Homogeneous Hydrogenation Catalyzed by Boranes

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Received July 9, 1962

The hydrogenation of organic compounds catalyzed by soluble catalysts has been reported rarely. Trialkyl and related boranes have now been shown to be effective homogeneous catalysts for reduction of olefinic linkages. Functional groups containing hetero atoms which inhibit borane-catalyzed isomerization also prevent reduction, hence only such compounds as ethers, alkyl sulfides, and tertiary amines may be present. Acetylenes do not inhibit but are themselves reduced. Benzene rings are normally not reduced. The reduction is effected by addition of B—H across an olefinic linkage, followed by hydrogenolysis of the carbon–boron bond. The reductions require high temperatures (190–225°). A relatively rapid addition–elimination of B—H accompanied by slow hydrogenolysis of the carbon–boron bond is indicated since olefin isomerization or deuterium rearrangement are simultaneous reactions which precede or accompany hydrogenation, and diglyme which catalyzes B—H addition does not accelerate hydrogenation. Increased temperature promotes the reaction, but there is little change in rate with hydrogen pressure. This catalyst system is particularly well suited for the reduction of high polymers in contrast to previously used heterogeneous catalysis which gives slow reactions and generally incomplete reduction. *cis*-1,4-Polybutadiene and *cis*-1,4-polyisoprene were reduced quantitatively (as indicated by infrared analysis) with borane catalysis. The former yields a crystalline polyethylene. The latter yields a tough elastomer equivalent to an alternating ethylene–propylene copolymer. Polypiperylene, free-radically polymerized butadiene, and styrene-butadiene rubber (SBR) have been quantitatively reduced. The reduction may be stopped at any desired conversion by quenching with an excess of a monoölefin.

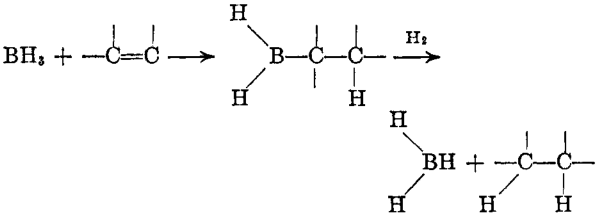
Saturation of the polymers derived from dienes should provide additional structural evidence and permit correlation of the degree of unsaturation with physical and chemical properties. Many such reductions have been carried out by heterogeneous catalysis. The reaction is frequently slow and the reduction incomplete.[1–3] Homogeneously catalyzed reactions of high polymers would be expected to proceed to completion without the impediment of an adsorption–desorption process involving polymeric molecules. This paper reports the discovery and characterization of a homogeneous hydrogenation catalyst for simple olefinic bonds. The reduction of a variety of polymers from diene monomers is also discussed.

Addition of molecular hydrogen to organic molecules with homogeneous catalysis has been reported for only a small fraction of the compounds which may be reduced by heterogeneous catalysis. Reduction of olefinic bonds has been observed frequently in the studies of hydroformylation. However, the utility of this method is limited since conditions have not been found which separate the reduction and hydroformylation reactions.[4]

More recently Halpern[5] and co-workers have reported the reduction of maleic acid catalyzed by a water-soluble ruthenium(III) salt. Walling and Bollyky[6] have reported the reduction of benzophenone and nitrobenzene in *t*-butyl alcohol catalyzed by potassium *t*-butoxide.

The facile addition reaction of boron hydrides to olefins has been developed by Brown[7] and co-workers. This has been shown to be a general reaction for olefinic bonds. The uncatalyzed hydrogenolysis of a number of carbon to metal bonds has been reported.[8,9] In particular, Köster[10,11] has reported the hydrogenolysis of a trialkyl borane to give a dialkyl boron hydride and a saturated hydrocarbon. These observations indicated that boranes might be effective homogeneous catalysts for the hydrogenation of olefins.

$$R_3B + 3H_2 \longrightarrow BH_3 + 3RH$$



$$BH_3 + -\overset{|}{C}=\overset{|}{C} \longrightarrow H_2B-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{H}{C}}- \xrightarrow{H_2} H_2BH + H-\overset{|}{C}-\overset{|}{\underset{H}{C}}-$$

