Our next consideration was to note how the curves in Fig. 3, reference 2, change, when one assumes an appreciable amount of dissociation. Theoretical intensity curves were therefore computed for models IVa, IVd, IVf, and IVb-c (final model previously given); also for V_a and V_b, assuming in each case that 50% of the sample was dissociated[5] (Fig. 2a). The resulting curves differ only slightly from those in which no dissociation was assumed (except for model IVa, which is no longer admissible); this is due to the fact that the amplitude of the intensity curve for the dissociated part of the sample, for S > 8, is only about half of the amplitude of the pattern of the associated molecules, while in the region S < 8 all the curves show the same qualitative features. The quantitative comparison is presented in Table Ia.

TABLE Ia

DIMETHYL ETHER–BORON TRIFLUORIDE

			s_0(calcd.)/s_0(obs.)					
			0% dissociated		50% dissociated			
Max.	Min.	s_0	I_{Av}	IV_{b-c}	IV_{b-c}	IV_d	IV_f	V_b
1		3.22	7	1.003	1.025	1.037	1.056	1.068
	2	4.44	−5	0.982	0.991	1.009	1.013	1.018
2		5.76	10	.993	1.021	1.035	1.042	1.052
	3	7.61	−6	.992	1.012	1.024	1.026	1.022
3		8.88	4.2	1.028	1.036	1.048	1.056	1.038
	4	10.07	−3	1.016	1.029	1.039	1.051	1.036
4		11.32	3.5	.996	1.005	1.019	1.028	1.016
	5	12.68	−2.8	.999	1.009	1.023	1.035	1.020
5		14.08	2.2	1.000	1.010	1.026	1.037	1.031
	6	15.24	−1.5	1.012	1.021	1.039	1.051	1.058
6		16.43	1	1.004	1.010	1.036	1.049	1.059
Average				1.002	1.015	1.030	1.040	1.038
Mean deviation				0.0093	0.0100	0.0094	0.0115	0.0155
Interatomic distances deduced			B–F	1.41	1.43	1.432	1.446	1.443
			B–O	1.52	1.54	1.493	1.446	1.495
			C–O	1.44	1.46	1.483	1.498	1.495

On replotting the average deviations for models IV, the minimum (0.0093) is found to be shifted from (B–F)/(B–O) = 0.925 to (B–F)/(B–O) = 0.955 with the average value for $s_{\text{calcd.}}/s_{\text{obs.}} = 1.028$. Hence the structure which is in best qualitative and quantitative agreement with the data—assuming 50% dissociation—is:

Boron and oxygen valence angles tetrahedral

B–F = 1.43 ± 0.03 Å. (previously 1.41 ± 0.02 Å.)

B–O = 1.50 ± 0.06 Å. (previously 1.52 ± 0.06 Å.)

C–O = 1.45 ± 0.03 Å. (previously 1.44 ± 0.03 Å.)

The situation also remains unchanged with regard to models V and VI; quantitatively these are not as satisfactory as the above model, but they cannot be eliminated. Due to the introduction of another variable, the degree of dissociation of the diffracting sample, the limits of error imposed on the final B–F distance is of necessity increased.

The case of dimethyl ether–boron trifluoride turned out to be more favorable for a structure determination than we had anticipated, due to the apparent insensitivity to the degree of dissociation of the complex. A similar electron diffraction attempt to determine the structure of the methyl cyanide–boron trichloride complex in the vapor phase clearly showed that the compound was completely dissociated at 95°, and this was substantiated by vapor density measurements.[6]

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[5] The exact per cent. dissociation in the sample doing the diffracting is not known. It probably was around 60%, as can be judged from the heights of the peaks at 2.84 Å. and 3.16 Å. of the R.D. curve. We assumed 50% dissociation rather than the somewhat larger value only because the computations are thus greatly simplified. We have shown below that the conclusions regarding the final structure are not sensitive to the fraction postulated.

[6] A. W. Laubengayer and D. C. Sears, THIS JOURNAL, **67**, 164 (1945).

ITHACA, N. Y.

RECEIVED JUNE 1, 1944

The Production of a Poison for Nickel Catalysts in the Absorption of Oxygen by Fieser's Solution[1]

BY W. B. BURFORD, III, AND J. C. W. FRAZER

In the early stages of work on the poisoning of nickel hydrogenation catalysts by water vapor[2] an attempt was made to remove oxygen from the ethylene by means of alkaline hydrosulfite in the form of Fieser's solution number 2,[3] using an equivalent amount of potassium hydroxide in place of the sodium hydroxide specified. Highly erratic results followed which suggested that the solution might be introducing some impurity into the ethylene. This was confirmed by the disappearance of the effect when purification by means of a precatalyst tube was substituted for the Fieser's solution.

