[CONTRIBUTION FROM JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Reaction of Hydrazoic Acid with Cinnamic Acids

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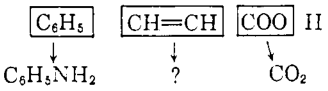
Received December 3, 1958

3-[*p*-Methoxyphenyl]-2-phenylacrylic acid yields *p*-anisidine, phenylacetaldehyde and *p*-methoxybenzyl phenyl ketone on treatment with hydrazoic acid. Cinnamylidene acetic acid under similar conditions gives aniline and benzaldehyde. These products may arise by addition of hydrazoic acid both to the olefinic bonds and to the carboxyl carbonyl group, followed by rearrangements.

Hydrazoic acid and cinnamic acid have been reported to react in a sulfuric acid–chloroform medium to give, after neutralization, aniline, phenylacetaldehyde, carbon dioxide, nitrogen, and ammonia.[1] The formation of aniline from cinnamic acid leaves two carbons unaccounted for in the isolated products, barring the unlikely possibility that they were oxidized to carbon dioxide.



$$\begin{array}{ccc}\boxed{C_6H_5} & \boxed{CH{=}CH} & \boxed{COO}\,H\\ \downarrow & \downarrow & \searrow\\ C_6H_5NH_2 & ? & CO_2\end{array}$$

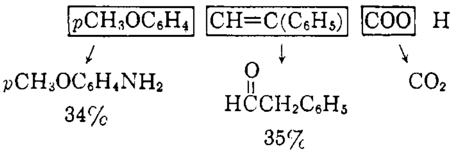
The phenylacetaldehyde has been suggested as being derived from styrylamine formed *via* the usual mechanism for the Schmidt reaction.[2]

$$C_6H_5CH{=}CHCOOH \xrightarrow[-CO_2]{HN_3} C_6H_5CH{=}CHNH_2 \rightleftarrows$$
$$C_6H_5CH_2CH{=}NH \xrightarrow{H_2O} C_6H_5CH_2CHO + NH_3$$

Our attempts to isolate a two-carbon fragment from the reaction were in vain. Under the reaction conditions the two-carbon fragment may have yielded the tar which was always found.

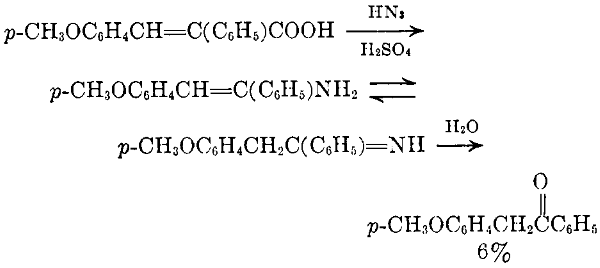
Finding a larger fragment than a two-carbon one might be more successful and, accordingly, the reaction of 3-[*p*-methoxyphenyl]-2-phenylacrylic acid with hydrazoic acid was studied. In this acid, an eight-carbon fragment (—CH=CC_6H_5—) corresponds to the two-carbon one (—CH=CH—) in cinnamic acid.

The reaction of this substituted acrylic acid with hydrazoic acid gave phenylacetaldehyde, an eight-carbon compound which could only have come from the cinnamic acid side chain. Other products were *p*-anisidine and *p*-methoxybenzyl phenyl ketone(I).



$$\begin{array}{ccc}\boxed{pCH_3OC_6H_4} & \boxed{CH{=}C(C_6H_5)} & \boxed{COO}\,H\\ \swarrow & \downarrow & \searrow\\ \underset{34\%}{pCH_3OC_6H_4NH_2} & \underset{35\%}{H\overset{\overset{O}{\|}}{C}CH_2C_6H_5} & CO_2\end{array}$$

