

3. For the solutions studied, those with pH greater than 7 have interfacial tensions greater than that of pure water-mercury; those with pH less than 7 have interfacial tensions less than that of pure water.

4. The pH of the solution has no direct bearing on the emulsification of mercury.

5. The electrocapillary curves of the systems

studied show that emulsifying and non-emulsifying agents give similar results with respect to maxima and form of curve.

6. Measurements of interfacial tensions made with the mercury and a fixed electrode in the solution shorted, give values less than that of pure water against mercury.

SEATTLE, WASH.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Silicon Compounds. I. The Use of Silicon Tetrafluoride in the Formation of Esters and Some Absorption Reactions

BY J. A. GIERUT, F. J. SOWA AND J. A. NIEUWLAND

It has been demonstrated recently in this Laboratory¹ that boron fluoride can be used to remove the elements of water and ammonia from alcohols and acids, and from alcohols and acetamide, to yield esters. Since silicon tetrafluoride resembles boron fluoride in many reactions of this type, we have studied its use in place of boron fluoride in the above reactions.

The silicon tetrafluoride was prepared either by heating to 150° a mixture of 156 g. of calcium fluoride, 300 g. (in excess) of finely pulverized silicon dioxide and 300-350 cc. of sulfuric acid, a slow stream of dry air being passed into the generator to assure a continuous flow of gas; or, more satisfactorily, by using a mixture of 100 g. of sodium fluosilicate, 15 g. of finely pulverized silicon dioxide and 250 cc. of concentrated sulfuric acid. The apparatus used was a modification of that of Adolph² with suggestions from the design of Armstrong.³

One mole each of the reacting substances was separately weighed into a 500-cc. Erlenmeyer flask fitted with a stopper carrying an outlet tube and an inlet tube which extended to within 2 cm. of the bottom of the flask. In the preparation of the benzoates, two moles of the alcohol were used to one of the acid. The amount of silicon tetrafluoride absorbed was ascertained by weighing the flask. In several cases where acetamide was used the alcohol was first saturated with silicon tetrafluoride and the acetamide then added.

The contents of the flask were refluxed for about twenty minutes. The upper layer which had then appeared was either distilled and then neutralized with a sodium carbonate solution or it was cooled and then neutralized directly. The ester layer was then separated, washed, dried over calcium chloride and fractionated.

Using acetic acid, between 0.1 and 0.3 mole of silicon tetrafluoride was absorbed per mole of methyl, ethyl, *n*- and *i*-propyl and *n*- and *i*-butyl alcohols. The yield of ester was practically quantitative for ethyl and methyl alcohol and between 20 and 60% for the other alcohols.

With benzoic acid similar amounts of silicon tetrafluoride were absorbed. A 40% yield of ester was obtained with methyl alcohol but only small yields, namely, 4-17%, with the other alcohols.

With acetamide between one-quarter and one-third of a mole of silicon tetrafluoride was absorbed with all of the alcohols and a yield between 13 and 20% of ester was obtained.

t-Butyl alcohol absorbed about 0.2 mole of silicon tetrafluoride and gave a yield of 4.3% ester with acetic acid. The phenol-acetic acid or acetamide solutions, although they absorbed some silicon tetrafluoride, gave either no ester or only a trace in all cases.

The absorption of silicon tetrafluoride by the alcohol alone was investigated using the same experimental arrangements. Methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *n*-amyl and *i*-amyl alcohols absorb about one-quarter of a mole of silicon tetrafluoride, the products being unstable addition compounds; phenol, ethyl ether, isopropyl phenyl ether, ethyl acetate and acetic acid do not absorb any silicon tetrafluoride. Acetamide absorbs about one-quarter and tributylamine about two-thirds of a mole, forming white solids.

Ammonia passed into an alcoholic solution of silicon tetrafluoride forms a white precipitate, which after removal can be sublimed without decomposition and appears to correspond to $SiF_4 \cdot (NH_3)_2$ as previously reported.⁴

It is interesting that in the case of isopropyl alcohol a white gelatinous substance began to form, indicating a possible slight dehydration of the alcohol, and indeed an absorption slightly greater than one-quarter of a mole was obtained in this case.

Summary

Various esters have been formed by treating acetic acid, benzoic acid or acetamide with alco-

(1) Sowa and Nieuwland, *THIS JOURNAL*, **55**, 5052 (1933); **56**, 271 (1936).

(2) Adolph, *ibid.*, **37**, 2500 (1915).

(3) Armstrong, *Ind. Eng. Chem., Anal. Ed.*, **5**, 315 (1933).

(4) Mixer, *Am. Chem. J.*, **2**, 153 (1881).

hols in the presence of silicon tetrafluoride. Practically the theoretical yields of methyl and of ethyl acetate are obtained.

