in the absence of methyl alcohol resulted in the partial disappearance of the insoluble solid. The reaction mixture was filtered from the unchanged material and the ethereal solution was washed with cold aqueous sodium hydroxide solution (to remove any unchanged material), then with water, dried, and evaporated. The colorless solid, so obtained, was crystallized from ethyl alcohol as colorless crystals, *ca.* 0.15 g., m.p. 169°. It was identified as 4-methoxy-9-xanthenone (melting point and mixed melting point[17]).

Acidification of the alkaline washings gave trace of unchanged 4-hydroxy-9-xanthenone.

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[CONTRIBUTION FROM THE ENTOMOLOGY RESEARCH DIVISION, AGRICULTURAL RESEARCH SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Synthesis of *beta*-(3,4-Methylenedioxyphenyl)tropic Acid and Its Derivatives. A Contribution to the Chemistry of the Perkin Reaction

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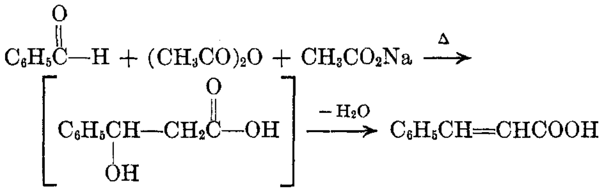
The belief that the Perkin synthesis involves an intermediate addition compound of the "aldol" type has been accepted since Perkin first described the reaction. Fittig reported the isolation of such an "aldol," but his compound was incapable of losing water, and therefore not a true intermediate. Hauser and Breslow prepared a true "aldol," and with their preparation the "aldol" view of the Perkin synthesis was regarded as established experimentally. Our synthesis of β-(3,4-methylenedioxyphenyl)tropic acid in good yield provides another example of a true "aldol" postulated in the Perkin reaction.

In connection with insecticide studies at Beltsville, Md., β-(3,4-methylenedioxyphenyl)tropic acid (V) and β-(3,4-methylenedioxyphenyl)atropic acid (VII) were synthesized and several of their esters tested as synergists for house flies. The synthesis of V in 65% yield provides another example of an "aldol"[1] intermediate postulated in the Perkin reaction.

Although the history of this interesting reaction dates from Perkin's synthesis of coumarin in the year 1868, uncertainty existed as to the roles of the acid anhydride and the sodium salt in the formation of "aldol" intermediates until just recently. Some textbooks in organic chemistry are still in opposition to Perkin's[2] original views that this synthesis of cinnamic acid involves the condensation of the aldehyde with the anhydride, the acid salt acting catalytically:

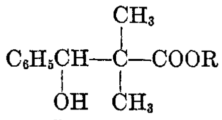


$$C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}\text{—}H + (CH_3CO)_2O + CH_3CO_2Na \xrightarrow{\Delta} \left[\underset{\underset{\displaystyle OH}{|}}{C_6H_5CH}\text{—}CH_2\overset{\overset{\displaystyle O}{\|}}{C}\text{—}OH\right] \xrightarrow{-H_2O} C_6H_5CH{=}CHCOOH$$

These writings on the subject follow the views of Fittig,[3] who by an incorrect interpretation of his data believed that the Perkin synthesis occurs between the aldehyde and the sodium salt of the acid in two stages: first an "aldol" is formed, *i.e.*, condensation took place between the aldehyde and the alpha carbon of the acid and then water was lost by the action of the anhydride.

The results of this investigation and a number of others provide substantial evidence in favor of Perkin's original view. Michael and Hartman[4] presented strong evidence that reaction was between the aldehyde and the anhydride in the production of intermediate "aldols." Studies by Breslow and Hauser[5] have led them to conclude that "there no longer need be any doubt that the anhydride condenses in the Perkin synthesis," and not the sodium salt.

Since the "aldol" view of the Perkin reaction has now received considerable support, its further substantiation by the actual isolation of the intermediate "aldols" becomes important. Fittig[6] reported the preparation of 2,2-dimethyl-3-phenylhydracrylic acid (I).



$$\underset{\underset{\displaystyle OH}{|}}{C_6H_5CH}\text{—}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\text{—}COOR$$

I R = H
II R = C_2H_5

Muller and co-workers[7] were unable to repeat this synthesis. Hauser and Breslow[1] were successful and prepared the ethyl ester (II) of I in 30% yield using

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(1) H. B. Watson, *Ann. Repts. Chem. Soc.* (*London*), **36**, 210 (1939), and C. R. Hauser and D. S. Breslow, *J. Am. Chem. Soc.*, **61**, 793 (1939), used the term "aldol" to represent *beta*-hydroxy intermediates.

