This gave 34.7 g. of pure acid; m.p. 197–199° (dec.).[6] An additional 2 g. of pure product was recovered from the mother liquor; total yield of pure product 36.7 g. (87% based on the ester, or 79% on the levulinic acid).

3-Ethylindole.—Thirty-nine and four-tenths gram (0.28 mole) of boron trifluoride etherate was slowly poured down the condenser into a solution of 20 g. (0.28 mole) of butyraldehyde and 32.8 g. (0.28 mole) of phenylhydrazine in 90 ml. of benzene. The solution refluxed a few minutes from the heat of reaction and separated into two phases. The mixture was refluxed for two hours and the benzene distilled off. The residue was triturated with water and the oily product extracted with ether. A small amount of unidentified solid insoluble in ether or water was filtered off and discarded. Distillation of the ether extract left an oil which was vacuum distilled to give 6.0 g. (15%) distilling at 138–139° at 6 mm. This product could not be crystallized from Skellysolve B, but was identified by the picrate with m.p. 114–115°[15] after one recrystallization from a benzene–Skellysolve B solution.

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[15] G. Plancher and O. Carrasco, *Atti. Accad. Lincei*, [5] **14**, II, 31 (1905).

AMES, IOWA RECEIVED APRIL 6, 1951

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Raney Nickel Desulfuration

BY CHARLES D. HURD AND BERNARD RUDNER[1]

Three modifications of Raney nickel were investigated in the desulfuration of three compounds containing the thiocarbonyl group, five thiazoles, and one thiophene derivative. From *o*-tolyl isothiocyanate or *o*-tolylthiourea the product obtained was *o*-toluidine. Thiobenzanilide gave rise to N-benzylaniline. Aniline was the major product from 2-mercaptobenzothiazole, with lesser quantities of *o*-aminothiophenol and benzothiazole. Acetophenone was formed in quantity from both 2-mercapto- and 2-amino-4-phenylthiazole: other products from the latter were methylamine and 1-phenylethylamine, and from the former 4-phenylthiazole. Acetamide and acetaldehyde were the chief products, respectively, from 2-amino- and 2-mercapto-4-hydroxythiazole. 2-Thienyl methyl ketone underwent desulfuration into 2-hexanone, but small quantities of acetaldehyde and ethyl alcohol were formed also.

The numerous recent reports on desulfuration of organic compounds[2,3] have prompted us to summarize our findings in this field. This paper reports new data regarding desulfuration by Raney nickel.

Three generally similar methods were used for preparing the nickel from its alloy $NiAl_2$: (A) the second procedure described by Mozingo[4]; (B) a procedure somewhat similar to that used for the Adkins–Pavlic W-4 nickel[5]; and (C) a procedure similar to that used by Ralls, Dodson and Riegel.[6] It was found that the hydrogenolytic activity of the nickels increased in the order (A), (B), (C). Nickel-C appeared to have a much greater amount of adsorbed hydrogen than the other two.

Three types of carbocyclic compounds and two heterocyclic systems were chosen for study. Each of the carbocyclics contained a nitrogen–carbon–sulfur triad: *o*-tolyl isothiocyanate, *o*-tolylthiourea and thiobenzanilide. Mozingo nickel in refluxing benzene converted *o*-tolyl isothiocyanate into *o*-toluidine in 64% of the theoretical yield. *o*-Tolylthiourea, with five times its weight of nickel-C, gave an 82% yield of *o*-toluidine. In neither reaction mixture could secondary amines or single-carbon compounds be detected. In spite of the report by Bougault and his co-workers that benzylthiourea yielded toluene rather than benzylamine on desulfuration,[7] Ashworth[8] only obtained an unidentifiable basic liquid from *p*-chlorophenylthiourea. Thiobenzanilide was reduced with seven to eight times its weight of nickel-B in benzene, producing an 86% yield of benzylaniline but no aniline.