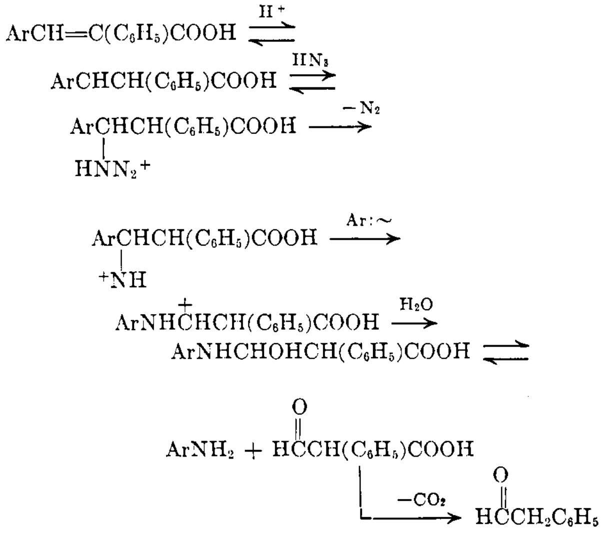
Average yields of *p*-anisidine and phenylacetaldehyde were roughly the same. The *p*-methoxybenzyl phenyl ketone apparently was formed in the same way as the phenylacetaldehyde from cinnamic acid itself.



$$p\text{-}CH_3OC_6H_4CH{=}C(C_6H_5)COOH \xrightarrow[H_2SO_4]{HN_3}$$
$$p\text{-}CH_3OC_6H_4CH{=}C(C_6H_5)NH_2 \rightleftarrows$$
$$p\text{-}CH_3OC_6H_4CH_2C(C_6H_5){=}NH \xrightarrow{H_2O}$$
$$\underset{6\%}{p\text{-}CH_3OC_6H_4CH_2\overset{\overset{O}{\|}}{C}C_6H_5}$$

I

The products (other than the *p*-methoxybenzy phenyl ketone) from 3-[*p*-methoxyphenyl]-2-phenylacrylic acid may be produced by addition of hydrazoic acid to the carbon-carbon double bond, followed by loss of nitrogen and a rearrangement of the *p*-methoxyphenyl group to positive nitrogen. The "missing" two-carbon fragment from cinnamic acid would be predicted to be acetaldehyde which polymerizes in the strong acid used for the reaction.



$$ArCH{=}C(C_6H_5)COOH \overset{H^+}{\rightleftarrows}$$
$$ArCHCH(C_6H_5)COOH \overset{HN_3}{\rightleftarrows}$$
$$Ar\underset{HNN_2^+}{\underset{|}{C}}HCH(C_6H_5)COOH \xrightarrow{-N_2}$$
$$Ar\underset{+NH}{\underset{|}{C}}HCH(C_6H_5)COOH \xrightarrow{Ar:\sim}$$
$$Ar\overset{+}{N}HCHCH(C_6H_5)COOH \xrightarrow{H_2O}$$
$$ArNHCHOHCH(C_6H_5)COOH \rightleftarrows$$
$$ArNH_2 + H\overset{\overset{O}{\|}}{C}CH(C_6H_5)COOH \xrightarrow{-CO_2} H\overset{\overset{O}{\|}}{C}CH_2C_6H_5$$

Nothing is known about when the decarboxylation step occurs. It may have occurred earlier than shown.

Addition of hydrazoic acid to the carbon-carbon double bond in cinnamic acids has an analogy in

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(1) M. Osterlin, *Angew. Chem.*, **45**, 536 (1932).

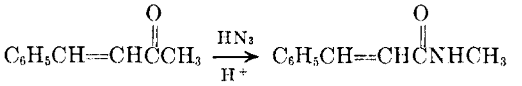
(2) H. Wolff, *Org. Reactions, III,* 307 (1947).

the addition of hydrazoic acid to olefins.[3] For example, 1,1-diphenylethylene gives acetophenone and aniline.[4]

The *p*-anisyl group has been shown to have a high migration aptitude in the Schmidt reaction of olefins.[5] Extensive rearrangements, presumably involving carbonium ions, have been observed with triethylacetic acid.[6]

In some cases, azides are formed from olefins or acetylenes and hydrazoic acid.[7] In strong acid azides are decomposed with loss of nitrogen and rearrangement.[8] It is possible that an azide could be a transient intermediate in our reaction.

It is interesting that cyclopropyl styryl ketone[9] and benzalacetone[10] apparently yield no products derived by addition of hydrazoic acid to the olefinic bond in strong acid.



$$C_6H_5CH{=}CH\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow[H^+]{HN_3} C_6H_5CH{=}CH\overset{\overset{O}{\|}}{C}NHCH_3$$

Perhaps in the acids a carboxyl group or a protonated carboxyl group is stabilized enough by resonance so that addition of hydrazoic acid may go elsewhere (*i.e.*, to a carbon-carbon double bond).