(2) W. H. Perkin, *J. Chem. Soc.*, 388 (1877); **53**, 181 (1868).

(3) R. Fittig, *Ann.*, **195**, 169 (1879); **216**, 97 (1883); **227**, 48 (1885); *Ber.*, **14**, 1824 (1881); **16**, 1436 (1883); **27**, 2658 (1897).

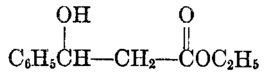
(4) A. Michael and R. N. Hartman, *Ber.*, **34**, 918 (1901); A. Michael, *J. Prakt. Chem.*, **60**, 364 (1899).

(5) D. S. Breslow and C. R. Hauser, *J. Am. Chem. Soc.*, **61**, 786 (1939).

(6) R. Fittig and H. W. Jayne, *Ann.*, **216**, 115 (1883); R. Fittig and P. Ott, *Ann.*, **227**, 48, 61 (1885).

(7) E. Muller, H. Gawlick, and W. Kreutzmann, *Ann.* **515**, 97 (1935); E. Muller, *Ann.*, **491**, 251 (1931).

sodium triphenylmethyl as the condensing agent. However, II and I are not true intermediates in the Perkin reaction because normal elimination of water does not occur. They isolated then the true "aldol," ethyl phenylhydroxypropionate (III), in 26% yield by stopping

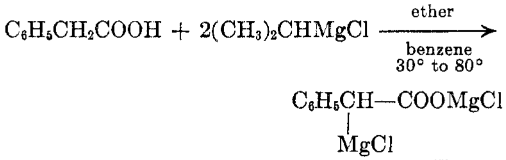


$$C_6H_5\overset{OH}{C}H{-}CH_2{-}\overset{O}{\overset{\|}{C}}OC_2H_5$$

III

their condensation after a reaction time of only one minute.

Another example of such a ture "aldol" has been prepared in this laboratory. Kalnin[8] had observed that inorganic and organic bases, for example potassium carbonate and triethylamine, may be substituted for the aliphatic acids salts in the Perkin reaction. We therefore heated potassium carbonate, piperonal, sodium phenylacetate, and acetic anhydride at 180° for 2 hr., and VII resulted in 46% yield. It followed that VII must have come from the intermediate V. Since V is related to tropic acid and because esters of tropic acid have been found useful in insecticide studies,[9] V was synthesized. This was accomplished by reacting phenylacetic acid and isopropyl magnesium chloride to give the Ivanov reagent[10] IV.



$$C_6H_5CH_2COOH + 2(CH_3)_2CHMgCl \xrightarrow[\text{benzene, } 30° \text{ to } 80°]{\text{ether}} \underset{\underset{MgCl}{|}}{C_6H_5CH}{-}COOMgCl + 2C_3H_8$$

(Ivanov reagent)

IV

The Ivanov reagent was heated with piperonal in the presence of benzene, and V was produced in 65% yield. This procedure is general and other "aldols," which have been difficult to isolate, may now be synthesized.[11] Treatment of V with acetic anhydride gave VII in 97% yield. A mixed melting point with VII from the Kalnin modification (the use of potassium carbonate) showed them to be identical. VIII, where R is methyl, was prepared in 83% yield with methanolic hydrogen chloride. De Schuttenbach[12] prepared this ester in 20% yield by the condensation of benzaldehyde with methyl α-(3,4-methylenedioxyphenyl) acetate in the presence of granulated sodium in toluene. VI was produced in quantitative yield from V. X where R′ is methyl or ethyl and R″ is acetyl or propionyl was prepared from VI in two steps with an overall yield of 36 to 56%.

