V or VI, the yield of the dinucleoside phosphate was 73% on the basis of the uridylic acid employed. Absorption peaks appeared at $\lambda_{max}^{pH\ 5.5}$ 259 mμ; $\lambda_{max}^{pH\ 3.1}$ 259 mμ (ε (p) 23,000).[14]

For the synthesis of adenylyladenosines VII or VIII the reaction of IIIa with adenosine 3′-phosphate was carried out in a manner analogous to that described above. The deblocked product[15] was homogeneous by paper chromatography: $R_f$ in ethyl alcohol–1 *N* ammonium acetate (5:2) 0.22, $R_f$ in *t*-amyl alcohol–formic acid–water (3:2:1) 0.15.[16] A spleen phosphodiesterase treatment under standard conditions[17] gave an equimolar mixture of adenosine 5′-phosphate and adenosine and undegraded dinucleoside phosphate (presumably adenylyl(2′-5′)adenosine (VIII)).[8] Yield of the isomeric diadenosine phosphates was 36%, $\lambda_{max}^{pH\ 7.1}$ 260 mμ (ε (p) 25,500).

(14) ε (p) = $A/Cd$, where $A$ = absorbance, $C$ = gram-atoms of phosphorus, and $d$ = internal cell length in centimeters.

(15) The 2′,3′-O-blocking group was removed by treatment of VIIb with 0.1 *N* acetic acid for 1 hr at room temperature.

(16) Chromatographic behaviors of our sample (VII) were identical with those reported of an isomeric mixture of adenylyladenosines prepared by Michelson.[8]

(17) W. E. Razzel and H. G. Khorana, *J. Biol. Chem.*, **236**, 1144 (1961).

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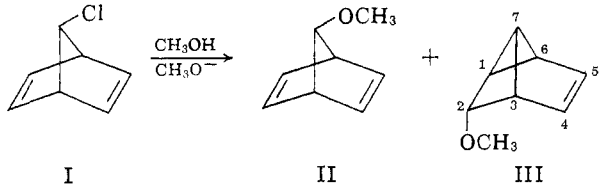
*Received November 27, 1965*

## Methanolysis of 7-Chloronorbornadiene under Alkaline Conditions. Evidence for the Formation of a Labile Tricyclic Intermediate

*Sir:*

The methanolysis of 7-chloronorbornadiene (I) in the absence of alkali proceeds quantitatively to the formation of 7-methoxynorbornadiene (II).[1] We wish to report that in the presence of an equivalent amount of sodium methoxide the solvolysis produces only 20% of the expected II together with another, highly labile species which is almost instantaneously converted by dilute acid into II. The characteristics of the labile species indicate that it is the hitherto unknown tricyclic derivative III. Consequently, it appears that nucleophiles other than borohydride[2,3] are capable of trapping the intermediate carbonium ion to yield tri-




I II III

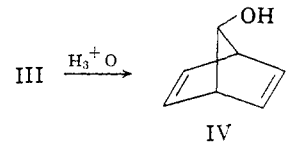
cyclic derivatives. This reaction appears highly promising, therefore, as a simple, convenient synthetic route to functional derivatives of the tricyclic structure, compounds which have not been available previously.

(1) G. Wittig and J. Otten, *Tetrahedron Letters*, **No. 10**, 601 (1963), reported 68% yield. On reinvestigation, we found quantitative formation of II.

(2) H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963).

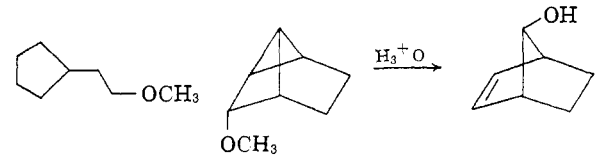
(3) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).

The methanolysis of I in methanol–dioxane (5:1) solution proceeded with a rate of $1.21 \times 10^{-4}$ sec$^{-1}$ at 16.8°. The same reaction in the presence of an equivalent amount of sodium methoxide gave a rate of $1.67 \times 10^{-4}$ sec$^{-1}$,[4] and the reaction mixture indicated the formation of a brown polymer beyond 80% reaction. Vapor phase chromatographic analysis showed only 20% yield of II at infinite time. However, when the reaction mixture was treated with dilute but sufficient perchloric acid to quench the action of sodium methoxide (a controlled experiment showed that this treatment quantitatively converts I into 7-norbornadienol (IV), but has no effect on II), the yield of IV indicated by vpc was larger than that of remaining I which was calculated by the rate constant. This excess, which approached maximum at about one half-life and then gradually decreased, strongly suggests the presence of a labile intermediate whose treatment with acid furnishes IV.




