0.042 mole), ethyl alcohol (100 ml.) and water (10 ml.). The reaction mixture was refluxed on a steam-bath for 36 hours, concentrated, and then poured into cold water (50 ml.). Filtration afforded a brown residue, which was dried and extracted with methylene chloride. The red extract was concentrated and adsorbed on alumina. Elution of the column with methylene chloride and concentration of the eluate gave pale yellow prisms (1.80 g., m.p. 207–210°), which were satisfactory for direct oxidation to the bis-sulfone. Further concentration of the eluate gave an additional crop of yellow sulfide, which was recrystallized from methylene chloride–ethanol, after treatment with charcoal, to yield 0.08 g. of pure VII as small white prisms, m.p. 213–217° dec. The total yield (1.88 g.) was 48%.

Anal. Calcd. for $C_{10}H_{10}S_2$: C, 61.81; H, 5.19; S, 33.00. Found: C, 61.61; H, 5.10; S, 32.81.

1,3,5,7-Tetrahydro[1,2-c:4,5-c′-dithiophene-2,2,6,6-tetroxide(VIII).—The bis-sulfide (1.74 g., 0.009 mole) was cautiously added over a period of 20 minutes to peracetic acid (60 ml.) which was cooled externally by means of an ice–water-bath. After the addition was complete, stirring was continued for 3 days at room temperature. The reaction mixture was diluted with cold water (100 ml.); the white crystalline product was removed by filtration and dried (2.1 g., 90%). Purification was accomplished by dissolving a small quantity of the product in warm dimethylformamide, adsorption on alumina, and continued elution of the column with warm dimethylformamide. Concentration of the eluate *in vacuo*, and addition of a small amount of water afforded the bis-sulfone as small white needles having no observable melting point below 400° dec.

Anal. Calcd. for $C_{10}H_{10}S_2O_4$: C, 46.50; H, 3.90; S, 24.83. Found: C, 46.38; H, 3.80; S, 24.94.

Benzo[1,2:4,5]dicyclobutene (V).—An intimate mixture of disulfone VIII (0.750 g.) and copper powder (0.350 g. was heated to 320° (salt-bath temperature) under a low pressure atmosphere of nitrogen (1 mm.) for two hours, the evolved vapors being passed through a glowing Nichrome coil (~600°) before being condensed on a cold finger.[6] The solid sublimate was washed off the condenser with ether and the ether solution was filtered and evaporated. The residue was extracted with a small amount of petroleum ether (40–70°) and the extract placed on a column (12 × 0.8 cm.) of Woelm neutral alumina. Elution of the column with ether afforded 0.150 g. (40%) of hydrocarbon V, m.p. 98–100°. The analytical sample, m.p. 101° (cor.), formed small white prisms after recrystallization from methanol.

An identical pyrolysis of sulfone–copper mixture gave only a 20% yield of V when the heating spiral was omitted; pyrolysis of the sulfone, undiluted by copper, gave also a 20% yield of V even though the spiral was employed; ultraviolet maxima (in ethanol): 276 mμ (log E 3.66), 280 mμ (log E 3.71), 286 mμ (log E 3.59).

