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
UNIVERSAL OIL PRODUCTS COMPANY
RIVERSIDE, ILLINOIS

RECEIVED JULY 22, 1948

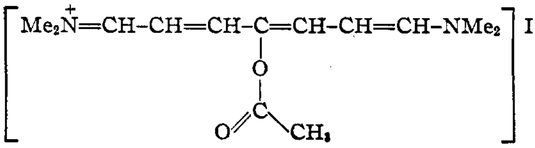
Two Simple Amidinium Vinylogs[1]

BY WILLIAM T. SIMPSON[2]

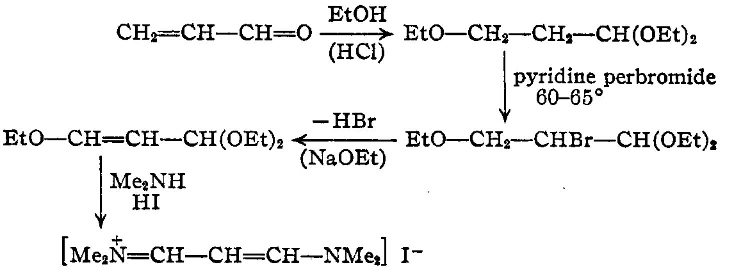
The vinylene homologous series

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

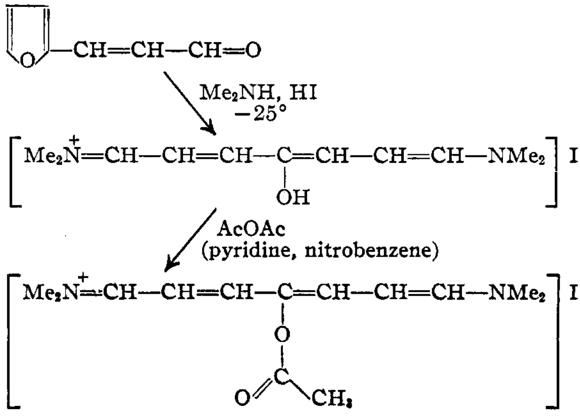
is interesting because of its simplicity[3] and yet its close relationship to several large families of dyestuffs. The second member ($n = 2$) was obtained by König and Regner.[4] Now the first member, ($n = 1$), N-methyl-(2-dimethylaminovinyl)-formimine methiodide, and a substance which is very closely 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



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.

N-Methyl-(6-dimethylamino-3-acetoxy-1,3,5-hexatrienyl)-formimine Methiodide.—Furylacrolein (1.0 g., 0.0082 mole) (Eastman Kodak Co., once recrystallized from ligroin), dissolved in 10 cc. of commercial isopropyl alcohol, was cooled to approximately −25°. A solution containing 1.4 g. (0.0079 mole) dimethylammonium iodide, 1.0 g. (0.0075 mole) of a 33% methanol solution of dimethylamine, and 5 cc. of isopropyl alcohol at room temperature was added to the furylacrolein suspension immediately upon its removal from the cooling bath. The addition, with shaking, required thirty seconds. The mixture was cooled immediately to −25° and kept at this temperature except for brief removal periods for stirring (at five-minute intervals). After thirty minutes the reaction mixture was removed from the cooling bath, 10 cc. of dry ether at 0° added, the solution stirred and filtered. The reaction flask and residue were washed with another cold 10-cc. ether portion. The residue was dried three minutes at the pump, and then transferred to a solution containing nitrobenzene (commercial) 100 cc., dry pyridine 10 cc., and acetic anhydride 10 cc. The solution was swirled until all of the crude material dissolved. The reaction required an hour at room temperature. The product was then thrown out with ether to give 1.2 g. (44%) of crude dye. Several recrystallizations from n-butyl alcohol gave an analytical sample with m. p. 191° (dec.). The crystals are a deep purple and possess a metallic luster.

Anal. Calcd. for $C_{13}H_{21}N_2O_2I$: C, 42.86; H, 5.81. Found: C, 42.89; H, 5.79.

I should like to thank Dr. L. G. S. Brooker for showing me an unpublished modification of reference 8, and Professors W. G. Dauben and G. E. K. Branch for much helpful advice.