Alcohols absorb silicon tetrafluoride in the ratio of four moles of alcohol to one mole of tetrafluoride,

the products being unstable addition compounds. Acetamide, ammonia and tributylamine form other stable white solids with silicon tetrafluoride.

NOTRE DAME, IND.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Contribution to the Multiplanar Isomerism of Cyclohexanes

BY R. F. MILLER¹ AND ROGER ADAMS

Quadrat-I-Khuda² reported the isolation of four forms of 4-methyl-1-carboxycyclohexyl acetic acid and explained their existence on the basis of the Sachse theory of two multiplanar rings. Goldschmidt and Gräfinger³ and Desai and Hunter⁴ however, have repeated these experiments without successfully obtaining more than two compounds. All other apparent compounds were mixtures of these two.

Quadrat-I-Khuda⁵ has also reported two forms of β,β -dimethylcyclohexanone but Dey and Linstead⁶ have shown one of these to be 2,2,4-trimethylcyclopentanone.

Although other authors have investigated types of compounds which might exist in the form of multiplanar isomers, no satisfactory evidence has as yet been offered to establish that such forms of cyclohexane or its derivatives can exist.⁷ Cohen⁸ on the basis of a geometrical analysis believes in two configurations for cyclohexane, one a "fixed" represented by the "Z" or chair modification and the other a "mobile" having an infinite number of modifications of which the "C" or boat form is one. Mills⁹ on the other hand, has pointed out

that the energy changes involved in the interconversion of one form to the other are so small as to exclude the likelihood of isolating the isomers as individuals.

The investigation described in this communication was undertaken to supplement the researches of Quadrat-I-Khuda,² from which he deduced that multiplanar isomers may be isolated in certain substituted cyclohexanes. The compound studied by Quadrat-I-Khuda, 4-methyl-1-carboxycyclohexyl acetic acid (I) exists in *cis-trans* modifications of the classical type. It may, therefore, hardly be considered ideal for the investigation of possible multiplanar forms since the stereochemical character of the product becomes more complex when *cis-trans* isomerism is possible. No attempt was made to repeat Quadrat-I-Khuda's experiments, the procedure followed by Goldschmidt and Gräfinger, and by Desai and Hunter, but analogous compounds were selected which would eliminate the complication just mentioned.

(1) Part of a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Quadrat-I-Khuda, *J. Ind. Chem. Soc.*, **8**, 277 (1931); *Nature*, **136**, 301 (1935).

(3) Goldschmidt and Gräfinger, *Ber.*, **68**, 279 (1935).

(4) Desai and Hunter, *Nature*, **136**, 608 (1935).

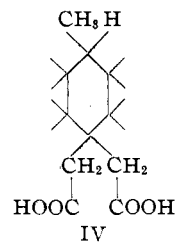
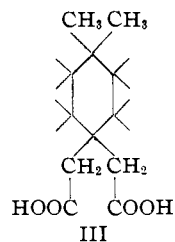
(5) Quadrat-I-Khuda, *ibid.*, **132**, 210 (1933).

(6) Dey and Linstead, *J. Chem. Soc.*, 1063 (1935).

(7) Schrauth and Görg, *Ber.*, **56**, 1900 (1923); Kursanoff, *J. Russ. Phys.-Chem. Soc.*, **34**, 221 (1902); Borsche and Lange, *Ber.*, **38**, 2766 (1905); Hell and Schaal, *ibid.*, **40**, 4162 (1907); Wallach, *ibid.*, **40**, 70 (1907); Werner and Conrad, *ibid.*, **32**, 3046 (1899); Böseken and Peek, *Rec. trav. chim.*, **44**, 841 (1925); Derx, *ibid.*, **41**, 312 (1922); Wightman, *J. Chem. Soc.*, **126**, 2541 (1926); Hopff, *Ber.*, **64B**, 2739 (1931); **65B**, 482 (1932); Unger, *ibid.*, **65B**, 467 (1932); Nenitzescu and Jonescu, *Ann.*, **491**, 189, 210 (1931); Zelinsky and Tarassova, *Ber.*, **65B**, 1249 (1932); *Ann.*, **508**, 115 (1934); Cornubert and Borrel, *Bull. soc. chim.*, **46**, 1148 (1929); Cornubert and Maurel, *ibid.*, **49**, 1498 (1931); Cornubert and de Demo, *Compt. rend.*, **197**, 1656 (1933); Desai, *Nature*, **135**, 434 (1935).

(8) Cohen, *Proc. Roy. Acad. Amsterdam*, **37**, 532 (1934).

(9) Mills, "Inst. intern. chim. Solvay Conseil chim." 4th Conseil, Brussels, 1931, p. 1-60.



Compounds II, III and IV in which no *cis-trans*