion show differences of structural rather than of space isomerism. The marked selective absorption of the pale yellow acid is that to be expected of a highly conjugated system.

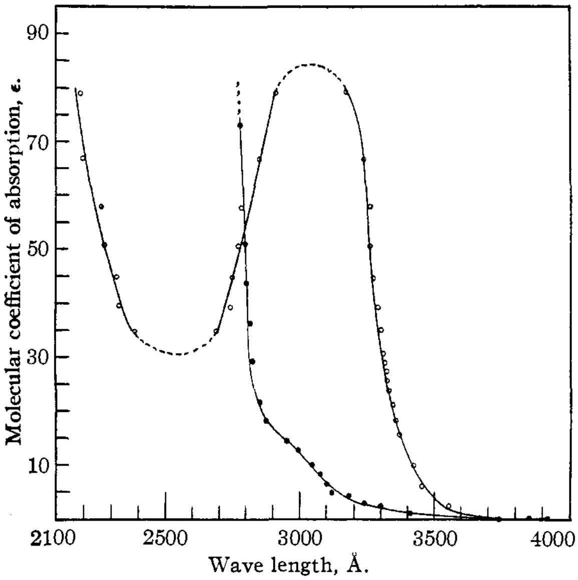


Fig. 1.—○—○—○—, Pale yellow acid (141–143°) in alcohol; -●—●—●-, colorless acid (144–145°) in alcohol.

The difference in chemical and physical characteristics of this pair of isomers, therefore, is in agreement with a chelated form for the colorless, an open chain form for the yellow acid. Further study of the behavior of this pair of acids, and of other analogous isomeric compounds, is in progress.

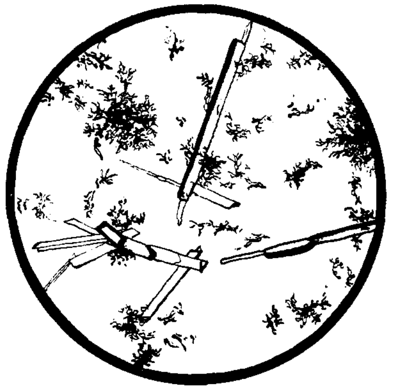


Fig. 2.—Needles of hydrated yellow acid with fine crystals of the colorless acid (× 30).

Fig. 3.—Hexagonal crystals of the hydrate of the colorless acid with hydrated needles of the yellow acid and some colorless acid (× 30).

Experimental Part

4-Bromobenzalpyruvic Acid, $4\text{-}BrC_6H_4CH{=}CHCOCOOH$, (143°).—The *p*-bromobenzaldehyde needed for the preparation of this acid was obtained in nearly 80% yield from *p*-bromotoluene by the method of Adams and Volweiler.[8] Twelve grams of the aldehyde was stirred into 36.6 ml. of a 25% solution of potassium hydroxide in methanol and to this mixture 5.8 g. of pyruvic acid was added rapidly enough so that the heat of reaction was suf-

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[3] Sidgwick, *J. Chem. Soc.*, **127**, 907 (1926).

[4] G. F. Zellhoefer, *Ind. Eng. Chem.*, **29**, 584 (1937); Copley, Zellhoefer and Marvel, THIS JOURNAL, **61**, 3550 (1939); Copley, Marvel and Ginsberg, *ibid.*, **61**, 3161 (1939); Copley and Holley, *ibid.*, **61**, 1599 (1939); Gordy and Stanford, *ibid.*, **62**, 497 (1940). This paper contains references to much of the earlier literature.

[5] Sidgwick, "The Electronic Theory of Valency," Oxford University Press, New York, N. Y., 1929; Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940; Blatt and Russell, THIS JOURNAL, **58**, 1903 (1936); Blatt, *ibid.*, **60**, 205 (1938); Lassettre, *Chem. Rev.*, **20**, 259 (1937); Hilbert, Wulf, Hendricks and Liddel, THIS JOURNAL, **58**, 548, 1991 (1936).

[6] We are indebted to Mr. R. H. Hay, of the Physics Department of Columbia University, for these determinations.

[7] Smakula, *Z. physik. Chem.*, **B25**, 90 (1934); Hahn and Evans, THIS JOURNAL, **50**, 806 (1928); Hahn and Dyer, *ibid.*, **52**, 2505 (1930).

