ically active species, diethylamine hydrochloride and aniline hydrochloride were tested, but they had no catalytic effect under these conditions.

EXPERIMENTAL

3-Trichlorosilylpropionitrile (I). A mixture of 106 g. (2 moles) of acrylonitrile, 271 g. (2 moles) of trichlorosilane, and 7.2 g. (0.1 mole) of dimethylformamide was refluxed for 24 hr. During this period the temperature increased from 37° to 83°.[12] Then an additional 135.5 g. of trichlorosilane was slowly added to the refluxing mixture over a period of 48 hr. The final reflux temperature was 105°. The lower boiling components were distilled from the mixture before the product was distilled at reduced pressure to give 272 g. (72%) of 3-trichlorosilylpropionitrile, m.p. 32–33°, b.p. 78–84° at 7–8 mm.

Anal. Calcd. for $C_3H_4NCl_3Si$: Si, 14.90; Neut. Equiv., 62.9. Found: Si, 15.3; neut. equiv., 62.6.

The amides listed in the table were evaluated as catalysts by refluxing equimolar amounts of trichlorosilane and acrylonitrile for 24 hr. in the presence of 2 mole % of the amide. The product was then distilled from the mixture in the yields shown.

CATALYSTS FOR THE CYANOETHYLATION OF TRICHLORISOLANE

Amide	% Yield in 24 Hr.
Dimethylformamide	42
N,N-Diethylbenzamide	38
N,N-Dibutylacetamide	38
N,N-Diethyldecanamide	42
p-Acetotoluide	43
Acetanilide	21
N,N-Dibutylbutyramide	35
N,N-Diethylpropionamide	34

3-Triethoxysilylpropionitrile (II).[1] A solution of 94 g. (0.5 mole) of I in 150 ml. of hexane was slowly added with stirring to a solution of 158 g. (2 moles) of pyridine, 92 g. of ethanol (2 moles), and 400 ml. of hexane. The mixture was cooled, filtered, and devolatilized. The residue was distilled at reduced pressure to give 86.7 g. (80%) of II, b.p. 108–110° at 10 mm., n_D^{22} 1.4121.

3-Methyldichlorosilylpropionitrile (III).[2] A solution of 0.5 mole of methyl magnesium bromide in 200 ml. of ether was added over a period of 1 hr. to a stirred solution of 94.2 g. (0.5 mole) of I in 200 ml. of ether. The stirring was continued for 0.5 hr., the solution was filtered, and the precipitate was washed with dry ether. The solvent was distilled from the combined filtrates, and the residue was distilled at 79–93° at 7–9 mm. to give 64 g. of crude product. Redistillation of the crude product gave 18.3 g. of pure III, b.p. 89° at 16 mm.; n_D^{22}, 1.4560; d_4^{25}, 1.206.

Anal. Calcd. for $SiC_4H_7NCl_2$: Neut. Equiv. 84.0. Found: 83.0.

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(12) An attempt to carry out this reaction in a sealed pressure bottle on a steam bath resulted in an explosion causing considerable damage to the surroundings.

Syntheses of *N*-Vinyl-secondary-amic Acids

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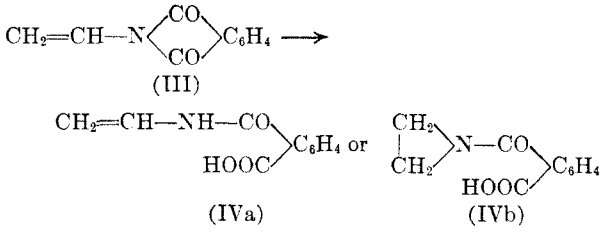
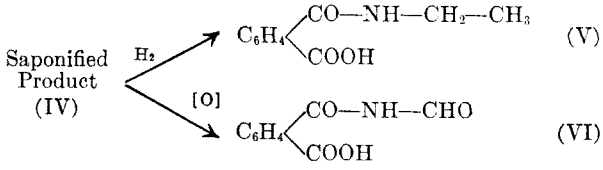
Since vinylamine (I) is unstable and is immediately isomerized into ethyleneimine (II) by the migration

$$CH_2{=}CH{-}NH_2 \quad (I) \qquad CH_2{-}{-}CH_2 \ (NH) \quad (II)$$

of hydrogen from nitrogen to carbon, all reactions intended to form vinylamines yield ethyleneimine.[1] On the other hand *N*-vinylimides, that is, *N,N*-disubstituted vinylamines such as *N*-vinylphthalimide (III), are stable. It is a matter of much interest whether the partially saponified product of III is *N*-vinylphthalamic acid (IVα) (*N*-vinyl secondary amide type structure) or *N*-(*o*-carboxybenzoyl)ethyleneimine (IVb).