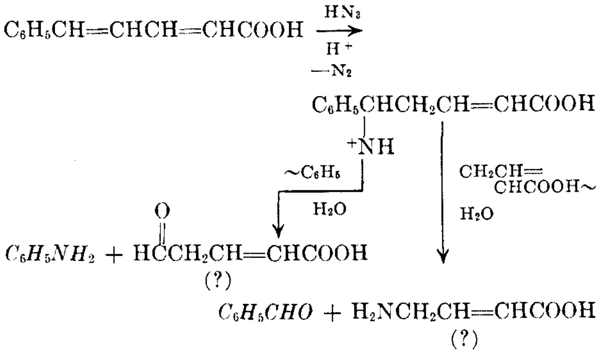
Anethole dibromide on treatment with hydrazoic acid yields *p*-anisidine and α-bromopropionaldehyde, presumably by displacement of the α-bromine by hydrazoic acid followed by migration of the *p*-methoxyphenyl group.[2]

A strong acid is required in the Schmidt reaction of α,β-unsaturated acids. Use of hydrochloric or phosphoric acids with cinnamic acid was unsuccessful. Cinnamic acid is reported not to react with hydrazoic acid in refluxing glacial acetic acid.[7b] Polyphosphoric acid did yield some reaction. The latter has been used with good results in the Schmidt reaction of ketones.[11]

Cinnamylidene acetic acid with hydrazoic acid gave aniline, benzaldehyde, nitrogen, and carbon dioxide. There may have been other products. In several instances, the odor of phenylacetaldehyde could be detected. The low yields may be due to the poor solubility of the acid in chloroform.

$$C_6H_5CH{=}CHCH{=}CHCOOH \xrightarrow[H_2SO_4]{HN_3} \underset{6\%}{C_6H_5NH_2} + \underset{13\%}{C_6H_5CHO} + CO_2 + N_2$$

These products may be explained by a mechanism involving addition of hydrazoic acid to an olefinic bond followed by migration of alkyl or aryl groups.



EXPERIMENTAL

3-[p-Methoxyphenyl]-2-phenyl acrylic acid. This was prepared by the method of Buckles, Bellis, and Coder from phenylacetic acid, anisaldehyde, and acetic anhydride.[12]

Reaction of 3-[p-methoxyphenyl]-2-phenyl acrylic acid with hydrazoic acid. The acrylic acid (12.5 g., 0.05 mole) was suspended in 24 ml. of chloroform in a 250-ml., three necked flask equipped with a dropping funnel, a mechanical stirrer and a gas outlet tube. The gases from the reaction were passed through three washing bottles (one empty and two containing concentrated barium hydroxide solution) into an inverted water-filled graduated cylinder. The barium hydroxide absorbed the carbon dioxide and the progress of the reaction was followed qualitatively by observing the displacement of the water level in the graduated cylinder by nitrogen.

Concentrated sulfuric acid (10 ml.) and chloroform (20 ml.) were added with vigorous stirring. During 1 hr., 41 ml. (0.06 mole) of 1.58*N* hydrazoic acid in chloroform (prepared from sodium azide and sulfuric acid[2]) were added slowly while the temperature was kept at 52–55°.

The acid reaction mixture was poured into 400 ml. of ice water and steam distilled. The distillation was continued until the odor of phenylacetaldehyde was no longer noticeable and a Schiff test[13] for aldehydes was negative. About 2 l. of distillate were collected.

This distillate was extracted with five or six portions of ether. The ether solution was washed with a saturated solution of sodium bisulfite, prepared by dissolving 400 g. of sodium bisulfite in 600 ml. of water, adding 180 ml. ethanol and filtering. The bisulfite solution (containing the aldehyde as the bisulfite addition compound) was treated with sodium carbonate and extracted with ether. The ether extract was dried over magnesium sulfate, the ether removed and the phenylacetaldehyde converted to a methone derivative,[14] m.p. 163–165° (lit.[15] m.p. 164–165°). It was also identified

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[3] L. P. Kuhn and J. Di Domenico, *J. Am. Chem. Soc.*, **72**, 5777 (1950); D. R. Nielsen and W. E. McEwen, *J. Am. Chem. Soc.*, **76**, 4042 (1954).