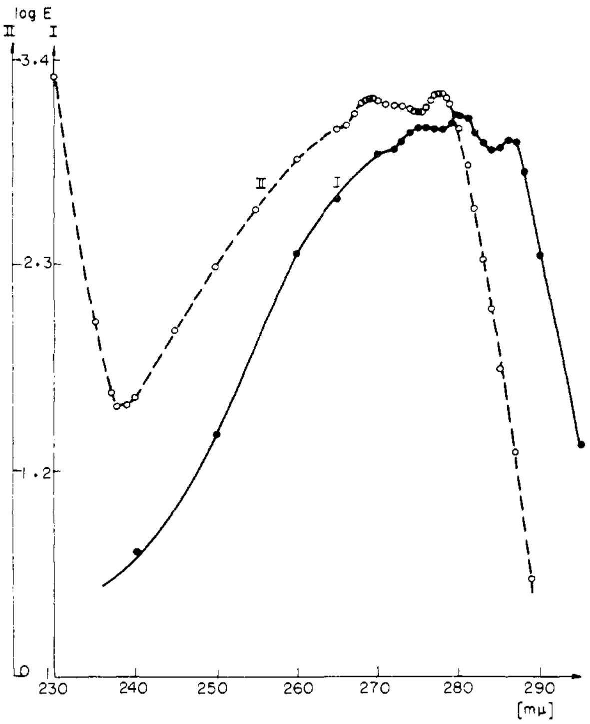

Fig. 1.—Spectra in 95% ethanol: I, benzo[1,2:4,5]dicyclobutene; II, 1,2,4,5-tetramethylbenzene (durene). (Solvent, 95% ethanol).

The maxima observed for durene in ethanol were: 269 mμ (log E 2.80), 278 mμ (log E 2.82).

Anal. Calcd. for $C_{10}H_{10}$: C, 92.26; H, 7.74; mol. wt., 130. Found: C, 92.30; H, 7.66; mol. wt. (Rast), 101.

Oxidation of Benzo[1,2:4,5]dicyclobutene(V).—A mixture of hydrocarbon V (0.024 g.), potassium permanganate (0.250 g.) and water (1.5 ml.) was shaken in a sealed tube at 100° for 18 hours. The brown precipitate of manganese dioxide was removed by filtration and the colorless filtrate was passed through a column (10 × 0.8 cm.) of Amberlite IR 120 resin (acid phase). Evaporation of the aqueous acidic eluate gave pyromellitic acid (IX) as white needles, converted by heating into the dianhydride. The sublimed anhydride weighed 0.017 g. (31%) and it was identical in melting point (283–285°) and infrared spectrum (KBr pellet) with material prepared from authentic pyromellitic acid

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[6] The apparatus used was identical with that described previously in ref. 1.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, TULANE UNIVERSITY]

Sodium Borohydride Reduction of Nitroso Groups and Furoxan Rings[1]

BY J. H. BOYER AND S. E. ELLZEY, JR.

RECEIVED SEPTEMBER 24, 1959

Sodium borohydride reduces both nitrosobenzene and β-phenylhydroxylamine to azoxybenzene, but transforms *p*-nitrosophenol into *p*-aminophenol. Both *o*- and *p*-dinitrosoaromatic derivatives and furoxans react with this reagent to give corresponding dioximes or their anhydrides, the furazans. Cyclohexanone oxime is reduced by sodium borohydride with lithium bromide to cyclohexylamine.

Nitrobenzene at 90–100°[2] and now nitrosobenzene below 45° are each reduced by sodium borohydride to azoxybenzene. An unexpected transformation, below 45°, of β-phenylhydroxylamine to azoxybenzene using sodium borohydride requires initial air oxidation to nitrosobenzene insofar as the probable transformation of each of these three staritng materials to azoxybenzene includes a condensation between nitrosobenzene and β-phenylhydroxylamine. Dismutation of β-phenylhy-

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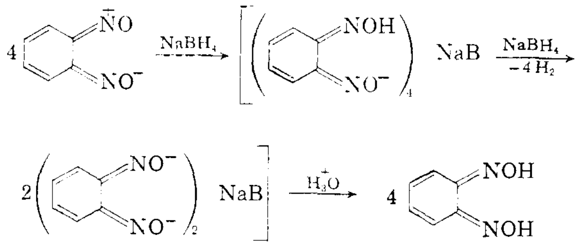
[1] Financial support by the Office of Ordnance Research, United States Army, under contracts No. DA-01-009-ORD-428 and DA-01-009-ORD-699 is gratefully acknowledged.

[2] C. E. Weill and G. S. Panson, *J. Org. Chem.*, **21**, 803 (1956).