DEPARTMENT OF CHEMISTRY
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RECEIVED AUGUST 9, 1948

NEW COMPOUNDS

Some Heterocyclic-Substituted Hydrazines

The condensation of a 2- or 4-chloroquinoline or of 2-amino-4-chloropyrimidine with benzenesulfonhydrazide was carried out in two ways. Refluxing a mixture of one mole of the halogen compound and two moles of benzenesulfonhydrazide in alcohol for two to six hours gave 40–50% yields of condensation product as the hydrochloride. In confirmation of the observations of Banks[1] it was found that the condensation of molal proportions of halogen compound and benzenesulfonhydrazide in the presence of one mole of hydrogen chloride (added as concentrated hydrochloric acid) increased the yields to 80–90%; the rate of condensation was also appreciably increased by this modification. The hydrochlorides were purified by crystallization from dilute or glacial acetic acid; excepting the pyrimidine derivative, the products were almost insoluble in water or dilute acids. Dilute bases produced the expected decomposition.[2]

1-Benzenesulfonyl-2-(7-chloroquinolyl-4)-hydrazine hydrochloride was also prepared, in 35% yield, by the action of benzenesulfonyl chloride on 7-chloro-4-hydrazinoquinoline in dry pyridine in the usual manner, followed by treatment of the product with dry hydrogen chloride in alcohol. The latter compound was prepared in 88.6% yield from 4,7-dichloroquinoline essentially by the general procedure of Koenigs and Loesch.[3] The compound formed white needles from alcohol, m. p. 231–232° (cor.) (dec.).

Anal. Calcd. for $C_9H_8ClN_3$: N, 21.70. Found: N, 21.68.

Surrey and Cutler[4] reported m. p. 220–221°.

1-Benzenesulfonyl-2-(5-nitropyridyl-2)-hydrazine was prepared from 2-hydrazino-5-nitropyridine[5] and benzenesulfonyl chloride in dry pyridine. This compound could not be prepared by the direct condensation of 2-chloro-5-nitropyridine with benzenesulfonhydrazide in either the presence or absence of hydrochloric acid.

The substituted hydrazines are listed in the accompanying table.

TABLE I

N^1-BENZENESULFONYL-N^2-SUBSTITUTED HYDRAZINE HYDROCHLORIDES

N^2-Substituent	M. p., °C.	Formula	Analyses, % Sulfur Calcd.	Sulfur Found	Chlorine Calcd.	Chlorine Found
Quinolyl-2-	207–209[a]	$C_{15}H_{14}ClN_3O_2S$	9.55	9.60	10.56	10.58
4-Methylquinolyl-2-[b]	171–172	$C_{16}H_{18}ClN_3O_3S$	8.72	8.69	9.64	9.65
5-Chloroquinolyl-4-	219.5–220.0[a]	$C_{15}H_{13}Cl_2N_3O_2S$	8.66	8.35	9.58[e]	9.56
7-Chloroquinolyl-4-	203–204[a]	$C_{15}H_{13}Cl_2N_3O_2S$	8.66	8.36	9.58[e]	9.66
7-Chloro-3-methylquinolyl-4-[c]	196–197[a]	$C_{18}H_{19}Cl_2N_3O_4S$	7.22	7.27	15.96	15.98
7-Phenoxyquinolyl-4-	209–210[a]	$C_{21}H_{18}ClN_3O_3S$	7.49	7.51	8.29	8.20
2-Aminopyrimidyl-4-	237–239[a]	$C_{10}H_{12}ClN_5O_2S$	10.63	10.52	11.75	11.61
5-Nitropyridyl-2-[d]	196–197[a]	$C_{11}H_{10}N_4O_4S$	10.89	11.00	...	...

[a] With decomposition. [b] As the monohydrate. [c] With one mole of acetic acid of crystallization. [d] Free base. [e] Ionic halogen only.

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(1) Banks, THIS JOURNAL, **66**, 1127 (1944).

(2) 1-Benzenesulfonyl-2-(7-chloroquinolyl-4)-hydrazine hydrochloride gave a 43.2% yield of 7-chloroquinoline, m. p. 31–32°, when steam distilled from excess sodium carbonate solution. 1-Benzenesulfonyl-2-(5-nitropyridyl-2)-hydrazine similarly gave a 32% yield of 3-nitropyridine, m. p. 39.5–40.5°. *Cf.* McFadyen and Stevens, *J. Chem. Soc.*, 584 (1936).

(3) Koenigs and Loesch, *J. prakt. Chem.*, **143**, 59 (1935); *cf.* Perkin and Robinson, *J. Chem. Soc.*, **103**, 1978 (1913).

(4) Surrey and Cutler, THIS JOURNAL, **68**, 2570 (1946).

(5) Rath, U. S. Patent 1,733,695.

STERLING–WINTHROP RESEARCH INSTITUTE
RENSSELAER, NEW YORK R. O. CLINTON

RECEIVED NOVEMBER 16, 1948

Preparation of Organic Silicon Chlorides[1]

The general method of synthesis was to add the appropriate Grignard reagent dropwise into an excess of silicon

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[1] This work was performed in 1945 as part of the research program of the Research and Development Branch, Military Planning Division, of the Office of the Quartermaster General. The opinions and conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or endorsement of the Department of the Army. Article not copyrighted. This work was performed with the assistance of Charles A. Miller, Joseph Rynasiewicz, Nelda Gulbransen, Esther Nielson and Eleanor Swenson.