which were available could be titrated with the Fischer reagent. Samples of triphenyltin hydroxide and triphenyllead hydroxide, on titration, gave 1.01 and 1.02 moles of apparent water found per mole hydroxide, respectively. Both compounds decolorized additional reagent on standing several hours. A sample of phenylboric acid, $C_6H_5B(OH)_2$, which had been freshly crystallized from water gave on titration 1.96 moles apparent water per mole of acid. On standing in the air or drying at 70° for several hours, the oxide $(C_6H_5BO)_3$, was formed which analyzed 0.99 mole apparent water per mole of oxide. Although organic hydroxy derivatives of germanium and arsenic have not yet been tested, it is probable that they, as well as the more basic organometallic hydroxides, can be determined by this method.

Other compounds tested which do not react with the Fischer reagent at all or do not react rapidly enough to be titrated are hexamethyldisiloxane, hexaphenyldisiloxane, ethyltriethoxysilane, tris-(*p*-chlorophenyl)-ethoxysilane, triphenylchlorosilane and tris-(*p*-dimethylaminophenyl)-silane.

Experimental

Five milliliters of pyridine or methanol was pipetted into a dry 50-ml. glass-stoppered volumetric flask and this solvent was titrated to the iodine end-point with Fischer reagent from a 10-ml. automatic buret. The weighed sample of silanol was then added quickly. (Liquid samples were weighed in a platinum boat). After washing down the neck with a little Fischer reagent, the flask was stoppered and shaken a few seconds to complete solution. This solution was then titrated to the same iodine end-point as that obtained with the solvent. The apparent millimoles of water found was calculated from the amount of Fischer reagent consumed by the silanol.

Tri-*p*-xenylmethoxysilane.—The solution remaining after the titration of tri-*p*-xenylsilanol (m.p. 200–201°) was diluted with water and filtered. The residue, 0.19 g. (91%), after washing with water and drying 1 hour at 120°, melted at 157–158°. This material would not react with the Fischer reagent. A portion of this residue was warmed with a solution of potassium hydroxide in ethanol–dioxane for 5 minutes, diluted with water, and filtered. The residue from this latter filtration melted at 200–202° and its mixed melting point with tri-*p*-xenylsilanol showed no depression. A sample of tri-*p*-xenylmethoxysilane was prepared by refluxing 0.23 g. of tri-*p*-xenylsilanol with 2.0 g. of anhydrous zinc chloride in 10 ml. of methanol for 40 hours.[6] The product was filtered and the residue was washed with methanol and acetone to leave 0.1 g. (42%) of white needles, m.p. 158°. A mixed melting point with the above compound isolated from the Fischer titration showed no depression.

Anal. Calcd. for $C_{37}H_{30}OSi$: Si, 5.42. Found: Si, 5.49.

Triphenyllead Hydroxide, Triphenyltin Hydroxide and Phenylboric Acid.—The samples of triphenyltin hydroxide, m.p. 122–124°, triphenyllead hydroxide and phenylboric oxide, m.p. 219°, had been prepared in these laboratories by C. E. Arntzen, R. K. Abbott and B. A. Hunter, respectively. A sample of the phenylboric oxide was recrystallized from water and the product was dried overnight at 70°. Titration of 0.120 g. (0.00115 mole) of the dried material required 18.94 ml. of Fischer reagent equivalent to 0.001144 mole of water or 99 mole per cent. calculated as $(C_6H_5BO)_3$. Another sample of the oxide was crystallized from water and dried 30 minutes at room temperature and 20 mm. pressure. Titration of 0.00755 mole of this product took 24.60 ml. of Fischer reagent, equivalent to 0.00148 mole or 98 mole per cent. calculated as phenylboric acid, $C_6H_5B(OH)_2$.

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[6] See reference (4b) for a related procedure for like compounds.

Isotopic Exchange between D_2O and $NaBH_4$

BY PETER R. GIRARDOT AND ROBERT W. PARRY

The observation that $NaBH_4$ is appreciably soluble in cold water has been previously recorded.[1] If it were dissolved in D_2O, any isotopic exchange between D and H would be apparent on subsequent evaporation of the solution and hydrolysis of the $NaBH_4$.