[4] W. E. McEwen, M. Gilliland, and B. I. Sparr, *J. Am. Chem. Soc.*, **72**, 3212 (1950).

[5] W. E. McEwen and N. B. Mehta, *J. Am. Chem. Soc.*, **74**, 526 (1952).

[6] C. Schuerch, Jr., and E. H. Huntress, *J. Am. Chem. Soc.*, **71**, 2238 (1949).

[7] (a) R. Westland and W. E. McEwen, *J. Am. Chem. Soc.*, **74**, 6141 (1952); (b) J. H. Boyer, *J. Am. Chem. Soc.*, **73**, 5248 (1951); (c) Y. A. Sinnema and J. F. Arens, *Rec. trav. chim.*, **74**, 901 (1955).

[8] S. N. Ege and K. W. Sherk, *J. Am. Chem. Soc.*, **75**, 354 (1953); C. H. Gudmundsen and W. E. McEwen, *J. Am. Chem. Soc.*, **79**, 329 (1957); J. H. Boyer, F. C. Canter, J. Hamer and R. K. Putney, *J. Am. Chem. Soc.*, **78**, 325 (1956).

[9] S. C. Bunce and J. B. Cloke, *J. Am. Chem. Soc.*, **76**, 2244 (1954).

[10] P. A. S. Smith and J. R. Horwitz, *J. Am. Chem. Soc.*, **72**, 3718 (1950); L. Briggs, G. de Ath, and S. Ellis, *J. Chem. Soc.*, **61** (1942).

[11] R. T. Conley, *J. Org. Chem.*, **23**, 1330 (1958).

[12] R. E. Buckles, M. P. Bellis, and W. D. Coder, Jr., *J. Am. Chem. Soc.*, **73**, 4972 (1951).

[13] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., John Wiley & Sons, Inc., New York, 1956, p. 114.

[14] Ref. 13, p. 220.

[15] K. Lin and R. Robinson, *J. Chem. Soc.*, 2005 (1938).

TABLE I

APPROXIMATE YIELDS IN THE REACTION OF 3-[*p*-METHOXYPHENYL]-2-PHENYL ACRYLIC ACID WITH HYDRAZOIC ACID

Acid Reacted, G.	*p*-Anisidine.HCl, G.	Per Cent	Methone Deriv. $C_6H_5CH_2CHO$, G.	Per Cent	2,4 DNP of Ketone, G.	Per Cent
4.1	0.76	29	1.86	30	0.29	4.5
3.7	.83	36	2.08	37	.38	6.5
3.9	.94	38	2.20	37	.40	6.5

as its 2,4-dinitrophenylhydrazone, m.p. 121–123° (lit.[16] m.p. 121°).

The residue from the steam distillation (nonvolatile material) was extracted with ether. The unreacted acrylic acid which was not extracted with the ether was recrystallized from ethanol. The ether extract was washed with sodium bicarbonate to remove unreacted starting material. The bicarbonate extract was neutralized and the 3-[*p*-methoxyphenyl]-2-phenyl acrylic acid recovered by this process was combined with that recovered earlier.

The ether extract from the steam distillate and from the residue were then combined and dried over anhydrous magnesium sulfate. The ether was removed and the *p*-methoxybenzyl phenyl ketone, m.p. 94–96° (lit.[17] m.p. 94.5–5°) was converted to its 2,4-dinitrophenylhydrazone, m.p. 179–182°. An oxime was prepared in several runs, m.p. 132–133° (lit.[18] m.p. 133°).

After the above ether extraction, the acidic residue from the steam distillation was made basic with 10% sodium hydroxide. The solution then was extracted with ether, the ether extract dried over anhydrous magnesium sulfate, and the ether removed to yield *p*-anisidine. It was identified as its benzenesulfonamide, m.p. 93–95° (lit.[19] m.p. 95°), *p*-toluenesulfonamide, m.p. 108–110° (lit.[19] m.p. 114°) and its acetamide, m.p. 124–126° (lit.[19] m.p. 127°).

