3,4-Dimethoxycinnamonitrile, m.p. 98°. *Anal.* Calcd. for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.82. Found: C, 69.99; H, 5.72.

2,5-Dimethoxycinnamonitrile.—The sodium salt of 2,5-dimethoxybenzylidenepyruvic acid was obtained by condensing 2,5-dimethoxybenzaldehyde with sodium pyruvate in aqueous methanol in the presence of alkali (50% more sodium hydroxide than required to neutralize the pyruvic acid).[10] The crude sodium salt was converted to the oxime which was dehydrated by heating with acetic anhydride. After distillation the yield was about 20%. The nitrile crystallizes in needles from methanol and melts at 75°. *Anal.* Calcd. for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.82. Found: C, 69.84; H, 5.72.

The authors wish to express their gratitude to Mr. Samuel Blackman for the micro-analyses here reported.

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(10) *Cf.* Erlenmeyer, *Ber.*, **37**, 1318 (1904).

THE WELLCOME RESEARCH LABORATORIES
TUCKAHOE 7, NEW YORK
RECEIVED AUGUST 7, 1950

Solubility of Nitroguanidine in Water

BY WILLIAM MCBRIDE, RONALD A. HENRY, JOSEPH COHEN AND SOL SKOLNIK

The approximate solubility of nitroguanidine, $NH_2C(NH)NHNO_2$, in distilled water at 25 and 100° has been given by Davis,[1] and at 19.3 and 100° by Thiele.[2] More exact determinations at 19.5, 50 and 100° have been reported by Desvergnes.[3] These determinations are not in good agreement, however, since they show a variation of almost 25% at 100° (see Fig. 1). Because of this divergence and because of the lack of data at the intermediate temperatures, the solubility of this compound in water has been carefully remeasured.

The results are plotted in Fig. 1. In the range 30 to 70°, the solubility can be expressed with an accuracy of 0.3% by the equation

$$\log (\text{solubility in g./100 g. of water}) = -1963.2/T + 6.1255$$

calculated from the data by the method of least squares. The *p*H of the solutions after equilibrium was attained varied between 6.7 and 7.0, measured at 25°. Above 70° the solubility can be expressed with an accuracy of 1.3% by the equation

$$\log (\text{solubility in g./100 g. of water}) = -2167.0/T + 6.7215$$

In this higher temperature range, because of the autocatalytic hydrolysis of nitroguanidine, the solutions become alkaline and the *p*H (25°) varied from 7.0 to 7.3, except for two determinations at 89 and 95° in which the *p*H increased to 8.3. It was noted that the *p*H of a saturated solution of nitroguanidine increased from 6.6 to 8.3 after one hour at 94.7°, or to 8.8 after 5.5 hours at 88.8°. Since nitroguanidine is amphoteric,[2,4] its solubility will increase as the solution becomes more alkaline. The variations in the solubility, as reported for 100°, could be explained if no control had been maintained over the *p*H of the solutions, or if long periods of time had been allowed for solution equilibrium to be reached. Extrapolation of the present data to 100° gives a solubility of 8.22 g./100 g. of water, lower than the previously reported values.

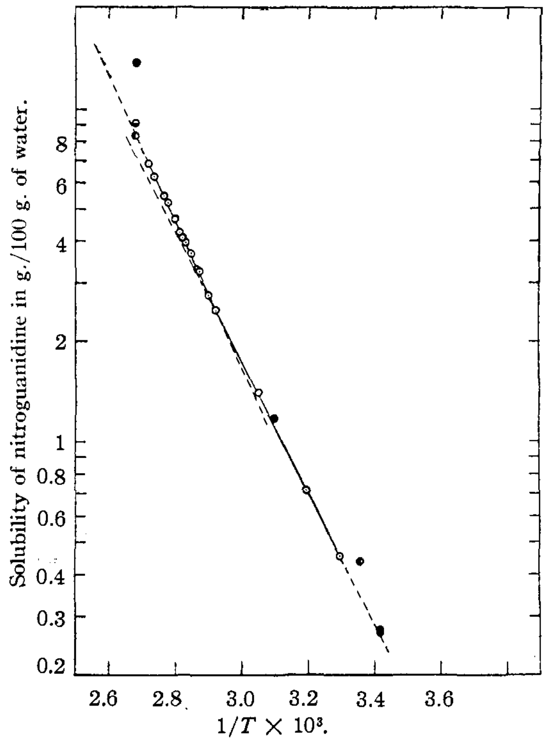

Fig. 1.—The solubility of nitroguanidine in water as a function of temperature: ⊙, present determination; ◐, Davis; ◒, Thiele; ●, Desvergnes.