We have recently observed the mass spectrum of the hydrogen evolved on hydrolysis after such a procedure, with the results shown below. Approximately 1.5 molal solutions of $NaBH_4$ were prepared in evacuated systems using 99.8% D_2O as the solvent. Hydrolysis of the $NaBH_4$ was reduced to a negligible amount by saturating the solution with $Ca(OD)_2$ (*p*H about 12). After standing 17.5 hours at 20–25°, the D_2O was distilled off, dry oxalic acid was added to the alkaline $NaBH_{4-x}D_x$ residue, the system was re-evacuated and hydrolysis effected by adding distilled water to the acid mixture. The reaction is

$$\mathrm{Na(BH_{4-x}D_x)} + 2\mathrm{H_2O} \xrightarrow{\mathrm{H^+}} \mathrm{NaBO_2} + x\mathrm{HD} + (4 - x)\mathrm{H_2}$$

The resulting H_2, HD mixture was analyzed in a Consolidated Isotope Ratio Mass Spectrometer. The upper limits for the HD:H_2 ratio are found in Table I.

TABLE I

Sample	Ratio HD:H_2 × 10^4
Blank using H_2O only	2.2
No. 1	7.4
No. 2	5.0
No. 3	8.0

Although the exact constant of the instrument converting these values to absolute ratios has not yet been determined, it is known that the constant will lie somewhere between 0.6 and 1.0; thus these values may be set as upper limits to the amount of exchange.

Natural abundance gives a D:H ratio reported variously as 1.45×10^{-4}(2) and 1.61×10^{-4}.(3) It is then apparent that the values found in this experiment do not indicate formation of significant amounts of HD, and we conclude that the hydrogen of sodium borohydride does not exchange with hydrogen of water.

(1) Albert E. Finholt, Ph.D. Dissertation, The University of Chicago, June, 1946.

(2) J. A. Swarthout and M. Dole, THIS JOURNAL **61**, 2025 (1939).

(3) A. J. Edwards, R. P. Bell and J. H. Wolfenden, *Nature*, **135**, 793 (1935).

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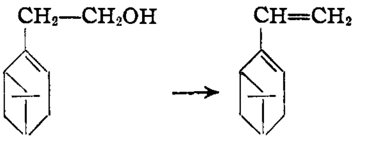
Nopadiene

BY LELAND J. KITCHEN

The conjugated diene 2-vinyl-6,6-dimethylbicyclo[3.1.1]-2-heptene was prepared by dehydration of nopol. Because of its derivation from nopinene and nopol, the diene is designated nopadiene.

Nopadiene acted as a retarder in copolymerization experiments. Retardation probably is due



to the allylic methylene group.[1] The allylic methinyl hydrogen atom in nopadiene would not be expected to retard because it occurs on a bridgehead carbon atom.[2]

Nopadiene derived from the *l*-nopinene of gum turpentine is optically active and presumably is pure levo isomer.

In the color test for conjugated unsaturation with *p*-nitrobenzenediazonium chloride reagent,[3] nopadiene gave a strong positive test. Several other dienes and terpenes were tested for comparison. Most of the dienes gave positive tests. Terpenes having a tendency to isomerize to monocyclics containing conjugated systems under acid conditions, such as the pinenes, gave delayed positive tests.

Experimental

Nopol was obtained from the Glidden Company, Jacksonville, Florida, and was prepared from commercial β-pinene (nopinene) from the same source, by the autoclave method.[4] The nopol had the properties, b.p. 135–136°, n^{25}_D 1.4918 (lit. 1.4920), and α^{23}_D −35.7° (10-cm. tube) (lit., α^{25}_D −35.5°).

A mixture of 77 g. (0.46 mole) of nopol, 20 g. (0.36 mole) of potassium hydroxide, 0.5 g. of phenyl-β-naphthylamine, and 150 g. of diethyleneglycol diethyl ether was refluxed under a fractionating column containing Raschig rings. During three hours 210 g. of distillate boiling in the range 98–185° was collected. After the distillate was washed thoroughly with water there remained 52 g. (75% yield) of nopadiene, n^{24}_D 1.5044.

In a similar experiment with tetraethyleneglycol dimethyl ether as diluent the reflux was carried out under vacuum. The yield of nopadiene was 50%.

When 166 g. (one mole) of nopol was dehydrated with 5.6 g. of potassium hydroxide with no diluent present, the distillate contained 16 g. of water and 15 g. (10% yield) of crude nopadiene. The material in the still-pot was separated from catalyst and distilled, giving 31 g. of distillate boiling up to 183° (3 mm.); the undistilled portion was a solid resin when cool.