In order to get an estimate of the yields, the phenylacetaldehyde in several runs was converted quantitatively to its methone derivative, the *p*-anisidine to its hydrochloride and the *p*-methoxybenzyl phenyl ketone to its 2,4-dinitrophenylhydrazone. The yield data are summarized in Table I. Yields are based on the amount of the acrylic acid reacted as calculated from the amount recovered. In all cases 12.5 g. (0.05 mole) of acid was used initially. The barium carbonate produced agreed well with the amount of acid consumed (over 90%).

Cinnamylidene malonic acid. This was prepared from cinnamaldehyde and malonic acid with pyridine as catalyst.[20]

Cinnamylidene acetic acid. This was prepared by decarboxylation of cinnamylidene malonic acid.[21]

Reaction of cinnamylidene acetic acid with hydrazoic acid. Cinnamylidene acetic acid (17.4 g., 0.1 mole) was dissolved in 50 ml. of chloroform in a 250-ml., three necked flask. The apparatus was the same as used in the previous reaction. Concentrated sulfuric acid (10 ml.) was added, followed by 70 ml. of 1.43*N* hydrazoic acid (0.1 mole) in chloroform. The temperature was maintained at 51–52°. After about an hour, the brown reaction mixture was poured into 500 ml. of ice water. The odor of benzaldehyde was observed.

Neutral and acidic substances were extracted with ether, and the acidic substances separated from neutral ones by extraction of the ether with sodium bicarbonate solution. Cinnamylidene acetic acid, 9.2 g., 53%, was recovered. Benzaldehyde was converted to its methone derivative,[14] (2.8 g., 13%), m.p. 192–193° (lit.[22] m.p. 193°). It was further identified as its semicarbazone, m.p. 218–220° (lit.[22] m.p. 217°).

Basic substances were obtained from the acid reaction mixture by neutralization and extraction with ether. The ether extract was dried and dry hydrogen chloride was passed into it to give a precipitate of an amine hydrochloride. This was treated with 5% sodium hydroxide, extracted with ether and the hydrochloride again made. The amine was identified as aniline by its hydrochloride (made quantitatively), 0.41 g., 6.4%, m.p. 193–196° (lit.[23] m.p. 198°), its benzenesulfonamide, m.p. 109–112° (lit.[24] m.p. 112°) and its acetyl derivative, m.p. 114° (lit.[23] m.p. 114°).

The barium carbonate (0.47 g.) recovered amounted to only 5% reaction based on acid consumed.

Reaction of cinnamic acid with hydrazoic acid. Hydrazoic acid (150 ml. of 2.125*N* solution in chloroform, 0.32 mole) was added dropwise to a stirred solution of cinnamic acid (49 g., 0.33 mole), concentrated sulfuric acid (98 ml.) and chloroform (150 ml.) in a three necked, 1-liter flask equipped with a mechanical stirrer, thermometer, gas outlet tube, and addition funnel. The temperature was between 45–50°.

After the addition of hydrazoic acid was completed and gas evolution ceased, the mixture was cooled, diluted with water, and steam distilled. A tar was produced on dilution. The distillate yielded phenylacetaldehyde, identified as its 2,4-dinitrophenylhydrazone, m.p. 120° (lit.[16] m.p. 121°).

The residue from the steam distillation was made alkaline and steam-distilled again. The distillate was led into hydrochloric acid solution which subsequently was evaporated to dryness. The residue was treated with sodium hydroxide to liberate aniline which was identified as its phenylthiourea, m.p. 152–153° (lit.[19] m.p. 154°). No evidence could be obtained in this or any other run for the presence of acetaldehyde or any other organic products (except the tar). Considerable amounts of cinnamic acid were usually recovered.

When polyphosphoric acid was substituted for sulfuric acid, reaction occurred but no new products were found. Hydrochloric acid or phosphoric acid could not replace sulfuric acid.

Acetaldehyde with concentrated sulfuric acid gave a dark brown viscous liquid. When acetaldehyde (0.2 mole) was added to the reaction mixture of cinnamic acid, hydrazoic acid, sulfuric acid, and chloroform during the reaction, only trace amounts of the aldehyde or none at all could be identified by the Simon's test.[25]

Acknowledgments. We are indebted to the University of Pennsylvania for a faculty summer scholarship (D. C. D.) and a summer research scholarship (A. S.).

PHILADELPHIA, PA.

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(24) Ref. 13, p. 288.

(25) Ref. 22, p. 43.