[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

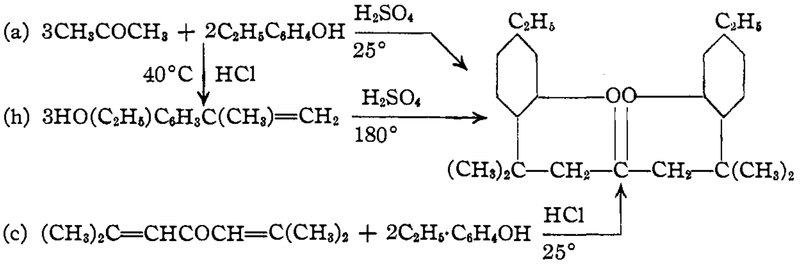
Spirochromans

BY JOSEPH B. NIEDERL AND RICHARD H. NAGEL[1]

The condensation of *m*- and *p*-cresol with acetone[2] was reinvestigated by W. Baker and D. M. Besley in 1939,[3] who not only confirmed both the empirical formulas and the "spirochroman" structures as advanced by J. B. Niederl,[4] but also assigned a similar "spirochroman" structure to their own hydroxyquinol–acetone condensation product.

To determine whether "spirochroman" formation was a phenomenon peculiar to the cresols, or whether it may be a general reaction of meta alkylated phenols with the position ortho to the phenolic hydroxyl group free, *m*-ethylphenol was condensed with acetone (a) and (b) and with phorone (c) in the presence of dry hydrogen chloride, as well as concentrated sulfuric acid. In the acetone condensation, the dimeric methovinylethylphenol, analogous to the dimer of methovinyl-methylphenol was obtained as the intermediate, when the condensation was carried out in the presence of dry hydrogen chloride at 40°. (b) This dimer was converted to the spirochroman according to the method of Böttcher[5] (b), by heating it to 180° with a small amount of sulfuric acid. The phorone condensation was direct and did not appear to have passed through any dimeric stage, which was also true in the case of the *m*- and *p*-cresol–phorone condensations.

Though the phorone product melted at 146° and the acetone compound at 114°, both gave the same tetranitro derivative, as evidenced by quantitative analyses and mixed melting point determinations. Furthermore, there was observed no depression in the melting point of an equal mixture of the two original crystalline condensation products and examination under the microscope showed that, though the crystals differed in form, it was possible to obtain crystallization by seeding a melt of the acetone compound crystals with a phorone compound crystal, and vice versa. This would seem to indicate that the dimorphism previously observed in the *m*- and *p*-cresol–acetone and the *m*- and *p*-cresol–phorone condensations and to be expected from stereochemical considerations is also exhibited by the ethyl homolog, and that the compound obtained in both cases is the 4,4,4′,4′-tetramethyl-7,7′-di-ethyl-bis-2,2′-spirochroman. Thus the course of the reaction may be presented as



Experimental

Acetone-*m*-ethylphenol

Dimeric Methovinylethylphenol (a and b).—One mole (122 g.) of *m*-ethylphenol and one-and-one-half moles (87 g.) acetone were placed in a 1-liter 3-necked round-bottomed flask provided with a reflux condenser and a gas inlet tube. Dry hydrogen chloride gas was passed into the reaction mixture at room temperature for six hours, and then the flask was tightly stoppered to keep the reactants in an atmosphere of the condensing agent, and let stand at room temperature for two weeks, in which time the mixture had turned dark brown in color and became quite viscous. The reaction mixture was poured into water and then repeatedly washed with 5% sodium carbonate solution and finally with distilled water, and then distilled. The main fraction (*ca.* 80 g.) distilled over between 200–207° at 12 mm. pressure, and on cooling an extremely viscous yellow liquid with a characteristic thymol-like odor was obtained.

Anal. Calcd. for $(C_{11}H_{14}O)_2$: C, 81.48; H, 8.64. Found: C, 81.55; H, 8.64.

Conversion to the Spirochroman (b).—Ten grams of the dimer was heated to boiling in a test-tube for half a minute with five drops of concentrated sulfuric acid. After two days, the solidified black mass was dissolved in boiling 95% ethyl alcohol and, on cooling, white rhombohedra crystallized out. These were recrystallized from the same solvent and were found to be insoluble in Claisen solution.

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[1] Abstracted from a portion of the thesis to be submitted by Richard H. Nagel to the faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of doctor of philosophy.

[2] J. B. Niederl, Ph.D. Thesis, Univ. of Graz (Austria) (1925); THIS JOURNAL, **50**, 2230 (1928); J. B. Niederl and R. Casty, *Monatsh.*, **51**, 1038 (1929); R. Casty, Ph.D. Thesis, Univ. of Graz (Austria) (1926); Th. Zincke and W. Gaebel, *Ann.*, **388**, 299 (1912); I. P. Tsukervanik and Z. N. Nazarova, *J. Gen. Chem.* (*U. S. S. R.*), **9**, 33 (1939).

[3] W. Baker and D. M. Besley, *J. Chem. Soc.*, 195 (1939).

