Anthraquinones.—Oxygen was bubbled through a solution of 1 g. of 2-phenyltetrahydroanthraquinone in 25 ml. of 0.2 *N* alcoholic sodium hydroxide for one hour; the dark red color of the solution was discharged and a yellow precipitate of 2-phenylanthraquinone appeared. Upon recrystallization from 95% ethanol, the product melted at 162–163° (lit.,[1,2] 162–163°).

2-(*p*-Tolyl)-anthraquinone, melting at 176°, and 2-(3,4-dichlorophenyl)-anthraquinone, melting at 228°, were also prepared by the above method.

4-Phenyl-Δ^4-tetrahydrophthalic Anhydride.—The anhydride was prepared by heating 2 g. of maleic anhydride, 3 g. of 2-phenyl-1,3-butadiene and 10 ml. of anhydrous benzene at 90° for four hours. Recrystallization from benzene gave a melting point of 105° (lit.,[2] 105–105.5°).

Summary

Procedures have been developed for the preparation of 4-aryl-4-methyl-1,3-dioxanes and 2-aryl-4-acetoxy-1-butenes by the reaction of formaldehyde with α-methylstyrenes in acetic acid solution. The corresponding 2-aryl-1,3-butadienes have been prepared by the pyrolysis of these compounds, and have been characterized by their Diels–Alder adducts with 1,4-naphthoquinone.

NOTRE DAME, INDIANA RECEIVED DECEMBER 17, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Aliphatic Aldehydes. I. Lauryl Aldehyde and Some New Aspects of the Stephen Reaction[1]

BY EUGENE LIEBER

Since Stephen[2] announced his "new synthesis of aldehydes" in 1925, there has been some controversy concerning its general applicability, particularly with regard to the higher aliphatic aldehydes.[3,4] In the Stephen procedure[2] anhydrous stannous chloride[5] is suspended in dry ether and saturated with dry hydrogen chloride gas until it dissolves. The nitrile is added and the criterion of the success of the reaction is based upon the precipitation from the reaction mixture of a crystalline "aldimine stannichloride," $(RCH{:}NH{\cdot}HCl)_2SnCl_4$. The complex is generally separated from the reaction mixture, washed with ether (hence *removing all ether soluble materials*) and then hydrolyzed with water or acid, usually by reflux, and the aldehyde recovered by distillation or extraction. Accordingly, failure to obtain an ether insoluble precipitate has been taken to indicate inapplicability of the Stephen reaction to the nitrile under consideration. The original Stephen procedure[2] has been modified at various times[6] because the tin complex was not obtained in the form and at the stage indicated in the original procedure. These modifications have been directed to inducing the formation of the ether insoluble complex.

The present paper summarizes the results of a study which has been made on the preparation of lauryl aldehyde (dodecyl aldehyde) from lauryl nitrile by means of the Stephen reaction. The main results of the study which will be discussed have revealed some new aspects of the Stephen reaction in which the prior criterion of an insoluble "aldimine stanni-complex" in this particular case is definitely misleading since, depending on the manner in which the reaction is conducted, both "liquid" and "solid" type lauryl nitrile–stannic chloride–hydrogen chloride complexes, which are, respectively, ether soluble and insoluble, can be isolated. Further, there seems to be no need for an *a priori* isolation of any complex whatsoever since the clear ether *solution* of a mixture of stannous chloride, hydrogen chloride and lauryl nitrile yields dimeric and trimeric lauryl aldehyde polymers when worked up after decomposition with water. The work has demonstrated the importance of examining the ether (or other solvent) solution of a Stephen reaction mixture, regardless of whether a precipitate has formed or not. The reduction of lauryl nitrile by the Stephen reaction has not been previously studied and this is the first recorded preparation of lauryl aldehyde by that means.

In the present study on the variables of the Stephen reaction the mode of attack and the main results obtained are summarized by Flow Plans A and B. Preliminary qualitative tests showed that anhydrous stannous chloride was quite insoluble in lauryl nitrile; however, by passing dry hydrogen chloride into the mixture, solution of the stannous chloride took place rapidly and the product was totally soluble in ether. By decomposing with water the presence of lauryl aldehyde was quite evident. Only a limited quantity of stannous chloride can be dissolved in lauryl nitrile, in the absence of solvent, by dry hydrogen chloride, the solution becoming very viscous, making further dissolution difficult. Quantitative experiments showed that this stage was reached at molar proportions of lauryl nitrile to hydrogen chloride to

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(1) Presented at the 115th meeting of the American Chemical Society, San Francisco, California, March 28, 1949.

