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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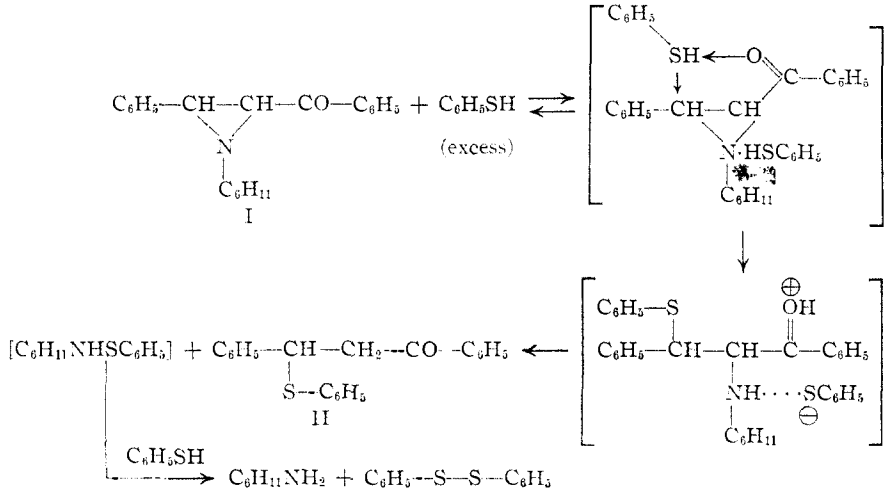
CHINA LAKE, CALIFORNIA RECEIVED JULY 17, 1950

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.

(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

(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).

of catalysts in each test. This was accomplished by suspending the catalysts in hardened cottonseed oil. In this form, the catalyst could be handled dry and weighed out accurately. The tests were made by adding a definite weight of the catalyst to a pressure bottle containing 50 g. of U.S.P. cottonseed oil. The bottle was attached to an Adams reductor and heated to 116 ± 1°. The bottle was evacuated and then the system was pressurized to 51 pounds per square inch and the reduction carried out in the usual manner. During the reduction the temperature was controlled between 116 and 120° by means of a jacket containing refluxing *n*-butanol. A record was kept of the pressure and time during the reduction.

Figure 1 shows aging curves for two samples of Raney nickel of the W-4[9] type. The activities shown are the initial rates of reductions carried out as described above.

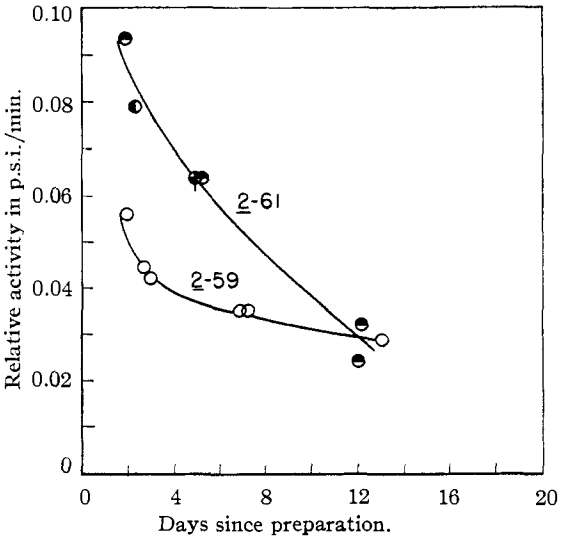

Fig. 1.—Aging of Raney nickel catalysts 2-59 and 2-61a.

The Oxygen Effect.—In order to determine what part oxygen plays in the loss of activity of this type of catalyst, another sample of W-4 Raney nickel was prepared. After the counter-current wash a small sample (about 10 g. of Ni) was removed and stored under distilled water, the bottle being kept completely filled. This sample was designated 2-69-a. The remainder of the catalyst was transferred to absolute alcohol by rinsing and decanting six times. At this point another sample was removed and stored in a bottle full of absolute ethanol as ordinarily recommended for the storage of Raney nickel. This sample was also about 10 g. and was called 2-69-b.

