The Reaction of Sodium Hydride with *p*-Nitrobenzaldehyde

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Sodium hydride reacts with *p*-nitrobenzaldehyde in tetrahydrofuran at room temperature to give *p*-nitrobenzoic acid plus smaller amounts of *p*-nitrobenzyl alcohol. From experiments with *p*-nitrobenzaldehyde-*α-d* it is concluded that *p*-nitrobenzyl alcohol arises through a Tischenko reaction or a Cannizzaro reaction involving oxygenated nucleophiles absorbed on the sodium hydride surface. The *p*-nitrobenzoic acid arises from these reactions and from the base-catalyzed autoxidation of *p*-nitrobenzyl alcohol. The results with *p*-nitrobenzaldehyde-*α-d* demonstrate that the nucleophilic addition of sodium hydride to the aldehyde carbonyl does not occur at a detectable level. A blue, oxygen-sensitive intermediate is obtained from either *p*-nitrobenzaldehyde or *p*-nitrobenzyl alcohol with sodium hydride under oxygen-free conditions.

Most of the literature concerning the reactions of sodium hydride and carbonyl compounds involves formation of an enolate ion.[1] There exists apparently only a single report of a reaction of sodium hydride with nonenolizable carbonyl compounds. Swamer and Hauser[2] observed that at elevated temperatures in hydrocarbon solvents sodium hydride failed to react with methyl benzoate, reduced benzophenone to benzhydrol, and converted benzaldehyde into benzyl benzoate.

We have found that sodium hydride reacts with *p*-nitrobenzaldehyde in tetrahydrofuran at room temperature to give, after hydrolysis, *p*-nitrobenzoic acid in yields up to 85% accompanied by smaller amounts of *p*-nitrobenzyl alcohol. The yields of neither product were quantitatively reproducible; typical product analyses for varying stages of aldehyde consumption are given in Table I. The highest yield of *p*-nitrobenzyl alcohol obtained was 30%. The system is heterogeneous; both the reactant sodium hydride (introduced as a small particle dispersion in mineral oil) and the sodium salts of the products are completely insoluble in tetrahydrofuran. A control reaction in which sodium hydroxide pellets were substituted for sodium hydride gave only 2% of *p*-nitrobenzoic acid after 1 hr.

TABLE I

THE REACTION OF SODIUM HYDRIDE WITH *p*-NITROBENZALDEHYDE[a]

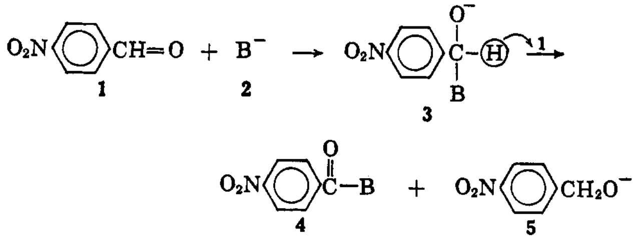
Reaction time, min.	*p*-Nitrobenzaldehyde, %[b]	*p*-Nitrobenzyl alcohol, %[b]	*p*-Nitrobenzoic acid, %[c]
10	74	16	13
10	58	22	19
20	47	22	23
20	26	19	47
40	40	12	46
48	1	12	82
60	2	13	78

[a] Molar excess (4:1) of sodium hydride in tetrahydrofuran at 25°. [b] Infrared analysis of hydrolyzed product. [c] Isolated.

It is apparent from the data that the ratio of *p*-nitrobenzoic acid to *p*-nitrobenzyl alcohol is unity within experimental error until about half of the *p*-nitrobenzaldehyde has disappeared. Thereafter the ratio increases rapidly. These observations suggest that *p*-nitrobenzaldehyde is being reduced to *p*-nitrobenzyl alcohol which is then autoxidized to *p*-nitrobenzoic acid.