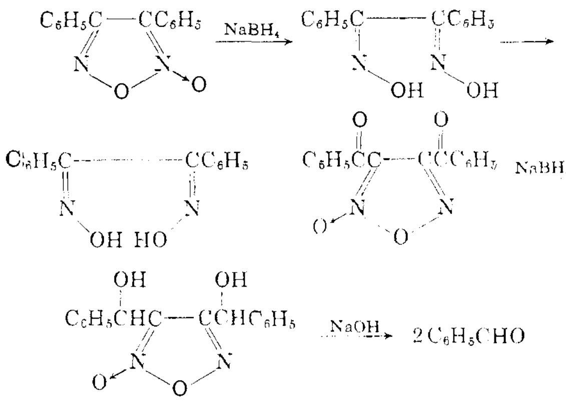
droxylamine to nitrosobenzene, and aniline, if it is occurring is negligible since neither aniline nor azobenzene can be detected in the reaction mixture. Reduction of *p*-nitrosophenol to *p*-aminophenol provides another demonstration that the presence of strong electron-donating ring substituents facilitates reduction of *β*-arylhydroxylamines to corresponding amines.[3]

Azoxy derivatives are not obtained from either *o*- or *p*-dinitrosoaromatic compounds and sodium borohydride. Instead, corresponding dioximes are produced in reactions which occur with greater difficulty with fused ring derivatives. Conceivably, two moles of *o*-(or *p*-)dinitrosobenzene may be transformed into the corresponding dioxime by one mole of sodium borohydride as is indicated in the equations for reactions which allow intermediates containing active hydrogen to react with sodium borohydride with the formation of hydrogen. Experimentally it has not been possible to realize the expected equimolar ratio between *o*-dinitrosobenzene and hydrogen evolved or a 2:1 molar ratio between *o*-dinitrosobenzene and sodium borohydride required (Table II). An excess of the reagent has been used to ensure maximum yield. The reaction, in the second step, between sodium borohydride and an oxime is apparently more complicated than represented in the equation since an average equimolar ratio between *o*-benzoquinone dioxime and sodium borohydride consumed in reacting with it is obtained instead of an expected 2:1 ratio and at the same time a 70% average yield of hydrogen is measured (Table II).



The results demonstrate that active hydrogen in an oximino group may not be quantitatively detected by sodium borohydride and suggest that oximes are reduced by sodium borohydride; however, reduction products other than oximes have not been isolated from reactions between sodium borohydride and either *o*- or *p*-dinitrosoaromatic compounds or furoxans.[4] In some cases glyoximes undergo dehydration to furazans. From cyclohexanone oxime and sodium borohydride with lithium bromide, cyclohexylamine is obtained.

Cleavage of a ring oxygen–nitrogen bond in furoxans by sodium borohydride accounts for the formation of corresponding dioximes. The exocyclic N→O bond in furoxans resembles the similar bond in azoxy derivatives in its resistance to attack by sodium borohydride. Dialkyl furoxans are less reactive than diaryl derivatives. Presumably *γ*-(*amphi*)-benzil dioxime is initially formed from diphenylfuroxan and undergoes isomerization to a *β*-(*syn*)-glyoxime which does not form a nickel chelate. Apparently carbonyl groups are reduced at lower temperatures than are furoxan rings since sodium borohydride transforms dibenzoylfuroxan into bis-(*α*-hydroxybenzyl)-furoxan, the identification of which is based on its infrared absorption, elemental analysis, molecular weight determination and release of benzaldehyde in alkaline solution.



Acknowledgment.—We are indebted to Mr. R. T. O'Connor of the Southern Regional Research Laboratory for infrared analytical data.

Experimental[5]

Reduction of Nitrosobenzene.—To a well stirred slurry of 3.21 g. (30.0 mmoles) of nitrosobenzene in 25 ml. of ethanol was added, over a period of 15 minutes, a solution of 0.72 g. (19 mmoles) of sodium borohydride, of at least 97% purity by volumetric or gasometric assay,[6] in 25 ml. of ethanol as the temperature of the exothermic reaction rose to 45° before cooling to 25–30° with an ice-bath. The mixture was stirred for 30 minutes at 25–30°, poured into 300 ml. of ice-water, stored a few hours and filtered. Crude orange azoxybenzene recrystallized from ethanol as light yellow needles; 2.16 g. (73%), m.p. and mixture m.p. 32–33° (lit.[7] m.p. 35–35.5°). A 75% yield of azoxybenzene was obtained after recrystallization when the order of addition of the reactants was reversed.