[4] J. B. Niederl, *Z. angew. Chem.*, **49**, 467 (1931); *Monatsh.*, **60**, 150 (1932).

[5] Böttcher, Ph.D. Thesis, University of Berlin, 1930.

The conversion was practically quantitative. The pure product melted at 114° (uncor.).

Anal. Calcd. for $C_{25}H_{32}O_2$: C, 82.42; H, 8.79. Found: C, 82.48; H, 8.92.

Tetra-nitro Derivative.—About 1 g. of the crystals was dissolved in an excess of concentrated nitric acid in an Erlenmeyer flask, warmed on a steam-bath until no more fumes were given off, and then the flask was heated directly with a small Bunsen flame until a clear solution had resulted. Water was added to the cold solution, precipitating a yellow crystalline mass, which was filtered and recrystallized from 95% ethyl alcohol. The yellow crystals melted between 246–248° (uncor.). They were not analyzed, but a mixed melting point determination showed them to be identical with those obtained from the phorone-*m*-ethylphenol condensation product.

Phorone-*m*-Ethylphenol

4,4,4′,4′-Tetramethyl-7,7′-di-ethyl-bis-2,2′-spirochroman.—Three-tenths of a mole (46 g.) of phorone and 0.6 mole (82 g.) of *m*-ethylphenol were placed in a 1-liter 3-neck round-bottomed flask and dry hydrogen chloride gas was passed into the reaction mixture for six hours, the flask was stoppered tightly and allowed to stand at room temperature for one week. An excess of Claisen solution was added, precipitating a brown gelatinous mass which was filtered through a large fluted filter. The residue was washed with distilled water and dissolved in hot 50% ethyl alcohol, and on cooling white plates crystallized out. These crystals could also be obtained, though not so readily, from 95% ethyl alcohol. The crystals are insoluble in Claisen solution and melt at 146° (uncor.).

Anal. Calcd. for $C_{25}H_{32}O_2$: C, 82.42; H, 8.79. Found: C, 82.43; H, 8.68.

Tetra-nitro Derivative.—One gram of the spirochroman was heated on the water-bath in an Erlenmeyer flask with an excess of concentrated nitric acid till no more brown fumes were evolved, then heated directly with a small Bunsen flame until a clear solution resulted. On cooling, yellow needles separated, which were filtered off on a sintered glass filter funnel, and recrystallized from 95% ethyl alcohol. The melting point was 246–248° (uncor.). A mixed melting point with the nitro compound prepared from the acetone condensation product produced no depression.

Anal. Calcd. for $C_{25}H_{28}O_{10}N_4$: C, 55.15; H, 5.15. Found: C, 54.96; H, 5.13.

Summary

The condensation of acetone with meta alkylated phenols was extended to include *m*-ethylphenol. Experimental results were obtained which are in full harmony with previously advanced postulations.

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Change of the Ultraviolet Absorption Spectrum of Acrolein with Time

BY A. M. BUSWELL, E. C. DUNLOP, W. H. RODEBUSH AND J. B. SWARTZ

During a study of the ultraviolet absorption spectra of solutions of pure organic compounds, we observed that in the case of acrolein the data were sometimes inconsistent. In one case a solution of a given strength showed less absorption than a solution of half the concentration had shown in a previous test. A check of the records showed that the weaker solution had been examined when freshly prepared, while the stronger solution was a few days old when its absorption was determined. This suggested a systematic study of the change of the absorption spectrum of acrolein with time to determine whether this effect was due to polymerization or some other reaction.

There are several articles in the literature[1] discussing the absorption spectrum of acrolein in the vapor phase, and in solution in alcohol, water and other solvents. They report a weak absorption band at about 3200 Å. and a very strong one extending from a sharp limit at 2500 Å. toward shorter wave lengths. There are no data showing what happens to the spectra of these solutions over a period of time. This point has been investigated and is reported herewith.

Experimental

The instrument used was a Bausch and Lomb medium quartz spectrograph with a sectorphotometer. The light source was a condensed iron-tungsten alloy spark. The cells were of glass with quartz windows and were 5.14 cm. in length.

The data were read from the plates by visual comparison using a hand lens to find the matched lines. The percentage transmission was known from the sector setting and the molecular extinction coefficient was calculated from the Lam-

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(1) (a) Blacet, Young and Roof, THIS JOURNAL, **59**, 608 (1937); (b) Eastwood and Snow, *Proc. Roy. Soc.* (London), **A149**, 446 (1935); (c) Thompson and Linnett, *Nature*, **134**, 937 (1934); (d) Purvis, *J. Chem. Soc.*, **127**, 9 (1925); (e) Henri, *Compt. rend.*, **199**, 849 (1934); **178**, 844 (1924); (f) Luthy, *Z. physik. Chem.*, **107**, 284 (1923); (g) Purvis and McClelland, *J. Chem. Soc.*, **103**, 433 (1913); (h) Bielecki and Henri, *Ber.*, **46**, 3627 (1913).