[8] Adams and Volweiler, *ibid.*, **40**, 1738 (1918).

ficient to keep the aldehyde in molten condition. By rapid stirring good contact was maintained and yields as high as 97% of potassium bromobenzalpyruvate were obtained. If the acid is added too rapidly much of the aldehyde is oxidized at the increased temperature and the yield of condensation product correspondingly lowered. The yellow granular salt, washed with alcohol and then with ether, was dissolved in water and the cooled solution acidified, giving yields of 80 to 90% of the unsaturated acid. After standing for five days over sulfuric acid the substance was crystallized from dried benzene. Two forms of crystals separated, a lower-melting hydrated form, and the pure acid. As longer standing over sulfuric acid dehydrated the acid very slowly, it was heated for at least one hour at 100°. The opaque crystals separated from boiling benzene in flat, lemon-yellow needles melting at 143°.

Anal. Calcd. for $C_{10}H_7O_3Br$: C, 47.06; H, 2.77; Br, 31.34. Found: C, 47.44; H, 2.78; Br, 31.50.

The dry acid is readily soluble in the usual organic solvents. It separates slowly from boiling water in stiff, hydrated needles which melt, with effervescence, around 120°. When the dry acid is left exposed to the air the melting point is gradually lowered and, after a few days, the hydration is complete.

Anal. Calcd. for $C_{10}H_7O_3Br \cdot H_2O$: C, 43.95; H, 3.29. Found: C, 44.13; H, 3.33.

The methyl ester, prepared by dissolving the dry acid in methanol saturated with hydrogen chloride, separates almost at once in clumps of pale yellow, soft, fine needles. After crystallization from methanol it melts at 122°.

Anal. Calcd. for $C_{11}H_9O_3Br$: C, 49.07; H, 3.39. Found: C, 48.98; H, 3.58.

The ethyl ester was prepared by a like procedure from a warmed solution. It crystallizes from hot ethyl alcohol in stiff bright yellow needles, or more slowly in flat plates, both forms melting at 77°.

Anal. Calcd. for $C_{12}H_{11}O_3Br$: C, 50.88; H, 3.88. Found: C, 51.20; H, 4.07.

The crystals that had crept up the sides of the beaker during this purification of the ethyl ester were found, after washing with alcohol, to be pure white and to melt at 167–168°. This is a dimeric form of the ester to be described later. The acid and the methyl ester change much more slowly in the light.

Oxidation of *p*-bromobenzalpyruvic acid with hydrogen peroxide takes place rapidly. When the acid, exactly neutralized by a 0.1% solution of sodium carbonate was treated with a slight excess of hydrogen peroxide (13 vols.) a solid began to separate in less than a minute and the yellow color of the solution faded rapidly. After one-half hour the mixture was filtered. The solid proved to be almost pure *p*-bromocinnamic acid, melting at 255–257°, identified by melting with an authentic sample prepared by the Perkin synthesis. A further quantity was obtained from the filtrate.

4-Bromobenzalpyruvic Acid Dibromide, $4\text{-}BrC_6H_4\text{-}CHBrCHBrCOCOOH$ (133°).—When the dried acid (143°) was suspended in dried chloroform and bromine added to the well cooled mixture, reaction took place slowly. After one molecular proportion of bromine had been added the red-brown mixture was shaken until clear and nearly colorless and a stream of dry air drawn through rapidly. The crystalline dibromide was washed with a few cubic centimeters of warm benzene and crystallized from a small volume of boiling benzene or from hot benzene to which an equal volume of high boiling ligroin had been added. Yields of 80% were obtained if the mixture was kept cold during bromination. The compound separated in hard clumps of fine needles melting at 133° with slow effervescence and browning. It is not affected by light nor by long exposure to the air.

Anal. Calcd. for $C_{10}H_7O_3Br_3$: C, 28.91; H, 1.71. Found: C, 29.31; H, 1.65.

The benzene residues from the washing and crystallization of the dibromide deposit slowly a heavy, red-brown oil to be discussed later.

The methyl ester, prepared from carefully purified dibromide by action of diazomethane in ether or with methanol and hydrogen chloride, crystallizes from methanol in shining stiff white needles, melting after several recrystallizations, without effervescence, at 113°.

