[CONTRIBUTION FROM THE B. F. GOODRICH RESEARCH CENTER]

A Pyrolysis Product of the Sorbic Acid–Maleic Anhydride Adduct

BY DAVID CRAIG

This paper reports on the structure of the methyl tetrahydrophthalic anhydride (Compound I) which results from the pyrolysis of the sorbic acid–maleic anhydride adduct according to Wicks, Daly and Lack.[1]

Compound I has now been found to have the carbon skeleton of the isoprene–maleic anhydride adduct. Thus, dehydrogenation by the bromination procedure of Newman and McCleary[2] gives 4-methylphthalic anhydride. Contrariwise, Wicks and others reported that 3-methylphthalic anhydride was formed by dehydrogenation over palladium. Since substances other than I are present in the pyrolysate and because of the report of Wicks, it was expected that some 3-methylphthalic anhydride would be isolated. However, none could be found. In support of the dehydrogenation reported here and opposed to that of Wicks, the hydrogenation of I in ethyl acetate over Raney nickel forms *trans*-4-methylhexahydro-*cis*,*cis*-phthalic acid[3] as a main product and the corresponding anhydride as a minor product, the combined yields of these compounds being forty-one per cent. The formation of the acid here where only anhydride was expected is worthy of further study.

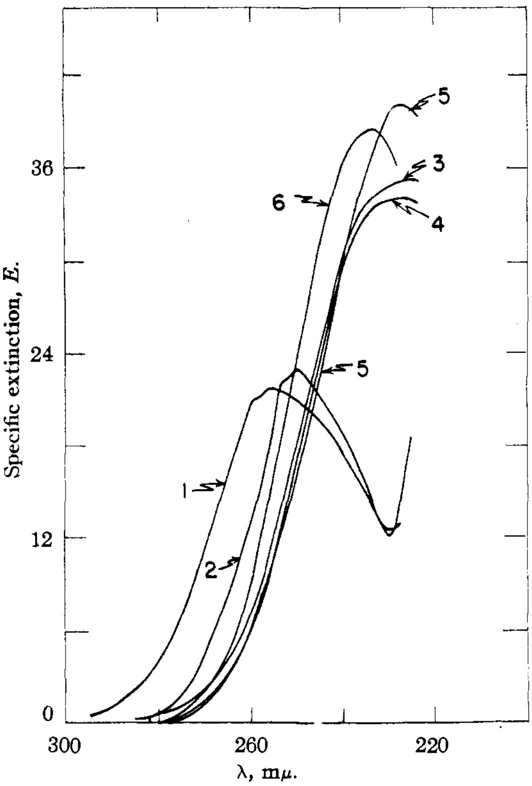

Fig. 1.—Spectra of I (1) 0.022 g./l. in MeOH immediately, (2) 0.014 g./l. in isoöctane, (3) 0.0125 g./l. in MeOH after standing for 3 hours, (4) 0.0125 g./l. in MeOH after standing for 120 hours, (6) 0.014 g./l. in 0.1 *N* KOH in MeOH; spectrum of acid of I (5) 0.010 g./l. in MeOH.

The hydrogenation of I and of the corresponding acid was attempted over platinum oxide in acetic acid solution. Hydrogen at one atmosphere pressure was not absorbed in the case of I. The acid of I absorbed about one-fourth of the expected amount of hydrogen at one atmosphere during twenty-four hours. These unexpected results and the very long time required (seventy-two hours) for the hydrogenation of I in ethyl acetate over Raney nickel indicates the presence of an unusually stable double bond such as one sterically hindered or one stabilized by conjugation. A recent study[3] of the hydrogenation of the 3- and 4-methyl-1,2,3,6-tetrahydrophthalic acids and anhydrides showed that these non-conjugated compounds absorb hydrogen rapidly.

The ultraviolet absorption of I is pronounced and dependent on the solvent.[4] The results depicted in Fig. 1 also show that the anhydride I, the corresponding acid and the potassium salt absorb differently. The absorption of I in alcohol varies with the age of the solution, presumably because of esterification. This reaction opens the anhydride ring and consequently causes a pronounced change in the resonance forms which are present. The results obtained are to be expected if the double bond of I is conjugated with both of the carbonyl groups.

The fact that I is stable to boiling water constitutes further evidence that the double bond is between the carbonyl groups, for it is known that anhydrides of this type, for example, dimethylmaleic anhydride,[5] resist hydrolysis. Resistance to hydrolysis and resistance to hydrogenation thus support each other and accordingly the structure assigned to I is that of 4-methyl-3,4,5,6-tetrahydrophthalic anhydride. This structure is planar and is presumably capable of intense resonance stabilization. Comparison to phthalic anhydride can be made here. This compound is also planar but it does not resist hydrolysis. However, the cross conjugation from the benzene ring probably prevents stabilization of the anhydride ring in this case.

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(1) Wicks, Daly and Lack, *J. Org. Chem.*, **12**, 713 (1947).

(2) Newman and McCleary, THIS JOURNAL, **63**, 1543 (1941).

(3) Craig, *ibid.*, **72**, 1678 (1950).

(4) The absorption of phthalic anhydride is reported to vary with the solvent; see Menczel, *Z. physik. Chem.*, **125**, 200 (1927).

(5) Compare also the behavior of 3,4,5,6-tetrahydrophthalic anhydride reported by Alder and Schumacher, *Ann.*, **564**, 98 (1949).

Experimental

Absorption Spectra.—These were measured by Earl Gregg and John Efroymson with a Beckman quartz spectrophotometer, Model DU.