Reaction of *β*-Phenylhydroxylamine with Sodium Borohydride.—To a well stirred solution of 2.18 g. (20.0 mmoles) of *β*-phenylhydroxylamine in 25 ml. of ethanol was added over a period of 15 minutes a solution of 0.72 g. (19 mmoles) of sodium borohydride in 20 ml. of ethanol. The solution was heated to 40–45°, stirred 15 minutes and poured into 250 ml. of water. Upon standing 36 hours in the refrigerator, crude yellow azoxybenzene, m.p. 30–32°, 0.93 g., precipitated. The filtrate and washings were combined and extracted with ether; the ether was evaporated and the residue, combined with the above product, was recrystallized from ethanol as small yellow needles of azoxybenzene, m.p. and mixture m.p. 36–37°, 1.06 g. (54%).

Reduction of *p*-Nitrosophenol.—A slurry of 1.23 g. (10.0 mmoles) of *p*-nitrosophenol in 15 ml. of water was made alkaline by the addition of 5 ml. of 10% sodium hydroxide solution. After the addition of 0.50 g. (13 mmoles) of sodium borohydride, the solution was heated with stirring for 5 hours at 50–60°, diluted with 50 ml. of water and acidified with 5 ml. of glacial acetic acid as the temperature was kept below 10° by external cooling. The solution was continuously extracted with ether for 17 hours and the dried extract

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(3) J. H. Boyer and H. Alul, THIS JOURNAL, **81**, 2136 (1959).

(4) E. Müller, H. Metzger and D. Fries, *Chem. Ber.*, **87**, 1449 (1954), reported reduction of *gem*-chloronitroso derivatives by sodium borohydride to oximes.

(5) Microanalyses by Dr. Alfred Bernhardt, Max Planck Institut, Microanalytisches Laboratorium, Mülheim (Ruhr), Germany. Molecular weight determination by Huffman Microanalytical Laboratories, Wheatridge, Colo. Melting points are uncorrected.

(6) W. D. Davis, L. S. Mason and G. Stegeman, THIS JOURNAL, **71**, 2775 (1949).

(7) S. Sugden, J. B. Reed and H. Wilkins, *J. Chem. Soc.*, **127**, 1525 (1925).

TABLE I

REDUCTION OF AROMATIC DINITROSO DERIVATIVES AND FUROXANS WITH $NaBH_4$

Dinitroso derivative or furoxan	Solvent	Temp., °C.	Time, hr.	Molar equiv. $NaBH_4$	Product	Yield, %
o-Dinitrosobenzene[a]	Diglyme	35–40	0.5	1.2	*o*-Benzoquinone dioxime[b]	54
p-Dinitrosobenzene[c]	Diglyme	30	1	1.3	*p*-Benzoquinone dioxime[d]	62
4-Methyl-1,2-dinitrosobenzene[e]	Ethanol	40–45	3	1.3	4-Methylbenzoquinone-1,2-dioxime	41
4-Methyl-1,2-dinitrosobenzene	Ethanol	78	1	2.0	5-Methylbenzofurazan	42
1,2-Dinitrosonaphthalene[f]	Diglyme	130–140	8	1.3	1,2-Naphthofurazan[f]	66
9,10-Dinitrosophenanthrene[g]	Diglyme	160	2	1.3	9,10-Phenanthrenefurazan[h]	57
3,6-Diphenyl-4,5-dinitrosopyridazine[i]	Ethanol	78	1	2.6	4,7-Diphenylfurazano [d] pyridazine[j,k]	48
Diphenylfuroxan[l]	Diglyme	160	2	1.3	β-Benzil dioxime[g]	43
Dibenzoylfuroxan[m]	Ethanol	25–30	2	0.6	Bis-(α-hydroxybenzyl)-furoxan[n]	45
Dimethylfuroxan[o]	Dioxane	102	10	1.0	Dimethylglyoxime[p]	4.3[q]
Tetramethylenefuroxan[g]	Dioxane	102	8	1.0	Nioxime[r]	10.7[s]
Tetramethylenefuroxan	Diglyme	160	2	1.3	Nioxime	18[t]