2-Mercaptobenzothiazole (Captax) was readily cleaved by nickel-C to yield 2.9% of benzothiazole, 20.7% of *o*-aminothiophenol and 54.6% of aniline. Nickel-A under similar conditions gave 31% of *o*-aminothiophenol, 12% of aniline and 36% of *o*-aminophenyl disulfide. The facile rupture of the heterocyclic ring was surprising in view of the report[9] that mercaptobenzothiazole is not altered by hydrogenation over Raney nickel.

2-Mercapto-4-phenylthiazole was considerably more resistant to cleavage than "Captax." Prolonged heating with eight to ten times its weight of nickel converted the thiazole to a tar and 15% of the theoretical yield of 4-phenylthiazole. From the tar acetophenone was obtained, both free and in a combined, acid-labile form, totalling 48% of the theoretical amount. A small quantity of unidentified basic tar was formed as well, and an even smaller quantity of starting material was recovered. 2-Amino-4-phenylthiazole proved even more resistant to hydrogenolysis. By prolonged heating with nickel-C, it was converted to acetophenone (45%), *dl*-phenylethylamine (9%) and methylamine (11.5%). An appreciable quantity of starting material was recovered. The ease of cleavage of thiazoles by Raney nickel is apparently dependent on the nature and position of the thiazole substituents. Heilbron and his co-workers[10] showed that although 2-hydroxy-4-phenyl-5-aminothiazole underwent cleavage and rearrangement to yield (phenylethylene)-urea, 2-mercapto-4-phenyl-5-aminothiazole formed only 4-phenyl-5-aminothiazole. Marrian[11] reported that desulfuration of substituted 2-amino-4-hydroxy-5-thiazoleacetamides gave sub-

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[1] The Texas Company fellow, 1948–1949.

[2] Cook, Heilbron and Hunter, *J. Chem. Soc.*, 1797 (1949); Blicke and Sheets, THIS JOURNAL, **71**, 4010 (1949).

[3] Rylander and Campaigne, *J. Org. Chem.*, **15**, 24 (1950).

[4] Mozingo, THIS JOURNAL, **66**, 1015 (1943).

[5] Adkins and Pavlic, *ibid.*, **69**, 3039 (1947).

[6] Ralls, Dodson and Riegel, *ibid.*, **71**, 3320 (1949).

[7] Bougault, Cattelain and Chabrier, *Compt. rend.*, **208**, 657 (1939).

[8] Ashworth, *J. Chem. Soc.*, 1716 (1948).

[9] Blomquist and Diuguid, *J. Org. Chem.*, **12**, 723 (1947).

[10] Cook, Heilbron and Levy, *J. Chem. Soc.*, 1598 (1947); Cook Heilbron and Hunter, *ibid.*, 1443 (1949).

[11] Marrian, *ibid.*, 1797 (1949).

stituted succinamides. Raney nickel has been shown[3] to convert 3-phenyl-2,4-thiazolidinedione 2-anil into aniline and acetanilide. We have found that 2-amino-4-hydroxythiazole (pseudothiohydantoin) gave, on cleavage with nickel-B, a 91% yield of acetamide. Under the same conditions, however, 2-mercapto-4-hydroxythiazole (rhodanine) gave a 72% yield of acetaldehyde.

2-Thienyl methyl ketone was subjected to desulfuration in the unrealized hope of obtaining 3,5-hexadien-2-one. Use of low temperatures, or relatively inactive nickel preparations, produced no reaction. Nickel-B converted the thienyl methyl ketone into ethanol, acetaldehyde and 2-hexanone in 7.6, 10 and 76.5% of their respective theoretical yields. Although ethanol was used in the preparation of some of the nickels, alcohol-free nickel was assured in these experiments by centrifugation with toluene. Also, comparable runs were obtained with nickels which had been washed free of water with isopropyl alcohol, and then washed free of the alcohol by xylene. Cleavage of carbonyl groups by Raney nickel has been noted by Metayer[12] as has the absence of olefinic products in the desulfuration of thiophene derivatives.[2]