We attempted to saponify III with alkali under mild conditions, obtaining a product whose composition was found to be $C_{10}H_9NO_3$ by analysis. This is equivalent to IVa or IVb. Through the catalytic hydrogenation of the saponified product under ordinary pressure and at room temperature, *N*-ethylphthalamic acid (V) was obtained. By oxidizing the saponified product with dilute aqueous potassium permanganate at room temperature, *N*-(*o*-carboxybenzoyl)formamide (VI) was obtained. (The ethyleneimine ring is stable to potassium permanganate.[2]) In the infrared spec-



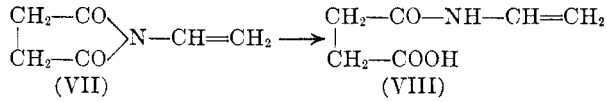
trum of the saponified product there are seen absorption bands at 3.02μ and 6.48μ which are considered to represent N—H of the secondary amide. If the saponified product were IVb, which is the tertiary imide and has no N—H group, these bands would not be expected. The absorptions at 6.02μ, 10.15μ, and 11.15μ, which are lacking in the infrared spectrum of the hydrogenated product (V), reveal the existence of a vinyl group, indi-

(1) C. C. Howerd and W. Markwald, *Ber.*, **32**, 2036 (1899).

(2) W. Markwald, *Ber.*, **33**, 765 (1900).

cating that the saponified product was IVa instead of IVb. In other words, a structure of the *N*-vinyl secondary amide type is stable.

By the similar saponification of *N*-vinylsuccinimide (VII), *N*-vinylsuccinamic acid (VIII), was obtained.



(VII) (VIII)

In the case of the saponification of *N*-vinylsaccharin, *o*-sulfamidobenzoic acid or saccharin was obtained.

EXPERIMENTAL

Materials. *N*-Vinylphthalimide,[3] *N*-vinylsuccinamide,[4] and *N*-vinylsaccharin were prepared by the pyrolysis of *N*-2-acetoxyethylphthalimide, *N*-2-acetoxyethylsuccinimide, and *N*-2-acetoxyethylsaccharin respectively. *N*-Vinylsaccharin is a new compound, m.p. 131–132° (from ethanol).

Anal. Calcd. for $C_9H_7NO_3S$: C, 51.67; H, 3.37; N, 6.70. Found: C, 51.61; H, 3.36; N, 6.64.

N-Vinylphthalamic acid (IVa). Five grams of *N*-vinylphthalimide (III) was added to 50 ml. of 10% aqueous potassium or sodium hydroxide while stirring at room temperature, after which most of III was neutralized with 5% sulfuric acid under ice-cooling. The precipitate which was filtered and washed with water, was extracted with ethanol and the solvent was concentrated under reduced pressure and at room temperature, and then IVa was obtained, m.p. 110–111.5° (dec.). IVa was also obtained by saponification with ethanolic potassium hydroxide.

Anal. Calcd. for $C_{10}H_9NO_3$: C, 62.82; H, 4.75; N, 7.32. Found: C, 62.72; H, 4.81; N, 7.25.

Hydrogenation of IVa. To 10 ml. of ethanol and 0.1 g. of Pd-black saturated with hydrogen in a hydrogenation vessel, 0.72 g. of IVa was added and hydrogenated with vigorous shaking under ordinary pressure and at room temperature. After hydrogenation was completed, the solution was filtered to remove the catalyst and the solvent was evaporated. Recrystallization of the residue from benzene gave 0.62 g. of *N*-ethylphthalamic acid (V), m.p. 133°. The mixed melting point of V with the authentic sample which was prepared by the saponification of *N*-ethylphthalimide was 132–133°.

Anal. Calcd. for $C_{10}H_{11}NO_3$: N, 7.25. Found: N, 7.13.