(2) H. Stephen, *J. Chem. Soc.*, **127**, 1874 (1925).

(3) J. W. Williams, THIS JOURNAL, **61**, 2248 (1939).

(4) A. W. Ralston, "Fatty Acids and Their Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 818.

(5) H. Stephen, *J. Chem. Soc.*, 2786 (1930).

(6) (a) F. E. King and R. Robinson, *J. Chem. Soc.*, 273 (1933); (b) C. R. Harrington and R. C. G. Moggridge, *ibid.*, 443 (1939); (c) F. E. King, P. L'Ecuyer and H. T. Openshaw, *ibid.*, 352 (1936); (d) F. E. King, J. W. Clifton and H. T. Openshaw, *ibid.*, 424 (1942); (e) G. Wittig, R. Kethur, A. Klein and R. Wietbrock, *Ber.*, **69B**, 2078 (1936); (f) G. Wittig and H. Hartmann, *ibid.*, **72B**, 1387 (1939).

stannous chloride of 1:1.5:0.3. In the ordinary Stephen procedure a molar ratio of stannous chloride to lauryl nitrile of 1 to 1.5 is used.

Experimental

Lauryl Nitrile.—A sample of commercial lauryl nitrile was fractionated three times by vacuum distillation through a vacuum-jacketed Stedman type column, concentrating the fraction boiling at 138–140° at 10 mm. pressure.[7] The freezing point determined was found to be 4.0°; reported 4.02°.[4]

Anal. Calcd. for $C_{11}H_{23}CN$: N, 7.73. Found: N, 7.70, 7.69.

Stannous Chloride.—According to Williams[8] the success of the Stephen reaction depends upon the quality of the catalyst. The procedure used in the present paper is described by Stephen.[5] This comprises stirring reagent grade stannous chloride dihydrate in acetic anhydride, filtering, washing with fresh acetic anhydride, then with dry ether and drying in a vacuum desiccator overnight. The product is kept in a tightly closed bottle until used.

Behavior of Lauryl Nitrile with the Stephen Reagents

Stannous Chloride.—Qualitative tests showed that anhydrous stannous chloride is quite insoluble in pure lauryl nitrile. However, if dry hydrogen chloride be passed into the mixture, *solution of the stannous chloride takes place rapidly and the product is totally soluble in dry ether.* The ether solution or the viscous mixture of lauryl nitrile, stannous chloride and hydrogen chloride, on decomposition with water, forms a white precipitate and the "lily-like" odor of lauryl aldehyde becomes at once noticeable.

Hydrogen Chloride.—A number of quantitative experiments were conducted to determine the molar proportion of hydrogen chloride absorbed by lauryl nitrile, in the absence of ether, alone and in the presence of stannous chloride. Using an excess of hydrogen chloride, it was found that absorption is quite slow, reaching maximum values. Typical data are given in Table I. It will be interesting to note that the mole proportion of stannous chloride, based on the lauryl nitrile used, in the normal Stephen reaction is 1.85.