Anal. Calcd. for $C_{11}H_9O_3Br_3$: C, 30.76; H, 2.09. Found: C, 30.79; H, 2.10.

β-Bromo-4-bromobenzalpyruvic Acid, 144–145°.—When the purified dibromide just described was boiled with water the filtered solution deposited slowly, on cooling, fine, pure white, feathery crystals of an unsaturated bromo acid. It separates from boiling benzene in soft, opaque needles which melt with browning and slow effervescence at 144–145°.

Anal. Calcd. for $C_{10}H_6O_3Br_2$: C, 35.92; H, 1.79. Found: C, 36.01; H, 2.05.

The acid is readily soluble in alcohol, benzene, glacial acetic acid and ether. The saturated solutions in benzene, after standing for several hours, deposit a mass of fine shining needles of the solvated acid which lose benzene rapidly on exposure to the air. In freshly prepared solutions the solubility of the acid was found to be: 4 g. in 100 ml. of benzene (21°); 0.03 g. in 100 ml. of water (23°). Benzene solutions on standing in diffused light become a brilliant greenish-yellow. From these solutions, exposed to bright sunlight, colorless, high molecular compounds separate.

The methyl ester of this acid cannot be prepared by long standing nor by boiling in methanol saturated with hydrogen chloride. It is readily obtained by action of diazomethane in ether from which it separates in fine, shining, colorless needles, melting at 101°.

Anal. Calcd. for $C_{11}H_8O_3Br_2$: C, 37.92; H, 2.29. Found: C, 37.94; H, 2.33.

The hydrate of the unsaturated bromo acid was formed by boiling the acid for several hours in water. The flat, transparent hexagonal plates formed on cooling were separated mechanically from unchanged acid, some bromobenzaldehyde and oily decomposition products. Methanol saturated with hydrogen chloride did not react with these crystals but excess of diazomethane gave a good yield of the ester melting at 101°.

Anal. Calcd. for $C_{10}H_6O_3Br_2 \cdot H_2O$: C, 34.08; H, 2.29. Found: C, 33.92; H, 2.26.

The hydrated crystals slowly disintegrate to give the colorless acid.

The Isomeric β-Bromo-4-bromobenzalpyruvic Acid, 141–143°.—One gram of carefully purified *p*-bromobenzalpyruvic acid dibromide (133°) was shaken with 250 ml. of 1% sodium carbonate solution for about two hours. The resulting clear, pale yellow liquid, on treatment with dilute hydrochloric acid, set to a deep cream-colored gel. When left in contact with the acid solution for twenty-four hours or longer, this changed to a quantity of shining needles, which rapidly became opaque on exposure to the air. The dry acid was purified by crystallization from benzene from which it separates in clumps of pale yellow, silky needles, melting at 141–143°.

Anal. Calcd. for $C_{10}H_6O_3Br_2$: C, 35.92; H, 1.79. Found: C, 36.04; H, 1.97

The acid is readily soluble in alcohol, ether and glacial acetic acid. The solubilities in benzene and in water are seen to be very different from those of the isomeric acid: 0.42 g. in 100 ml. of benzene (21°); 0.24 g. in 100 ml. of water (23°). A benzene solution of this pale yellow acid shows no change in color on long exposure to diffused light nor to direct sunlight. Benzene solutions, on boiling, however, take on a bright, greenish-yellow color. The dry acid is sensitive to light, changing rapidly in bright light to a pinkish-brown color. This reaction has not been investigated.

The methyl ester was obtained readily, in quantitative yield, by dissolving the acid in cold methanol saturated with hydrogen chloride. The ester separated from this solution only when practically all the alcohol had evaporated, indicating combination with the solvent. It crystallizes from a small volume of boiling hexane in rosets of fine pale yellow needles melting at 75°. It also can be readily prepared by diazomethane in ether.

Anal. Calcd. for $C_{11}H_8O_3Br_2$: C, 37.92; H, 2.29. Found: C, 38.19; H, 2.51.

