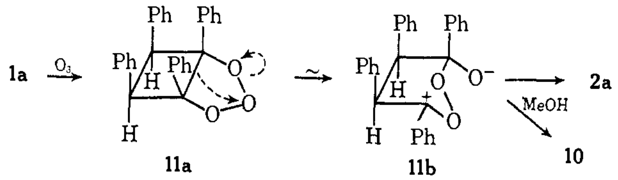
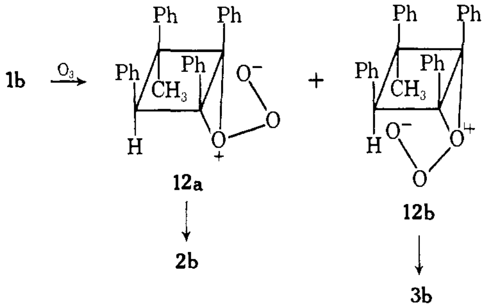
Scheme I

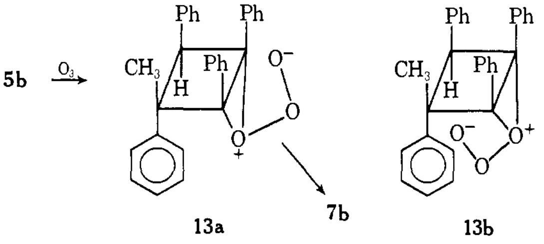


close to ozonide or be intercepted by methanol to form **10**. Scheme I requires that 2a and not 3a be produced.[12]

For the 3,4-trisubstituted cyclobutenes we propose that primary ozonide formation is sterically prohibited, and that attack takes place only at the olefinic carbon adjacent to and from the same side as the lone H to form



both σ complexes **12a** and **12b**. These, on concerted rearrangement,[1a,b] lead, respectively, to the *exo* and *endo* isomeric ozonides **2b** and **3b**. However, when a phenyl group is *cis* to the proton, as in **5b**, its preferred conformation is such that only **13a** can be produced, **13b** being sterically inaccessible. Accordingly, we predict that concerted rearrangement of the single σ complex produced from **5b** affords only **7b**.



[12] An X-ray structure determination of this compound is currently being carried out by F. P. Boer.

[13] Dow-Eastern Research Laboratory, Postdoctoral Research Fellow, 1967–1968.

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Received June 10, 1968

The Reaction of Trialkylboranes with Diazoacetone. A New Ketone Synthesis

Sir:

The interaction of trialkylboranes with nucleophiles (*i.e.*, ylides,[1] carbanions[2]) has been demonstrated to constitute an essential primary step in the elaboration of olefins to various homologated functionalized derivatives (alcohols,[1] esters,[1,2] amides,[1] α-haloesters,[2] dialkylacetic acid esters[2]). Based on this principle we find it possible to add to the already existing wealth of organoborane-based synthetic methods a new ketone synthesis.

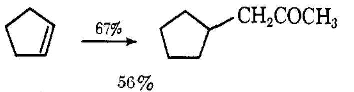
We wish to report that the reaction of diazo ketones with organoboranes[3] (available from olefins *via* hydroboration), followed by treatment with alkaline hydrogen peroxide, or, more conveniently, alkaline hydrolysis in the absence of peroxide,[4] provides a convenient new method of homologating olefins to ketones (eq 1).

$$R_3B + CH_3COCHN_2 \xrightarrow{-N_2} \xrightarrow{\text{hydrolysis}} RCH_2COCH_3 \qquad (1)$$

Yields[5] of ketones are in the range 36–89% for a variety of olefins (eq 2–6).

$$CH_3(CH_2)_2CH{=}CH_2 \xrightarrow{85\%} CH_3(CH_2)_5COCH_3 \qquad (2)$$

$$CH_3(CH_2)_3CH{=}CH_2 \xrightarrow{89\%} CH_3(CH_2)_6COCH_3 \qquad (3)$$



(4)

$$(CH_3)_2C{=}CH_2 \xrightarrow{56\%} (CH_3)_2CH(CH_2)_2COCH_3 \qquad (5)$$

$$CH_3CH{=}CHCH_3 \xrightarrow{36\%} CH_3CH_2CH(CH_3)CH_2COCH_3 \qquad (6)$$

Similarly, 1-pentene is converted to hexyl phenyl ketone and 1-hexene to heptyl phenyl ketone, each in 91% yield[5] (78% isolated yield), by treatment of the respective trialkylborane with diazoacetophenone followed by hydrolysis. The reaction of diazo ketones with trialkylboranes thus appears to be fairly general and complements the recent,[6b] elegant methyl ketone synthesis involving four-carbon homologation.