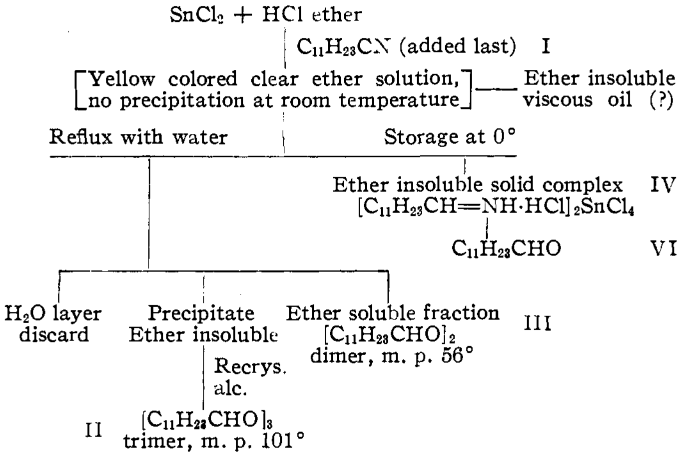
TABLE I

ABSORPTION OF HCl AT 25° BY LAURYL NITRILE AND LAURYL NITRILE–STANNOUS CHLORIDE IN ABSENCE OF ETHER

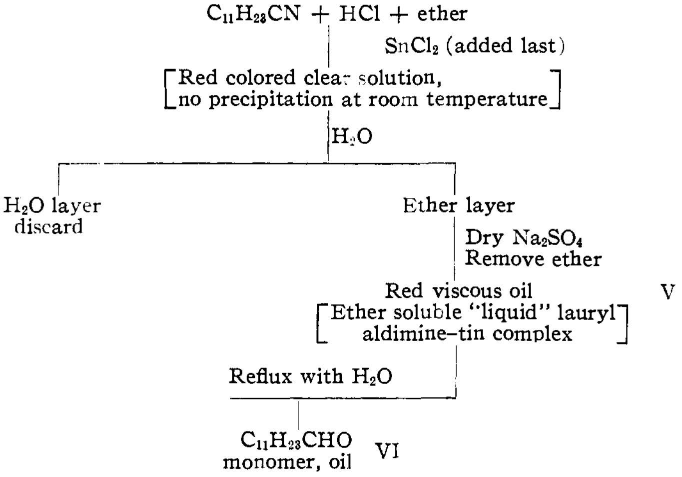
Time, min.	Absorbent	Moles $SnCl_2$[a]	Ratio HCl/ $C_{11}H_{23}CN$
30	$C_{11}H_{23}CN$	None	0.25
60	$C_{11}H_{23}CN$	None	.50
90	$C_{11}H_{23}CN$	None	.50
155	$C_{11}H_{23}CN$-$SnCl_2$	0.093[b]	.85
195	$C_{11}H_{23}CN$-$SnCl_2$	.186	1.10
235	$C_{11}H_{23}CN$-$SnCl_2$	.30	1.45
265	$C_{11}H_{23}CN$-$SnCl_2$	.30	1.45

[a] Molar proportion based on lauryl nitrile used. [b] The stannous chloride was added in increments of 0.093 mole proportion based on lauryl nitrile. The first addition dissolves rapidly. Succeeding increments of stannous chloride dissolve more slowly until 0.3 mole proportion has dissolved. The solution at this point is quite viscous and will not dissolve any further quantity of stannous chloride, even when heated to 100°.

FLOW PLAN "A"—STEPHEN PROCEDURE



FLOW PLAN "B"—CATALYST IN LAST



Lauryl Aldehyde Trimer, High Melting Form (II).—Fifty grams (0.28 mole) of lauryl nitrile was added to a solution of 97.5 g. (0.51 mole) of anhydrous stannous chloride in dry ether–hydrogen chloride according to the procedure of Stephen.[2] After standing overnight at room temperature no precipitation of aldimine stanni-chloride took place, although a small lower viscous layer was found to be present. The ether layer, colored yellow, was decanted and the lower viscous layer washed with fresh ether. The ether extracts were combined. The ether layer on water washing precipitates a small amount of white crystalline material (3.5 g.) which did not melt at 280° and had a high ash content (13%). After removing the ether, 37 g. of a white crystalline product was obtained. This was purified by successive recrystallizations from ethyl alcohol to a fine white crystalline powder, m. p. 101° (uncorrected).[9] Purification removes a small but very persistent ash which is present in the product; final yield, 32 g. (63%).

Anal. Calcd. for $C_{36}H_{72}O_3$: C, 78.05; H, 13.11; mol. wt., 552–556. Found: C, 77.46; H, 13.04; mol. wt. Rast (sealed tube), 505, 518, 510.

The viscous lower layer, separated from the above

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[7] G. W. Hoerr, E. F. Binkerd, W. O. Pool and A. W. Ralston, *J. Org. Chem.*, **9**, 68 (1944).

[8] J. W. Williams, *Org. Syn.*, **23**, 64 (1943).

[9] As pointed out by one of the reviewers of this paper, the appearance of a trimer of lauryl aldehyde of m. p. 101° is anomalous and suggests the necessity of a complete re-investigation of the whole dimer–trimer question with respect to the higher fatty aldehydes.

operation, was refluxed for sixteen hours with water, gradually depositing a curdy yellow precipitate. This was filtered and air dried; yield 14 g. (28%). It gave positive aldehyde tests. One recrystallization from ethyl alcohol gave a fine white powder melting at 100–101° (uncorrected). No depression of mixed melting point was found with the 101° m. p. product isolated from the ether layer. High melting lauryl aldehyde trimer (II) when isolated in crude form gives a strong positive aldehyde reaction with all reagents. However, on successive recrystallizations, the tests became entirely negative.