Hydrogenation of Simple Olefins.—The anticipated reduction was observed using cyclohexene. This compound and caprylene were used as model compounds for characterization of the reduction process. In the initial experiment (Table I) cyclohexene (1 mole) containing triisobutylborane (0.04 mole) was charged into the reactor. Triisobutylborane was chosen for convenience in handling, but the reaction scheme indicates that borane or any simple alkyl borane should be effective. The autoclave was purged and pressured to 2500 p.s.i. with hydrogen. The temperature was raised in 50° increments to 225° or until pressure drop was observed. The products were analyzed by

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[2] A. I. Yakubchik and G. N. Gromova, *J. Gen. Chem. USSR*, **26**, 1823 (1956).

[3] A. I. Yakubchik and B. I. Tikhomirov, *ibid.*, **30**, 135 (1960).

[4] For a review and discussion, *cf.* M. Orchin, *Advan. Catalysis*, **5**, 385 (1953).

[5] J. Halpern, J. F. Harrod, and B. R. James, *J. Am. Chem. Soc.*, **83**, 753 (1961).

[6] C. Walling and L. Bollyky, *ibid.*, **83**, 2968 (1961).

[7] H. C. Brown, *Tetrahedron*, **12**, 117 (1961).

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[9] W. Ipatieff, G. Razuwajeff, and I. F. Bogdanow, *Ber.*, **63**, 335, 1110 (1930).

[10] R. Köster, *Angew. Chem.*, **68**, 383 (1956).

[11] R. Köster, B. Gunter, and B. Paul, *Ann.*, **644**, 1 (1961).

Table I

Hydrogenation of Simple Olefins

Olefin	Moles	i-Bu_3B, moles	Temp., °C.	Time, hr.	Initial H_2 press.	% reduction
Cyclohexene	0.5	0.03	235	5	2500	100[a]
Octene-1	1.0	.03	225	3	2000	100[a]
Caprylene[d]	1.0	.03	235	5	2500	100[a]
Caprylene[d]	0.25	.03	235	15	500	[b]
Cyclohexene	1.18	.04	225	11	2000	[c]

[a] By infrared analysis. [b] Gas chromatographic analysis: 10% low boil, 81% n-octane, 6% octene-1, 3.0% octene-2. [c] Final pressure at room temperature = 200 p.s.i.; initial hydrogen present = 1.4 moles; 72% cyclohexane. [d] Mixture of 25% octene-1 and 75% octene-2.

gas chromatography. Table I summarizes the data for cyclohexene and caprylene.

Hydrogenation at an appreciable rate was not observed below 200°. As indicated, temperatures between 225 and 240° gave complete reduction in a few hours. The absolute hydrogen pressure necessary for reduction is quite low as indicated by the drop to 200 p.s.i.g. when a 1.4/1.2 hydrogen to olefin ratio was used. The rate of hydrogenation was not as sensitive to hydrogen pressure as it was to temperature over the range studied.

The hydrogenation of simple olefins in the presence of other compounds is summarized in Table II.

Table II

The Hydrogenation of Simple Olefins in the Presence of Other Compounds

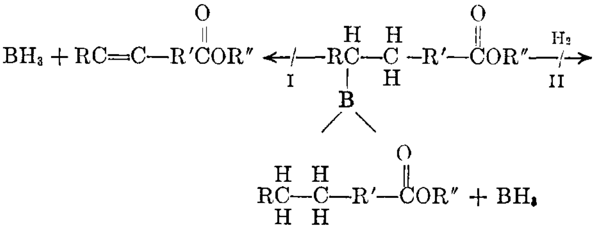
Olefin (0.5 mole)[a]	Compound	Moles	Temp., °C.	Time, hr.	% reduction[b]
CAP[c]	Diglyme	0.075	238	5	~100
CAP	NEt_3	.075	235	5	~100
CAP	$HNEt_2$	.04	125–225	8[d]	None
CAP	$TiCl_4$	.03	125–225	8[d]	[e]
CYC[c]	BF_3·EtOEt	.03	125–225	8[d]	[f]
CYC	n-BuCl	.05	240	5	43
CYC	MeSMe	.05	240	5	60
CYC	Furan	.05	240	5	86
CYC	Pyridine	.05	240	5	43
CYC	Cyclohexanone	.05	240	5	1.3
CYC	2,4-Dimethyl sulfolane	.05	240	5	37
CYC	Thiophene	.05	240	5	99
CYC	CCl_4	.05	240	5	None
CYC	EtOAc	.05	240	5	None
CYC	Hexyne-1	.05	240	5	~100
CYC	Acetal	.05	240	5	~30