Experimental

Nickel Preparation. Nickel-A.—The procedure used was the second of two described by Mozingo.[4]

Nickel-B.—The procedure used was similar to that used in the preparation of W-4 nickel.[5] To a stirred solution of 128 g. of sodium hydroxide in 500 ml. of water at 35° was cautiously added 100 g. of Raney nickel alloy, the rate of addition being such that the temperature of the solution was kept at 50–55°. Addition was completed in approximately two hours, and the bubbling gray suspension was stirred for an additional hour at 50–55°. After settling, it was decanted. The residue was washed by decantation with five 300-ml. portions of water. The dark gray solid was washed into a one-liter graduate cylinder fitted with an air-driven stirrer and an inlet tube extending from the bottom of a 25-liter distilled water reservoir to the bottom of the graduate cylinder. Application of pressure from a nitrogen cylinder to the reservoir gave a controllable, air-free, automatic washing of the nickel in the cylinder. The effluent was neutral to litmus after 13 liters of water had been used; washing was continued for an additional 5 liters (four hours total time). The nickel was then washed in a nitrogen atmosphere into a 250-ml. centrifuge bottle. There it was washed by stirring and centrifuging, first with three 150-ml. portions of 95% alcohol, then with the same amount of absolute alcohol. It was then washed into a wide mouth, glass stoppered bottle, and stored there under absolute alcohol. When an alcohol-free nickel was desired, fresh nickel was prepared and washed free of alcohol by centrifugation with three 150-ml. portions of sulfur-free toluene.

Nickel-C.—As suggested by J. Ralls, a more active nickel was prepared by varying procedure B to permit addition of the nickel alloy at 0–10°. The suspension was allowed to stand at 20–25° overnight before it was washed and worked up as before. The final product was a black, almost colloidal powder which evolved hydrogen for approximately a week after preparation.

The time required for 1 g. of nickel to remove sulfur from 0.1 ml. of thiophene in 99.9 ml. of refluxing xylene to the extent where an indophenin test was no longer obtainable was taken as a measure of the activity of the nickel. Freshly prepared nickel-B had a desulfuration time of 17–20 minutes. Nickel-C had a desulfuration time of approximately five minutes.

Desulfuration Studies: *o*-**Tolyl Isothiocyanate.**—A solution of 0.5 g. of *o*-tolyl isothiocyanate in 150 ml. of benzene was refluxed over 16 g. of nickel-A for 14 hours, then filtered. The benzene-washed residue contained no organic material soluble in 1% hydrochloric acid. Preliminary tests showed that the 200-ml. combined volume of filtrate and washings contained no organic acids, aldehydes or ketones but did contain a primary aromatic amine. Half the solution was extracted with two 30-ml. portions of *N* hydrochloric acid. From half the extract there was obtained, by Schotten–Baumann technique, 126 mg. of a crude benzenesulfonyl derivative, m.p. 123–125°. Recrystallization from 80% ethanol gave white plates of m.p. 125–126°. Similarly prepared was a benzoyl derivative which, after two recrystallizations, melted at 144–145°. *o*-Toluidine is reported to form derivatives of m.p. 124 and 145°, respectively. No secondary or tertiary amine was detected in the sulfonylation reaction mixture. The acid-extracted benzene solution gave on evaporation only negligibly small quantities of brown tar. Distillation of the rest of the benzene solution revealed no other components. The amount of benzenesulfon-*o*-toluidide obtained corresponded to 0.23 g. of *o*-toluidine or 64% of the theoretical.

o-**Tolylthiourea.**—Four grams of *o*-tolylthiourea, m.p. 158–160°, in 200 ml. of benzene was refluxed over 20 g. of nickel-C for four hours, then cooled and filtered. The 280-ml. volume of combined filtrate and washings was extracted with three 30-ml. portions of 5% hydrochloric acid and two 30-ml. portions of water. Evaporation of half the benzene solution gave 0.12 g. of a light yellow residue of m.p. 147–151°. After two recrystallizations from alcohol the residue melted at 157–159°, a melting point not depressed after addition of the starting material. The acid extract gave, on treatment with alkali, extraction with ether, and evaporation, 2.11 g. (82%) of *o*-toluidine, the identity of which was established by conversion to a benzenesulfonyl derivative of m.p. 124–124.5° and a benzoyl derivative of m.p. 142–143°. There was no evidence for secondary amines.