Lauryl Aldehyde 2,4-Dinitrophenylhydrazone.—Both 101° m. p. lauryl aldehyde trimers on reaction with 2,4-dinitrophenylhydrazine gave, respectively, yellow-orange crystals melting sharply at 106° (uncor.).[10]

Anal. Calcd. for $C_{18}H_{28}O_4N_4$: N, 15.32. Found: N, 15.01, 15.07.

Depolymerization of 101° m. p. Trimer.—Attempts to depolymerize the high melting lauryl aldehyde trimer by distillation under high vacuum (0.10 mm.) at 240–260° gave only very small amounts of a liquid over long periods of time. This was found to have a m. p. of 11° corresponding to one of the monomeric forms of lauryl aldehyde as reported by Zaar.[11]

Lauryl Aldehyde Dimer (III).—Thirty-six grams (0.2 mole) of lauryl nitrile was added to a solution of 68 g. (0.36 mole) of stannous chloride in ether–hydrogen chloride according to the procedure of Stephen.[2] The reaction mixture was allowed to stand twelve days at room temperature. *No precipitation of aldimine stanni-chloride took place,* the only noticeable change comprising the conversion of the original yellow ether solution to one having a reddish-orange color. Careful addition of water *to the entire solution* produced an upper yellow ether layer and a lower aqueous layer which was drawn off and discarded. The ether layer was then refluxed in the presence of water for eight hours, with frequent agitation. The refluxed mixture comprised a large amount of a white precipitate suspended in the ether. This was filtered off, washed with ether and air dried; yield 17 g. (46%). Recrystallization from ethyl alcohol gave a fine white powder, m. p. 101° (uncor.), identical with lauryl aldehyde trimer (II). It yielded a 2,4-dinitrophenylhydrazone, m. p. 105–106° (uncor.).

The ether extracts collected from above were water washed, dried with anhydrous sodium sulfate, filtered and the ether removed by distillation. The product comprised a granular waxy solid; yield 14 g. (38%), m. p. 54–56° (uncor.), which showed positive aldehyde reactions with all reagents. This corresponds to the dimeric lauryl aldehyde polymer of Zaar[11] and Guenther.[12] A Stillman–Reed analysis[13] showed a monomeric lauryl aldehyde content of 31%. This was readily separated by vacuum distillation at 10 mm. pressure, b. p. 120–125°, yielding the 11° m. p. monomeric form. Both the dimeric and monomeric lauryl aldehydes yield 2,4-dinitrophenylhydrazones melting at 106°.

Liquid-Type Lauryl Nitrile Stanni-chloride Complex.—Dry hydrogen chloride gas was passed into a solution comprising 25 g. (0.14 mole) of lauryl nitrile in 300 cc. of dry ether for two hours. At this time approximately 92 g. of hydrogen chloride had been absorbed. Forty-eight grams (0.25 mole) of anhydrous powdered stannous chloride was added at the rate of 8 g. every thirty minutes. Dry hydrogen chloride gas was passed through the reaction continuously. Each addition of stannous chloride dissolved instantly, forming an orange colored solution. On storage either at room temperature or at 0–10° F., *no precipitation took place,* even over a period of three weeks, the solution remaining clear and of a reddish-orange color. On careful addition of water (the initial addition of water forms a clear ether solution) two layers are formed, an upper deep reddish-orange solution and a lower aqueous layer, which was drawn off and discarded. The ether layer was dried with anhydrous sodium sulfate, filtered and the ether removed by distillation. A residue of 83 g. of a *viscous red oil* was obtained as product. Repetition of this experiment repeatedly yielded 80–90 g. of the same product when carried out in exactly the same manner. This corresponds to a quantitative yield on the basis that reagents lauryl nitrile, hydrogen chloride and stannic chloride are present approximately in the ratio $1:4:{}^1/_2$.

Anal. Calcd. for $C_{11}H_{23}CN{\cdot}4HCl{\cdot}{}^1/_2SnCl_4$: SnO_2, 16.5. Found: SnO_2, 15.9, 16.1.

