Dr. D. L. Turner and Dr. J. M. Vandenbelt. We thank Parke, Davis and Company for their assistance.

Summary

1. Twelve new sapogenins and two new pro-sapogenins have been isolated. The original isolation procedure for each is described. Additional sources for these have been reported previously.[3]
2. Chemical interrelationships between these and the previously characterized sapogenins have been carried out. Structures for the new sapogenins and the pro-sapogenins have been proposed.
3. Neochlorogenin, β-neochlorogenin, 7-ketogitogenin, 7-ketoyuccagenin and 6-ketotigogenin have been prepared.
4. The positions of the hydroxyl groups in digitogenin have been further established at C-2, C-3 and C-15.
5. Diosgenin and tigogenin have been interrelated with kryptogenin, further illustrating the spiro-ketal nature of the sapogenin side-chain.
6. Bethogenin has been shown to be a derivative of kryptogenin.
7. A biogenetic relationship of the sapogenins has been proposed and correlated with the seasonal changes of the steroidal content of various plants.

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(123) Original manuscript received June 26, 1944.

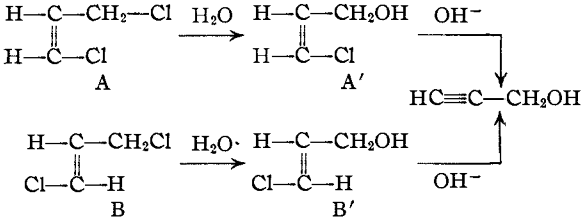
NOTES

The *cis-trans* Isomers of 1,3-Dichloropropene

BY LAWRENCE J. ANDREWS AND RICHARD E. KEPNER

The terms *alpha* and *beta* were formerly used to designate, respectively, the low and high boiling isomers of 1,3-dichloropropene.[1] On the basis of comparative studies of the rates of hydrolysis of the isomeric dichlorides as catalyzed by the cuprous chloride–chloride ion complex and of the comparative rates of dehydrochlorination of the corresponding 3-chloro-2-propen-1-ols the *alpha* isomer has been assigned the *trans* and the *beta* isomer the *cis* configuration.[2] In surveying the evidence on which these assignments of structure are based we have noted that there is still doubt as to the correct geometric configurations of the two compounds.

For purposes of discussion the two dichlorides will be designated A and B and the corresponding alcohols as A′ and B′, as represented below.



The catalytic action of cuprous chloride in the hydrolysis of allyl chloride in dilute hydrochloric acid solution has been explained on the assumption that the reaction is facilitated by formation of an intermediate complex between the olefin and $CuCl_2^-$.[3] Since the rate of hydrolysis of *beta* 1,3-dichloropropene under these conditions is much more rapid than that of the *alpha* isomer, it has been assumed that formation of an olefin–$CuCl_2^-$ complex occurs more readily with the *beta* than with the *alpha* isomer.[2] Hatch and Roberts have made the further assumption that the factors influencing the formation of such a complex are similar to those involved in the mercuration of an olefin. Since *cis*-methyl cinnamate and *cis*-stilbene are mercurated faster than the corresponding *trans* isomers,[4] they have concluded that beta 1,3-dichloropropene is the *cis* isomer. Though Hatch and Roberts do not show structural formulas, it seems likely that the *cis* isomer to which they refer should be represented by formula A, in which the two hydrogen atoms attached to the ethylenic linkage are *cis* with respect to each other.

In a mercuration reaction of the type under consideration it has been shown that the mercurating agent, methoxymercuric acetate, adds to the double bond of the olefin.[5] On the other hand the hydrolysis of a dichloropropene is a substitution reaction. However the formation of a complex between dichloropropene and $CuCl_2^-$, resulting in an enhanced rate of hydrolysis of the unsaturated halide, might be explained on the assumption that the complex were formed by addition of the $CuCl_2^-$ to the double bond of the olefin. There is still no experimental evidence to indicate that the mechanism of formation of this complex would be similar to or different from that of the

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(1) Hatch and Moore, THIS JOURNAL, **66**, 285 (1944).

(2) Hatch and Roberts, *ibid.*, **68**, 1196 (1946).

(3) Hatch and Estes, *ibid.*, **67**, 1730 (1945).

(4) Thomas and Wetmore, *ibid.*, **63**, 136 (1941), have assigned the *cis* configuration to the 2-butene isomer which mercurates faster.

(5) (a) Wright, *ibid.*, **57**, 1993 (1935); (b) Romeyn and Wright, *ibid.*, **69**, 697 (1947).

mercuration reaction. At present, therefore, it seems unwise to the authors to attempt an assignment of geometric configuration to the dichloropropenes on the basis of an interpretation of their $CuCl_2^-$ catalyzed hydrolysis rates in terms of the steric course of mercuration reactions.

The chloroalcohol obtained by hydrolysis of α-1,3-dichloropropene is readily dehydrochlorinated by aqueous sodium hydroxide while that obtained from the *beta* isomer is not.[1] On the basis that chlorofumaric acid is dehydrochlorinated more readily than chloromaleic acid, Hatch and Roberts concluded that the *alpha* dichloride and chloroalcohol were the *trans* isomers (presumably B and B′).