[a] Initial hydrogen pressure of 2500 p.s.i. and 0.03 mole i-Bu_3B used in all experiments. [b] Calculated from gas chromatographic data. [c] CAP = caprylene; CYC = cyclohexene. [d] Temperature increased from 125 to 225° in 25° increments over a period of 8 hours. [e] No reduction using 0.03 mole of the following also: $SnCl_4$, $SbCl_3$, $BiCl_3$, $AlCl_3$, $VOCl_2$, PCl_3, and $CuCl_2$. [f] No reduction. Polymerization to tetramer.

Lewis acids showed a strong inhibitory effect on the reduction. Lewis bases, diglyme in particular, which catalyzes the addition of B—H to olefinic linkages did not lower the temperature required for reduction. These data indicate that the rate-determining step must be associated with hydrogenolysis of the carbon–boron bond. Additional evidence for a relatively rapid addition–elimination of B—H to the olefin followed by slow hydrogenolysis is discussed in connection with the hydrogenation of polymers.

The inclusion of compounds with various functional groups in cyclohexene reduction served to demonstrate any inhibition or catalysis of cyclohexene reduction as well as indicate the reducibility of the added compound. Diglyme and benzene were essentially inert diluents in the olefin reduction. Hexyne was reduced with no adverse influence on the olefin reduction. No attempt was made to determine the relative rates of acetylenic and olefinic reductions. Some inhibition of the olefin reduction was noted in the presence of butyl chloride, dimethyl sulfide, furan, and pyridine. Less olefin reduction was observed in the presence of diethyl acetal and 2,4-dimethyl sulfolane. Complete inhibition was found with ethyl acetate, cyclohexanone, and carbon tetrachloride.

Esters, ketones, and alcohols have been reported to inhibit borane-catalyzed olefin isomerization but do not inhibit borane formation. For example, ethyl oleate gives a borane by reaction with BH_3 but no isomerization.[12,13] These reagents which inhibit isomerization also inhibit hydrogenation. This suggests a parallel between reaction I, required for isomerization, *i.e.*, the cleavage of a carbon–boron bond by reaction with the neighboring carbon–hydrogen bond, and reaction II, the cleavage of a carbon–boron bond by reaction with hydrogen.



A small amount of white solid could be isolated from the hydrogenated products, and qualitative tests on this solid indicated the presence of boron. Volatile boranes polymerize at elevated tempera-

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[12] S. P. Fore and W. G. Bickford, *J. Org. Chem.*, **24**, 920 (1959).

[13] T. J. Logan, *ibid.*, **26**, 3657 (1961).

TABLE III

THE BORANE-CATALYZED HYDROGENATION OF *cis*-1,4-POLYISOPRENE[a]

Moles olefin	Solvent	Concn., %	*i*-Bu_3B, moles	Cyclohexene, moles	Temp., °C.	Time, hr.	Notes	Product
0.62	Benzene	5	0.066	2.5	190	48	Reaction complete after 24 hours	Completely saturated tough rubbery product
.14	HPT[b]	5	.03	0.5[c]	230	5	Infrared shows complete reduction	Tough rubbery product
.53	Benzene	5	.09	1.5	240	10	Infrared shows complete reduction	Liquid polymer
.14	HPT[b]	5	.03	0.5[d]	230	5	Infrared shows complete reduction	Semisolid polymer
1.4	HPT[b]	7	.12	5.6[e]	240	5	Infrared shows moderate *trans* band at 10.3 μ	Tough rubbery product
1.4	HPT[b]	8.9	.12	[f]	240	5	Infrared shows moderate *trans* band at 10.3 and small $CH_2{=}C<$ band at 11.25 μ	Tough rubbery product

[a] Initial hydrogen pressure for all experiments was 2500 p.s.i. [b] HPT = hydrogenated propylene trimer. [c] Diglyme, 25 ml. also present. [d] Triethylamine, 42 ml. also present. [e] Diglyme, 100 ml. also present. [f] Propylene trimer, 6.9 mole and diglyme, 100 ml. present.

