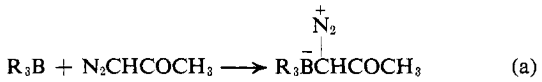
Although no mechanistic studies have been undertaken, it is reasonable to postulate a sequence[10] involving (a) Lewis acid–Lewis base interaction of the diazo ketone with the trialkylborane; (b) rapid 1,2-alkyl shift from boron to carbon with simultaneous expulsion of nitrogen; (c) boron–carbon bond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



$$R_3B + N_2CHCOCH_3 \longrightarrow R_3\bar{B}\overset{\overset{+}{N_2}}{C}HCOCH_3 \qquad (a)$$

$$R_3\bar{B}\overset{\overset{+}{N_2}}{C}HCOCH_3 \longrightarrow R_2BCHRCOCH_3 + N_2 \qquad (b)$$

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

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.

[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.

John Hooz, Siegfried Linke[11]
Department of Chemistry, University of Alberta
Edmonton, Alberta, Canada

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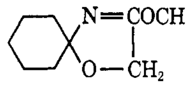
Organic Synthesis by Electrolysis. II. Anodic Methoxylation of Isocyanide

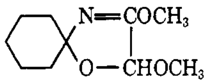
Sir:

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.

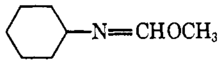
The electrolysis (1 A, 20 V, 20 hr) was carried out with carbon electrodes at the boiling temperature of the solvent. The concentration of I was 1 mole/l. in methanol containing sodium methoxide (0.5 mole/l.). The electrolysis gave seven products (II–VIII) and each product was isolated by fractional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



II



III



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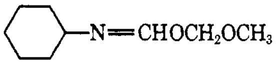

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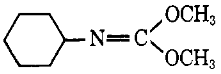

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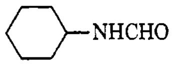
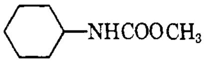


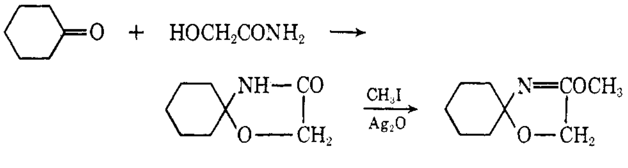
VII



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).

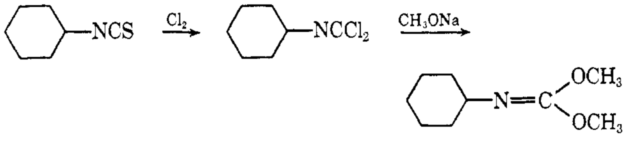
[4] H. O. L. Fischer, D. Dangschat, and H. Stettiner, *Chem. Ber.*, **65**, 1032 (1932).

cm^{-1} (C=N). Compound IV was identical in every respect with an authentic specimen prepared by the published procedure.[5]

Compound V had bp 90° (5 mm); nmr spectrum, τ 8.0–9.0 (multiplet, 10 H), 6.8, 6.2 (two broad singlets, ratio 2:1, total 1 H), 6.83, 6.81 (two singlets, ratio 2:1, total 3 H), 5.47, 5.35 (two singlets, ratio 2:1, total 2 H), 2.0, 1.85 (two singlets, ratio 2:1, total 1 H); the nmr data suggest that compound V is a mixture (2:1) of two geometric isomers; ir spectrum, 1680 cm^{-1} (C=N); mass spectrum, *m/e* 171, 156, 140, 126, 110. *Anal.* Calcd for $C_9H_{17}NO_2$: C, 63.13; H, 10.00; N, 8.18. Found: C, 62.96; H, 10.26; N, 8.12. The electrolysis of IV under the same reaction condition gave V. Thus, the structure assigned to V is convincing.

Compound VI had bp 93–95° (22 mm); nmr spectrum, τ 8.1–8.95 (multiplet, 10 H), 6.75 (broad singlet, 1 H), 6.38 (singlet, 3 H), 6.39 (singlet, 3 H); ir spectrum, 1685 cm^{-1} (C=N); mol wt (mass spectrum), 171. *Anal.* Calcd for $C_9H_{16}NO_2$: C, 63.13; H, 10.00; N, 8.18. Found: C, 63.07; H, 10.35; N, 7.95. The iminocarbonate VI was synthesized independently by the route[6] shown in Scheme II and the structure proposed for VI is convincingly established.

Scheme II



The structures of compounds VII and VIII were established by elemental analysis and comparisons of their spectroscopic data with those of authentic samples.

