$$RB\text{---}CR_2$$
$$\underset{\text{V}}{\overset{|\quad\;|}{OH\;\;OH}}$$

According to this mechanism, the successful trapping of intermediate II would provide a valuable means of converting olefins into their methylol derivatives. This is described in the following communication.[8]

(7) Hillman realized only dialkylcarbinols in his oxidations, with only traces of dialkyl ketones. We are unable to account for the difference between his results and our own, unless the presence of the diglyme protects the intermediate V from the hydrolysis by the base prior to the addition of the hydrogen peroxide. We have been able to obtain dialkylcarbinols by subjecting the reaction product to hydrolysis with aqueous alkali at elevated temperatures prior to oxidation with alkaline hydrogen peroxide.

(8) M. W. Rathke and H. C. Brown, *J. Am. Chem. Soc.*, **89**, 2740 (1967).

(9) National Science Foundation Fellow, 1964–1966.
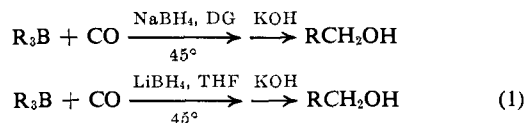
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Received March 28, 1967

## Reaction of Carbon Monoxide at Atmospheric Pressure with Trialkylboranes in the Presence of Sodium or Lithium Borohydride. A Convenient Procedure for the Oxymethylation of Olefins *via* Hydroboration

*Sir:*

We wish to report that both sodium and lithium borohydrides markedly catalyze the rate of absorption of carbon monoxide at atmospheric pressure by trialkylboranes in ether solvents. The reaction can be controlled to achieve the transfer of but one alkyl group from boron to carbon. Consequently, hydrolysis of the reaction intermediate with ethanolic potassium hydroxide produces the homologated alcohol (1).

$$R_3B + CO \xrightarrow[45°]{\text{NaBH}_4,\ DG} \xrightarrow{\text{KOH}} RCH_2OH$$

$$R_3B + CO \xrightarrow[45°]{\text{LiBH}_4,\ THF} \xrightarrow{\text{KOH}} RCH_2OH \qquad (1)$$

Consequently, carbonylation of organoboranes can now be controlled to achieve migration of all three groups from boron to carbon, providing the trialkylcarbinol;[1] two groups, providing the ketone or dialkylcarbinol;[2] or one group, providing the corresponding methylol derivative of the olefin.

By means of this latter reaction, described in this communication, we have been able to achieve the conversion of 1-octene into 1-nonanol, cyclopentene into cyclopentylmethanol, cyclohexene into cyclohexylmethanol, and norbornene into 2-*exo*-norbornylmethanol, in yields of 70–85%.

In previous experiments[1,2] we found it necessary to operate at 100–125° in order to achieve absorption of carbon monoxide by trialkylboranes at a convenient rate. However, the rate of absorption is markedly enhanced by the presence of alkali metal borohydrides. Thus, the presence of 200 mmoles of sodium borohydride in a solution of 100 mmoles of triethylborane in 100 ml of diglyme caused the uptake of carbon monoxide to be complete in 1 hr at 45°. Hydrolysis with

(1) H. C. Brown and M. W. Rathke, *J. Am. Chem. Soc.*, **89**, 2737 (1967).
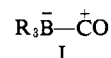
(2) H. C. Brown and M. W. Rathke, *ibid.*, **89**, 2738 (1967).

Table I. The Reaction of Carbon Monoxide at Atmospheric Pressure with Solutions of Triethylborane (1.00 $M$) at 45° in the Presence of Varying Amounts of Sodium Borohydride

| Sodium borohydride, mmoles | Triethylborane, mmoles | Carbon monoxide absorbed, mmoles | Products, mmoles | |
|---|---|---|---|---|
| | | | Ethanol | 1-Propanol |
| 200 | 100 | 142 | 180 | 80 |
| 100 | 100 | 142 | 195 | 85 |
| 50 | 100 | 140 | 202 | 82 |
| 25 | 100 | 81 | 240 | 42 |

ethanolic potassium hydroxide, followed by oxidation with hydrogen peroxide, produced 180 mmoles of ethanol, 80 mmoles of 1-propanol, and 12 mmoles of diethylcarbinol. No trace of 1-butanol, corresponding to the doubly homologated alcohol, was found by glpc analysis.[3]

It is possible that the borohydride functions by reducing the initially formed carbonyl (I) of the proposed mechanism.[2] This would be followed by transfer of one alkyl group from boron to carbon. However, at this stage we were more concerned with exploring the scope of this new synthesis than in investigating the mechanism.

$$\underset{\text{I}}{R_3\bar{B}\text{---}\overset{+}{C}O}$$

The data summarized in Table I indicate the stoichiometry for sodium borohydride to be $0.5\text{NaBH}_4/\text{Et}_3\text{B}$.

