Notes A department for short papers of immediate interest.

The Nuclear Magnetic Resonance Spectrum of Feist's Acid[1]

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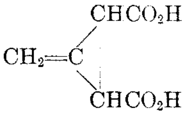
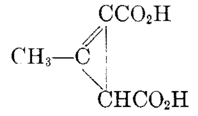
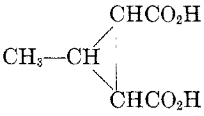
Feist's acid[3] is generally accepted to be either I


I


II


III

or II. Cogent evidence in favor of I has been obtained by Ettlinger[4] and his structural assignment has been confirmed by x-ray diffraction analysis.[5] Unequivocal evidence that Feist's acid is I and not II has now been obtained from its nuclear magnetic resonance (NMR) spectrum (Fig. 1) in a solution of excess sodium deuteroxide in heavy water. Three peaks of almost equal area were obtained (see Curve A) corresponding from left to right to the two methylene hydrogens, the two carboxyl hydrogens (present as water) and the 1,2-ring hydrogens respectively. The center peak was clearly due to H_2O because it increased markedly on addition of a drop of ordinary water to the solution (compare Curve B). If the acid actually had Structure II, the C—H peaks would be in the ratio of one (the ring hydrogen) to three (the methyl hydrogens).[6] The NMR spectrum (Curve C) of the hydrogenation product of Feist's acid (III) is in satisfactory agreement with the assigned structure although, in this case, the three varieties of hydrogen attached to carbon absorb too closely together to permit clear resolution.

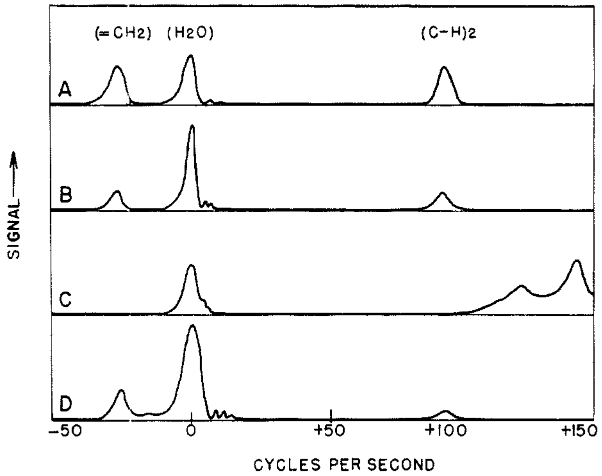


Fig. 1.—Nuclear Magnetic Resonance Spectra of 5-mm. Samples at 40 mc. and 9400 gauss (12-sec. sweep) with Varian Associates Model V-4300B High Resolution Spectrometer. A, 0.19 g. of I dissolved in 0.46 g. of a solution prepared from 0.12 g. of sodium and 0.8 g. of deuterium oxide; B, same solution plus one drop of ordinary water; C, 0.14 g. of III dissolved in 0.36 g. of a solution prepared from 0.10 g. of sodium and 0.8 g. of deuterium oxide; D, solution as for B after five days at room temperature.

After five days at room temperature, the NMR absorption of the 1,2-ring hydrogens of I decreased about 75% relative to the methylene hydrogens showing that the 1,2-hydrogens were exchanging with the solvent. No additional bands were noted in the spectrum after 60 days at room temperature. Removal of the solvent under reduced pressure, dissolution of the residue in fresh deuterium oxide, and equilibration reduced the absorption of the 1,2-hydrogens to negligible proportions without effect on the absorption of the methylene hydrogens. The occurrence of hydrogen-deuterium exchange was confirmed by examination of the infrared spectrum (potassium bromide pellet) of the deuterated acid and regeneration of I by equilibration of a sample of the deuterated acid with a solution of sodium hydroxide. The strong absorption band at 910 cm.$^{-1}$ characteristic of the protated acid was absent from the infrared spectrum of the deuterated material. The specificity of the exchange (*i.e.*, no exchange of the methylene hydrogens) precludes any possibility of a facile base-induced equilibration between forms I and II under these conditions. The spectrum of the deuterium oxide solution of III did not appear to change over 60 days at room temperature.

The recent reassertion that Feist's acid is II[7] because of its infrared spectrum, has been controverted by Ettlinger and Kennedy.[6] Ozonization of the diethyl ester of Feist's acid is reported to

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[1] Supported in part by the Petroleum Research Fund of the American Chemical Society.

[2] National Science Foundation Predoctoral Fellow, 1954–1957.

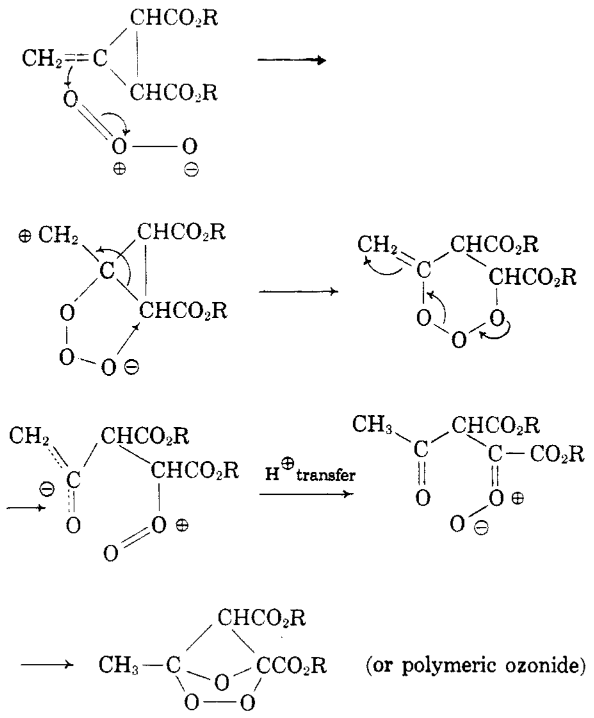
[3] F. Feist, *Ber.*, **26**, 747 (1893); *Ann.*, **436**, 125 (1924).