From a statistical analysis of the data it can be concluded that the change in slope of the solubility curve is probably continuous throughout the range 30 to 100°, and that there is no justification for assuming a sharp inflection and a phase change at the temperature corresponding to the intersection of the two linear equations. The absence of a change of phase in this temperature range has also been confirmed experimentally by means of thermal differential analysis, dilatometric studies and X-ray studies.

Experimental

The nitroguanidine was a sample of commercial material that had been recrystallized twice from water (50 g./liter). Since the melting point of nitroguanidine is not a good criterion of purity, several attempts were made to determine its purity by the method of phase analysis.[5] Although the results were not completely satisfactory, they indicated a purity of better than 99.5%.

For the solubility determination, 2 to 10 g. of nitroguanidine was suspended in 125 ml. of distilled water, and the solution brought to equilibrium with stirring. Below 70°, 2 to 17 hours, depending on the particular temperature, were allowed for equilibrium to be reached; above 70°, one-half to one hour was allowed. Below 85°, equilibrium was approached from both the hot and cold sides; above 85°, from the hot side only. Fifteen- to 25-g. samples of the solution were removed by pressure filtration through a fine pored, sintered Pyrex glass disk into a receiver which was an integral part of apparatus immersed in the bath. Adequate precautions were taken to prevent evaporation losses during the sampling. The samples were sealed, cooled, weighed and evaporated to dryness in a vacuum desiccator at room temperature so as to avoid hydrolysis. Final drying to constant weight of solute was accomplished by heating at 100° for one to two hours. The average deviation for duplicate determinations below 85° was 2.2 parts per 1000;

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(1) Davis, "Chemistry of Powder and Explosives," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 381; also see Davis, THIS JOURNAL, **47**, 1063 (1925).

(2) Thiele, *Ann.*, **270**, 18 (1892); also see Pritchard and Wright, *Can. J. Research*, **25F**, 257 (1947).

(3) Desvergnes, *Rev. chim. ind.*, **38**, 265 (1929).

(4) Hahn, Pribyl, Lieber, Caldwell and Smith, THIS JOURNAL, **66**, 1223 (1944).

(5) Webb, *Ind. Eng. Chem., Anal. Ed.*, **20**, 100 (1948).

above this temperature the average deviation was about 12 parts per 1000.

The *p*H was measured at 25° on filtered samples of solution after equilibrium had been established.

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CHINA LAKE, CALIFORNIA

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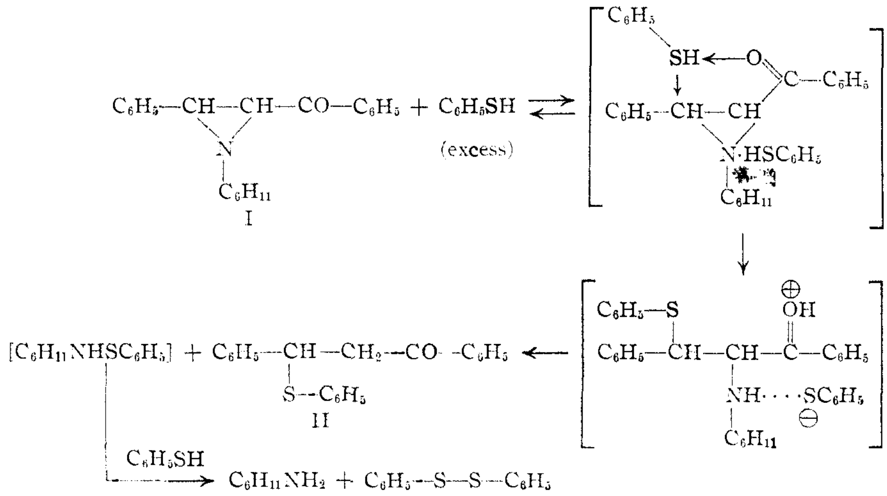
The Reaction of 1-Cyclohexyl-2-benzoyl-3-phenylethylenimine with Thiophenol