The feasibility of the latter step was demonstrated by treatment of *p*-nitrobenzyl alcohol with sodium hydride under the previous reaction conditions: an 81% yield of *p*-nitrobenzoic acid was obtained after 1 hr. The formation of *p*-nitrobenzyl alcohol, however, does not occur by direct addition of sodium hydride to *p*-nitrobenzaldehyde (**1** → **3a**). When *p*-nitrobenzaldehyde-*α-d* was allowed to react with sodium hydride, the *p*-nitrobenzyl alcohol produced was completely deuterated at the benzylic carbon. The analysis was obtained by the n.m.r. spectra of samples from two different reactions using concentrations that would have allowed as much as 5% of the methylene proton signal to be detected. This exclusive deuteration eliminates both the reaction and work-up solvents as hydrogen sources and clearly requires a concerted hydrogen transfer from one molecule of *p*-nitrobenzaldehyde to another.

The peculiar combination of a specific hydrogen transfer and the formation of both the corresponding alcohol and carboxylic acid from an aldehyde indicates a Cannizzaro reaction or possibly a Tischenko reaction if the Tischenko ester could be hydrolyzed under the reaction conditions. Of these two possibilities the latter would actually seem to be the more probable, not only in view of the findings of Swamer and Hauser,[2] but also because the Tischenko reaction is known[3] to be an ionic chain reaction requiring only a catalytic amount of initial alcohol (**1** → **4b**). The required amount of *p*-nitrobenzyl alcohol could conceivably be small enough to be produced by direct sodium hydride reduction and still escape detection in the deuterium experiments.



a, B = H
b, B = $O_2NC_6H_5CH_2O$
c, B = OH, O^-
d, B = O_2H, O_2^-

In support of this route *p*-nitrobenzyl *p*-nitrobenzoate (**4b**) was found to hydrolyze quantitatively under the work-up conditions. Further, in an experiment in

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(1) For a review of the organic chemistry of sodium hydride, see "Sodium Hydride Dispersed in Oil," Technical Bulletin of Metal Hydrides, Inc.

(2) F. W. Swamer and C. R. Hauser, *J. Am. Chem. Soc.*, **68**, 2647 (1946).

(3) See, for example, O. Kamm and W. F. Kamm, "Organic Syntheses," Coll. Vol. I, H. Gilman and A. H. Blatt, Ed., John Wiley and Son, Inc., New York, N. Y., 1932, p. 104.

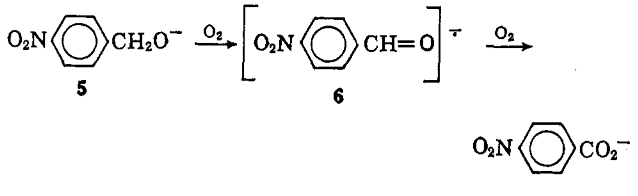
which the *p*-nitrobenzaldehyde–sodium hydride reaction mixture was filtered instead of hydrolyzed, the presence of *p*-nitrobenzyl *p*-nitrobenzoate could be detected. Quantitatively, however, the yield of ester in this experiment as determined from the infrared spectrum was only 8% under conditions which generally produced over 50% of *p*-nitrobenzoic acid. In another experiment, *p*-nitrobenzyl *p*-nitrobenzoate was subjected to the same reaction conditions for 1 hr. and then filtered; the ester was recovered from the filtrate in 69% yield. The persistance of 12–13% of *p*-nitrobenzyl alcohol as shown in Table I and the failure to obtain more than an 85% yield of *p*-nitrobenzoic acid even after 4 hr. probably reflect the limit of the amount of Tischenko ester formed.

These findings indicate that the majority of the *p*-nitrobenzoic acid obtained from the longer reaction times does not come from *p*-nitrobenzyl *p*-nitrobenzoate either by hydrolysis or autoxidation. Most of the acid obtained in these experiments must come either from *p*-nitrobenzyl alcohol through the demonstrated autoxidation or from *p*-nitrobenzaldehyde directly. If the former is the correct path, then the stability of the Tischenko ester toward autoxidation and the studies with deuterated aldehyde indicate that a Cannizzaro reaction is responsible for an appreciable amount of the formation of *p*-nitrobenzyl alcohol.

