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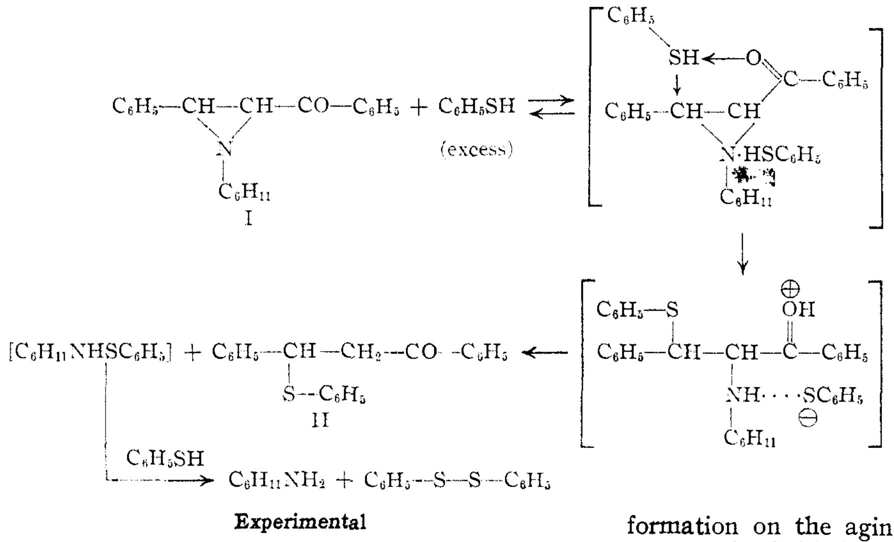
The Reaction of 1-Cyclohexyl-2-benzoyl-3-phenylethylenimine with Thiophenol

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).