[4] M. G. Ettlinger, *J. Am. Chem. Soc.*, **74**, 5805 (1952).

[5] Unpublished work by J. H. Sturdivant and D. R. Petersen; D. R. Petersen, Ph.D. Thesis, California Institute of Technology, 1955. A less complete analysis has been reported by D. Lloyd, T. C. Downie, and J. C. Speakman, *Chemistry & Industry*, 222, 492 (1954).

[6] Similar conclusions have been reached from NMR spectra of dimethyl and diethyl esters of Feist's acid by M. G. Ettlinger and F. Kennedy, *Chemistry & Industry*, 166 (1956). We are grateful to Dr. Ettlinger for information regarding these results in advance of publication.

[7] G. R. Boreham, F. R. Goss, and G. J. Minkoff, *Chemistry & Industry*, 1354 (1955).



IV

yield ethyl acetoxaloacetate and no formaldehyde as expected of esters of II.[8] However, it should be noted that methylenecyclopropane yields but 2% of formaldehyde on ozonization.[9] Furthermore, if attack of ozone is electrophilic in character, esters of I might afford acetoxaloacetates by a sequence of reasonable reactions like the following (here presented in condensed form) which involves a rather common type of ring-opening process as the key step. IV can be regarded as the normal ozonide of II.

We are indebted to Dr. Martin G. Ettlinger for helpful discussions and generous samples of I and III.

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A Note on the Dechlorination Condensation of Benzal Chloride and Benzotrichloride by Iron and Water

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Several years ago, one of the authors reported on the dechlorination condensation by iron powder suspended in water, whereby dibenzyl was produced from benzyl chloride, *trans*-stilbene (II) from benzal chloride, and *trans*-α,α'-dichlorostilbene (IV) from benzotrichloride.[1] This procedure has been applied by several other investigators to the condensation of *p*-(α-halogenoalkyl)anisoles[2] and their derivatives,[3,4] to prepare hexestrol and its derivatives.

$$2\,C_6H_5CHCl_2 \xrightarrow{Fe\,+\,H_2O} \underset{I}{C_6H_5CHCl{-}CHClC_6H_5} \xrightarrow{Fe\,+\,H_2O} \underset{II}{C_6H_5CH{=}CHC_6H_5} \quad (A)$$

$$2\,C_6H_5CCl_3 \xrightarrow{Fe\,+\,H_2O} \underset{III}{C_6H_5CCl_2{-}CCl_2C_6H_5} \xrightarrow{Fe\,+\,H_2O} \underset{IV}{C_6H_5CCl{=}CClC_6H_5} \quad (B)$$

It is natural to consider that the reaction of benzal chloride or benzotrichloride proceeds *via* path (A) or (B), respectively.

The present paper describes the isolation of the intermediate α-stilbene dichloride (I) and tolane tetrachloride (III) in the very early stages of the dechlorination reaction of benzal chloride and benzotrichloride, respectively. Moreover, it has been ascertained that intermediate (I) on the further dechlorination with iron gave *trans*-stilbene (II) and intermediate (III) gave *trans*-α,α'-dichlorostilbene (IV). These condensations probably proceed by way of unstable organoiron chlorides as in the case of magnesium or zinc. But the organoiron compounds are so unstable and highly reactive toward another chlorine atom that they are difficult to detect. It is of interest to note that the organoiron intermediate hardly reacts with water, and this property differentiates it from the organomagnesium or organozinc compound. The role of the water in the reaction is not only to keep the fluidity of the mixture but to prevent the occurrence of Friedel-Crafts reactions leading to polymeric substances.

EXPERIMENTAL

All melting points are corrected. The syntheses under optimum conditions are described.

α-Stilbene dichloride (I) *from benzal chloride.* In a flask equipped with a reflux condenser were placed water (200 cc.) and finely divided iron (reduced iron powder) (35 g., 0.632 mole). The flask was dipped in a boiling water-bath and to it was added benzal chloride (50.9 g., 0.316 mole) with vigorous stirring in one minute. The stirring then was continued for 3 minutes. The reaction mixture was extracted with benzene and the solvent was evaporated to dryness to produce crude material. The crude crystals were washed with petroleum ether, aqueous ammonia, and then

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[8] F. R. Goss, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, **123**, 327 (1923).

[9] J. T. Gragson, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **75**, 3344 (1953).

[1] Ogata, Tsuruta, and Oda, *Bull. Phys. Chem. Research (Tokyo)*, 21, 616 (1942) [*Chem. Abstr.*, **43**, 2194 (1949)].

[2] Sisido and Nozaki, *J. Am. Chem. Soc.*, **70**, 778 (1948).

[3] Sisido, Nozaki, and Kuyama, *J. Org. Chem.*, **14**, 1124 (1949).

[4] Buu-Hoï and Hoán, *J. Org. Chem.*, **14**, 1023 (1949).