Any Cannizzaro process requires the presence of substantial amounts of some oxygen nucleophile (**2c** or **2d**). Although no studies of the surface composition of sodium hydride have been reported, it is reasonable to suspect the presence of sodium hydroxide, sodium oxide, sodium hydroperoxide, or sodium peroxide from the absorption of water vapor and atmospheric oxygen.[4] To test whether these substances in a finely divided form are capable of effecting a Cannizzaro reaction with *p*-nitrobenzaldehyde, experiments were run in which sodium hydride was replaced by equal weights of either powdered sodium hydroxide or sodium peroxide. For reaction times that produced *p*-nitrobenzoic acid in over 50% yields with sodium hydride, powdered sodium hydroxide and sodium peroxide gave 64 and 37% yields, respectively, of *p*-nitrobenzoic acid. In addition, it was observed that sodium hydride from cans that had been opened extensively gave higher yields of *p*-nitrobenzoic acid than fresh samples.[6]

Hydroperoxide ion is known to be a good nucleophile,[7] and, by implication, peroxide ion should be also. Attack by either hydroxide or oxide ion on *p*-nitrobenzaldehyde would lead directly to *p*-nitrobenzoic acid (**4c**), attack by either hydroperoxide or peroxide ion would lead to *p*-nitroperbenzoic acid (**4d**). Although no *p*-nitroperbenzoic acid was ever isolated, *p*-nitroperbenzoate ion would be expected to decompose rapidly to oxygen and *p*-nitrobenzoate ion.[8]

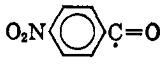
The base-catalyzed autoxidation of benzyl alcohols is a much studied reaction,[9] the mechanism apparently involving a radical-ion intermediate. In this regard we observed that combination of *p*-nitrobenzyl alcohol, sodium hydride, and tetrahydrofuran under vacuum led to the formation of an intense blue solution whose color persisted until either air or water was admitted. From this behavior and the report of radical ions in a closely similar system[9a] we assume that the blue color is due to a relatively stable radical ion, in all probability the *p*-nitrobenzaldehyde radical ion (**6**).[10] This radical ion is the expected intermediate in the reaction of *p*-nitrobenzylate ion with oxygen (**5** → **6**); its formation under evacuated conditions probably involves small amounts of residual molecular oxygen as the initial hydrogen atom acceptor.



5 **6**

The same blue solution could also be prepared from *p*-nitrobenzaldehyde, sodium hydride, and tetrahydrofuran in an evacuated system. It would seem possible that a *p*-nitrobenzaldehyde radical ion could be formed directly by a one-electron transfer from sodium hydride to *p*-nitrobenzaldehyde, but apparently this does not happen. Treatment of *p*-nitrobenzophenone, a reasonable equivalent of *p*-nitrobenzaldehyde in electron acceptor ability, with sodium hydride in an evacuated system gave no color. Under the same conditions metallic sodium readily converted *p*-nitrobenzophenone to a blue-green species.[13]

The evidence for most of the *p*-nitrobenzoic acid at high conversions of *p*-nitrobenzaldehyde coming from the autoxidation of *p*-nitrobenzyl alcohol is circumstantial. There are other possible mechanisms which have been established for similar systems: a free radical induced autoxidation[15] involving the *p*-nitrobenzaldehyde radical (**7**) or a carbanion electron-transfer process[9a] involving the *p*-nitrobenzaldehyde carbanion (**8**).



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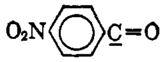

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Although we have no definitive evidence against either process, both seem less likely on the basis of results already in the literature than the steps proposed here.

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[4] Metallic sodium, which shares some similar chemistry with sodium hydride, has been reported to absorb rapidly traces of water vapor and oxygen to give sodium oxide and hydroxide.[5]

[5] L. G. McKnight, Ph.D. Thesis, University of Michigan, 1962.

[6] The data given in Table I are for reasonably fresh samples of sodium hydride. An experiment run in a good drybox with a previously unopened can of sodium hydride gave 24% of *p*-nitrobenzoic acid after 20 min.

[7] W. P. Jencks and J. Carrinolo, *J. Am. Chem. Soc.*, **82**, 1778 (1960).

[8] D. Swern, *Chem. Rev.*, **45**, 1 (1949).

[9] See, for example, (a) G. A. Russell and E. G. Janzen, *J. Am. Chem. Soc.*, **84**, 4153 (1962); (b) A. Le Berre, *Bull. soc. chim. France*, 1198 (1961).