Analysis of the solutions for residual hydride indicated the following over-all stoichiometry (2).

$$2R_3B + 3CO + 4H^-(\text{NaBH}_4) \longrightarrow \longrightarrow$$
$$4ROH + 2RCH_2OH \quad (2)$$
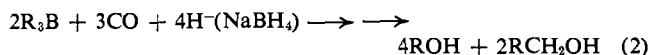
The amount of carbon monoxide consumed in these reactions is not yet understood. We observed approximately 1.5 moles of carbon monoxide to be absorbed per mole of trialkylborane in all cases investigated, although the homologated alcohols isolated, the major product, plus the much smaller by-product of dialkylcarbinol, accounted for only 1 mole of the gas. Possibly the excess consumption of carbon monoxide is the result of a direct reduction by an intermediate.

The observation that the reaction proceeds rapidly at 45° suggested the desirability of utilizing the more convenient solvent, tetrahydrofuran, for both the hydroboration and carbonylation stages. Lithium borohydride was therefore selected for its solubility in this solvent. Results obtained with this system are summarized in Table II

The following procedure for the synthesis of *exo*-2-norbornylmethanol is representative. A dry 300-ml flask, equipped with thermometer well, septum inlet, and magnetic stirrer, was attached to the carbonylation apparatus, set up as previously described.[1] The system was flushed with nitrogen. Then, a solution of 14.2 g (150 mmoles) of norbornene in tetrahydrofuran (26.6 ml) was introduced into the flask and the latter was immersed in an ice–water bath. Hydroboration was achieved by adding dropwise 23.4 ml of a solution of

(3) The convenient synthesis of homologated alcohols by the reaction of dimethyloxosulfonium methylide with trialkylboranes has recently been reported: J. J. Tufariello and T. L. C. Lee, *ibid.*, **88**, 4757 (1966). However, this procedure produces appreciable amounts of the higher homologated alcohols.

**Table II.** Conversion of Olefins into the Corresponding Methylol Derivatives by the Hydroboration–Carbonylation Reaction

| Olefin | Product | $T_{50\%}$, min | $T_{100\%}$, min | Yield,[a] % |
|--------|---------|------|------|------|
| Ethylene | 1-Propanol | 15 | 87 | 80 |
| 1-Butene | 1-Pentanol | 55 | 216 | 72 |
| 1-Octene | 1-Nonanol | 130 | 400 | 70 |
| Cyclopentene | Cyclopentyl-methanol | 56 | 230 | 69 |
| Cyclohexene | Cyclohexyl-methanol | 35 | 125 | 80 |
| Norbornene | 2-exo-Norbornyl-methanol[b] | 100 | 350 | 85 |

[a] By glpc comparison with authentic samples. The yield is based on a theoretical production of 1 mole of alcohol from 1 mole of $R_3B$ (1). [b] The absence of the endo isomer was indicated by nmr (<4%).

diborane (25 mmoles) in tetrahydrofuran, followed by stirring at room temperature for 0.5 hr. Then 1.09 g (50 mmoles) of lithium borohydride was added and the solution was heated to 45°. The system was flushed with carbon monoxide and reaction initiated by stirring the contents of the flask magnetically. After 6 hr, absorption of carbon monoxide ceased and a solution of 7 g of potassium hydroxide in 25 ml of absolute ethanol was added. The reaction mixture was heated to 70° for 1 hr to hydrolyze the intermediate. Then the flask was cooled in an ice–water bath and 22 ml of 30% hydrogen peroxide was added dropwise to oxidize the borinic acid, keeping the temperature at 30–35°. (It is purely a convenience to convert the organoboron intermediate to alcohols and boric acid.) The solution was stirred for 1 hr and then saturated with potassium carbonate. The supernatant liquid was analyzed by glpc, and a yield of 42.5 mmoles of exo-norbornylmethanol, 85%, was established.

In the present three communications[1,2] we have reported the use of hydroboration–carbonylation for the synthesis of trialkylcarbinols, dialkyl ketones, and monoalkylmethanols from the corresponding olefins. We have also found it possible to utilize this synthetic approach for the synthesis of cyclic and polycyclic derivatives and mixed ketones, as well as aldehydes and carboxylic acids. Finally, both hydroboration and carbonylation can tolerate a wide selection of functional groups. Consequently, it is now possible to synthesize many types of compounds, previously available only through Grignard syntheses, while utilizing building blocks containing reactive functional groups. We are actively exploring this new exciting development and will communicate additional developments shortly.