The viscous red oil is positive to all aldehyde tests. It was found to be very soluble in ether, benzene, chloroform, dioxane, acetone and ethyl alcohol. In the latter solvent it slowly decomposes, depositing a white powder. It was found to be insoluble in petroleum ether and cyclohexane. In water the viscous oil ($d^{27}{}_4$ is 1.4258) settles to the bottom and slowly decomposes with the formation of a colloidal white precipitate and an oil which rises to the surface. This was identified after isolation as monomeric lauryl aldehyde.

Hydrolysis of Liquid Lauryl Nitrile Stanni-chloride Complex.—On boiling with water, the liquid complex decomposes with the separation of an oil which rises to the surface. This can be isolated by extraction with ether. The product so obtained after a brief reflux (thirty minutes) still had a very high ash content (6.3%) but gave a Stillman–Reed analysis of 85% lauryl aldehyde content. In order to determine the stability of the liquid complex to hydrolysis, it was refluxed for various periods of time with 2 *N* hydrochloric acid, the oil isolated, and the ash content determined. The data summarized below showed the liquid complex to be very resistant to hydrolysis.

Time, hr.	0	1	2	8	16	24
Ash, %	16.0	9.2	5.3	7.3	1.7	0.6

The oil obtained was converted to a 2,4-dinitrophenylhydrazone, m. p. 106–108° (uncor.) corresponding to lauryl aldehyde. On oxidation in an acetone solution of potassium permanganate, 2.0 g. was converted to lauric acid (recovery 2.3 g.) identified by melting point (45°) and conversion to the *p*-bromophenacyl ester of m. p. 76°.

Lauryl Aldimine Stanni-chloride Complex, Solid Form (IV).—A normal type of Stephen reaction was carried out with 36 g. (0.2 mole) of lauryl nitrile by adding to 69 g. (0.24 mole) of anhydrous stannous chloride dissolved in ether with dry hydrogen chloride. The clear solution of the reaction mixture which shows no precipitate at room temperature begins to deposit white crystals when stored at 0 to −5°. After ten days of storage at −5°, a considerable quantity of crystals had deposited. These were washed with fresh ether by decantation several times, and then recovered by filtration; yield 64 g. (83.2%) of white feathery-like crystals. This was identified as dodecanaldimine hydrochloride stannic chloride complex by analysis and hydrolysis to monomeric lauryl aldehyde.

Anal. Calcd. for $[C_{11}H_{23}CH{:}NH{\cdot}HCl]_2SnCl_4$: N, 3.99; Cl, 30.37. Found: N, 3.99, 3.97; Cl, 29.92, 29.97.

Hydrolysis of Solid Complex.—Thirty-five grams (0.05 mole) of the white crystalline material was added to 500 cc. of water and refluxed vigorously for eight hours. It was observed that very shortly after reflux starts a yellowish oil gradually separates, while a white very voluminous precipitate forms and remains colloidally suspended throughout the water (anhydrous stannous chloride exhibits this behavior on hydrolysis). After cooling, the oil was recovered by ether extraction; yield 17.6 g. (96%) of a reddish oil having a persistent lily-of-the-valley-like odor. It responds to all aldehyde tests and shows a 92% monomeric lauryl aldehyde content by a Stillman–Reed analysis. This corresponds to an over-all yield of

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(10) C. F. H. Allen, This Journal, **52**, 2958 (1930).

(11) B. Zaar, *J. prakt. Chem.*, **132**, 69 (1931).

(12) E. Guenther and E. E. Langenau, This Journal, **65**, 959 (1943).

(13) R. C. Stillman and R. M. Reed, *Perfumery and Essential Oil Record*, **23**, 278 (1932).

88% lauryl aldehyde based on the solid complex. The 2,4-dinitrophenylhydrazone was found to melt at 106° (uncor.). Oxidation with an acetone solution of potassium permanganate yields lauric acid, m. p. 44–45° (uncor.) in quantitative yield.

This investigation is being continued with the purpose of elucidating the mechanism of the reactions involved in order to arrive at an explanation as to why the reactions take a different course with variation in experimental technique.

Summary

Lauryl aldimine stannic chloride precipitate cannot be obtained by the Stephen reaction by adding lauryl nitrile to stannous chloride dissolved in ether with dry hydrogen chloride. By working up the ether solutions, di- and trimeric lauryl aldehyde polymers are isolated in approximately quantitative yield. The trimeric lauryl aldehyde, m. p. 101°, has not been reported previously.

