relevant picture published by these authors seems to refer to some foreign substance which contaminated their preparation of wood pulp fibers.

We have invariably found with all kinds of cellulose fibers that, in order to study fibrillation, grinding in the wet condition is to be preferred and then yields more interesting pictures.

Acknowledgment.—The electron micrographs were taken by the "Institute for Electron-microscopy" at the Technical College in Delft, Netherlands.

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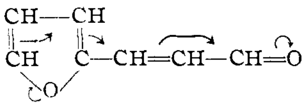
Diene Reaction of Some Furans

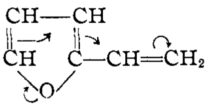
BY WERNER HERZ

In a brief communication several years ago, Van Campen and Johnson[1] included among a number of furans which did not undergo the Diels–Alder reaction with maleic anhydride compounds containing an ethylenic group attached to the furan nucleus. The substances exhibiting such inactivity were not specified. On the other hand, Paul[2] has reported successful addition of maleic anhydride to furylethylene. Attachment did not, however, occur at the alpha carbon atoms of the furan nucleus, but at the beta atoms of the side chain and ring.

In view of this discrepancy, it seemed of interest to subject some easily accessible derivatives of furfural containing an ethylenic bond in the side chain to the action of maleic anhydride. Furylacrolein, furylacrylic acid and 2-(β-nitrovinyl)-furan were found to be inactive. This is not surprising if it is assumed that the Diels–Alder synthesis is initated by an anionoid–cationoid reaction in which the diene is nucleophilic and the beta carbon atom of the dienophile is electrophilic, as has been suggested.[3] In the three compounds named the strongly electrophilic groups attached to the beta carbon atom of the side chain deactivate this atom and, through conjugation, the nucleus (I). In furylethylene, on the other hand, extended conjugation favors attack of the dienophile on the beta carbon atom of the side chain (II), as actually observed by Paul.



I



II

According to this concept, if the conjugation in the three compounds cited is destroyed by saturation of the side chain, reaction with maleic anhydride should lead to the normally obtained epoxytetrahydrophthalic anhydrides. Furylpropionic acid and maleic anhydride, mixed in equimolecular proportions in boiling ether, gave a product which was assumed to have the structure of a normal Diels–Alder adduct and not that of the mixed anhydride $C_4H_3O—CH_2CH_2CO—O—COCH=CHCO_2H$, as no similar anhydride could be isolated from the reaction mixture furylacrylic acid–maleic anhydride. To obtain a substance of unequivocal structure, furylpropionic ester and maleic anhydride reacted under identical conditions and yielded a compound having the correct neutral equivalent and analysis.

Experimental[4]

Reaction of Furylpropionic Acid with Maleic Anhydride. To a solution of 13 g. of furylpropionic acid in 50 ml. of ether was added 11 g. of maleic anhydride with boiling until completely dissolved. At intervals, the mixture was shaken vigorously; crystals soon appeared and the mixture became a solid crystalline mass in two hours. The product was separated by filtration, washed with a little ether and purified by dissolving in acetone, treating with charcoal and diluting with benzene. Eleven grams of the substance in the form of white needles melting at 96° were isolated. More could be recovered from the ether washings. The compound is soluble in alcohol, acetone and water, insoluble in benzene and slightly soluble in ether.

Anal. Calcd. for $C_{11}H_{10}O_6$: C, 55.46; H, 4.20; neut. equiv., 79. Found: C, 55.43; H, 4.18; neut. equiv., 79.

Analysis and neutral equivalent are equally correct for either a Diels–Alder adduct or a mixed anhydride. When the substance was titrated after having been dissolved in alcohol, a neutral equivalent of 113 was obtained, indicating esterification of one carboxyl group. This may be due to spontaneous esterification of an adduct or alcoholysis of an anhydride. Treatment with boiling water yielded crystals of furylpropionic acid, m. p. 57–58°.

3-(β-Carbethoxy)-ethyl-3,6-epoxy-1,2,3,6-tetrahydro-*o*-phthalic Anhydride.—Nine grams of ethyl furylpropionate and 4 g. of maleic anhydride were mixed in boiling ether. The yellow color characteristic of the diene reaction was observed and long needles began to appear after two hours. The mixture was allowed to stand for twenty-four hours and the separated solid was filtered and washed with cold ether. Nine grams of product, m. p. 90°, was obtained. It could be purified without further change in melting point by dissolving in a minimum of cold acetone and reprecipitating with ligroin. It was soluble in acetone, hot alcohol and benzene, dilute base, acetic acid, ethyl acetate and chloroform, partially soluble in carbon tetrachloride and insoluble in ligroin and dilute acid. Boiling in water regenerated the constituents.

Anal. Calcd. for $C_{13}H_{14}O_6$: C, 58.65; H, 5.26; neut. equiv., 133. Found: C, 58.59; H, 5.22; neut. equiv., 130.

No compound, other than the reactants, could be isolated after two weeks of standing from mixtures containing furylacrylic acid, furylacrolein or 2-(β-nitrovinyl)-furan, each with an equivalent amount of maleic anhydride in boiling ether. Refluxing in benzene solution for eight to ten hours gave similar results. A solution of equivalent quantities of furylacrylic acid and maleic anhydride in ether, allowed to stand at room temperature for two months, gave no precipitate upon being chilled in the refrigerator for several days and on removal of the solvent yielded only a mixture of the reactants.

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(1) Van Campen and Johnson, THIS JOURNAL, **55**, 430 (1933).

(2) Paul, *Compt. rend.*, **208**, 1028 (1939); *Bull. soc. chim.*, **10**, 163 (1943).

(3) Hudson and Robinson, *J. Chem. Soc.*, 715 (1941); Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, New York, N. Y., 1943, p. 131.

(4) Melting points are uncorrected.