82% conversion of halide to Grignard reagent was achieved as determined by titration.[6]

Experimental

Three moles (402 g.) of *t*-butylbenzene was placed in a long reaction tube which was strongly illuminated. Chlorine, which was first bubbled through a sulfuric acid absorption tube, was slowly bubbled through the hydrocarbon over a period of three hours until a total of three moles had passed. Subsequent rectification yielded 90 g. (0.67 mole) of *t*-butylbenzene, 240 g. (1.42 moles) of 1-chloro-2-methyl-2-phenylpropane, 45 g. of polychlorinated material and 70 g. of still residue. The physical constants of 1-chloro-2-methyl-2-phenylpropane are b. p. 111-112° (18 mm.), $n^{20}{}_D$ 1.5245, and $d^{20}{}_4$ 1.047.

Anal. Calcd. for $C_{10}H_{13}Cl$: Cl, 21.02. Found: Cl, 21.0, 21.0.

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[6] Gilman, *et al.*, This Journal, **45**, 150 (1923).

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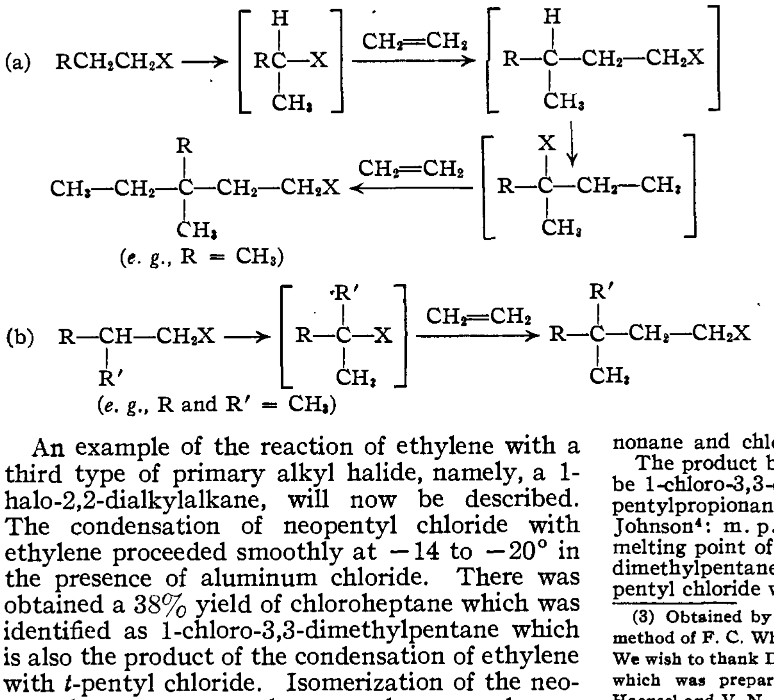
Condensation of Saturated Halides with Unsaturated Compounds. VII. Condensation of Neopentyl Chloride with Ethylene[1]

By Louis Schmerling and E. E. Meisinger

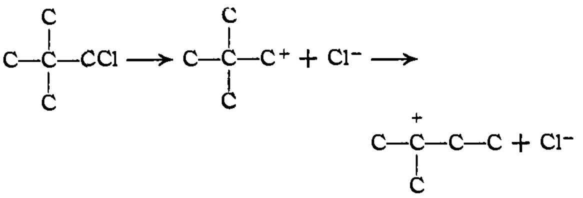
The metal halide catalyzed condensation of ethylene with alkyl halides (particularly chlorides and bromides) containing at least three carbon atoms offers a means of preparing 1-halo-3,3-dialkylalkanes.[2] The reaction of typical primary alkyl halides may be illustrated as:



(*e. g.*, R = CH_3)

(*e. g.*, R and R′ = CH_3)

An example of the reaction of ethylene with a third type of primary alkyl halide, namely, a 1-halo-2,2-dialkylalkane, will now be described. The condensation of neopentyl chloride with ethylene proceeded smoothly at −14 to −20° in the presence of aluminum chloride. There was obtained a 38% yield of chloroheptane which was identified as 1-chloro-3,3-dimethylpentane which is also the product of the condensation of ethylene with *t*-pentyl chloride. Isomerization of the neopentyl group to *t*-pentyl apparently occurred



The dissociation of the neopentyl chloride into the unstable positive neopentyl ion and the negative chloride ion is probably brought about by formation of a complex with the catalyst, $(CH_3)_3CCH_2^+AlCl_4^-$.