[10] Although the *p*-nitrobenzaldehyde radical ion is a known species, the color is of little diagnostic value. Apparently the colors of nitroaromatic radical ions vary considerably with solvent (or other factors). For example, the *p*-nitrotoluene radical ion has been reported to be yellow-brown in aqueous ethanol[11] and dimethylformamide,[12] red in *t*-butyl alcohol,[9a] and blue-green in dimethyl sulfoxide.[9a] The single report of the color of the *p*-nitrobenzaldehyde radical ion listed it as yellow-brown in aqueous ethanol.[11]

[11] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963).

[12] W. Kemula and R. Sioda, *Bull. acad. polon. sci., Ser. sci. chim.*, **11**, 395 (1963).

[13] The report of a blue color by Swamer and Hauser[2] during the prolonged treatment of benzophenone and sodium in boiling xylene under nitrogen indicating the presence of benzophenone ketyl is probably due to the initial conversion of xylene to its anion by sodium hydride; carbanions are known to be efficient one-electron transfer agents.[14] The reduction to the isolated[2] benzhydrol would then be completed by a hydrogen transfer from xylene.

[14] G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.* **86**, 1807 (1964).

[15] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc. New York, N. Y., 1957, pp. 399–401.

The formation of the *p*-nitrobenzaldehyde radical (7) from *p*-nitrobenzaldehyde is abnormally slow; 14 hr. is required for the complete autoxidation of *p*-nitrobenzaldehyde in the presence of ozone.[16] The formation of carbanions from weak acids with sodium hydride is extremely slow; little or no reaction was detected between sodium hydride and triphenylmethane in 1,2-dimethoxyethane over a long period of time.[17]

Several attempts were made to detect by deuterium exchange any *p*-nitrobenzaldehyde carbanion present. Heavy water was injected directly into the blue solution formed from *p*-nitrobenzaldehyde and sodium hydride under vacuum with a hypodermic syringe through a rubber septum. In each case any deuterium incorporation in either the isolated *p*-nitrobenzaldehyde or *p*-nitrobenzyl alcohol was below the limit ($\pm 2\%$) of the analytical method. Injecting light water into the same reactions of *p*-nitrobenzaldehyde-α-*d* led to no loss of deuterium in the recovered aldehyde within $\pm 3\%$.

The steps proposed here for the formation of *p*-nitrobenzyl alcohol and for its conversion to the *p*-nitrobenzaldehyde radical ion must be heterogeneous. Both sodium hydride and sodium *p*-nitrobenzylate are completely insoluble in tetrahydrofuran.[18] In unstirred vacuum experiments the blue color is observed to form at the surface of the sodium hydride and slowly diffuse into the tetrahydrofuran solution. The surface reaction is undoubtedly enhanced by the small particle size produced by the dispersion of the sodium hydride in mineral oil. Indeed, in our view the contribution of sodium hydride, aside from assuring that all of the *p*-nitrobenzyl alcohol is present as the alcoholate ion, is to provide a large surface area for the absorption of oxygen, the conversion of oxygen to oxygenated nucleophiles, and the absorption of the organic reactants. The considerable difference in reactivity for sodium hydroxide in pellet and powdered form also demonstrates the importance of the surface area. In view of the heterogeneous nature of this system, it is not surprising that the mechanism deduced here is somewhat different from that found by Russell and Janzen[9a] for *p*-nitrobenzaldehyde and a strong base in a homogeneous system.

Cannizzaro reactions have not been reported previously with sodium hydride and aldehydes because the more rapid reactions with α-hydrogens have always been possible. The report by Swamer and Hauser[2] is apparently the only other exception. The difference in reaction found by these authors must be attributed to their exclusion of oxygen from the reaction mixture and to the greatly decreased tendency for benzyl alcohol compared with *p*-nitrobenzyl alcohol to form radical ions.