The procedure is simple. A solution of olefin in tetrahydrofuran is treated with sufficient diborane in tetrahydrofuran to ensure complete conversion to the corresponding trialkylborane.[7] An equimolar quantity of diazo ketone in tetrahydrofuran is added. In the case of a tri-*n*-alkylborane a mildly exothermic reaction ensues with immediate evolution of nitrogen, whereas the reaction with a more sterically hindered organoborane requires a reflux period.[8] After hydrolysis the ketone is conveniently isolated by extraction and distillation.

It is immediately apparent that the more hindered organoboranes[8] give the lowest yields of homologated product (eq 4–6). Attempts to increase the yields by employing a large excess of diazo ketone or by addition of copper or copper salts[9] were unsuccessful.

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[1] (a) J. J. Tufariello and L. T. C. Lee, *J. Am. Chem. Soc.*, **88**, 4757 (1966); (b) J. J. Tufariello, L. T. C. Lee, and P. Wojtkowski, *ibid.*, **89**, 6804 (1967), and references cited therein.

[2] (a) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **90**, 818 (1968); (b) *ibid.*, **90**, 1911 (1968).

[3] The reactions of diazoalkanes with boron compounds have recently been reviewed by C. E. H. Bawn and A. Ledwith, *Progr. Boron Chem.*, 1, 345 (1964).

[4] These conditions[1,2] simplify isolation of the desired ketone by avoiding oxidation of boron-bound alkyl groups of the intermediate α-boryl ketone to the unhomologated alcohol.

[5] Yields are by glpc analysis and are the average values of three independent runs. Here, as in other examples of organoborane homologative functionalizations,[1,2,6] only one of the alkyl groups of R_3B is constructively consumed.

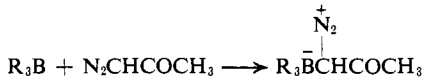
[6] (a) M. W. Rathke and H. C. Brown, *J. Am. Chem. Soc.*, **89**, 2740 (1967); (b) A. Suzuki, A. Arase, H. Matsumoto, M. Itoh, H. C. Brown, M. M. Rogić, and M. W. Rathke, *ibid.*, **89**, 5708 (1967); (c) H. C. Brown, M. M. Rogić, M. W. Rathke, and G. W. Kabalka, *ibid.*, **89**, 5709 (1967); (d) H. C. Brown, R. A. Coleman, and M. W. Rathke, *ibid.*, **90**, 499 (1968).

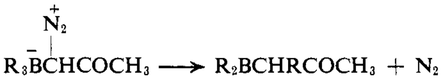
[7] (a) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962; (b) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963).

[8] Six hours of reflux was required for reactions with boranes derived from 1,1- and 1,2-disubstituted olefins and 3 hr of reflux for tricyclopentylborane before nitrogen evolution ceased.

[9] An example of a reaction of a carbene with a trialkylborane is provided by the recent study of D. Seyferth and B. Prokai, *J. Am. Chem. Soc.*, **88**, 1834 (1966).

Although no mechanistic studies have been undertaken, it is reasonable to postulate a sequence[10] involving (a) Lewis acid–Lewis base interaction of the diazo ketone with the trialkylborane; (b) rapid 1,2-alkyl shift from boron to carbon with simultaneous expulsion of nitrogen; (c) boron–carbon bond fission of the functionalized derivative.


$$R_3B + N_2CHCOCH_3 \longrightarrow R_3\overset{-}{B}(\overset{+}{N_2})CHCOCH_3 \qquad (a)$$


$$R_3\overset{-}{B}CH(\overset{+}{N_2})COCH_3 \longrightarrow R_2BCHRCOCH_3 + N_2 \qquad (b)$$

$$R_2BCHRCOCH_3 \longrightarrow RCH_2COCH_3 \qquad (c)$$

The method is illustrated for the preparation of 2-nonanone. 1-Hexene (60 mmoles) was converted[7] to trihexylborane by treatment with BH_3 (20 mmoles) in tetrahydrofuran. An azotometer was connected to the reaction vessel. A solution of diazoacetone (20 mmoles) in 15 ml of tetrahydrofuran was added over a period of *ca.* 20 min while the magnetically stirred reaction mixture was kept at 20° by ice cooling. Over 90% of the theoretical amount of nitrogen was evolved at this stage. The mixture was stirred for 30 min at room temperature, then refluxed for 30 min to liberate the remaining nitrogen. The solution was cooled in an ice bath and treated with 20 ml of 3 *N* potassium hydroxide solution. After being stirred at room temperature for 2 hr, the mixture was poured into water and extracted with pentane (three 60-ml portions). Glpc analysis at this stage indicated an 89% yield of 2-nonanone and a trace amount of 1-hexanol. The solution was dried (Drierite), and the residue remaining after removal of solvent was distilled to afford 1.86 g (65%) of 2-nonanone, identical in all respects with an authentic sample.