However a survey of the literature indicates that in general dehydrohalogenation of vinyl halides takes place most readily when the hydrogen and halide are *trans* to each other.[6] For example, chlorofumaric acid,[6] *trans*-2-bromo-2-butene[7] and *cis*-dichloroethylene[8] all dehydrohalogenate more readily than the isomers of opposite geometric configuration. From these facts it would seem better to reach a conclusion opposite to that of Hatch and Roberts and to assign the structures A and A′ to the *alpha* isomers and B and B′ to the *beta* isomers.

In the opinion of the authors a definite assignment of geometric configuration for the 1,3-dichloropropenes cannot be made on the basis of available experimental evidence. It is possible that further studies of the mechanisms of dehydrohalogenation of substituted vinyl halides and of the cuprous chloride–chloride ion complex catalyzed hydrolysis reactions would clarify this situation.

[6] (a) Michael, *J. prakt. Chem.*, [2] **52**, 289 (1895); (b) Michael, THIS JOURNAL, **40**, 704, 1674 (1918).

[7] Wislicenus and Schmidt, *Ann.*, **313**, 216 (1900).

[8] Chavanne, *Compt. rend.*, **154**, 776 (1912).

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Nicotinic Anhydride

BY C. O. BADGETT

Preparation of nicotinic anhydride by the reaction of nicotinyl chloride with sodium nicotinate and subsequent distillation of the anhydride from the reaction mixture has been reported previously.[1] However, the synthesis of pure nicotinyl chloride from nicotinic acid[2,3] or from nicotinic acid nitrate[4] is difficult, time-consuming, and poorly productive because of the troublesome separation of the acid chloride from pyridine hydrochloride by distillation.

A simplified method for the preparation of nicotinic anhydride from nicotinic acid has been developed in this Laboratory. Excellent yields of essentially pure product are obtained by a process in which distillation procedures are eliminated and the anhydride is crystallized from the liquid portion of the reaction mixture. The improvement over previously reported methods is achieved by high temperature removal of hydrogen chloride from nicotinyl chloride hydrochloride in inert solvents.

Preparation

Into a 500-cc. three-necked, round-bottom flask equipped with a condenser fitted with a calcium chloride drying tube, air-tight stirrer and dropping funnel, were placed 40.6 g. (0.33 mole) of nicotinic acid and 100 cc. of anhydrous nitrobenzene. Over a period of ten minutes, 39.3 g. (0.33 mole) of redistilled thionyl chloride was added dropwise. The temperature of the reaction mixture was raised gradually to 210° and maintained for one hour, or until all gas evolution had ceased. The reaction mixture was allowed to cool, then 53.1 g. (0.33 mole) of potassium nicotinate was introduced in one portion, and the mixture was heated to 210° for three hours, after which it was allowed to cool to approximately 100° and poured into a 1500-cc. beaker. One liter of anhydrous benzene and 10 g. of Norit were added. The mixture was then boiled for about ten minutes and filtered through a heated Buchner funnel, and the filtrate was cooled to room temperature. The 49.5 g. of nicotinic anhydride which crystallized had a melting point of 119.8–121.5°.[5] Concentrating the mother liquors to approximately 150 cc. gave a second crop of crystals, which weighed 14.6 g. and had a melting point of 119.1–121.3°. A third crop of 2.5 g. was obtained by further concentration and crystallization, bringing the total weight of nicotinic anhydride to 66.6 g. This represented a yield of 88.9%. The combined crops of crystals recrystallized once from hot benzene gave a pure anhydride melting at 122.5–123.5°. However, the crude anhydride was of sufficient purity to be used in most syntheses.

Anal. Calcd. for $C_{12}H_8N_2O_3$: C, 63.16; H, 3.53; N, 12.28. Found: C, 63.15; H, 3.63; N, 12.23.

Direct reaction of 1 mole of potassium nicotinate with 0.5 mole of thionyl chloride gave lower yields than this procedure. Use of other solvents in the preparation of nicotinic anhydride was investigated. Nitrobenzene gave the best yields and product. The following table shows the solvent used and yield of anhydride obtained.

Solvent	Yield, %
Nitrobenzene	88.9
o-Dichlorobenzene	78.3
Deobase[6]	47.9
p-Cymene	26.6

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[1] Graf, *Biochem. Z.*, **229**, 164–168 (1930).

[2] Späth and Spitzer, *Ber.*, **59B**, 1477–1486 (1926).

[3] Meyer and Graf, *ibid.*, **61**, 2202–2215 (1928).

[4] Douglass and Forman, THIS JOURNAL, **56**, 1609 (1934).

[5] Melting points reported are uncorrected.

[6] Deobase is deodorized kerosene. It was redistilled and only the cut boiling at 205–215° was used.

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The Preparation of 1-Phenyl-1,3-butadiene

BY E. C. COYNER AND G. A. ROPP[1]

In connection with a study of Diels–Alder reactions of aryl-substituted dienes, an investiga-

[1] Research Corporation Fellow.