TABLE IV

HYDROGENATION OF OTHER OLEFINIC POLYMERS[a]

Polymer	Moles C=C	Concn. in benzene, %	*i*-Bu_3B, moles	Temp., °C.	Time, hr.	
1,2-Polybutadiene	0.204	9.0[b]	0.01	225	18	Product is a viscous liquid
1,4-Polybutadiene[f]	.167	3.0	.006	225	14	A severely degraded liquid product
SBR (MW 250,000)[h]	1.37	5.6	.028	225	5	Product is a semisolid (mol. wt. 94,000 = 20%).
cis-1,4-Polybutadiene	0.093	5[c]	.004	225	4	Product is a crystalline solid
Neoprene 834	.057	5	.007	225	19	No H_2 uptake. Liquid product HCl evolved
Polypiperylene[g]	.16	[d]	.03	240	5	Liquid product with an infrared spectrum identical to that of reduced *cis*-1,4-polyisoprene
cis-1,4-Polyisoprene-3[d]	.04	[e]	.03	235	5	Semisolid product. Infrared spectrum showed extensive deuterium exchange

[a] Infrared spectra showed that all products, except neoprene, contained completely saturated aliphatic double bonds. Initial hydrogen pressure 2000 p.s.i. [b] Cyclohexane, 110 g. also added. [c] Cyclohexane, 100 ml. also added. [d] A 6.0% solution in cyclohexane. Diglyme, 20 ml. also added. [e] A 2.4% solution in cyclohexene. Diglyme, 5 ml. also added. [f] Emulsion polymerized. [g] Poly-1,3-pentadiene prepared by Ziegler catalysis. [h] Styrene–butadiene rubber.

tures to form boron hydrides of higher molecular weight.[14] The white solid isolated is probably a mixture of higher boron hydrides. Thermal cracking of these higher boron hydrides has been reported.[15,16] These considerations imply that any boron hydride, alkyl-substituted boron hydride, or trialkyl borane may function as a hydrogenation catalyst.

Hydrogenation of Unsaturated Polymers.—Borane-catalyzed hydrogenation was applied to *cis*-1,4-polybutadiene in benzene solution. Benzene had been shown to be inert under reduction conditions. Tables III and IV indicate the complete reduction of *cis*-1,4-polybutadiene and several other hydrocarbon polymers. A general molecular weight drop is indicated in the reductions as the temperature is increased above 200°. Pyrolytic decomposition of this class of polymers has been reported in this temperature range.[17] The extent of thermal degradation is a function not only of the reduction temperature but also of the original polymer. Free radical polymers (Table IV) generally gave more severe breakdown than those prepared by Ziegler catalysis.

cis-1,4-Polybutadiene (infrared spectrum[18]) yielded a crystalline polymer with an infrared spectrum and melt characteristics of a high density, moderate molecular weight polyethylene. The broad *cis* olefin peak at 13.55 μ and the small *trans* and vinyl in the 10–11-μ region have completely disappeared. The deep sharp doublet at 13.70 and 13.92 μ are characteristic of crystalline

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(14) D. T. Hurd, "Chemistry of Hydrides," John Wiley & Sons, Inc., New York, N. Y., 1952, p. 78.

(15) H. I. Schlesinger and A. B. Burg, *Chem. Rev.*, **31**, 1 (1942), and J. K. Bragg, L. V. McCarty, and F. J. Norton, *J. Am. Chem. Soc.*, **73**, 2134 (1951).