Currently we are exploring the scope of the reactions of organoboranes with a wide variety of mono- and difunctionally substituted diazoalkanes, N_2CHX and N_2CXY, respectively. Preliminary studies indicate that ethyl diazoacetate reacts with trialkylboranes at a faster rate than does diazoacetone and provides the two-carbon homologated ester. Detailed results of this and related studies will be dealt with in future publications.

Acknowledgment. We wish to thank the National Research Council of Canada for financial support of this work.

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[10] Analogous proposals have appeared to account for the reactions of trialkylboranes with ylides[1] and carbanions.[2] See also ref 3.

[11] Postdoctoral Research Fellow, 1967–1968.

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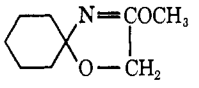
Received July 15, 1968

Organic Synthesis by Electrolysis. II. Anodic Methoxylation of Isocyanide

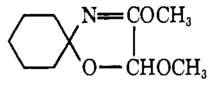
Sir:

Anodic methoxylation of some aromatic compounds or aliphatic unsaturated compounds has been studied by several workers[1] and most of the mechanisms of these reactions have been elucidated by the formation of a cationic intermediate. On the other hand, the nucleophilic character of isocyanide has been well established[2] and, furthermore, substantial reactivity of isocyanide toward free radicals has been observed in our previous study.[3] Thus, it seemed interesting to study the anodic formation of a cationic species from an isocyanide or the attack of an anodically generated methoxy radical on an isocyanide. In this communication, we wish to report the anodic methoxylation of cyclohexyl isocyanide (I) to yield some unusual products of intriguing synthetic potentialities. In addition, a novel one-step methoxylation reaction of aliphatic ethers is suggested by the present study.

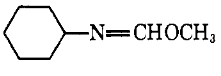
The electrolysis (1 A, 20 V, 20 hr) was carried out with carbon electrodes at the boiling temperature of the solvent. The concentration of I was 1 mole/l. in methanol containing sodium methoxide (0.5 mole/l.). The electrolysis gave seven products (II–VIII) and each product was isolated by fractional distillation or preparative gas chromatography.



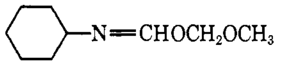
II



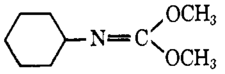
III



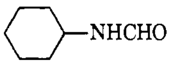
IV



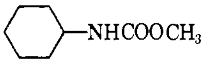
V



VI



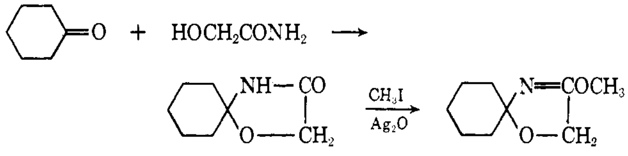
VII



VIII

Compound II had bp 115° (25 mm); nmr spectrum, τ 8.47 (singlet, 10 H), 6.23 (singlet, 3 H), 5.98 (singlet, 2 H); mol wt (mass spectrum), 169; ir spectrum, 1675 cm^{-1} (C=N). *Anal.* Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.94; N, 8.28. Found: C, 63.72; H, 9.13; N, 8.06. The 3-oxazoline (II) was synthesized independently by the route[4] shown in Scheme I and the structure of II was thereby established.

Scheme I



Compound III had bp 120° (25 mm); nmr spectrum, τ 8.43 (singlet, 10 H), 6.60 (singlet, 3 H), 6.20 (singlet, 3 H), 4.88 (singlet, 1 H); ir spectrum, 1695 cm^{-1} (C=N). *Anal.* Calcd for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60; N, 7.03. Found: C, 60.13; H, 8.62; N, 7.25. The fact that the electrolysis of II under the same reaction condition as that for I gave III strongly supports the structure proposed for III.

Compound IV had bp 61° (15 mm); nmr spectrum, τ 8.1–8.9 (multiplet, 10 H), 7.0 (broad singlet, 1 H), 6.40 (singlet, 3 H), 2.49 (singlet, 1 H); ir spectrum, 1660

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[1] S. D. Ross, M. Finkelstein, and R. C. Petersen, *J. Am. Chem. Soc.*, **88**, 4657 (1966), and references cited therein.

[2] I. Ugi, *Angew. Chem.*, 74, 9 (1962).

[3] T. Shono, M. Kimura, Y. Ito, K. Nishida, and R. Oda, *Bull. Chem. Soc. Japan*, 37, 635 (1964).

[4] H. O. L. Fischer, D. Dangschat, and H. Stettiner, *Chem. Ber.*, **65**, 1032 (1932).