4-Methyl-3,4,5,6-tetrahydrophthalic Acid.—Compound I was prepared in nearly theoretical crude yield according to Wicks, Daly and Lack from a sample of the adduct (m. p. 178–182°). After extraction with an equal volume of boiling water it froze at about −40° and melted at about −10°. It was sharply dibasic. When the titration solution was concentrated and acidified with excess concentrated hydrochloric acid in the presence of benzene, crystals of the acid corresponding to I formed readily. They were washed with benzene and a small amount of water. They melted at 125–126° with decomposition when heated rapidly.

Anal. Calcd. for $C_9H_{12}O_4$: C, 58.66; H, 6.57; neut. equiv., 92.0. Found: C, 58.74; H, 6.75; neut. equiv., 92.5.

The melting point of I when prepared by distilling this acid was found to be −5°. Crude and pure I had the same refractive index, $n^{20}{}_{D}$ 1.5002.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.02; H, 6.08. Found: C, 65.03; H, 5.98.

When the pure anhydride was reconverted to the acid the yield amounted to 80% and when the crude anhydride was used to only 55–72%. These low yields are believed due in part to the instability of the acid.

4-Methylphthalic Anhydride.—An authentic specimen was prepared from the isoprene–maleic anhydride adduct by the sulfur dehydrogenation method which Newman[6] used for preparing 3-methylphthalic anhydride from the piperylene adduct. The yield of 4-methyl derivative amounted to 59% of a product which melted at 91–92°. Mayer and Gunther[7] reported 92°. The bromine dehydrogenation of 5.0 g. of crude I according to Newman and McCleary[2] resulted in a yield of 0.8 g. (16%) of crystals, m. p. 91–92° alone or mixed with the authentic specimen. Efforts to isolate 3-methylphthalic anhydride from the mother liquors were not successful.

Dehydrogenation of crude I with sulfur (2 moles per mole of I) during thirty minutes at 240–260° supplied a 7% yield of 4-methylphthalic acid melting at 150–151°. This acid was isolated by acidifying the alkaline extract of the reaction product. No evidence could be found for the presence of 3-methylphthalic acid or of 3-methylphthalic anhydride.

The Hydrogenation of I.—Sixteen and six-tenths grams (0.1 mole) of crude I, 100 ml. of ethyl acetate and 20 g. of Raney nickel were shaken at three atmospheres pressure of hydrogen and at 25° for seventy-two hours. During this time 0.09 mole of hydrogen was absorbed. The Raney nickel which had been stored under water was washed with alcohol and then with ethyl acetate just prior to use. The catalyst was filtered off and most of the solvent distilled away. The crystals which formed in the remaining filtrate when it was cooled were filtered off and washed with ethyl acetate. They melted at 170–175° and, including a small amount recovered from the hydrolysis of the anhydride in the filtrate, weighed 7.6 g. (41%). Recrystallization from dilute alcohol raised the m. p. to 177–179° and this was not depressed by admixture with authentic *trans*-4-methylhexahydro-*cis,cis*-phthalic acid.[3]

Summary

The main component in the pyrolysis product of the sorbic acid–maleic anhydride adduct has been found to be 4-methyl-3,4,5,6-tetrahydrophthalic anhydride. Saponification yielded the salt of the corresponding acid and hydrogenation accompanied by hydrolysis yielded *trans*-4-methylhexahydro-*cis,cis*-phthalic acid.

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[6] Newman, This Journal, 59, 1004 (1937).

[7] Mayer and Gunther, *Ber.*, 63, 1458 (1930).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Frontal Analysis of Ethers and Sulfides

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Indifferent compounds such as ethers or sulfides may often be separated from mixtures by distillation, but one can visualize mixtures where this approach is closed, as with ethyl hexyl ether and 1,2-diethoxyethane, both of which boil at 119°. Thermal instability may also invalidate distillation analysis, as in sulfide mixtures containing mustard gas, since the latter, on heating, is reported[2] to change into 1,8-dichloro-3,6-dithiaoctane, $ClCH_2CH_2SCH_2CH_2SCH_2CH_2Cl$, 1,11-dichloro-3,6,9-trithiahendecane, $(ClCH_2CH_2SCH_2CH_2)_2S$, and other products.

Analysis of mustard gas by chemical methods is difficult also. Thus, the method of Rosser, Meade and Glover reported by Fuson[2] was carried out by treating the 2-chloroethyl sulfide with sodium methyl sulfide followed by distillation of the methyl mercapto derivative. According to Meade and Moggridge,[3] however, this reaction gives rise not only to the expected (2-methylmercapto)-ethyl sulfide, $(CH_3SCH_2CH_2)_2S$, but also to about 1% of 2,5,8,11-tetrathiadodecane, $CH_3S–(CH_2CH_2S)_3–CH_3$, and 0.02% of 2,5,8,11,14-pentathiapentadecane, $CH_3S–(CH_2CH_2S)_4–CH_3$. These investigators pointed out that analyses of mixtures such as $Cl(CH_2CH_2S)CH_2CH_2Cl$, $Cl(CH_2CH_2S)_2CH_2CH_2Cl$ and $Cl(CH_2CH_2S)_3CH_2CH_2Cl$ by this method "can at best only be regarded as rough approximations."

Adsorption analysis seemed well suited for such mixtures. It was first planned in the present study to analyze mixtures containing mustard gas by chromatographic adsorption after first converting the chloro sulfide into *p*-phenylazophenoxyethyl sulfide, $(PhN{=}N{-}C_6H_4{-}O{-}CH_2CH_2)_2S$, by reaction with the sodium salt of *p*-hydroxyazobenzene. Although it was possible to obtain this orange derivative, m. p. 151°, in good

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[1] Department of Chemistry, Boston University, Boston, Massachusetts.

[2] Fuson, Lipscomb, McKusick and Reed, *J. Org. Chem.*, 11, 513 (1946).

[3] Meade and Moggridge, *J. Chem. Soc.*, 813 (1946).