[a] P. A. S. Smith and J. H. Boyer, *Org. Syntheses*, **31**, 14 (1951). [b] T. Zincke and P. Schwarz, *Ann.*, **307**, 28 (1899). [c] Hypohalite oxidation transformed *p*-benzoquinone dioxime into *p*-dinitrosobenzene (J. H. Trepagnier and J. V. Vaughen, U. S. Patent 2,419,976; *C. A.*, **41**, 5897 (1947)). The crude yellow product darkened at 200°, did not melt under 300° and sublimed at 95–120° (0.02–0.1 mm.) into a green amorphous solid collected on a surface cooled by acetone containing Dry Ice. The green solid became yellow below room temperature, had no sharp m.p. and appeared to be electrified. Lowering the temperature did not, but resublimation as described above did, bring about restoration of the green solid. A m.p. 174–175°, reported for the green form (J. H. Boyer, U. Toggweiler and G. Stoner, THIS JOURNAL, **79**, 1748 (1957), has not been reproduced. [d] M.p. 235–240° dec.; R. Nietzki and F. Kehrmann, *Ber.*, **20**, 613 (1887), reported m.p. 240° dec. The diacetate ester of *anti-p*-benzoquinone dioxime, m.p. 199–203° dec., was prepared from this product (F. Kehrmann, *ibid.*, **28**, 340 (1895), reported a m.p. 190° dec.). [e] A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **101**, 2452 (1912). [f] A. G. Green and F. M. Rowe, *ibid.*, **111**, 612 (1917). [g] J. H. Boyer and U. Toggweiler, THIS JOURNAL, **79**, 895 (1957). [h] J. Schmidt and J. Söll, *Ber.*, **40**, 2454 (1907). [i] H. R. Snyder and N. E. Boyer, THIS JOURNAL, **77**, 4233 (1955). [j] The initial crude product is a brick-red dioxime of 3,6-diphenyl-4,5-diazabenzquinone-1,2 which upon oxidation with alkaline hypohalite is converted into 3,6-diphenyl-4,5-dinitrosopyridazine (71% over-all recovery) with no trace of a furazan. The red dioxime in boiling acetone is converted into the corresponding furazan in 39% yield. The furazan was indifferent to alkaline hypochlorite. [k] E. Durio, *Gazz. chim. ital.*, **61**, 589 (1931). [l] E. Beckmann, *Ber.*, **22**, 1588 (1889). [m] A. F. Hollemann, *ibid.*, **20**, 3359 (1887). [n] M.p. 107–117°; repeated recrystallization from a mixture of methylene chloride and hexane gave colorless needles, m.p. 132.2–132.6° cor. Calcd. for $C_{16}H_{14}N_2O_4$: C, 64.43; H, 4.73; N, 9.39; O, 21.46; mol. wt., 298. Found: C, 64.20; H, 4.63; N, 9.68; O, 21.28; mol. wt., 224. Infrared absorption from a KBr disk (possible furoxan bands italicized): 3390s, 3040m, *1585s*, *1484s*, *1445s*, 1403m, *1344m*, 1314m, 1266m, 1232m, *1192m*, 1096s, 1064s, *1028s*, 1005s, 923m, 867w, *845s*, 814m, 784m, 765s, 746s, 722s, 694s, 658s. [o] R. Scholl, *Ber.*, **23**, 3490 (1890). [p] L. Wolff, *Ann.*, **288**, 1 (1895). [q] This includes 1.8% isolated as the nickel chelate salt; starting material (15%) was recovered. [r] M.p. 170–176° dec.; O. Wallach, *Ann.*, **437**, 148 (1924), reported 189–190° dec. [s] The product was isolated as the free dioxime (3.6%) plus its nickel chelate (7.1%). [t] Product isolated as its nickel chelate salt.