The odor of exhausted solutions strongly indicated a sulfur containing compound. Tests for sulfur dioxide and hydrogen sulfide were both negative, but a positive test for carbon disulfide was obtained by the procedure of Vogel.[4] This consists of passing the gases into alcoholic potassium hydroxide and precipitating any xanthate formed with copper sulfate as the dark yellow-green insoluble copper xanthate.

Tests were made by bubbling gas through the hydrosulfite solution at about 55 ml. per min. for one-half to one hour and passing the exit gases through alcoholic potassium hydroxide. The yellow-green color of the precipitate formed was observed readily against filter paper after filtration.

Using ethylene containing 2% oxygen a positive test was obtained in fifteen minutes. However, with 0.1% oxygen at least half an hour was required and it was necessary to heat the hydrosulfite. A faint positive test was obtained when air alone was passed through for fifteen minutes but none if pure nitrogen was used.

Various brands and purities of reagents produced no change in these observations.

It is concluded that the action of ethylene–oxygen mixtures or of air on Fieser's solution pro-

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[1] Original manuscript received January 27, 1943.

[2] W. B. Burford, III, and J. C. W. Frazer, THIS JOURNAL, **67**, 331 (1945).

[3] L. F. Fieser, *ibid.*, **46**, 2639 (1924).

[4] Vogel, *Ann.*, **86**, 369 (1853).

duces a detectable amount of a volatile material giving the xanthate test for carbon disulfide. Mere oxygen concentration does not seem to govern the amount produced, for the test with air was very faint. The results also strongly suggest that ethylene alone is without effect.

The poisoning effect of carbon disulfide on nickel catalysts is well known and may account for the erratic results obtained using Fieser's solution.

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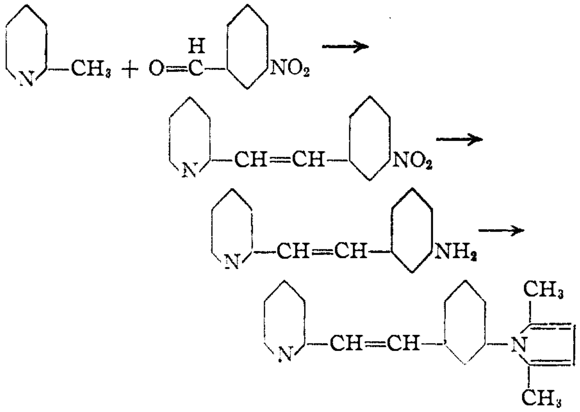
Some Styrylpyridines and -Quinolines

BY H. GILMAN AND GEORGE KARMAS

Incidental to a study of anils, several substituted styrylpyridines and -quinolines have been prepared. Some of the nitrostyryl types were reduced to the corresponding aminostyryls, and these in turn were condensed with acetonylacetone to give the corresponding 2,5-dimethylpyrrylstyryl compounds. The following is an illustrative sequence of transformations:



Experimental

The condensations of aldehydes with the picolines, quinaldine, and lepidine were effected by conventional procedures.[1,2] In a few comparative preparations it was observed that the method using acetic anhydride was better than the one in which anhydrous zinc chloride was used. The general results are given in Table I. Tests on the following compounds will also be reported later: α-(*p*-dimethylaminostyryl)-quinoline[3]; α-(*m*-aminostyryl)-quinoline[4]; α,α′-(di-*m*-nitrostyryl)-pyridine[5]; α- and γ-(*m*-nitrostyryl)-pyridine[2,5]; α-(*m*-nitrostyryl)-quinoline[6]; α-(*p*-nitrostyryl)-quinoline[7]; α-(*m*-2,5-dimethylpyrrylstyryl)-quinoline; α- and γ-(*p*-nitrostryl)-pyridine[2,5]; and α- and γ-(*m*-aminostyryl)-pyridines.[8]

The authors are grateful to Parke, Davis and Company for arranging the tests.