Thiobenzanilide.—A stirred suspension of 4 g. of thiobenzanilide, 200 ml. of benzene and 30 g. of nickel-B was refluxed for ten hours, then cooled and filtered. The 280 ml. of benzene filtrate and washings was extracted successively with (a) 160 ml. of water, which was also used to wash the nickel residue; (b) 60 ml. of 5% hydrochloric acid followed by 40 ml. of water; and (c) 60 ml. of 2% sodium hydroxide solution and 40 ml. of water, which combination was also used to wash the nickel residue. The alkaline extract was quickly chilled and acidified with concentrated hydrochloric acid, precipitating 0.44 g. of starting material, m.p. 98–99° after two recrystallizations from alcohol. The benzene solution contained no characterizable groups, but on evaporation left 18 mg. of a yellow solid. On washing with 2% sodium hydroxide solution and recrystallizing from 30% ethanol, this was converted to 11 mg. of benzanilide, m.p. 164–166°. The neutral, aqueous extract was found to be free of organic matter. The acid extract was found to contain a secondary amine. Evaporation of half the solution and drying *in vacuo* gave 1.61 g. of hygroscopic light pink needles of m.p. 211–213° after recrystallization from alcohol. The hydrochloride was converted by the Schotten–Baumann method into an alkali-insoluble benzenesulfon-(N-benzylanilide), m.p. 117–118°, and by the Einhorn procedure with benzoyl chloride and pyridine, into benzo-(N-benzylanilide) of m.p. 106.5–107°, white needles from ethanol.

The derivatives of N-benzylaniline are reported to have the following melting points: the hydrochloride, 214–216°; benzenesulfonyl, 119°; and benzoyl, 107°. Thus N-benzylaniline was obtained in 86% yield, and 10.8% of the starting material was recovered. Kornfeld[13] recently has reported finding benzylaniline in 59% yield using Raney nickel.

2-Mercaptobenzothiazole.—Four grams of 2-mercaptobenzothiazole in 200 ml. of refluxing ethanol and 15 ml. of concentrated ammonium hydroxide was desulfurized over 32 g. of nickel-C for six hours. The combined filtrate and washings were treated with 100 ml. of 10% hydrochloric acid and distilled to dryness on a steam-bath. The distillate contained no detectable organic compounds other than alcohol. The 2.6 g. of dark green distillation residue was suspended in 50 ml. of 5% caustic and extracted with three 20-ml. portions of benzene. The combined organic solutions were in turn extracted with three 20-ml. portions of 5% hydrochloric acid. The acid-washed benzene solution

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(12) Metayer, *Compt. rend.*, **[illegible]**, 500 (1948).

(13) Kornfeld, *J. Org. Chem.*, **16**, 133 (1951).

contained only traces of other organic compounds. The alkaline solution was found to contain only amphoteric 2-aminothiophenol, which was identified by its oxidation, by boiling 1% ferric chloride solution to a total of 0.61 g. of 2-aminophenyl disulfide, m.p. 91–92° after recrystallization from 80% alcohol. On reaction of the acid extract with 2 ml. of benzenesulfonyl chloride and aqueous caustic, there was obtained 1.86 g. of benzenesulfonanilide, m.p. 110–111° after recrystallization from alcohol. A benzene extract of the alkaline Hinsberg reaction mixture was found to contain 95 mg. of basic, steam-volatile benzothiazole, identified as its picrate, needles from 90% alcohol, m.p. 178–179.5°. In all, there was obtained 0.095 g. (2.9% of the theoretical yield) of benzothiazole, 0.62 g. (20.7%) of 2-aminothiophenol and 1.29 g. (54.6%) of aniline.