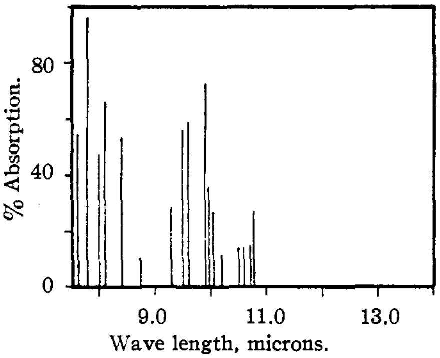


Fig. 1.—Infrared absorption spectrum of 1-chloro-3,3-dimethylpentane.

Experimental

Condensation of Neopentyl Chloride with Ethylene.—A mixture of 40 g. (0.37 mole) of neopentyl chloride,[3] 50 g. of *n*-pentane diluent and 5 g. of aluminum chloride was placed in a three-necked flask immersed in a Dry Ice-acetone-bath. Ethylene was bubbled into the stirred mixture while the temperature was permitted to rise from −70 to −15° at which point absorption began (determined by difference of gas rates in inlet and outlet bubblers). The temperature was maintained at −14 to −20° for the duration of the addition of ethylene (three quarters of an hour) during which time the catalyst gradually coagulated. The liquid product was decanted from the 12 g. of yellow sludge and powder, washed with water, dried and distilled. There was obtained 19 g. (0.14 mole) of product b. p. 50-51° at 20 mm. pressure (150-151° at 760 mm.); $n^{20}{}_D$ 1.4300. There was also obtained 22 g. of unidentified higher-boiling material which apparently consisted largely of chlorononane and chlorohendecane.

The product boiling at 50-51° at 20 mm. was shown to be 1-chloro-3,3-dimethylpentane by converting it to β-*t*-pentylpropionanilide by the method of Schwartz and Johnson[4]: m. p. 95-96°. This anilide did not depress the melting point of the analogous derivative of 1-chloro-3,3-dimethylpentane prepared by the condensation of *t*-pentyl chloride with ethylene.[2]

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[1] Preceding paper in this series, This Journal, **71**, 107 (1949).

[2] L. Schmerling, *ibid.*, **67**, 1152 (1945).

[3] Obtained by the chlorination of neopentane according to the method of F. C. Whitmore and G. H. Fleming, *ibid.*, **55**, 4161 (1933). We wish to thank Dr. Vladimir Haensel for the sample of neopentane which was prepared by the demethylation of neohexane: V. Haensel and V. N. Ipatieff, *Ind. Eng. Chem.*, **39**, 853 (1947).

[4] A. M. Schwartz and J. R. Johnson, This Journal, **53**, 1063 (1931); see also H. W. Underwood, Jr., and J. C. Gale, *ibid.*, **56**, 2117 (1934).

Comparison of the infrared spectrum[5] (Fig. 1) of the product boiling at 50–51° at 20 mm. with that of the 1-chloro-3,3-dimethylpentane prepared from *t*-pentyl chloride and ethylene showed that samples contained at least 95% material in common.

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(5) We are indebted to Dr. W. S. Gallaway, Physics Division, Universal Oil Products Company, for the infrared absorption analysis. For a description of the procedure used, see THIS JOURNAL, **69**, 1124 (1947).

RESEARCH AND DEVELOPMENT LABORATORIES
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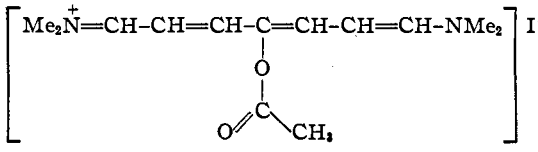
Two Simple Amidinium Vinylogs[1]

BY WILLIAM T. SIMPSON[2]

The vinylene homologous series

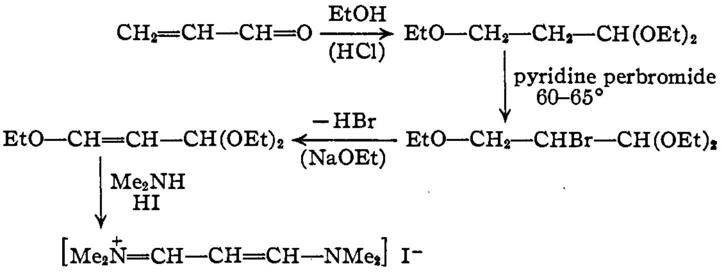
$$[\mathrm{Me_2\overset{+}{N}{=}CH{-}(CH{=}CH)_{\mathit{n}}{-}NMe_2}]\ \mathrm{X^-}$$

is interesting because of its simplicity[3] and yet its close relationship to several large families of dyestuffs. The second member (n = 2) was obtained by König and Regner.[4] Now the first member, (n = 1), N-methyl-(2-dimethylaminovinyl)-formimine methiodide, and a substance which is very closely related to the third member (n = 3) have been synthesized. The latter compound is N-methyl-(6-dimethylamino-3-acetoxy-1,3,5-hexatrienyl)-formimine methiodide