TABLE I

STYRYL DERIVATIVES

Product	M. p. (cor.), °C.	Anal., % N Calcd.	Anal., % N Found
α,γ-$(C_5H_3N)(CH{=}CHC_6H_4NO_2$-*m*$)_2$[a]	242–243	10.80	11.02
γ-$(C_5H_4N)CH{=}CHC_6H_4N(CH_3)_2$-*p*[b]	240–241	12.50	12.37
γ-$(C_9H_6N)CH{=}CHC_6H_4N(CH_3)_2$-*p*[c]	141–142	10.23	10.36
γ-$(C_5H_4N)CH{=}CHC_4H_3O$-α (picrate)[d]	212–214	14.00	14.25
α-$(C_9H_6N)CH{=}CHC_6H_4CF_3$-*m*[e]	104–105	4.68	4.18
α-$(C_5H_4N)CH{=}CHC_6H_4NH_2$-*m*[f]	103–104	14.30	14.32
γ-$(C_5H_4N)CH{=}CHC_6H_4NH_2$-*m*[g]	189–190	14.30	14.45
α-$(C_5H_4N)CH{=}CHC_6H_4NC_6H_8$-*m*[h]	87–88	10.20	10.40
α-$(C_9H_6N)CH{=}CHC_6H_4NC_6H_8$-*m*[i]	132–133	8.63	8.70

[a] This condensation product of α,γ-lutidine and *m*-nitrobenzaldehyde was crystallized from tetrachloroethane. The yield was 34%. [b] Crystallization of the condensation product from *p*-dimethylaminobenzaldehyde was from methanol. [c] Crystallization was from petroleum ether (b. p. 80–110°). [d] The condensation product with furfural distilled at about 200° (18 mm.), and because of its instability in air was converted to the picrate which was crystallized from ethanol. [e] This compound was synthesized in 65% yield by condensation with *m*-trifluoromethylbenzaldehyde (prepared by F. Yeoman), and was crystallized from dilute ethanol. [f] The nitrostyrenes were reduced to the corresponding amines by refluxing an ethanol solution with a saturated aqueous solution of sodium sulfide. The hemi-hydrate of this *m*-aminostyryl derivative of α-picoline was reported to melt at 85° [Schuftan, *Ber.*, **23**, 2717 (1890)]. Our product, obtained in 49% yield, was crystallized from dilute ethanol. [g] No m. p. was given for this compound. See Deutsche Hydrierwerke Akt.-Ges., French Patent 775,101 (June 27, 1934) [*Chem. Zentr.*, **106**, I, 3853 (1935)]. Our product, obtained in 47% yield, was crystallized from ethanol. [h] The *m*-2,5-dimethylpyrrylstyryl compound, obtained by condensation of the *m*-aminostyryl product with acetonylacetone, distilled as a viscous light yellow oil at 180–190° (0.001 mm.). This solidified after a short time, and crystallization from dilute methanol gave small, colorless flakes. [i] The reduction of α-(*m*-nitrostyryl)-quinoline by sodium sulfide gave the corresponding amine in a 57% yield and melting at 160–161°. The m. p. reported by Wartanian, *Ber.*, **23**, 3648 (1890), is 158–159°. In addition to the amine we isolated a small quantity of an orange colored compound which was insoluble in hot ethanol, but crystallized from dioxane as fine, orange needles melting at 226–227°. This may be the azo compound, $C_9H_6NCH{=}CHC_6H_4N{=}NC_6H_4CH{=}CHC_9H_6N$. *Anal.* Calcd. for $C_{34}H_{24}N_4$: N, 11.46. Found: N, 11.21. The *m*-(3,5-dimethylpyrrylstyryl) product, obtained in 72% yield by condensation of the amine with acetonylacetone, distilled at 200–210° (0.001 mm.). Crystallization from ethanol gave fine, buff platelets.

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(1) Kaplan and Lindwall, THIS JOURNAL, **65**, 927 (1943).

(2) Shaw and Wagstaff, *J. Chem. Soc.*, 77 (1933).

(3) Noelting and Witte, *Ber.*, **39**, 2750 (1906). Our m. p. for this compound was 181–182°, and they reported 177°.

(4) Wartanian, *Ber.*, **23**, 3648 (1890). Our m. p. for this compound was 160–161°, and he reported 158–159°.

(5) Wagstaff, *J. Chem. Soc.*, 277 (1934).

(6) Taylor and Woodhouse, *ibid.*, 2971 (1926).

(7) Bulach, *Ber.*, **20**, 2047 (1887).

(8) See footnotes *f* and *g* in Table I.

Fluorescence Chromatography of the Methyl Glucoses[1]

BY ETHELDA J. NORBERG, IRVING AUERBACH[2] AND R. M. HIXON

Several investigators have attempted, by chromatographic techniques, the quantitative separation of the ultimate hydrolysis products of methylated starch: *i. e.*, 2,3-dimethyl glucose,

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(1) Journal Paper No. J. 1244 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project 817. Supported in part by a grant from the Corn Industries Research Foundation.

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