The total yield of the products was in the range of 20% and an example of product composition was as follows: II, 21.9%; III, 16.7%; IV, 9.5%; V, 4.9%; VI, 2.5%; VII, 4.3%; VIII, 22.6%. Although the detection of any radical intermediate by esr spectrometry could not be achieved, the formation of II–IV may be explained by a homolytic mechanism in which anodically generated methoxy radical plays an important role. A polarographic study of I indicated that I did not give any oxidation wave at below +2.5 V (*vs.* sce), while the discharge potential of methanol or methoxide anion may be around +2.5 V (*vs.* sce). Furthermore, the electrolysis of I in methanol using tetraethylammonium *p*-toluenesulfonate or ammonium nitrate as the supporting electrolyte did not give II–VI. Thus, it is conceivable that the primary attacking species is the methoxy radical. However, the possibility that the radicals generated from I yield cationic species by the anodic oxidation cannot be ignored. A detailed study of the mechanism of this novel electrolytic reaction is currently in progress. In addition, the fact that III and V could be obtained from II and IV, respectively, suggests a one-step electrolytic methoxylation reaction of aliphatic ethers. The mechanism and scope of this novel methoxylation reaction will be reported elsewhere.

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(5) T. Saegusa and Y. Itô, *Tetrahedron Letters*, 1273 (1967).

(6) T. Fujisawa, Y. Tamura, and T. Mukaiyama, *Bull. Chem. Soc. Japan*, 37, 793 (1964).

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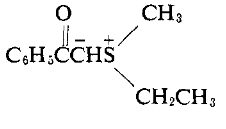
Tatsuya Shono, Yoshihiro Matsumura
Department of Synthetic Chemistry, Faculty of Engineering
Kyoto University, Kyoto, Japan

Received August 12, 1968

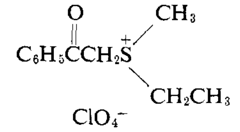
The Preparation and Racemization of an Optically Active Sulfonium Ylide. (−)-Ethylmethylsulfonium Phenacylide

Sir:

A number of reports[1–4] have indicated that sulfonium ylides have a pyramidal structure and should be capable of exhibiting optical activity. We wish to report on the preparation and isolation of the optically active ylide ethylmethylsulfonium phenacylide (I) and on its racemization.


$C_6H_5C(=O)\bar{C}H\overset{+}{S}(CH_3)CH_2CH_3$

I


$C_6H_5C(=O)CH_2\overset{+}{S}(CH_3)CH_2CH_3\ ClO_4^-$

II

The ylide I is readily formed in solvent methanol from ethylmethylphenacylsulfonium perchlorate (II) by treatment with sodium methoxide. The formation of the ylide is indicated by the ultraviolet spectrum of the solution. Compound II has λ_{max}^{MeOH} 250 mμ (log ϵ 4.14) in neutral or acidic methanol and exhibits λ_{max} 297 mμ (log ϵ 4.0) in methanol containing 3–7 equiv of sodium methoxide. Using optically active II[5] the same changes in the ultraviolet spectrum are observed. Compound II racemizes very slowly in neutral or acidic methanol at room temperature. In basic methanol II is converted to I and racemization is relatively fast.

The optically active ylide I can be isolated as a solid using the method described by Ratts and Yao for the preparation of stable sulfonium ylides.[6] The preparation involves treatment of optically active II with 5% aqueous sodium hydroxide and extraction of the solution with chloroform. The chloroform extracts were washed with water and dried over magnesium sulfate and the chloroform was removed using a rotary evaporator. The residual yellow oil crystallized on drying *in vacuo*. The active ylide, after recrystallization from benzene–Skellysolve B, had mp 83–85° and $[\alpha]^{25}D$ −137° (*c* 0.487, benzene). *Anal.* Calcd for $C_{11}H_{14}OS$: C, 68.0; H, 7.26; S, 16.50. Found: C, 68.06; H, 7.33; S, 16.47.

The first-order rate constants for racemization of I in a variety of solvents are summarized in Table I. The ylide does not decompose under the conditions required for racemization. For example, after 4 half-lives (160 min) for racemization of I in solvent carbon tetrachloride at 50.0° less than 5% of the ylide has decomposed as gauged by ultraviolet spectroscopy.

As regards the mechanism of the racemization only two nondestructive processes need be considered. The

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(1) K. W. Ratts, *Tetrahedron Letters*, 4707 (1966).

(2) A. Hochrainer and W. Silhan, *Monatsh. Chem.*, **97**, 1477 (1966).

(3) H. Nozaki, D. Tunemoto, Z. Morita, K. Nakamura, H. Watanabe, M. Takaku, and K. Kondo, *Tetrahedron*, **23**, 4279 (1967).

(4) A. F. Cook and J. G. Moffatt, *J. Am. Chem. Soc.*, **90**, 740 (1968).

(5) D. Darwish, S. H. Hiu, and R. L. Tomilson, *ibid.*, **90**, 5631 (1968).

(6) K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **31**, 1185 (1966).