Experimental

Melting points were determined on a Fisher-Johns block and are uncorrected. Infrared spectra, unless otherwise specified, were determined on a Beckman IR-5. N.m.r. values were determined in deuteriochloroform on a Varian A-60. The sodium hydride used was a 53% dispersion in mineral oil supplied by Metal Hydrides, Inc. All transfers of sodium hydride were made as rapidly as possible and the top was resealed with paraffin after each use. The *p*-nitrobenzaldehyde was recrystallized from water and dried thoroughly. The melting point, 106–107° (lit.[20] m.p. 106.5°), was unaltered after months of handling and storage in an ordinary screw-cap bottle. An n.m.r. spectrum showed the *p*-nitrobenzaldehyde to be free of *p*-nitrobenzyl alcohol. The *p*-nitrobenzyl alcohol was prepared by sodium borohydride reduction of *p*-nitrobenzaldehyde. The deterioration of *p*-nitrobenzyl alcohol was quite rapid and before each experiment it was freshly recrystallized from aqueous ethanol, m.p. 93–94° (lit.[20] m.p. 93°). The tetrahydrofuran was freshly distilled from lithium aluminum hydride before each experiment and was gas chromatographically pure.

Reaction of Sodium Hydride with *p*-Nitrobenzaldehyde.—The reactants, 240 mg. (1.6 mmoles) of *p*-nitrobenzaldehyde, 280 mg. (6.2 mmoles) of sodium hydride, and 50 ml. of tetrahydrofuran, were combined in a flask fitted with a calcium sulfate drying tube and a magnetic stirrer. Colors and color sequences were often observed in the solution, yellow to brown to purple being most common. The yields of products obtained were not related to the colors or to their absence. After a given amount of reaction time at room temperature the reaction mixture was poured on ice (vigorous reaction, but no sparking) and the resulting solution was extracted several times with dichloromethane. The combined organic layers were dried over Drierite and concentrated in a rotatory evaporator at room temperature. The residue was either chromatographed through a Florisil column or analyzed directly through its infrared spectrum. The aqueous layer was acidified and extracted several times with ether. The residue from the evaporated ether solution was dried under vacuum at 100° and weighed. The *p*-nitrobenzoic acid isolated always melted in the range 230–238° (lit.[20] m.p. 242°). There was a trace of an impurity (possibly *p*-nitrophenol) which was yellow in base and colorless in acid but which could not be detected in the infrared spectrum of the *p*-nitrobenzoic acid isolated.

In the column chromatography of the neutral fraction, mineral oil was rapidly eluted with benzene. A 20:1 benzene–ether mixture eluted first *p*-nitrobenzaldehyde and then *p*-nitrobenzyl alcohol. In a typical experiment, one in which the yield of *p*-nitrobenzoic acid was 24%, the following results were obtained: fractions 4–6, 124 mg. of *p*-nitrobenzaldehyde, m.p. 102–105° (52% recovery); fractions 7 and 8, 15 mg., m.p. 70–103°; and fractions 9–11, 46 mg. of *p*-nitrobenzyl alcohol, m.p. 90–93° (19% yield).

A control reaction in which an equivalent weight of sodium hydroxide pellets was substituted for sodium hydride gave a 2% yield of *p*-nitrobenzoic acid after a 1-hr. reaction time.

Attempts were made to standardize the stirring rate in each experiment, although this apparently was not critical; reactions in which stirring was omitted altogether gave comparable results.

Analysis of Reaction Mixtures.—Working curves were prepared from the absorbance at several concentrations for the carbonyl band at 5.84 μ of *p*-nitrobenzaldehyde and for the unbonded hydroxyl band at 2.82 μ of *p*-nitrobenzyl alcohol. The indicated error is $\pm 5\%$.

Reaction of Sodium Hydride with *p*-Nitrobenzyl Alcohol.—The same procedure was used as given above for *p*-nitrobenzaldehyde. Combination of the reactants caused an immediate blue color which quickly faded as stirring was begun. At the end of 1 hr. the yield of *p*-nitrobenzoic acid was 81%.

Preparation of *p*-Nitrobenzaldehyde-α-*d*.—This compound was synthesized by the method of Brown and Subba Rao[21] from *p*-nitrobenzoyl chloride and lithium tri-*t*-butoxyaluminodeuteride (prepared from *t*-butyl alcohol and lithium aluminum deuteride). The yellow reaction mixture was chromatographed through a Florisil column (benzene elution) to give a 57% yield of material, m.p. 99–107°. Recrystallization from ligroin (b.p. 60–90°) raised the melting point to 107°. The absence of any carbonyl proton signal at τ −0.13 showed the aldehyde to be better than 97% deuterated. The C–H stretching and bending frequencies had been replaced by C–D bonds at 2121 (m), 2067 (w), and

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[16] C. R. Dick and R. F. Hanna, *J. Org. Chem.*, **29**, 1218 (1964); see also C. Walling and E. A. McElhill, *J. Am. Chem. Soc.*, **73**, 2927 (1951).