III IV

The methanolysis mixture with methoxide at one half-life was reduced at 0° over $PtO_2$ with about 2 mole equiv of hydrogen. The reduced mixture was divided into two parts, A and B; part A was worked up under a basic condition and part B was treated with sufficient perchloric acid to remove the methoxide. The capillary vpc analysis (45-m Ucon LB-550-X) showed, besides the 50% recovery of 7-chloronorbornane: in part A, 7-methoxynorbornane, (2-methoxyethyl)cyclopentane (V),[5-7] bp 74° (48 mm), $n^{21}$D 1.4313, and an unknown compound (VI) in the relative peak areas of 24, 22, and 54, respectively (total yield 97%); in part B, 7-methoxynorbornane, V, and *anti*-7-norbornenol (VII) in the relative areas of 24, 18, and 58, respectively. Therefore, it can be concluded that VI observed in part A




V VI VII

was converted into VII in part B. For isolation of VI, part A was treated with elution chromatography on Merck standardized alumina using a mixed solvent of pentane and ether (99:1). After elution of 7-chloro- and 7-methoxynorbornane and V, a sample of VI, bp 90° (bath temperature) at 110 mm, contaminated with about 15% of V, was obtained.[8] The infrared spectrum of VI in $CS_2$ showed cyclopropyl CH at 3040

(4) Second-order plots showed upward curvature. The presence of 0.128 *M* sodium perchlorate, instead of sodium methoxide, gave $1.98 \times 10^{-4}$ sec$^{-1}$. Therefore, the slightly increased rate in this case over that in the methanolysis without methoxide was ascribed to a salt effect.

(5) Satisfactory analyses were obtained for all compounds described.

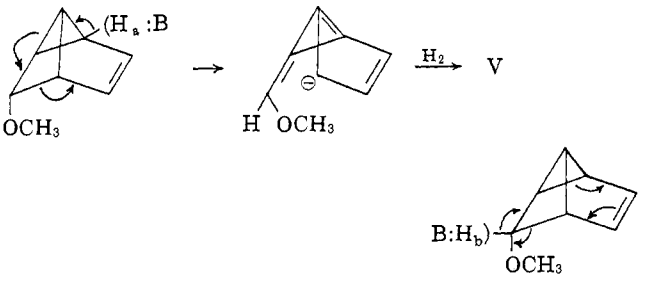
(6) Isolated by elution chromatography and identified with the sample independently prepared by methanolysis of β-cyclopentylethyl bromide.[7]

(7) C. R. Noller and R. Adams, *J. Am. Chem. Soc.*, **48**, 2444 (1926).

(8) Standing on the alumina for 2–3 hr induced the isomerization of VI into *anti*-7-methoxynorbornene, bp 80° (25 mm), $n^{25}$D 1.4630.

(m), 810 (m), and 795 (m) $cm^{-1}$, and $CH_3O$ absorption at 1118 $cm^{-1}$. The existence of a cyclopropyl ring was also supported by the first overtone of the cyclopropyl CH stretching vibration observed at 6020 $cm^{-1}$.[9] The nmr peaks (in $CCl_4$) of a $C_2$ proton at $\tau$ 6.29 (quartet, $J_{C_1-H,C_2-H}$ = 3.8, $J_{C_2-H,C_3-H}$ = 8.0 cps (apparent $J$ value)), of a $C_3$ proton at $\tau$ 7.35 (multiple doublet), and of three cyclopropyl and four $C_4$,$C_5$ protons at $\tau$ 8.0–8.7 (complex multiplets) were entirely consistent with the structure of 2-methoxytricyclo[4.1.0.$0^{3,7}$]-heptane. The coupling constants of the $C_2$ proton indicated the methoxyl substituent to be exclusively in the *endo* orientation as observed in some related reactions.[10,11] Consequently, the structure of the labile intermediate, the main product obtained in the methanolysis, was established as *endo*-2-methoxytricyclo-[4.1.0.$0^{3,7}$]hept-4-ene (III).

The formation of ring-opened V would be rationalized by base-catalyzed isomerization of III into 1-(2-methoxyvinyl)cyclopentadiene, which involves abstraction of the acidic cyclopropyl proton $H_a$ and generation of a stable cyclopentadienide ion, followed by saturation of three double bonds.[12,13] The use of $H_b$, instead of the bridgehead $H_a$, may be another possibility. The




formation of VI was also observed in the methanolysis of *anti*-7-norbornenyl *p*-toluenesulfonate with alkali, but in only 1% yield.

While the results obtained here have interesting implications as to the structure of the cation from I and similar derivatives,[2,3] we prefer not to examine these implications at this time.

(9) Refer to H. Tanida, Y. Hata, Y. Matsui, and I. Tanaka, *J. Org. Chem.*, 30, 2259 (1965).
(10) P. R. Story, *J. Am. Chem. Soc.*, 83, 3347 (1961).
(11) H. Tanida and Y. Hata, *J. Org. Chem.*, 30, 977 (1965). The cyano substituent in 2-cyanotricyclo[4.1.0.$0^{3,7}$]heptane obtained in the reaction of *anti*-7-chloronorbornene with sodium cyanide was recently proved to be exclusively in the *endo* position by the coupling constants of the $C_2$ proton at $\tau$ 6.81 (in $CCl_4$, quartet), $J_{C_1-H,C_2-H}$ = 3.7, $J_{C_2-H,C_3-H}$ = 8.3 cps, and by hydrogenolysis to *endo*-2-cyanonorbornane.
(12) Highly strained small-ring hydrocarbons are said to have unusually high acidity. Refer to G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, 85, 2022 (1963).
(13) We acknowledge the suggestion of this mechanism to a referee.