Oxidation of the acid with a slight excess of hydrogen peroxide (13 vols.) in 2% sodium carbonate solution began at once and proceeded rapidly. After two hours the colorless solution was acidified. The pure white precipitate was crystallized from a large volume of boiling water from which it separated in fine stiff needles, melting at 221°. The acid is not readily soluble in any of the usual organic solvents at room temperature, but soluble in boiling benzene from which it separates in shining plates containing solvent, which it loses very slowly, from boiling acetone and glacial acetic acid. The compound is unsaturated and analysis shows it to be a bromo-*p*-bromocinnamic acid.

Anal. Calcd. for $C_9H_6O_2Br_2$: C, 35.29; H, 1.96. Found: C, 35.11; H, 2.06.

The methyl ester of this acid was prepared by the diazo methane reaction and by methanol and hydrogen chloride. It can be crystallized from a small volume of methanol by adding water to the alcoholic solution until a faint cloudiness persists. It separates in shining flat plates, melting at 72°.

Anal. Calcd. for $C_{10}H_8O_2Br_2$: C, 37.50; H, 2.50. Found: C, 37.59; H, 2.36.

Transformation of the yellow to the colorless acid can be accomplished by heating the former just above its melting point for a few minutes. As there is considerable decomposition at this temperature, a better procedure is to surround the sample with a bath of boiling xylene (138–140°) for about fifteen minutes. The solution of the product in boiling water deposits on cooling the characteristic feathery needles of the colorless acid. The ready isomerization at this temperature accounts for the fact that the two acids have nearly the same melting point. It would be reasonable to expect the open chain acid to have a higher melting point than its chelated isomer.[9] When 0.5 g. of the yellow acid was boiled with 75 ml. of water for an hour or more, and the solution cooled slowly, the characteristic hexagonal crystals of the hydrate of the colorless acid were formed in quantity. These soften at 90° and melt, with effervescence, around 120°. The form of the crystals, the analysis and the action of excess of diazomethane to give the ester melting at 101°, prove this substance to be the same as that obtained from the colorless acid on longer boiling. After standing over sulfuric acid the colorless acid was obtained. This same change to the hydrate of the colorless acid takes place when the yellow acid is left for several months suspended in cold water in the dark.

The reverse transformation of the colorless to the pale yellow acid is as readily brought about. When 1 g. of colorless acid was shaken with 50 ml. of 2% sodium carbonate solution, it dissolved rapidly and a mass of shining, plate-like crystals of a sodium derivative separated at once. These were filtered, washed with ice water, since they were found to be extremely soluble in alcohol, and analyzed.

Anal. Calcd. for $C_{10}H_5O_3Br_2Na$: Na, 6.46. Found: Na, 6.51.

These crystals are soluble in a large volume of water, the solution depositing the colorless acid on acidification. This acid was obtained also from the sodium carbonate solution from which the crystals had been filtered, if acidified at once. When the sodium derivative was left in contact with the alkaline solution it dissolved after four or five days, more rapidly with continued shaking. The solution, from which a few needles of the hydrolytic product, *p*-bromobenzaldehyde, were filtered, deposited on acidification the pure yellow acid.

This ready transformation of the colorless to the yellow acid in alkaline solution accounts for the fact that oxidation of the colorless acid with hydrogen peroxide in sodium carbonate solution gives the same bromocinnamic acid as was obtained from the yellow acid. The fact that this oxidation takes several days for completion while that of the yellow acid is complete in an hour or less would seem to show that it is the yellow, not the colorless, acid that is oxidized. This is substantiated by treatment of the two acids in alcoholic solution with hydrogen peroxide. After standing overnight the solution of the yellow acid had deposited a good yield of the bromocinnamic acid. The colorless acid was not affected after many days in the alcoholic hydrogen peroxide solution but crystallized unchanged on evaporation of the solvent.

α-Bromo-4-bromostyrene, 4-$BrC_6H_4CH{=}CHBr$.—The *p*-bromobenzalpyruvic acid dibromide, from which these two isomeric acids were obtained, was purified by crystallization from benzene. The benzene residues from the crystallization deposited a heavy, reddish oil, evidently a mixture from which no pure substance has been obtained. That

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(9) W. Baker, *J. Chem. Soc.*, 1684 (1934).

an isomeric dibromide is present in this oil is shown by its behavior. When treated with a 2% solution of sodium carbonate the oil became cloudy and a white solid separated rapidly. This was washed repeatedly with sodium carbonate solution and with water. The neutral, unsaturated product, insoluble in water but readily soluble in organic solvents, was purified by crystallization from a small volume of boiling glacial acetic acid to which a few drops of water were added. The substance separated in sharp, colorless needles, melting at 81°. It was proved by analysis and by oxidation in cold permanganate solution to *p*-bromobenzoic acid, to be α-bromo-4-bromostyrene.