A sample of nopadiene purified by distillation through a column (glass helices; 28 theor. plates) had the following properties: b.p. 179° (738 mm.); b.p. 85.5–86.5° (30 mm.); d^{25}_4 0.8842; n^{25}_D 1.5044; α^{23}_D −30.16° (10 cm. tube).

Molecular refraction: Calcd. for $C_{11}H_{16}$: 47.66 (D). Found: 49.69 (D). Exaltation: +2.03. An exaltation of +0.48 has been assigned to the cyclobutane ring of the pinene ring system.[5] The remaining exaltation, +1.55, is due to conjugation, comparing with an exaltation of +1.67 due to conjugation in 2,4-hexadiene.[6]

Anal. Calcd. for $C_{11}H_{16}$: C, 89.12; H, 10.89. Found: C, 88.61; H, 11.01.

Test for Conjugated Unsaturation.—The materials which were tested were purified by distillation. Tests were carried out in acetic acid–dioxane solution with *p*-nitrobenzenediazonium chloride in acetic acid, according to the directions of Fieser and Campbell.[7] A positive test was formation of an orange or red color which was more pronounced after five minutes than immediately after addition of the reagent.

Nopadiene and alloöcimene gave immediate red colorations, and 2-methylpentadiene, 2,3-dimethylbutadiene and myrcene, orange colorations, which were darker in color in 15 minutes. Isoprene, piperylene, naphthalene, nopol, terpinolene and dipentene gave weak tests, the colorations being unchanged light yellow at first and amber or orange within five minutes. The tests on α-pinene and nopinene showed no color change in five minutes, but had turned from light yellow to orange within 15 minutes. Chloroprene gave a negative test, remaining light yellow after 15 minutes.

Polymerization Tests.—A test-tube containing a few ml. of nopadiene and a granule of benzoyl peroxide was placed under a General Electric RS sunlamp. After 40 hours it was a sticky yellow polymer. Nopadiene without benzoyl peroxide, similarly exposed, was yellow in color and still fluid.

Sealed tubes each containing 7 g. of nopadiene and a few granules of benzoyl peroxide under carbon dioxide were oven-aged at 85°. After 160 hours contents of a tube containing nopadiene was still liquid, as was the contents of a tube containing equal amounts of methyl methacrylate and nopadiene. A third tube containing methyl methacrylate and benzoyl peroxide without nopadiene contained solid polymer within 15 hours.

Bottles were charged with water 100, sodium lauryl sulfate 0.2, ammonium persulfate 0.2, sodium bicarbonate 0.4 and monomer 25.0 parts; after being flushed with carbon dioxide and capped, the bottles were placed in a 50° polymerizer. After 19.5 hours, a bottle containing acrylonitrile alone as monomer was filled with a stiff paste of polyacrylonitrile; from a bottle charged with 1:1 acrylonitrile and nopadiene, four grams of pasty polymer resembling polyacrylonitrile was isolated; and from a third bottle, charged only with nopadiene as monomer, was recovered 24 g. (96%) of nearly pure nopadiene, n^{25}_D 1.5048.

A bottle charged with 180 parts (72 g.) of water along with stearic acid 4.63, sodium hydroxide 0.67, potassium persulfate 0.30, modifier ($C_{12}H_{25}SH$) 0.6, butadiene 75 and nopadiene 25 parts was agitated in a 50° polymerizer. After 66 hours it contained 33.5 g. of copolymer and a considerable amount of unreacted butadiene. This represented a monomer conversion of 76%, the theoretical yield of copolymer being 40 g. Coagulated with aluminum sulfate (phenyl-β-naphthylamine present) and dried, the polymer had good milling characteristics.

Acknowledgment.—The writer wishes to acknowledge the assistance of Mr. E. F. Kluchesky, who carried out the emulsion polymerization experiments.

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The Beckmann Rearrangement of O-Picrylbenzophenone Oxime[1]

BY B. B. LAMPERT AND F. G. BORDWELL

By their kinetic studies of the rearrangement of O-picrylbenzophenone oximes and related compounds Chapman and co-workers[2] contributed greatly to our understanding of the Beckman rearrangement. They represented their rearrangements, carried out in anhydrous inert solvents, as shown for O-picrylbenzophenone oxime (I).

In view of their isolation of N-picrylbenzanilide (III), Chapman and Howis[2a] suggested that the previously reported[3] rearrangement of O-benzene-

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[1] The work was supported by the Office of Naval Research under Contract No. N7-onr-45007.

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