was treated with Norite and filtered. The filtrate, concentrated to about 50 ml., was combined with an equal volume of benzene and upon chilling deposited 0.46 g. (42%) of *p*-aminophenol as gray platelets, m.p. 182–184° dec. (bath preheated to 165°) (lit.[8] m.p. 184° dec.). A small sample of the reduction product was treated with benzoyl chloride and 10% sodium hydroxide. The product, twice recrystallized from aqueous ethanol, formed small colorless needles of O,N-dibenzoyl-*p*-aminophenol, m.p. and mixture m.p. 240–241° (lit.[9] m.p. 231°).

Reduction of Cyclohexanone Oxime.—To a solution of 2.00 g. (51.3 mmoles) of sodium borohydride in 50 ml. of diglyme (diethylene glycol dimethyl ether), b.p. 85–86° (50 mm.), $n^{25}D$ 1.4050, was added 4.51 g. (51.9 mmoles) of lithium bromide. The solution was cooled to room temperature, stirred for 15 minutes, treated with 5.66 g. (50.0 mmoles) of cyclohexanone oxime, heated at gentle reflux with stirring for 4 hours, and distilled at 49–52 mm. until 30 ml. of distillate, b.p. 85°, was collected. To the distillation residue was added 25 ml. of diglyme, and another 35 ml. of distillate, b.p. 85–87°, was collected at 49 mm. The combined distillates were saturated with dry hydrogen chloride and, upon evaporation of the steam-bath with an air stream, deposited 0.90 g. (19%, based on recovered starting material and assuming quantitative formation of the hydrochloride derivative) of colorless needles of cyclohexylamine hydrochloride, m.p. 209–210° (lit.[10] m.p. 206–207.5°) after recrystallization from anhydrous isopropyl alcohol and ethyl acetate. A small sample of the hydrochloride treated with benzoyl chloride and 10% sodium hydroxide gave N-cyclohexylbenzamide, m.p. 150–151° (lit.[11] m.p. 149°), after two recrystallizations from dilute methanol. From the distillation residue, treated with 50 ml. of water, acidified below 15° with 10 ml. of 50% acetic acid and placed in the refrigerator for 15 hours, impure cyclohexanone oxime was recovered, m.p. 75–82°, 1.74 g. (31%). A methanol solution of the recovered oxime treated with a hot solution of 2,4-dinitrophenylhydrazine gave the 2,4-dinitrophenylhydrazone of cyclohexanone, m.p. 160–162°.

When the reaction was carried out at 100° for 15 hours a 5% yield of cyclohexylamine hydrochloride was obtained and cyclohexanone oxime (23%) was recovered.

Reduction of *o*-Dinitrosobenzene.—To a solution of 0.36 g. (9.2 mmoles) of sodium borohydride in 20 ml. of diglyme was added with stirring during a period of about two minutes 1.00 g. (7.35 mmoles) of *o*-dinitrosobenzene. The blood-red solution was warmed to 35–40°, stirred at that temperature (with external cooling when necessary) for 30 minutes, poured into about 150 ml. of ice-water, acidified carefully with 5 ml. of glacial acetic acid, cooled to 0–5° and upon filtration gave a brown solid, 0.55 g. (54%), m.p. 146–148° dec., which recrystallized from dilute ethanol as small tan needles of *o*-benzoquinone dioxime, m.p. 148–149° dec. (lit.[12] m.p. 142° dec). The dioxime gave a black precipitate when treated in ethanol with aqueous nickelous nitrate. Ether extraction of the acidic filtrate yielded, upon evaporation of the solvent, 0.14 g. of an unidentified black-brown solid.