Anal. Calcd. for $C_8H_6Br_2$: C, 36.64; H, 2.29. Found: C, 36.09; H, 2.33.

The sodium carbonate filtrates deposited the yellow acid on acidification. The fact that no styrene derivative was formed when the pure, crystalline dibromide was similarly treated, shows that the red, oily residues contain a diastereoisomeric dibromide. After standing for several weeks at room temperature the oil had changed to the stable, solid form.

When the pure, crystalline dibromide was shaken with a 10% solution of sodium carbonate a small amount of a solid, similar in appearance to the styrene derivative just described, separated from the solution. It softens, however, at 100° and melts at 120° with vigorous effervescence. Analysis proves it to be a hydrate of the dibromide.

Anal. Calcd. for $C_{10}H_7O_3Br_3H_2O$: C, 27.71; H, 2.09. Found: C, 27.34; H, 2.10.

All of the ketonic acids here described dissolve in concentrated sulfuric acid to give an orange solution slowly changing to a persistent dark brown color. The brilliant color changes characteristic of the methoxy substituted acids do not take place.

Summary

4-Bromobenzalpyruvic acid was prepared for the purpose of studying the influence on the side-chain of the *p*-bromine atom as compared with that of other *para* substituents. The unusual stability of the dibromo addition product has made possible the preparation of isomeric β-bromo-4-bromobenzalpyruvic acids, believed to be chelated and open-chain isomers.

New York, N. Y. Received June 26, 1940

[Contribution from the Bureau of Entomology and Plant Quarantine, U. S. Department of Agriculture]

The Non-crystalline Constituents of *Tephrosia virginiana* Roots

By Lyle D. Goodhue and H. L. Haller

The increasing demand for insecticides, such as rotenone and related compounds, that are nontoxic to man has intensified the search for new sources of these materials. The isolation of rotenone by Clark[1] from the roots of (*Cracca*) *Tephrosia virginiana* L., the most abundant species of *Tephrosia* indigenous to the United States, has stimulated interest in the development of a domestic source of this group of insecticides. Analytical studies[2] of samples of this plant, commonly known as devil's shoestring, have shown considerable variation in the amount of the insecticidal constituents, but recent selective breeding experiments[3] now make it possible to produce a root of uniformly higher quality. These new varieties are now available in limited amounts and have permitted further studies on the chemical constituents. This paper reports the results of such an investigation.

The extractives from a sample of root that analyzed 2.4% rotenone and 7.4% total extractives was divided into four fractions, namely, rotenone, alkali-soluble portion, neutral resin, and oil. Except for rotenone these fractions are for the most part noncrystalline mixtures.

The alkali-soluble portion, which was removed from an ether solution of the extractives with 5% potassium hydroxide, consists mainly of phenolic substances. In addition to the usual dehydro compounds and tephrosin that separate at this stage, a new substance having a melting point of 76° was isolated. Although it appeared in this fraction, the purified compound is not soluble in aqueous alkali. Attempts to isolate other crystalline substances or to prepare crystalline derivatives from this fraction were unsuccessful.

The neutral-resin fraction contains deguelin, which is easily obtained in the racemic form by treatment of the resin with dilute methanolic alkali. Although deguelin has been found in other species of *Tephrosia*, it has not previously been isolated from *T. virginiana*. Two other crystalline compounds also have been isolated by adsorption on activated carbon. One is an orange-

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[1] Clark, *Science*, **77** (n. s.), 311 (1933).

[2] Jones, Campbell and Sullivan, *Soap*, **11**, [9] 99 (1935).

[3] The material used in these studies was furnished by G. A. Russell, of the Bureau of Plant Industry, U. S. Department of Agriculture, and V. A. Little, of the Texas Agricultural Experiment Station, for whose coöperation we wish to express our appreciation.