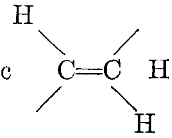
(16) R. Klein, A. Bliss, L. Schoen, and A. G. Nadeau, *ibid.*, **83**, 4131 (1961).

(17) "Latex and Rubber Derivatives and Their Industrial Applications," F. Marchionna, Vol. III, The Rubber Age, New York, N. Y., 1937, p. 1118.

(18) G. Natta, *Rubber Plastics Age*, **38**, No. 6 (1947).

polyethylene. The small peak at 7.3 μ attests to a small amount of methyl groups.

Under similar conditions, *cis*-1,4-polyisoprene (Ameripol SN[19]) gave a tough rubbery polymer very similar in infrared analysis to a random copolymer of ethylene and propylene prepared by Ziegler catalysis.[20] Again the olefinic peaks at 11.95 and 6.05 μ have disappeared and the —CH_2— sequence peak at 13.6 μ is present. In addition, polypiperylene (infrared spectrum[21]) was hydrogenated to give an infrared spectrum quite similar to the hydrogenated polyisoprene. This spectrum was good evidence that the original polypiperylene which had been obtained by Ziegler catalysis had polymerized in a 1,4 manner.

Partial reduction of *cis*-1,4-polybutadiene was also achieved by conducting the reaction in the presence of a simple olefin or by an olefin quench. Reactions terminated by limited hydrogen or by temperature drop resulted in gels which could be solubilized by heating with propionic acid. Borane formation by reaction of boron hydride with residual unsaturation in two chains would give the observed cross-linking. This requires that addition of B—H to the olefin even in the absence of diglyme is more rapid than the hydrogenolysis; otherwise the cross-links would be cleaved by hydrogen. Examination of the infrared spectrum of the partially reduced *cis*-1,4-polyisoprene provided additional evidence of a rapid addition–elimination process involving B—H and the olefinic linkage; the broad *cis* unsaturation band at 13.9 μ was completely eliminated and a rather intense *trans* unsaturation characteristic  $HC{=}CH$ had developed at 10.3 μ in addition to the —CH_2— sequence sharp peak at 13.6 μ.

Cyclic boranes could be formed by interaction of BH_3 with two double bonds in a single chain. Available data do not indicate whether this type of reaction makes a significant contribution to the over-all process.

The borane-catalyzed hydrogenation of *cis*-1,4-polyisoprene-3-*d* (infrared spectrum[22]) was undertaken since the infrared spectrum of the product should be useful in the interpretation of the infrared spectrum of ethylene–propylene copolymers prepared by Ziegler catalysis. The spectrum of the product obtained by reduction at 240° indicated extensive deuterium elimination. The sharp 3-*d* peak at 4.5 μ in the starting material had shifted as expected to 4.65 μ in the saturated product, but it was greatly reduced in intensity. Addition–elimination reactions[23,24] proceeding at a more rapid rate than hydrogenolysis readily account for the observed results.