The remainder of the catalyst was covered with hardened cottonseed oil and warmed on the hot-plate 6 hours to remove most of the ethanol. The maximum temperature was 80°. This mixture was stirred rapidly while cooling to maintain a uniform dispersion of catalyst in oil. The solidified catalyst was broken into small particles and separated into five portions according to particle size as follows: 2-69-c larger than 4 mesh, 2-69-e (8–14 mesh), and 2-69-g (smaller than 20 mesh) were stored in air; 2-69-d (the 4–8 mesh portion) was stored in an atmosphere of nitrogen, air was rigorously excluded by a heavy layer of paraffin over the tightly closed tube; 2-69-f was from 14 to 20 mesh and was stored in an atmosphere of pure oxygen.

Tests run as soon as possible after the preparation of these catalysts showed about the same activity, as would be expected since they were all part of the same original preparation. Figure 2, however, shows that after 3 days there was already a definite difference in the catalysts stored in hardened cottonseed oil, the smaller particles losing their activity the fastest. At the end of 12 days the samples stored in alcohol, water and hardened cottonseed oil had approximately equal activities.

Comparisons were also made of catalysts 2-69-d (stored in nitrogen), 2-69-e (stored in air) and 2-69-f (stored in oxygen) 10 days after their preparation. These are given

(9) Pavlic and Adkins, THIS JOURNAL, **68**, 1471 (1946).

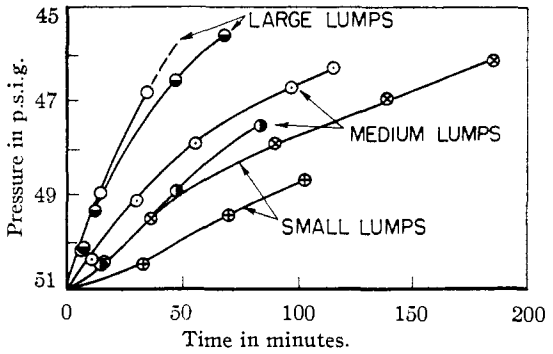

Fig. 2.—Reductions with Raney nickel 2-69; age 3 days.

in Fig. 3. The sample stored in nitrogen retained its original activity whereas the sample stored in air was much less active. Storage in oxygen was even more harmful to the catalyst. This would indicate that the loss of activity of Raney nickel is either caused by the reaction of oxygen with the nickel or the loss of hydrogen from the catalyst (presumably in this case by reaction with oxygen to form water) or both.

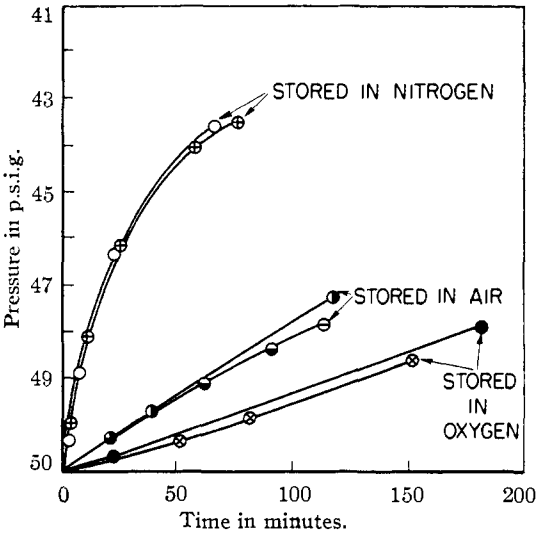

Fig. 3.—Effect of oxygen on Raney nickel 2-69; age 10 days.

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Esters of Benzoic and Chlorobenzoic Acids

BY EZRA MONROE AND CLARE R. HAND

The esters were prepared by the well known Schotten–Bauman reaction. The properties and analyses of the esters prepared are summarized in Table I. Yields are not reported since they would be based on single experiments and thus would not necessarily be representative of what may be obtained. These compounds have been tested against the two-spotted spider mite and Mexican bean beetle.[1]

(1) Kenaga, *J. Econ. Entomol.*, **42**, 999 (1949).