Oxidation of IVa *with potassium permanganate.* To the solution in which 1.7 g. of IVa was suspended by vigorous stirring in 30 ml. of water was added in 0.5 hr. another solution made by dissolving 0.86 g. of potassium permanganate in 60 ml. of water. Stirring was further continued for 20 min. after addition of potassium permanganate was completed. After addition of sodium hydrogen sulfide to the solution, the latter was extracted with 10 portions of 20 ml. of ethyl acetate. The extract was dried with anhydrous sodium sulfate and the solvent was evaporated. Recrystallization of the residue from ethanol gave 1.7 g. of VI, m.p. 150–151°.

Anal. Calcd. for $C_9H_7NO_4$: C, 55.96; H, 3.65; N, 7.25. Found: C, 55.77; H, 3.75; N, 6.98.

N-Vinylsuccinamic acid (VIII). Five grams of *N*-vinylsuccinimide (VII) was dissolved in 20 ml. of 10% aqueous sodium hydroxide. After the solution was filtered, the filtrate was neutralized with 5% sulfuric acid under ice-cooling. The solution was extracted with ether and the solvent was removed after the extract was dried with anhydrous calcium chloride. Recrystallization of the residue from ether gave VIII, m.p. 93–94°.

Anal. Calcd. for $C_6H_9NO_3$: N, 9.79. Found: N, 9.98. Hydrogenation of VIII gave *N*-ethylsuccinamic acid, m.p. 96–97°.

Saponification of N-vinylsaccharin. Two grams of *N*-vinylsaccharin was dissolved in a mixed solution of 10 ml. of ethanol and 10 ml. of aqueous potassium or sodium hydroxide, then the solution was filtered and the filtrate was neutralized with 5% hydrochloric or sulfuric acid and extracted with ethyl acetate. After drying the extract with anhydrous calcium chloride, the solvent was distilled under reduced pressure. Recrystallization of the residue from ethanol gave saccharin, m.p. 224°. The mixed melting point with an authentic sample was 222–223°. The infrared spectra of the two coincided. The product obtained by saponification with 10% ethanolic potassium hydroxide in a similar method was also saccharin. The product of saponification with 10% aqueous sodium hydroxide was *o*-sulfamidobenzoic acid, m.p. 164–165°. The mixed melting point with the authentic sample[5] was 164–165°. The infrared spectra of the two perfectly coincided.

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(3) W. E. Hanford and H. B. Stevenson, U. S. Patent **2,276,840**; *Chem. Abstr.*, **36**, 4637 (1942).

(4) W. E. Hanford and H. B. Stevenson, U. S. Patent **2,231,905**; *Chem. Abstr.*, **35**, 3267 (1941).

(5) *Beilsteins Handbuch der Organischen Chemie*, 4te. Auflage, Julius Springer, Berlin, 1928, *Bd. XI*, 376. (Wilson, *Am. Chem. J.*, **30**, 354).

16-Hydroxylated Steroids. VIII.[1] 5β-Dihydrocortisone Approach to the Synthesis of Triamcinolone

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In 1956, this laboratory[2] announced the synthesis of triamcinolone (9α-fluoro-16α-hydroxy-prednisolone), a compound which has found considerable use in the treatment of rheumatoid arthritis and other disorders.[3] The importance of triamcinolone therefore merited further work on its preparation.[4]

One of the original syntheses of triamcinolone proceeded *via* 16α,21-diacetoxy-17α-hydroxy-4,9-

(1) Paper VII, S. Bernstein, M. Heller, R. Littell, S. M. Stolar, R. H. Lenhard, W. S. Allen, and I. Ringler, *J. Am. Chem. Soc.*, in press.

(2) S. Bernstein, R. H. Lenhard, W. S. Allen, M. Heller, R. Littell, S. M. Stolar, L. I. Feldman, and R. H. Blank, *J. Am. Chem. Soc.*, **78**, 5693 (1956). A detailed paper on this work has been submitted for publication to the *Journal of the American Chemical Society*.

(3) L. Hellman, B. Zumoff, M. K. Schwartz, T. F. Gallagher, C. A. Berntsen, Jr., and R. H. Freyberg, Paper presented before Am. Rheumatism Assoc. Meeting, Bethesda, Md., Nov. 30, 1956; R. H. Freyberg, C. A. Berntsen, Jr., and L. Hellman, *Arthritis and Rheumatism*, **1**, 215 (1958).

(4) A synthesis of triamcinolone based essentially on the introduction of the 16α-hydroxyl group by *Streptomyces roseochromogenus* has been announced by R. W. Thoma, J. Fried, S. Bonanno, and P. Grabowich, *J. Am. Chem. Soc.*, **79**, 4818 (1957).