In an earlier run, using a 4:1 ratio of nickel-A, the products included 31% of 2-aminothiophenol, 36% of 2-aminophenyl disulfide and 12% of aniline. Conditions of this earlier run were such as to make detection of benzothiazole impossible.

2-Mercapto-4-phenylthiazole.—Preliminary trials using four to six times the weight of nickel-A or -B gave little evidence for ring cleavage. Four grams of the thiazole in 200 ml. of ethanol containing 10 ml. of ammonium hydroxide was refluxed over 42 g. of nickel-C until no more ammonia was evolved (18 hours). The combined filtrate and alcoholic washings were distilled through a 10-inch Vigreux column to yield only ethyl alcohol as distillate. The purple-black, tarry distillation residue was dissolved in 50 ml. of benzene and to this added the equal volume of benzene used to extract the nickel residue. The dark solution was extracted first with an equal volume of 5% sodium hydroxide, then an equal volume of 5% hydrochloric acid. The alkaline extract, on neutralization with dilute hydrochloric acid, precipitated 0.15 g. of starting material, m.p. 163–165°, after recrystallization from alcohol. The benzene solution contained no elements detectable by sodium fusion. It was found to contain acetophenone, identified and determined as 3.1 g. of acetophenone 2,4-dinitrophenylhydrazone, dark red needles, after two recrystallizations from nitromethane, m.p. and mixed m.p. 248–249°. The brown acid extract rapidly turned turbid and developed an odor of acetophenone. It was allowed to stand for three hours, then extracted twice with 25-ml. portions of benzene. From the organic extract was obtained 97 mg. of acetophenone 2,4-dinitrophenylhydrazone, m.p. 246–248°. The acid extract did not contain additional ketone, even after boiling. It contained two amines, one a black gum, 0.224 g., which failed to react with benzenesulfonyl chloride, and which could not be induced either to crystallize or form crystalline derivatives with hydrochloric or picric acids. The second amine, isolated by distillation of the neutralized extract, was 0.502 g. of 4-phenylthiazole, identified as its hydrochloride, m.p. 76–78°, and picrate, m.p. 162–163°. The yields obtained were 15% of the theoretical of 4-phenylthiazole and 48% acetophenone.

2-Amino-4-phenylthiazole.—Four grams of 2-amino-4-phenylthiazole, in 200 ml. of refluxing absolute alcohol, was treated with 36 g. of nickel-C for 72 hours, until no more ammonia was evolved. Half of the combined filtrate and washings was treated with 50 ml. of 10% hydrochloric acid and evaporated to dryness on a steam-bath. The gummy brown semi-solid residue, which smelled of acetophenone, was triturated twice with 15-ml. portions of benzene, to remove acetophenone, identified as 1.32 g. of its 2,4-dinitrophenylhydrazone, fine red needles from nitromethane, m.p. 245–246°. The benzene-insoluble residue, a brown solid, was taken up in 20 ml. of water and treated with 3 g. of potassium hydroxide pellets. The volatile amine which was generated was distilled into 20 ml. of 10% hydrochloric acid. The distillate was evaporated dry to yield 38 mg. of hygroscopic methylammonium chloride, m.p. 223–226°, identified as benzo-(methylamide), m.p. 78–79° after recrystallization from water. The alkaline residue from which the methylamine had been distilled contained both a solid and an oil. It was chilled and filtered, yielding 0.269 g. of starting material, m.p. 147–149°, mixed m.p. 148–151°, with authentic 2-amino-4-phenylthiazole. The oil was extracted from the filtrate with two 15-ml. portions of benzene and then extracted from the benzene solution with an equal volume of 5% hydrochloric acid. Evaporation of the acid extract gave 0.125 g. of crude, hygroscopic light brown 1-phenylethylammonium chloride, which was converted to a mat of fine gray needles of m.p. 169–171° after one recrystallization. For confirmation, the salt was converted by the Schotten–Baumann technique to benzo-(1-phenylethylamide), fine white needles of m.p. 118–119° after recrystallization from 80% alcohol. In summary, from 3.462 g. of unrecovered 2-amino-4-phenylthiazole, there was obtained 81 mg. (13.3%) of methylamine, 0.212 g. (9%) of *dl*-(1-phenylethyl)-amine, and 1.06 g. (44.9%) of acetophenone.