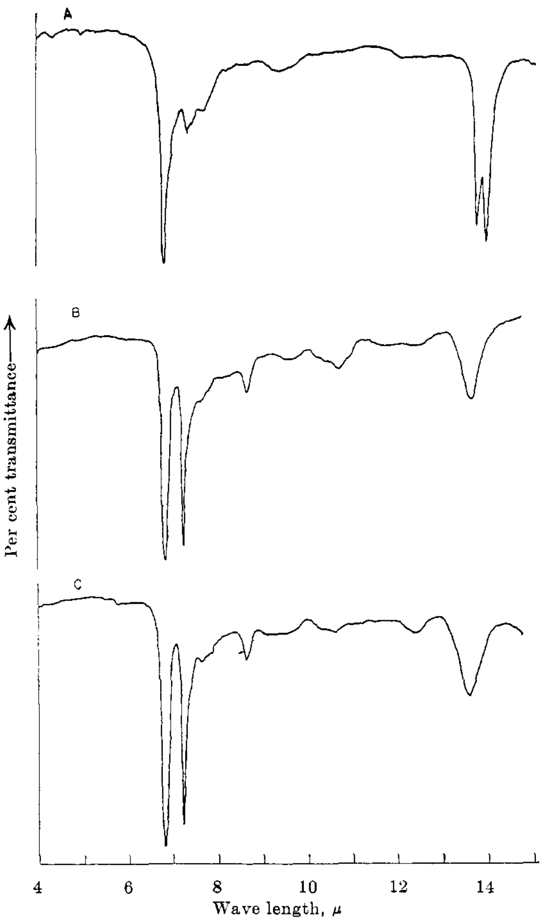


Figure 1

As previously noted, hydroboration of olefins is catalyzed by diglyme. However, diglyme does not increase the over-all rate of hydrogenation; this implies that the boron hydride addition step is not rate-determining. This leads to the postulate that the hydrogenolysis of the carbon to boron bond is the rate-determining step. Olefin isomerization, deuterium elimination, and gel formations cleaved by propionic acid[25] are all in accord with this postulate. A co-catalyst to promote reduction at a lower temperature was sought but none found; however, pyrolytic chain cleavage can be minimized at the minimum temperature giving an appreciable reaction rate (200°).

Experimental

Materials.—The triisobutylborane, caprylene, and cyclohexene used in this work were commercial materials used without additional purification.

Polybutadiene and SBR were prepared by standard emul-

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[19] S. E. Horne, Jr., J. P. Kiehl, J. J. Shipman, V. L. Folt, and C. F. Gibbs, *Ind. Eng. Chem.*, **48**, 784 (1956).

[20] Von Therese Gössl, *Makromol. Chem.*, **42**, 1 (1960).

[21] John Binder, *J. Polymer Sci.*, in press (1962).

[22] J. J. Shipman and M. A. Golub, *J. Appl. Polymer Sci.*, **5** (16) (1962).

[23] H. C. Brown, *Tetrahedron*, **12**, 117 (1961).

[24] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6434 (1959).

[25] H. C. Brown and K. Murray, *ibid.*, **81**, 4108 (1959).

sion free radical polymerization recipes. *cis*-1,4-Polyisoprene, *cis*-1,4-polybutadiene, and piperylene were prepared by Ziegler catalysts.

Hydrogenation of Simple Olefins (Table I).—Into a 100-ml. steel autoclave was placed 0.5 mole of the olefin to be reduced (cyclohexene, caprylene, or octene-1) together with 7.5 ml. (0.03 mole) of the triisobutylborane. The autoclave was purged with nitrogen, charged to 2500 p.s.i. with hydrogen, and heated at 235° for 5 hr. Under these conditions, quantitative reduction was realized as shown by infrared spectroscopy and gas phase chromatography. Extensive hydrogenation of simple olefins has also been observed at lower temperatures (180–190°) but the reaction may usually be driven rapidly to completion at the higher temperature.

Hydrogenation of *cis*-1,4-Polyisoprene (Table III).—Into a 4500-ml. steel autoclave was placed a 5% benzene solution of *cis*-1,4-polyisoprene (42 g. of polymer), 16.5 ml. (0.067 mole) of triisobutyl borane, and 205 g. (2.5 moles) of cyclohexene. The autoclave was purged with nitrogen, charged to 2500 p.s.i. with hydrogen at room temperature, and heated at 190° for 48 hr. There was no further decrease in hydrogen pressure after 24 hr. and a total pressure drop of 500 p.s.i. was observed. The polymer was precipitated from the reaction mixture by addition of methanol and dried in a vacuum oven at 45° for 7 hr. An infrared spectrum of the tough rubbery product closely resembled that of a random copolymer of ethylene and propylene (B).

Hydrogenation of Other Olefinic Polymers (Table IV).—Exploratory experiments were carried out as indicated below. Into a 2960-ml. steel autoclave was placed a 5.6% benzene solution of styrene–butadiene rubber (100 g. of polymer) and 7.0 ml. (0.028 mole) of triisobutylborane. The autoclave was purged with nitrogen, charged to 2000 p.s.i. with hydrogen at room temperature, and heated at 225° for 5 hr. The polymer was precipitated from the cooled reaction mixture by addition of methanol and dried in a vacuum oven. The product was a semisolid whose infrared spectrum showed that the aliphatic double bonds had been completely saturated.