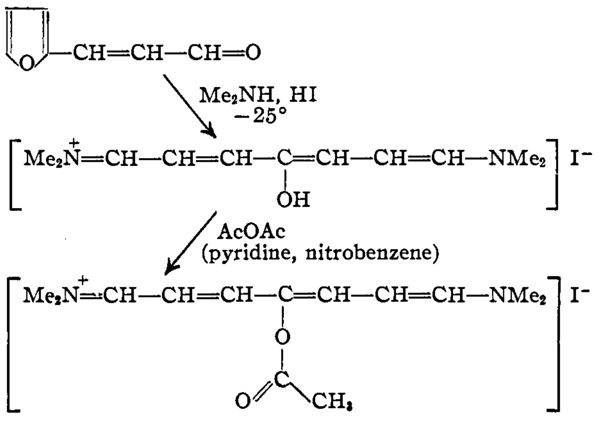


$$\left[\mathrm{Me_2\overset{+}{N}{=}CH{-}CH{=}CH{-}\underset{\displaystyle \underset{|}{O}{-}C({=}O)CH_3}{C}{=}CH{-}CH{=}CH{-}NMe_2}\right]\mathrm{I^-}$$

The former substance was prepared according to the scheme



The latter was synthesized by a splitting of the furan ring,[5] followed immediately by acetylation.



Experimental

β-Ethoxypropionaldehyde Diethylacetal.—This material was prepared substantially as described by Pingert.[6] Since the yield of acrolein acetal is not important, the following changes in the procedure were made. The starting material, 80 g. (95 cc., 1.36 mole) of acrolein (95% with stabilizer) was combined with 325 cc. (5.56 mole) of absolute ethanol (commercial). Approximately 0.7 g. of hydrochloric acid was used as a catalyst. The alcohol was removed under reduced pressure at 40–50°. The yield was 125.1 g. (52%); b. p. 95–97° (39 mm.). The material was used without further purification in the next step.

Bromination of β-Ethoxypropionaldehyde Diethylacetal.[7]—The acetal (67 g., 76 cc., 0.38 mole) and 30 g. (30.5 cc., 0.38 mole) of dry pyridine were combined. Then 61 g. (19.5 cc., 0.38 mole) of bromine was added at a rate of several drops a second. A mechanical stirrer operated continuously until the reaction was complete. After the bromine had been added the temperature was adjusted to 60–65°. The reaction was complete in two to four hours, as indicated by the disappearance of the red color of the pyridine perbromide. The reaction vessel was then washed with dry ether and the precipitate triturated with dry ether. Combined ether extracts were dried over anhydrous potassium carbonate and stored in an ice chest. Removal of the ether left 81 g. (83%) of the crude product. It was found that distillation of the crude material produced decomposition to the extent that a better yield in the next step was obtained if purification at this stage had been eliminated.

Dehydrobromination was carried out as described by Reitzenstein and Bonitsch.[8]

N-Methyl-(2-dimethylamino-vinyl)-formimine Methiodide.—Dimethylammonium iodide (6.0 g., 0.034 mole), 6.0 g. (0.034 mole) β-ethoxyacrolein diethylacetal, 4.8 g. (0.036 mole) 33% dimethylamine in methanol, and 10 cc. absolute methanol were sealed in a bomb tube. The tube was heated at 100° for five hours in the dark. The reaction mixture was washed with 200 cc. of ether; the precipitate which formed filtered and purified by several recrystallizations from acetic anhydride followed by ether throwdown. The material was dissolved in acetic anhydride at 100° and maintained at this temperature for five or ten minutes during each recrystallization. (This heating during recrystallization converted unchanged dimethylammonium iodide into ether soluble materials.) The yield after three recrystallizations was 3.8 g. (44%). An analytical sample was obtained after several additional recrystallizations from *n*-butyl alcohol. The pure material is crystalline, white with a faint suggestion of a metallic luster: m. p.[9] 188–188.5°.

Anal.[10] Calcd. for $C_7H_{15}N_2I$: C, 33.08; H, 5.95. Found: C, 33.18; H, 5.95.

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[1] Taken from the writer's Ph.D. thesis.

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[3] Simpson, *J. Chem. Phys.*, **16**, 1124 (1948).

[4] König and Regner, *Ber.*, **63**, 2823 (1930).

[5] König, *ibid.*, **67**, 1274 (1934).

[6] Pingert, *Org. Syn.*, **25**, 1 (1945).

[7] This procedure was taken from the work of McElvain and Walters, THIS JOURNAL, **64**, 1963 (1942).

[8] Reitzenstein and Bonitsch, *J. prakt. Chem.*, **86**, 1 (1912).

[9] All melting points are corrected.

[10] The analyses were performed under the direction of Mr. Charles Koch.