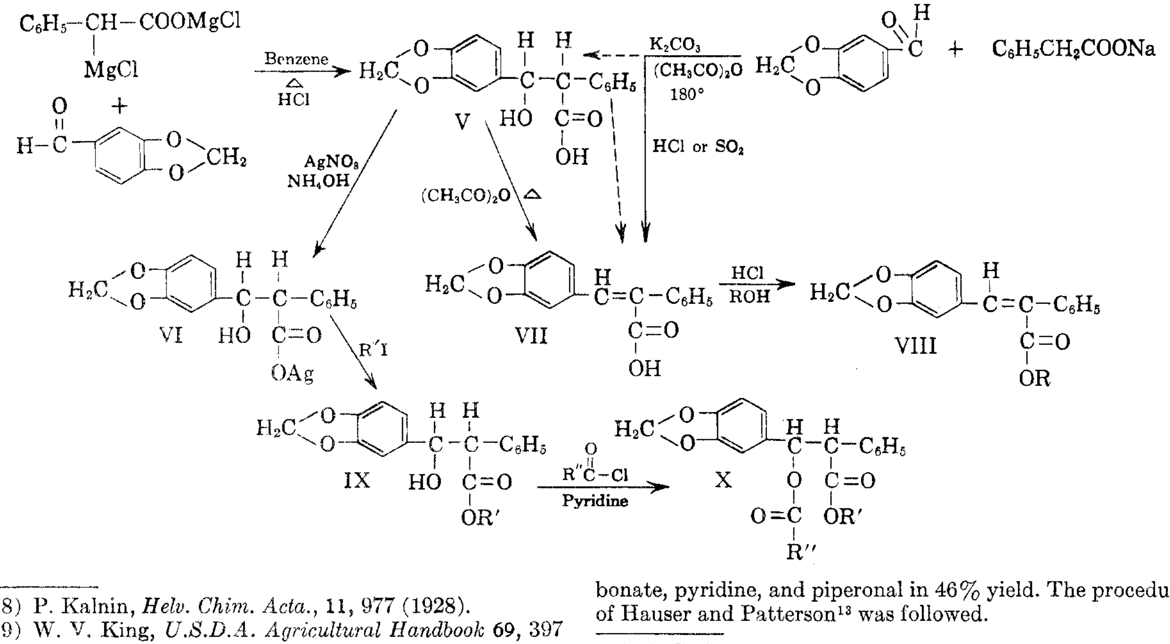
EXPERIMENTAL

β-(3,4-Methylenedioxyphenyl)tropic acid (V), was prepared according to the directions of Blicke *et al.*;[10] piperonal dissolved in benzene was substituted for their paraformaldehyde; m.p. 169° (dec.), recrystallized from 50% aqueous alcohol; yield 65%.

Anal. Calcd. for $C_{16}H_{14}O_5$: C, 67.13; H, 4.93. Found: C, 66.82; H, 5.02.

β-(3,4-methylenedioxyphenyl)atropic acid, (VII), was prepared from V (0.4 mole) by stirring with 95% acetic anhydride (900 ml.) and anhydrous sodium acetate (0.9 mole) at 100° for 1 hr. It was cooled at 25° and poured into cracked ice. On standing crystallization occurred; m.p. 232–235° (lit. 231–232°) recrystallized from alcohol; yield 97%.

VII was also prepared by the Kalnin modification from sodium phenylacetate, acetic anhydride, potassium carbonate, pyridine, and piperonal in 46% yield. The procedure of Hauser and Patterson[13] was followed.



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[8] P. Kalnin, *Helv. Chim. Acta.*, 11, 977 (1928).

[9] W. V. King, *U.S.D.A. Agricultural Handbook* 69, 397 pp. (1954).

[10] D. Ivanov and S. Spassov, *Bull. soc. chim. France*, 49, 19 (1931); F. F. Blicke, H. Raffelson, and B. Barna, *J. Am. Chem. Soc.*, 74, 253 (1952); H. E. Zimmerman and M. D. Traxler, *J. Am. Chem. Soc.*, 79, 1920 (1957).

[11] C. S. Rondestvedt, Jr., and M. E. Rowley, *J. Am. Chem. Soc.*, 78, 3804 (1956).

[12] Y. de Schuttenbach, *Ann. chim.*, 6, 53 (1936).

[13] C. R. Hauser and M. Patterson, *Org. Reactions*, Vol. 1, 252 (1942).

β-(3,4-Methylenedioxyphenyl)atropic acid, methyl ester (*VIII, R* = *CH_3*), was prepared from V (0.15 mole) by refluxing with 3% methanolic hydrogen chloride (200 ml.) for 4 hr.; m.p. 110–111° (lit. 106–107°) recrystallized from alcohol; yield 83%.

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.34; H, 5.00. Found: C, 72.34; H, 4.93.

β-(3,4-Methylenedioxyphenyl)atropic acid, ethyl ester (*VIII, R* = *C_2H_5*) was prepared as the methyl ester (described above); m.p. 100–102° (lit. 104°) recrystallized from alcohol; yield 56%.

Anal. Calcd. for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.80; H, 5.38.

β-(3,4-Methylenedioxyphenyl)tropic acid, silver salt (*VI*), was prepared as follows: V, 200 g. (0.7 mole), was stirred in water, 1800 ml., at 5°. Concentrated ammonium hydroxide, 80 ml. (0.7 mole) was added until the solution was just neutral to indicator paper. Silver nitrate, 121 g. (0.71 mole) was then added slowly and the mixture was kept at 5° overnight. After filtering, the residue was washed with cold water and then it was air-dried in the dark. The product was further dried *in vacuo* over phosphorus pentoxide. Yield 272 g., or 99% of theory.