2-Amino-4-hydroxythiazole (Pseudothiohydantoin).—A mixture of 2 g. of twice recrystallized pseudothiohydantoin, 20 g. of nickel-C, and 200 ml. of ethanol was refluxed for six hours, then allowed to stand overnight. The ammoniacal vapor which formed during the reaction was passed into a solution of benzenesulfonyl chloride in benzene. There was obtained from the trap 63 mg. of benzenesulfonamide, white plates of m.p. and mixed m.p. 150–152°, after recrystallization from water. The filtrate from the desulfuration reaction mixture was evaporated dry on a steam-bath, leaving 2.18 g. of a greasy yellow solid as residue. All but approximately 5 mg. of this was soluble in benzene. The insoluble portion was yellow, alkali soluble and melted at 210° (dec.); it was considered to be pseudothiohydantoin. The benzene-soluble portion, 2.1 g. melting at 63–71°, was water soluble and contained only nitrogen as detected by sodium fusion. Recrystallization from a 1:4 ether–ethanol mixture gave colorless prisms of m.p. 85–86°; its mixture with authentic acetamide of m.p. 84–85° showed no melting point depression. As confirmation, the desulfuration product was hydrolyzed and the hydrolysis products characterized. From 1 g. of acetamide was obtained 2.0 g. of benzenesulfonamide, m.p. 150–151°, and 3.31 g. of *p*-phenylphenacyl acetate, m.p. 110–111°. From 4 g. of pseudothiohydantoin there was obtained 2.1 g. of acetamide (91%) and 13.7 mg. (2.3%) of ammonia.

2-Mercapto-4-hydroxythiazole (Rhodanine).—A mixture of 2 g. of once-recrystallized rhodanine, 20 g. of nickel-C and 200 ml. of water was refluxed for 4 hours, then allowed to stand overnight. During that period of approximately 20 hours, both acetaldehyde and ammonia vapors escaped from the top of the condenser. Half of the reaction filtrate and washings, *i.e.*, 180 ml., was mixed with an equal volume of a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid. Filtration after 2 days gave 1.21 g. of crude acetaldehyde 2,4-dinitrophenylhydrazone which after recrystallization from alcohol, melted at 163–165° and did not depress the melting point of authentic acetaldehyde 2,4-dinitrophenylhydrazone. From 2 g. of rhodanine was obtained 0.475 g. or 72% of acetaldehyde.

The remaining half of the combined filtrate and washings was evaporated, leaving as residue 0.21 g. of dark oil, somewhat water-soluble, readily soluble in dilute hydrochloric acid with the formation of acetaldehyde. The oil was heated with 20 ml. of 10% hydrochloric acid for ten minutes, and filtered to clarify the light brown solution which was then divided into two parts. One half was treated with three volumes of dinitrophenylhydrazine reagent; there was obtained 43 mg. of acetaldehyde 2,4-dinitrophenylhydrazone, m.p. 163–165° after recrystallization from alcohol. The second half of the filtrate was shaken vigorously with benzenesulfonyl chloride, and 20% aqueous sodium hydroxide. There was obtained, after acidification, partial evaporation, and filtration, approximately 10 mg. of crude benzenesulfonamide, m.p. 148–150°.