Similar yields of the dioxime were obtained at a reaction temperature of 55°. When the reaction was run at 15° a dioxime was not isolated (although the red color of the solution indicated its probable formation) and 37% of the starting material, m.p. 67–68°, was recovered. Benzofurazan was not isolated upon ether extraction of the steam distillate from the acidic reaction mixture.

In several cases where the solid dinitroso compound was rapidly added to the solution of sodium borohydride the temperature rose rapidly to 65–85° and then began to drop after about 10 minutes. The yield of the dioxime isolated

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(8) W. Lossen, *Ann.*, **175**, 271 (1875).

(9) O. Hinsberg and L. Udranszky, *ibid.*, **254**, 252 (1889).

(10) W. Markownikoff, *ibid.*, **302**, 1 (1898).

(11) O. Wallach, *ibid.*, **343**, 40 (1905).

(12) T. Zincke and P. Schwarz, *ibid.*, **307**, 28 (1899).

TABLE II

HYDROGEN EVOLUTION FROM REACTIONS OF *o*-DINITROSOBENZENE (DNB) AND OF *o*-BENZOQUINONE DIOXIME (BQD) WITH SODIUM BOROHYDRIDE (SBH)

Compound[a]	G.	Mmole	SBH,[a,b] mmole	Hydrogen evolved during reaction[c] Cc.	Hydrogen evolved during reaction[c] Mmole	Hydrogen evolved by acid Cc.	Hydrogen evolved by acid Mmole	Excess SBH,[d] mmole	SBH consumed in reaction, mmole
DNB	0.0890	0.654	0.745	12.5	0.509[e]	18.7	0.761	0.190	0.555
DNB	.0902	.663	.745	13.5	.550	18.8	.765	.191	.554
BQD	.0839	.608	.701	20.4	.833	14.2	.580	.145	.556
BQD	.0350	.254	.701	9.2	.375	39.1	1.59	.398	.303

[a] Samples dissolved in 3 ml. of diglyme purified by distillation from lithium aluminum hydride and redistilled, b.p. 88-90° (52 mm.). [b] SBH (0.769 mmole) which assayed 97.0% used with DNB; SBH (0.769 mmole) which assayed 91.2% used with BQD. [c] Blank runs with sodium borohydride in purified diglyme gave no more than 0.1 cc. of evolved gas after 2.5 hours at 35–40°. For DNB, reaction time was 3 hours at 35–40°; for BQD, reaction time was 1.5 hours at 35–40°; hydrogen measured at 27° (762 mm.). [d] One-fourth of the mmoles of hydrogen evolved by acid according to the equation $NaBH_4 + H_2SO_4 + 3H_2O \rightarrow 4H_2 + H_3BO_3 + NaHSO_4$. [e] Sample calculation: $n = (762/760)0.0125/0.08205\ (300) = 0.000509$ mole = 0.509 mmole.

ranged from 0–30%. The initially acidified reaction mixture was made strongly alkaline with sodium hydroxide with the precipitation of 0.1–0.2 g. of a yellow or brown solid which did not melt below 300° and was insoluble in hot methylene chloride or *n*-hexane but very soluble in hot ethanol. It dissolved readily in cold concentrated hydrochloric acid or glacial acetic acid and gave a wine colored solution in each case; it was insoluble in cold 10% sodium hydroxide. It could be sublimed with difficulty at 170–180° (0.02 mm.) whereupon a red-orange solid which did not melt below 300° was obtained.

Reduction of nitroso derivatives and furoxans is summarized in Table I.

In two experiments, *o*-dinitrosobenzene was treated with excess sodium borohydride (assayed by hydrogen evolution in a reaction with sulfuric acid) in diglyme following a procedure[13] which allowed the collection over mercury of evolved hydrogen. Excess borohydride was removed with dilute sulfuric acid. Based on hydrogen evolution measured before and after treatment with acid, the amount of sodium borohydride used in reduction was calculated. A sample of the gas collected above water during the reduction burned explosively in air and gave negative tests for the presence of boron compounds. Under similar conditions *o*-benzoquinone dioxime was treated with sodium borohydride. The results obtained with each compound are described in Table II.