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# Organic Photochemistry. II. The Photosensitized Cross-Addition of Butadiene to α-Acetoxyacrylonitrile[1]

*Sir:*

Although the photosensitized cross-addition of dienophiles to olefins is well-known,[2] the corresponding

(1) Part I: W. L. Dilling, Chem. Rev., 66, 373 (1966).

photosensitized addition of dienophiles to dienes is much less common. Examples of the latter reaction have been confined to the addition of dienes to α,β-unsaturated carbonyl compounds,[3] other dienes,[4] the haloethylenes,[5] and a simple olefin.[6] The photosensitized dimerization of the dienes themselves[4a,7] (the predominant reaction even in the presence of dienophiles[5,6]) may be regarded as a special case, but other examples are lacking, and the reaction has not yet been demonstrated to be general.[6]

The major products from these photosensitized diene-dienophile cross-additions are solely[3a,b,d] or predominantly[3c,4,5] cyclobutanes with the exception of the photosensitized addition of 1,3-cyclohexadiene to cyclopentene[6] (a poor dienophile[8]). When cyclohexenes are formed, they appear to be different (e.g., exo rather than endo in the case of cyclic dienes[3c]) from the expected Diels–Alder (thermal) adducts. This fact, plus the observation of entirely different product ratios when the expected Diels–Alder adducts are formed, has led to the postulate that the photo- and thermal adducts result from quite different reaction paths.[3c,5,7b,h]

We now wish to report what appears to be the first photosensitized cycloaddition of an α,β-unsaturated nitrile to a simple diene to yield products *identical* with those formed in the thermal (Diels–Alder) reaction, albeit in different ratios.

Irradiation of an equimolar mixture of butadiene (1) and α-acetoxyacrylonitrile (2) in the presence of 0.2 mole of a sensitizer through 7740 Pyrex glass ($\lambda$ >280 m$\mu$)[9] with a 450-w medium-pressure Hanovia mercury arc lamp at ca. 30° gave the three cross-adducts 3–5 (in yields of 30–50% of the total dimeric products, depending on the sensitizer[10]), previously observed from the thermal reaction,[11] along with the three butadiene dimers 6–8.[7i,12] The products were identified

(2) (a) G. S. Hammond and N. J. Turro, Science, 142, 1541 (1963); (b) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 194; (c) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 536.

(3) (a) G. O. Schenck, W. Hartmann, S.-P. Mannsfeld, W. Metzner, and C. H. Krauch, Chem. Ber., 95, 1642 (1962); (b) G. O. Schenck, W. Hartmann, and R. Steinmetz, ibid., 96, 498 (1963); (c) G. O. Schenck, J. Kuhls, and C. H. Krauch, Z. Naturforsch., 20b, 635 (1965); Ann., 693, 20 (1966); (d) H.-D. Scharf and F. Korte, Chem. Ber., 99, 1299 (1966).

(4) (a) R. S.-H. Liu, Ph.D. Thesis, California Institute of Technology, 1965; (b) G. Sartori, V. Turba, A. Valvassori, and M. Riva, Tetrahedron Letters, 211, 4777 (1966).

(5) N. J. Turro and P. D. Bartlett, J. Org. Chem., 30, 1849 (1965).

(6) R. S. H. Liu and G. S. Hammond, J. Am. Chem. Soc., 86, 1892 (1964).

(7) (a) G. S. Hammond, N. J. Turro, and A. Fischer, ibid., 83, 4674 (1961); (b) N. J. Turro and G. S. Hammond, ibid., 84, 2841 (1962); (c) G. O. Schenck and R. Steinmetz, Bull. Soc. Chim. Belges, 71, 781 (1962); (d) D. J. Trecker, R. L. Brandon, and J. P. Henry, Chem. Ind. (London), 652 (1963); (e) G. S. Hammond and R. S. H. Liu, J. Am. Chem. Soc., 85, 477 (1963); (f) G. S. Hammond, N. J. Turro, and R. S. H. Liu, J. Org. Chem., 28, 3297 (1963); (g) D. Valentine, N. J. Turro, Jr., and G. S. Hammond, J. Am. Chem. Soc., 86, 5202 (1964); (h) G. O. Schenck, S.-P. Mannsfeld, G. Schomburg, and C. H. Krauch, Z. Naturforsch., 19b, 18 (1964); (i) R. S. H. Liu, N. J. Turro, Jr., and G. S. Hammond, J. Am. Chem. Soc., 87, 3406 (1965); (j) R. B. Cundall and P. A. Griffiths, Trans. Faraday Soc., 61, 1968 (1965); (k) J. E. Baldwin and J. P. Nelson, J. Org. Chem., 31, 336 (1966).

(8) (a) A. S. Onishchenko, "Diene Synthesis," L. Mandel, Translator, Daniel Davey & Co., Inc., New York, N. Y., 1964, p 278; (b) H. A. Bruson and T. W. Riener, J. Am. Chem. Soc., 67, 723 (1945).

(9) Reference 2c, p 742.

(10) W. L. Dilling, J. Am. Chem. Soc., 89, 2742 (1967).

(11) J. C. Little, ibid., 87, 4020 (1965).

(12) At butadiene conversions greater than ca. 20%, depending on the sensitizer, a copolymer of 1 and 2 was also formed. The products of the reaction, 3–8, were relatively stable under the reaction conditions