β-(3,4-Methylenedioxyphenyl)tropic acid, methyl ester, acetate (*X, R′ and R″* = *CH_3*), was prepared from VI. Methyl iodide (0.084 mole) was added dropwise to VI (0.076 mole) in 250 ml. of ether with stirring. The mixture was refluxed 18 hr. and then was filtered. Pyridine, 18 ml., was added to the filtrate and while stirring there was added acetyl chloride (0.1 mole). The mixture was refluxed for 4 hr. and then kept at room temperature overnight. Ether and 5% aqueous hydrochloric acid were added and two layers separated. The ether layer was washed with 5% hydrochloric acid, water, 5% sodium bicarbonate, and then with saturated sodium chloride. After removal of the ether, crystallization occurred. Recrystallized twice from alcohol, the compound melted at 122–123°; yield 54%.

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.73; H, 5.14.

β-(3,4-Methylenedioxyphenyl)tropic acid, methyl ester, propionate (*X, R′* = *CH_3, R″* = *C_2H_5*), was prepared from VI as described except that propionyl chloride was used instead of acetyl chloride; m.p. 82°–83° after recrystallization from alcohol; yield 56%.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.03; H, 5.60.

β-(3,4-Methylenedioxyphenyl)tropic acid, ethyl ester, acetate (*X, R′* = *C_2H_5, R″* = *CH_3*) was prepared as described above; m.p. 108°–110° after recrystallization from alcohol; yield 36%.

Anal. Calcd. for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found: C, 67.02; H, 5.66.

Acknowledgment. The authors gratefully acknowledge the aid of Ray W. Ihndris. All microanalyses were performed by Kathryn Gerdeman, of the Chemistry Department, University of Maryland.

BELTSVILLE, MD.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

Sulfonation of Phenanthrene by Dioxane-Sulfotrioxide[1]

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Phenanthrene is converted by dioxane-sulfotrioxide to 1-, 2-, 3- and 9-phenanthrene sulfonic acids. The salts of these isomeric acids are isolated in yields of 5–7%, 4–6%, 27–32% and 24–30%, respectively.

Earlier reports[2] on the sulfonation of phenanthrene in which sulfuric acid was used indicated the need for temperatures of 120–125° for a short reaction time. Losses due to polysulfonation and sulfone formation had to be accepted and only the phenanthrene-2- and the phenanthrene-9-sulfonates were isolated. At lower temperatures, very long reaction times were needed. The yields were still unsatisfactory although some phenanthrene-1- and phenanthrene-9-sulfonates were isolated. Table I summarizes this earlier work.

The fractionation and isolation of the isomers were a long and tedious process especially when all four isomers resulted from the sulfonation.

Suter *et al.*[3] have reported facile sulfonation of naphthalene by dioxane-sulfotrioxide. This reagent turned out to be well suited for the monosulfonation of phenanthrene. Generally, 94–96% of the phenanthrene was converted into water soluble material during the sulfonation and over 90% of the water soluble product could be precipitated as an insoluble sodium salt by the addition of a saturated solu-

TABLE I

Author	Temp., °C.	Reaction Time, Hrs.	Yields, % of Phenanthrene Sulfonates			
			-1-	-2-	-3-	-9-
Fieser[a]	120–125	3–7	...	17–21	24–26	...
	60	72	4–8	18	19	13
Werner[b]	120–130	5	...	12	18.6	...
	100	8	...	7	9–11	4
Sanqvist[c]	20	400	...	...	...	7–14.6
Ioffe[d]	...	...	...	17–37	...	...

[a] *Cf.* Ref. 4. [b] A. Werner, B. Löwenstein, A. Wack, T. Frey, M. Kunz, K. Rekner, A. Ney, H. Heil, A. Scherrer, H. Schwabacher, J. Kunz, and A. Grob, *Ann.*, **321**, 248 (1902). [c] H. Sandqvist, *Ann.*, **392**, 76 (1912). [d] I. S. Ioffe, *J. Gen. Chem.* (*U.S.S.R.*), **3**, 448 (1933), *Chem. Abstr.*, **28**, 1694 (1934).

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(1) Presented before the Division of Organic Chemistry, AMERICAN CHEMICAL SOCIETY, 130th Meeting, Atlantic City, September 1956.

(2) References to earlier reports are given by L. E. Fieser, *Org. Syntheses*, Coll. Vol. II, 482 (1943).

(3) C. M. Suter, P. B. Evans, and J. M. Kiefer, *J. Am. Chem. Soc.*, 60, 538 (1938).