Reaction of Bis-(α-hydroxybenzyl)-furoxan with Sodium Hydroxide.—A suspension of 0.30 g. (1.0 mmole) of the furoxan in 15 ml. (38.0 mmoles) of 10% sodium hydroxide solution was stirred at room temperature for 45 minutes. The solid slowly dissolved as the solution became pink and finally yellow and the odor of benzaldehyde was noted. After acidifying with 5 ml. of glacial acetic acid, a solution of 2,4-dinitrophenylhydrazine was added, the mixture was heated to the boiling point, cooled to 0° and filtered. The crude product recrystallized from methanolic hydrochloric acid as small orange plates of benzaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixture m.p. 243–245°, 0.12 g. (21%).

NEW ORLEANS 18, LA.

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[13] J. C. Rankin and C. L. Mehltretter, *Anal. Chem.*, **28**, 1012 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF FLORIDA]

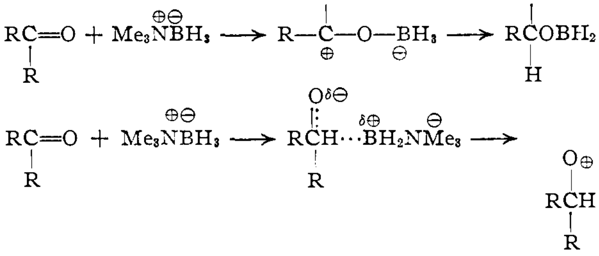
Amine Borane Reductions. The Stereochemistry of the Reduction of 4-*t*-Butylcyclohexanone with Trimethylamine Borane in the Presence and Absence of Boron Fluoride

BY W. M. JONES

RECEIVED OCTOBER 9, 1959

The reduction to the alcohol of 4-*t*-butylcyclohexanone with trimethylamine borane and diborane in neutral, non-aqueous solvents was found to give approximately 16% of the *cis* isomer in each case. These results suggest that the two reactions have a common intermediate. On the other hand, the reduction of 4-*t*-butylcyclohexanone with trimethylamine borane and diborane in the presence of boron fluoride gave, under the same conditions, 46–52% and 16% *cis*-4-*t*-butylcyclohexanol, respectively. These results are rationalized in terms of the trimethylamine borane reduction proceeding by initial complexing of the boron fluoride with the carbonyl oxygen followed by intermolecular hydride transfer from the amine borane. Evidence is also presented which indicates that the resulting ionic intermediate I decompose to 4-*t*-butylcyclohexyldifluoroboronite II and III.

Of the many substituted boranes and borohydrides that have been found in the past few years to be effective reducing agents[1] one which we feel has potential for becoming especially useful due to its stability[1b,2] and convenience to deal with is trimethylamine borane.[3] The possibility that carbonyl reductions involving this reagent might well proceed by either of the general paths



$$\underset{\displaystyle R}{\underset{|}{RC}}{=}O + Me_3\overset{\oplus\ominus}{N}BH_3 \longrightarrow R{-}\overset{\displaystyle R}{\underset{\oplus}{C}}{-}O{-}\underset{\ominus}{BH_3} \longrightarrow R\overset{\displaystyle R}{\underset{\displaystyle H}{C}}OBH_2$$

$$\underset{\displaystyle R}{\underset{|}{RC}}{=}O + Me_3\overset{\oplus\ominus}{N}BH_3 \longrightarrow \underset{\displaystyle R}{\overset{O^{\delta\ominus}}{RCH}}\cdots\overset{\delta\oplus}{B}H_2\overset{\ominus}{N}Me_3 \longrightarrow \overset{O^{\oplus}}{\underset{\displaystyle R}{RCH}}$$

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[1] (a) N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956; (b) Callery Chemical Co., Technical Bulletin C-200, Callery, Penna., April 1, 1958.

[2] A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 780 (1939).

[3] Commercially available from Callery Chemical Co., Callery, Penna. The trimethylamine borane employed in these investigations was most generously supplied by this company.