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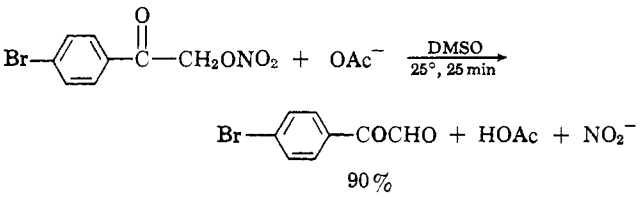
## A New and Convenient Synthesis of Glyoxals, Glyoxalate Esters, and α-Diketones

*Sir:*

We wish to describe a convenient synthesis of glyoxals, glyoxalate esters, and α-diketones, the utility of which may be appreciated when it is recognized that Tables I and II record the yields of analytically pure products. The reaction upon which the synthesis depends is the conversion of nitrate esters to carbonyl compounds under the influence of sodium acetate, *e.g.*




In practice, one may start with the corresponding halide, convert it to the nitrate ester, and, without isolating, transform this into the carbonyl compound; the yields (Table I) are almost identical with those obtained on starting with pure nitrates (Table II).[1]

**Table I.**[a] Conversion of >CHBr to >C=O

| Halide | Product | Yield, % |
|---|---|---|
| *p*-$BrC_6H_4COCH_2Br$ | *p*-$BrC_6H_4COCHO \cdot H_2O$ | 85 |
| *p*-$ClC_6H_4COCH_2Br$ | *p*-$ClC_6H_4COCHO \cdot H_2O$ | 82 |
| *p*-$O_2NC_6H_4COCH_2Br$ | *p*-$O_2NC_6H_4COCHO$[c] | 83 |
| *p*-$C_6H_5C_6H_4COCH_2Br$ | *p*-$C_6H_5C_6H_4COCHO \cdot H_2O$ | 86 |
| $C_6H_5COCHBrC_6H_5$ | $C_6H_5COCOC_6H_5$ | 95 |
| $CH_3(CH_2)_3CHCH_2OCCH_2Br$[b] (with $C_2H_5$, O) | $CH_3(CH_2)_3CHCH_2OCCHO$ (with $C_2H_5$, O) | 82 |

[a] All reactions in DMSO at 20–25° for 25 min using 10 mole % sodium acetate trihydrate except as otherwise noted. [b] One equivalent of sodium acetate trihydrate. [c] Isolated as the dimedon derivative.

**Table II.**[a] Conversion of $>CHONO_2$ to >C=O

| Nitrate | Product | Yield, % |
|---|---|---|
| *p*-$BrC_6H_4COCH_2ONO_2$ | *p*-$BrC_6H_4COCHO \cdot H_2O$ | 90 |
| *p*-$ClC_6H_4COCH_2ONO_2$ | *p*-$ClC_6H_4COCHO \cdot H_2O$ | 85 |
| *p*-$O_2NC_6H_4COCH_2ONO_2$ | *p*-$O_2NC_6H_4COCHO$[c] | 86 |
| *p*-$C_6H_5C_6H_4COCH_2ONO_2$ | *p*-$C_6H_5C_6H_4COCHO \cdot H_2O$ | 94 |
| $C_6H_5COC(C_6H_5)HONO_2$ | $C_6H_5COCOC_6H_5$ | 98 |
| $C_6H_5COC(CH_3)HONO_2$[b] | $C_6H_5COCOCH_3$ | 94 |

[a] All reactions in DMSO at 20–25° for 25 min using 10 mole % sodium acetate trihydrate, except as otherwise noted. [b] One equivalent of anhydrous sodium acetate for 55 min. [c] Isolated as the dimedon derivative.

It is an important feature of this synthesis that anhydrous conditions are not necessary. Sodium acetate trihydrate works as well as anhydrous sodium acetate, and, since nitrite ion is liberated in the reaction,[2] it would be anticipated that a catalytic amount of acetate would suffice; this, indeed, proves to be the case. Most of the reactions were carried out with a

(1) Nitrate esters may, of course, also be prepared by esterification of alcohols: R. Boschan, R. T. Merrow, and R. W. Van Dolah, *Chem. Rev.*, 55, 485 (1955); E. G. Ausell and J. Honeyman, *J. Chem. Soc.*, 2779 (1952); J. Honeyman and J. W. W. Morgan, *ibid.*, 3660 (1955); A. F. McKay, R. H. Meen, and G. F. Wright, *J. Am. Chem. Soc.*, 70, 430 (1948).
(2) We shall subsequently present evidence that the oxidizing agent is not DMSO and that we deal here with a base-catalyzed elimination of nitrate esters.