1,2-Polybutadiene.—The product was a liquid whose infrared spectrum was essentially identical to that of polybutene.

1,4-Polybutadiene.—Complete reduction gave a severely degraded liquid polymer.

***cis*-1,4-Polybutadiene.**—The product was insoluble in benzene and was recrystallized from hot xylene. The infrared spectrum and melt characteristics were those of a high density polyethylene of moderate molecular weight (A).

Polypiperylene.—A liquid product resulted. The infrared spectrum closely resembled that of completely hydrogenated *cis*-1,4-polyisoprene (C).

***cis*-Polyisoprene-3*d*.**—A completely saturated *cis*-1,4-polyisoprene whose infrared spectrum showed that extensive deuterium exchange had occurred.

A Facile Conversion of Aldehydes to Nitriles

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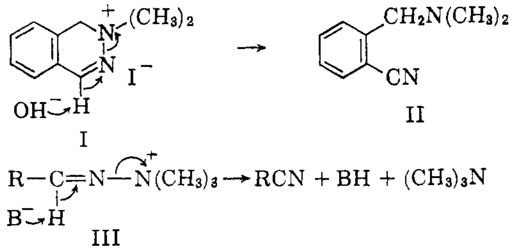
Received July 13, 1962

Aldehydes were conveniently converted to the corresponding N,N,N-trimethylhydrazonium salts [$RCH{=}NN(CH_3)_3{}^+X^-$]. These salts underwent a beta elimination reaction when treated with methanolic sodium methoxide to give high yields of the corresponding nitriles.

The recent observation[1] in these laboratories that 2,2-dimethyl-1,2-dihydrophthalazinium iodide (I) is transformed to α-N,N-dimethylamino-*o*-toluonitrile (II) on treatment with aqueous sodium hydroxide suggested that N,N,N-trimethylhydrazonium salts derived from aldehydes (III) might also undergo an analogous beta elimination reaction to give the corresponding nitriles.[2]



$$R{-}\underset{\underset{B^-\ H}{|}}{C}{=}N{-}\overset{+}{N}(CH_3)_3 \rightarrow RCN + BH + (CH_3)_3N$$

It was found that quaternary salts of type III (Table I) could be simply prepared by the reaction of either methyl iodide or methyl *p*-toluenesulfonate with solutions of the N,N-dimethylhydrazones[3] which were obtained by refluxing the aldehyde and N,N-dimethylhydrazine in either benzene or alcohol.

The crude quaternary salts were smoothly converted to the corresponding nitriles by methanolic sodium methoxide. Fifteen different nitriles were synthesized by this method (Table II). Benzonitrile and *p*-methoxybenzonitrile were obtained in excellent yields by employing methanolic potassium hydroxide as the basic medium in the elimination reaction, but this method gave only poor yields of *p*-nitrobenzonitrile. However, the use of methanolic sodium methoxide afforded *p*-nitrobenzonitrile in 92% yield.

The nitrile synthesis described in this paper resembles the base-catalyzed conversion of aromatic chloroimines ($ArCH{=}NCl$) to nitriles reported by Hauser and Gillaspie[4] with our beta elimination differing only in the nature of the leaving group.

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(1) R. F. Smith and E. D. Otremba, *J. Org. Chem.*, **27**, 879 (1962).

(2) For other recently reported methods of converting aldehydes to nitriles and leading references on older methods see: (a) H. M. Blatter, H. Lukaszewski, and G. de Stevens, *J. Am. Chem. Soc.*, **83**, 2203 (1961); (b) J. H. Hunt, *Chem. Ind.* (London), 1873 (1961); (c) J. H. Pomeroy and C. A. Craig, *J. Am. Chem. Soc.*, **81**, 6340 (1959).

(3) (a) D. Todd, *ibid.*, **71**, 1353 (1949); (b) R. H. Wiley, S. C. Slaymaker, and H. Kraus, *J. Org. Chem.*, **22**, 204 (1957).

(4) C. R. Hauser and A. G. Gillaspie, *J. Am. Chem. Soc.*, **52**, 4517 (1930).