[17] H. O. House and V. Kramar, *J. Org. Chem.*, **27**, 4146 (1962). The reaction time is not specified in this paper, but by implication it is much longer than the 18 hr. reported for successful reaction of potassium with triphenylmethane.

[18] Although no quantitative data are available, such information is known for a similar system: the solubility of lithium hydride in ether at room temperature could not be detected down to 50 parts per billion.[19]

[19] D. A. Brandreth and M. C. Molstad, *J. Chem. Eng. Data*, **7**, 494 (1962).

[20] "Handbook of Chemistry and Physics," C. D. Hodgman, Ed., 38th Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1956.

[21] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **80**, 5377 (1958).

894 cm.$^{-1}$ (m) (Beckman IR-7); the C=O stretching frequency had been shifted from 5.84 to 5.92 μ. Otherwise the infrared spectra of the protium and deuterium aldehydes were identical. The absence of any absorption around 2.8 μ indicated that less than 2% of the corresponding alcohol could be present. The absence of any absorption around 7.9 μ indicated that less than 1% of the corresponding Tischenko ester could be present. A 17% yield of *p*-nitrobenzyl alcohol-α-d_2, m.p. 91–92°, was obtained from the last chromatography fractions (elution with 10:1 benzene–ether).

Reaction of Sodium Hydride with *p*-Nitrobenzaldehyde-α-*d*.—Two experiments were performed using the same procedure as given above for the protium aldehyde. The reaction time in each case was 30 min. The *p*-nitrobenzyl alcohol, m.p. 91–92°, isolated by column chromatography (10% yield in both cases) possessed an infrared spectrum identical with that of the completely deuterated alcohol described above. The absence of any methylene proton signal around τ 5.17 indicated that the alcohol in each case was better than 95% deuterated. The n.m.r. spectrum of the recovered *p*-nitrobenzaldehyde showed the amount of deuteration was still better than 97%.

Preparation of *p*-Nitrobenzyl *p*-Nitrobenzoate.—This compound was prepared from *p*-nitrobenzoyl chloride and *p*-nitrobenzyl alcohol in pyridine, m.p. 168–170° (lit.[22] m.p. 169–170°).

Reaction of Sodium Hydride with *p*-Nitrobenzyl *p*-Nitrobenzoate. A. Protic Work-Up.—The procedure given above for *p*-nitrobenzaldehyde was used with a reaction time of 50 min. The isolated yields of *p*-nitrobenzoic acid and *p*-nitrobenzyl alcohol were 96 and 90%, respectively.

B. Aprotic Work-Up.—After a 15-min. reaction time the reaction mixture was filtered several times through glass wool plugs until clear. The filtrate was evaporated and the residue was washed several times with petroleum ether to remove mineral oil leaving 169 mg. (69% recovery) of ester, m.p. 168–170°. In a similar experiment with *p*-nitrobenzaldehyde, comparison of the infrared spectrum of the evaporated filtrate with synthetic spectra showed the presence of a 25% yield of *p*-nitrobenzaldehyde and an 8% yield of *p*-nitrobenzyl *p*-nitrobenzoate.

Reaction of Other Nucleophiles with *p*-Nitrobenzaldehyde.—Sodium peroxide was taken directly from a previously unopened container. Reagent grade sodium hydroxide pellets were finely ground and dried at 130° for 1 hr. The same procedure as described for *p*-nitrobenzaldehyde was used. The yields of *p*-nitrobenzoic acid obtained after a 1-hr. reaction time were 37% for sodium peroxide and 64% for sodium hydroxide.