BY GARBIS MEGUERIAN AND LEALLYN B. CLAPP

In one of a series of papers describing the reactions of ketoimines, Cromwell[1] has shown that the high melting isomer of 1-benzyl-2-benzoyl-3-phenylethylenimine reacts with excess hydrogen chloride in ether solution to give predominantly α-benzylamino-β-chlorobenzylacetophenone hydrochloride. The weaker acid, thiophenol, however, does not give an analogous product with the related ketoimine, 1-cyclohexyl-2-benzoyl-3-phenylethylenimine (I) (m.p. 107°) but, instead, results in a reductive cleavage. Thus, in the absence of solvents, (I) reacted with thiophenol to produce β-phenylmercaptobenzylacetophenone (II), instead of the expected α-amino-β-mercaptoketone. Diphenyl disulfide was also identified in the reaction mixture. However, the reaction did not take place in the presence of the solvents, ether nor alcohol, even at the reflux temperatures.

A plausible route for the reaction is presented in the scheme



Experimental

Seven grams (0.023 mole) of 1-cyclohexyl-2-benzoyl-3-phenylethylenimine[2] (m.p. 107°) was treated with 14 g. (0.125 mole) of thiophenol at 45° for 20 hours in a closed tube. Addition of 50 ml. of petroleum ether (b.p. 35–40°) and cooling in ice gave 3.8 g. (40%) of white needles. After several recrystallizations from 95% ethanol, a pure sample of the β-phenylmercaptobenzylacetophenone (II) gave a m.p. 119–120°.

Anal. Calcd. for $C_{21}H_{18}OS$: S, 10.06. Found: S, 10.06.

The filtrate was distilled under reduced pressure in a nitrogen atmosphere. After thiophenol was collected, a yellow oil, b.p. 160–169° (6 mm.), was obtained which solidified on cooling; m.p. 60–61°, after seven recrystallizations from 40% ethanol. A mixed m.p. with diphenyl disulfide did not produce a depression.

Identification of the compound prepared by the method described above was accomplished by comparing the infrared spectrum of this compound with that of β-phenylmercaptobenzylacetophenone, prepared by the method of Ruhemann,[3] from benzalacetophenone and thiophenol in the presence of a little piperidine; m.p. 119–120°, recrystallized from 40% ethanol. A mixed m.p. of the two samples gave no depression.

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[1] Cromwell and Wankel, THIS JOURNAL, **70**, 1320 (1948); **71**, 711 (1949).

[2] Cromwell, Babson and Harris, *ibid.*, **65**, 312 (1943).

[3] Ruhemann, *J. Chem. Soc.*, **87**, 461 (1905).

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Some Factors Influencing the Activity of Raney Nickel Catalyst. II. The Role of Oxygen in the Aging of Raney Nickel Catalyst[1]

BY JOHN N. PATTISON[2] WITH ED. F. DEGERING[3]

The keeping qualities of Raney nickel have not been extensively studied. Paul[4] tacitly assumes that Raney nickel is easily preserved whereas Mozingo[5] warns that the catalyst may deteriorate on standing. He gives six months as the practical half-life of Raney nickel prepared by his method. Aubry[6] found that the surface of Raney nickel stored in the presence of water was slowly oxidized to nickel hydroxide. Schröter[7] remarks that hydrogen is slowly lost on storage of the catalyst. He also says that the activity of the catalyst decreases as the hydrogen is released but that the two effects are not parallel. Adkins and Billica[8] give a preparation for a very active catalyst (W-6) whose high activity appears to depend to a large extent upon its high hydrogen content when fresh. They say the activity of this catalyst becomes ordinary after standing. Schröter claims that the active metal can be stored in a well-sealed container without much loss in activity. Many, including the present author, have found catalysts a year or more old to be quite active.

As a result of these observations it was decided to obtain some factual information on the aging of Raney nickel. As an outgrowth of this investigation it was shown that oxygen was responsible for the major part of the loss in activity.

Experimental

Because of the variation in reduction rate with the amount of catalyst used it was necessary to take the same amount

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[1] From the Ph.D. Thesis of John N. Pattison, Purdue University, June, 1948.

[2] Battelle Memorial Institute, Columbus, Ohio.

[3] Miner Laboratories, Chicago, Illinois.

[4] R. Paul, *Bull. soc. chim.*, **7**, 296–346 (1940).

[5] Drake, *Org. Syntheses*, **21**, 15 (1941).

[6] Aubry, *Bull. soc. chim.*, **5**, 1333 (1938).

[7] Schröter, *Angew. Chem.*, **54**, 229, 252 (1941).

[8] Adkins and Billica, THIS JOURNAL, **70**, 695 (1948).