By conducting the Stephen reaction in an inverse manner, *i. e.*, addition of stannous chloride to an ether solution of lauryl nitrile saturated with hydrogen chloride, an ether soluble "liquid" type metallo complex of lauryl nitrile can be isolated in quantitative yield. It is quite resistant to hydrolysis, yielding monomeric lauryl aldehyde.

The ether insoluble "solid type" lauryl aldimine stannic chloride complex can be precipitated in high yield from a normal type of Stephen reaction by storing the clear solution at low temperatures. It has the composition postulated by Stephen of $[C_{11}H_{23}CH:NH \cdot HCl]_2SnCl_4$.

CHICAGO, ILLINOIS RECEIVED JANUARY 22, 1949

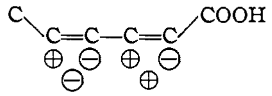
[CONTRIBUTION FROM TEMPLE UNIVERSITY]

Ethyl Sorbate in the Diene Synthesis

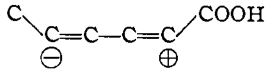
BY M. WESLEY RIGG AND RUDOLPH ROSENTHAL

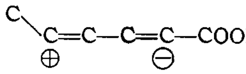
The recent literature contains numerous references to the polymerization reactions involving diene olefins and acrylic esters; however, very little work has been reported on the successful polymerization of sorbic acid and its esters. Thermal polymerization reactions[1,2,3,4a,b] have been reported; the results indicate that only dimeric and trimeric products were obtained. The principal reactions were Diels–Alder additions. Carpmaels and Ransford[5] report a mixed polymer of rubber-like properties obtained on emulsion polymerization of butadiene and ethyl sorbate. A mixed polymer was also obtained when butadiene or isoprene was polymerized with 3,5-heptadiene-2-one. Several Diels–Alder addition products of sorbic acid and its esters with maleic anhydride, acrylyl chloride, and vinyl phenyl ketone have been reported.[6,7,8,9] Houtz and Adkins[10] found that sorbic acid in dioxane was unaffected by the catalyst diisobutylene ozonide both at 23° and at 100°. It was also found that ethyl sorbate showed a 70% increase in viscosity using 3% pinene ozonide as catalyst, and 24% increase without catalyst in seventy-six days at 23°. In nine days at 100°, the viscosity increased six-fold without catalyst, and ten-fold with 3% ozonide as catalyst.

According to the charge distribution on the double bonds assigned by Price,[11] the carbon atoms should have charges as indicated in the formula



Heinanen[12] also predicted the same charge distribution on the ethyl sorbate molecule but did not discuss the question of olefin addition. Farmer and Morrison-Jones,[4] as a result of their work on the thermal polymerization of methyl sorbate in which dimeric esters were obtained, pointed out that either both polarized forms must exist at the same time or that the addition is a free radical reaction.





Their decision was based upon the isolation of two dimeric forms and a residue which they predicted might contain the remaining two isomeric forms which would be expected from a free radical mechanism.

Since little information is available concerning the successful polymerization of ethyl sorbate or sorbic acid, it was considered of interest to determine the activity of ethyl sorbate under the influence of various catalysts which are known to cause polymerization: namely, heat, peroxide in bulk, peroxide in solvent, persulfate in emulsion, and low temperature polymerization by

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(1) Doebner, *Ber.*, **35**, 2129 (1902).

(2) Lennartz, *Ber.*, **76B**, 1006 (1943).

(3) Kuhn and Deutsch, *Ber.*, **65B**, 43 (1932).

(4) (a) Farmer and Morrison-Jones, *J. Chem. Soc.*, 1339 (1940); (b) Wheeler, THIS JOURNAL, **70**, 3467 (1948).

(5) Carpmaels and Ransford, British Patent 387,381, Feb. 6, 1933.

(6) Diels and Alder, *Ann.*, **470**, 91 (1929).

(7) Wicks, Daly and Lack, *J. Org. Chem.*, **12**, 713 (1947).

(8) Wagner-Jauregg and Helmert, *Ber.*, **71B**, 2535 (1938).

(9) Allen, Bell, Bell and Van Allan, THIS JOURNAL, **62**, 656 (1940).

(10) Houtz and Adkins, *ibid.*, **55**, 1614 (1933).

(11) C. C. Price, "Reactions of the C–C Double Bond," Interscience Pub. Co., New York, N. Y., 1946, pp. 33, 49.

(12) P. Heinanen, *Ann. Acad. Sci. Fennicae*, **A49**, No. 4, 112 pp. (1938).