2-Thienyl Methyl Ketone.—A mixture of 4 g. of distilled ketone, 20 g. of nickel-B and 200 ml. of sulfur-free xylene was heated under reflux at 100° for 6 hours, then allowed to stand overnight. Distillation of the combined filtrate and washings through a Vigreux column gave three fractions (ml., b.p.): (a) 0.2, 29–83°; (b) 310, 111–148°; and (c) residue, 1.5 g. Fraction (a) contained both aldehyde and alcohol. It was dissolved in 10 ml. of benzene and extracted with two 5-ml. portions of 5% aqueous sodium bisulfite. The extract, on treatment with 50 ml. of a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* hydrochloric acid, precipitated 0.55 g. of acetaldehyde 2,4-dinitrophenylhydrazone, orange needles from alcohol which melted at 167–168° both alone and mixed with an authentic sample. The bisulfite-washed benzene solution was subjected to a Schotten–Baumann reaction with 5 ml. of 20% sodium hydroxide solution and 0.5 g. of 3,5-dinitrobenzoyl chloride. The benzene layer was washed and evaporated to yield 0.4 g. of light yellow ethyl 3,5-dinitrobenzoate which, after recrystallization from alcohol, had a m.p. and mixed m.p. of 93–94°.

Half of fraction (b) was extracted with four 20-ml. portions of 5% sodium bisulfite, and half of the bisulfite solution was treated with twice its volume of dinitrophenylhydrazine solution. There was obtained 1.24 g. of 2-hexanone 2,4-dinitrophenylhydrazone, orange-red rods of m.p. 104–105°, after recrystallization from alcohol. An attempted acylation of (b) after being washed with bisulfite using 2 g. of 3,5-dinitrobenzoyl chloride and 5 ml. of pyridine gave less than 15 mg. of yellow solid, m.p. 29–32°.

The clear, brown oily residue (c) was dissolved in 15 ml. of benzene and extracted with five 10-ml. portions of 5% bisulfite solution. From the aqueous extract was obtained, as before, 2.26 g. of 2-thienyl methyl ketone *p*-nitrophenylhydrazone, red needles from nitromethane, m.p. and mixed m.p. 181–182°. Reaction of the benzene solution with 3,5-dinitrobenzoyl chloride gave less than 10 mg. of yellow solid, m.p. 70–78°. From 2.81 g. of unrecovered thienyl methyl ketone was obtained 0.108 g. (10.6%) of acetaldehyde, 77 mg. (7.2%) of ethanol and 1.77 g. (76.5%) of 2-hexanone.

When the desulfuration was repeated using nickel which had been washed free of water with isopropyl alcohol rather than ethanol, and then washed free of alcohol by xylene, there was obtained a 12.5% conversion to acetaldehyde, 9.2% to ethanol and 63.5% to 2-hexanone. There was no evidence for the presence of either isopropyl alcohol or acetone in the reaction mixture. Distillation of the xylene in which the nickel had been stored for two days between preparation and use showed no evidence for the presence of either alcohols or carbonyl compounds.

EVANSTON, ILLINOIS RECEIVED MARCH 12, 1951

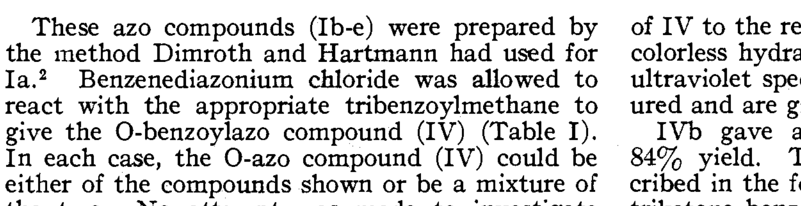
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

The Effect of Substituents on the Thermal Rearrangement of Phenylazotribenzoylmethanes[1a]