Reactions in an Evacuated System.—Sodium hydride and *p*-nitrobenzaldehyde (or *p*-nitrobenzyl alcohol) were placed in the receiver of a small distillation apparatus. Tetrahydrofuran and sodium hydride were placed in the distilling flask which was immersed in a Dry Ice–acetone bath. The system was evacuated at 0.1 mm. for 1 hr. At the end of this time the Dry Ice–acetone bath was switched to the receiver resulting in a rapid condensation of tetrahydrofuran there. After approximately 20 min. the stopcock to the vacuum pump was closed and the cooling bath was replaced with a magnetic stirrer. Within 5 min. (for both *p*-nitrobenzaldehyde and *p*-nitrobenzyl alcohol) a blue color appeared which gradually intensified. After another 20 min., the reaction was quenched by either admitting air and pouring onto ice or by injecting water with a hypodermic syringe through a rubber septum. The admission of air resulted in a gradual change of color to either a green or a dirty brown; both instantly changed to a pale yellow on ice. The injection of water resulted in a vigorous reaction and an instantaneous color change to yellow. The product yields were quite variable: the yield of *p*-nitrobenzoic acid ranged from 3 to 31%.

Experiments in which heavy water was injected into the blue solution led to no deuterium incorporation in either *p*-nitrobenzaldehyde or *p*-nitrobenzyl alcohol. The infrared spectra of the reaction mixtures showed no bands in the 4.7–5.0-μ region at concentrations which would have allowed 2% of either deuterated aldehyde or alcohol to be detected. An experiment in which *p*-nitrobenzaldehyde-α-*d* which had been combined with sodium hydride in an evacuated system and injected with ordinary water showed no loss of deuterium in the recovered aldehyde by either infrared (examination of the 2121-, 2067-, and 894-cm.$^{-1}$ bands with a Beckman IR-7; precision ±3%) or n.m.r. (examination of the τ -0.13 region; sensitivity 3%) spectroscopy.

Experiments with *p*-nitrobenzophenone resulted in only a slight yellow color after several hours. Substitution of sodium for sodium hydride resulted in a dark blue-green color within 10 min.

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[22] M. Davis, *J. Chem. Soc.*, 3981 (1956).

The Competition of Trimethylhalosilanes and Styrene for Organolithium Reagents[1]

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The addition of an organolithium reagent, RLi, to a mixture of trimethylhalosilane and styrene in tetrahydrofuran gives the organotrimethylsilane, RSiMe$_3$ (I), and a silane, Me$_3$SiCHPhCH$_2$R (II), in which one styrene unit has been inserted between the silicon and organo group. The ratios of I–II with trimethylchlorosilane and alkyllithium reagents (3, 3, 0, and 0 with R $\equiv$ *n*-butyl, isobutyl, *sec*-butyl, and *t*-butyl, respectively) and the complete absence of structures containing more than one styrene unit show that (a) primary alkyllithium reagents react at comparable rates with the chlorosilane and styrene; (b) secondary and tertiary alkyllithium reagents react exclusively with styrene; and (c) all intermediate benzylic organolithium reagents, formed *via* the addition of the alkyllithium to styrene, react exclusively with the chlorosilanes. These data and previous estimates of the relative rates of initiation and propagation in the *n*-butyllithium-catalyzed polymerization of styrene show that the intermediate benzylic organolithium reagents are at least 250 times as reactive as *n*-butyllithium toward trimethylchlorosilane in tetrahydrofuran. Phenyl- and vinyllithium gave only I. The preparation of 2,2-dimethyl-4-phenylpentane by substitution of dimethyl sulfate for chlorosilane in this competitive scheme (R $\equiv$ *t*-butyl) provides an alternative method of trapping the intermediate benzylic organolithium reagent. The lithium reagent from the addition of *t*-butyllithium to α-methylstyrene reacts with trimethylchlorosilane to yield *p*-silyl rather than α-silyl derivatives.

Among the facile reactions of organolithium reagents are the coupling with chlorosilanes[2] (see eq. 1) and

$$\mathrm{RLi} + \mathrm{R'_3SiCl} \longrightarrow \mathrm{R'_3SiR} + \mathrm{LiCl} \qquad (1)$$

the addition across the double bond of aryl olefins. This latter reaction is one example of the widely useful anionic polymerization of monoaryl olefins.[3]

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[1] Presented before the Organic Section at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Aug. 1964.

[2] C. Eaborn, "Organosilicon Compounds," Butterworth and Co. (Publishers) Ltd., London, 1960, Chapter 2.

[3] M. Szwarc, *Macromol. Chem.*, **35**, 132 (1960).