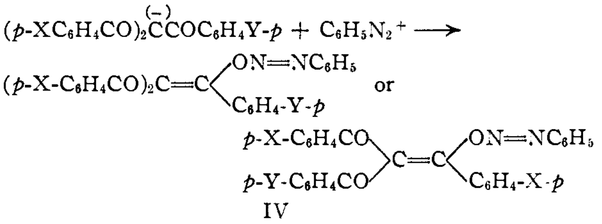
BY DAVID Y. CURTIN[1b] AND CHARLOTTE SANANES RUSSELL

The effect of *p*-nitro and *p*-methoxyl substituents on the thermal rearrangement of phenylazotribenzoylmethane to diphenyl triketone benzoylphenylhydrazone has been investigated. For this purpose the O-phenylazo derivatives of *p*-nitrotribenzoylmethane, *p,p'*-dinitrotribenzoylmethane. *p*-methoxytribenzoylmethane and *p,p'*-dimethoxytribenzoylmethane were prepared and rearranged through the C-phenylazo isomer to the corresponding mixture of hydrazones which was then analyzed. The results show that a *p*-nitrobenzoyl migrates slower than benzoyl and *p*-methoxybenzoyl migrates at about the same rate as or somewhat faster than benzoyl. Evidence for the intramolecularity of the rearrangement has also been obtained.

Dimroth and Hartmann,[2] over 40 years ago, discovered a thermal rearrangement of phenylazotribenzoylmethane (Ia) to diphenyl triketone benzoylphenylhydrazone (IIa). Little attention has since been paid to this rearrangement. It was the purpose of the present work to examine the effect of *p*-substituents on the rearrangement by investigating the relative amounts of rearrangement products (II and III) obtained in the rearrangement of a series of *p*-substituted derivatives of I (Ib-e).



(a) X = Y = H
(b) X = H, Y = NO_2
(c) X = NO_2, Y = H
(d) X = H, Y = OCH_3
(e) X = OCH_3, Y = H



These azo compounds (Ib-e) were prepared by the method Dimroth and Hartmann had used for Ia.[2] Benzenediazonium chloride was allowed to react with the appropriate tribenzoylmethane to give the O-benzoylazo compound (IV) (Table I). In each case, the O-azo compound (IV) could be either of the compounds shown or be a mixture of the two. No attempt was made to investigate this point. The O-azo compounds (IVb-e) were allowed to rearrange at 120°. Since the C-azo compounds (Ib-e) which are first formed[2] were difficult to isolate, they were allowed to rearrange in the reaction mixture in which they were prepared, directly to the hydrazones (IIb-e and IIIb-e). That the rearrangement of the O-azo compound (IV) proceeded through the C-azo compound (I) in every case was supported by the initial change of the yellow color of IV to the red color of I which then faded as the colorless hydrazone (II or III) was formed.[3] The ultraviolet spectra of Ia, IVd and IIIb were measured and are given in Figs. 1 and 2.

IVb gave a single rearrangement product in 84% yield. This substance was shown, as described in the following paper,[4] to be *p*-nitrophenyl triketone benzoylphenylhydrazone (IIIb)—formed

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[1a] Taken from the Ph.D. thesis submitted by Charlotte S. Russell to Columbia University.

[1b] Department of Chemistry, University of Illinois, Urbana, Illinois.

[2] (a) O. Dimroth, *Ber.*, **40**, 2404 (1907); (b) O. Dimroth and M. Hartmann, *ibid.*, **40**, 4460 (1907); (c) O. Dimroth and M. Hartmann, *ibid.*, **41**, 4012 (1908).

[3] When the rearrangement of IVc was conducted at 120° side reactions leading to extensive decomposition to tars occurred. This compound was therefore heated at 75° until the color of the C-azo compound (Ic) had just begun to fade and the rearrangement was completed at 120°. It is of interest that this rearrangement apparently took place entirely in the solid state.

[4] D. Y. Curtin and C. S. Russell, THIS JOURNAL, **73**, Nov. (1951).