(IX) of magnamycin (or leucomycin) obtained by synthesis.[13]

$$\underset{\text{VIII}}{CH_3(CH_2)_7CH(CH_3)CH_2CH(CH_3)(CH_2)_5CH_3}$$

$$\underset{\text{IX}}{CH_3(CH_2)_7CH(CH_3)CH_2CH(C_2H_5)(CH_2)_4CH_3}$$

In the mass spectra of the hydrocarbon obtained from spiramycin and the hydrocarbon IX, *m/e* (rel intensity) 253 (M − CH_3) (0) and 239 (M − C_2H_5) (14) were characteristically observed, accompanying a weak molecular ion at *m/e* 268 (3), and in that of VIII, *m/e* 253 (M − CH_3) (4) and 239 (M − C_2H_5) (4) were characteristically compared with a strong molecular ion, *m/e* 268 (13). These facts indicate that the α position of the aldehyde is a methylene group in the spiramycins, as in magnamycin and leucomycin, and that the spiramycin skeleton should be corrected to a 16-membered ring.

Stereochemical Considerations. In the nmr spectrum (100 Mcps) of the spiramycin, the absorptions in the olefinic region (5.5–7 ppm), H_{12} (5.60 ppm; $J_{12,13}$ = 15.4 cps), H_{13} (6.55 ppm; $J_{13,14}$ = 15.3 cps), and H_{14} (6.05 ppm; $J_{14,15}$ = 15.2 cps) indicate the *trans, trans* conformation, as in leucomycin.[4c] These facts show that the fundamental structure of the spiramycins is correlated to the absolute structure of leucomycin[4] and that spiramycins have steric structures indicated by IIa,b,c, excluding the nature of the anomeric center linking the forosamine[6] portion.

Acknowledgment. We are indebted to the Kyowa Hakko Kogyo Co., Ltd., for the supply of spiramycins, and thank Dr. Uzu of that company for making the nmr spectral data for spiramycin-A and -C available for the present work.

[13] The skeletal hydrocarbons, VIII and IX, were synthesized as follows. 2-Bromodecane (**1**) was condensed with diethyl malonate; the product was decarboxylated to 2-methylundecylenic acid (**2**) which was chlorinated to form its acid chloride (**3**). The Wurtz reaction, used for the synthesis of tuberculostearic acid,[12] was applied to the reaction of **3** and diamylcadmium in benzene and afforded 8-methylhexadecan-6-one (**4**) which was treated with ethylmagnesium iodide, followed by dehydration and catalytic reduction over platinum, to obtain 6-ethyl-8-methylhexadecane (IX) (*m/e* 268).

$$CH_3(CH_2)_7CHBrCH_3\ (\mathbf{1}) \longrightarrow CH_3(CH_2)_7CH(CH_3)CH_2COOH\ (\mathbf{2}) \longrightarrow CH_3(CH_2)_7CH(CH_3)CH_2CHCl\ (\mathbf{3}) \longrightarrow CH_3(CH_2)_7CH(CH_3)CH_2CO(CH_2)_4CH_3\ (\mathbf{4}) \longrightarrow \mathbf{VIII}$$

7,9-Dimethylheptadecane (VIII) was prepared from **3** and dipentylcadmium under the same conditions as above, followed by Grignard reaction with methylmagnesium iodide, dehydration, and finally catalytic reduction over platinum.

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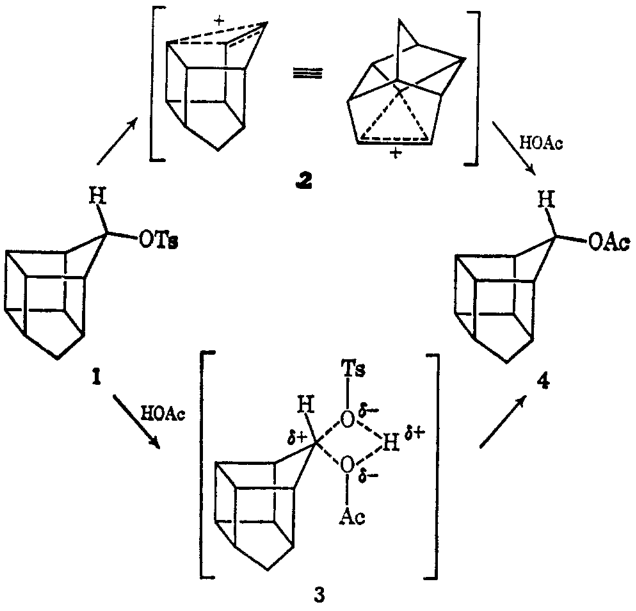
Received April 29, 1969

Pentacyclodecane Chemistry. VI. Acetolysis and Formolysis of Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]dec-6-*d*-*syn*-6-yl Tosylate. Evidence for a Symmetrical Intermediate[1]

Sir:

We present evidence which establishes the intermediacy of a symmetrical bridged carbonium ion, **2**, or its equivalent of two rapidly equilibrating classical ion pairs, in the solvolysis of the *syn*-1,3-bishomocubyl tosylate **1**.[1] Preliminary rate data for solvolysis and internal return in both acetic and formic acids are also presented.

An alternate explanation to the bridged ion **2** for the almost complete retention of stereochemistry observed in the acetolysis of the *syn*-tosylate **1**[1] is a front-side displacement, perhaps with assistance by the leaving group (see **3**),[2] as has been proposed for several acyclic systems.[3,4] The latter explanation predicts no skeletal rearrangement of the pentacyclodecane nucleus while the former implies that one-half of the product acetate **4** would be rearranged to the enantiomer of that shown for **4**.[5]



The α-deuterated tosylate **5** and acetate **6** were prepared in manners analogous to those reported previously for the nondeuterated compounds.[1] Lithium aluminum deuteride, or better, aluminum deuteride,[1,6] was substituted for lithium aluminum hydride in the reduction of *endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one. The formate **8** was prepared by the procedure described by Vogel.[7,8] All of the esters were 100% deuterated in the α (6) position as determined by the absence of nmr resonances at −4.51, −4.71, and −4.99 ppm[9] which appear in the spectra of the nondeuterated ana-

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[1] Part V: W. L. Dilling, C. E. Reineke, and R. A. Plepys, *J. Org. Chem.*, in press.

[2] Six-membered-ring transition states may also be drawn.

[3] (a) H. L. Goering and S. Chang, *Tetrahedron Letters*, 3607 (1965); (b) H. L. Goering, R. G. Briody, and J. F. Levy, *J. Am. Chem. Soc.*, **85**, 3059 (1963); (c) H. Hart and H. S. Eleuterio, *ibid.*, **76**, 1379 (1954).

[4] 7-Norbornyl tosylate and brosylate have been shown to undergo solvolysis with 80–90% retention of configuration. No skeletal rearrangement occurs in these reactions leading to 7-norbornyl products. See (a) P. G. Gassman and J. M. Hornback, *J. Am. Chem. Soc.*, **89**, 2487 (1967); (b) F. B. Miles, *ibid.*, **89**, 2488 (1967); **90**, 1265 (1968); (c) P. G. Gassman, J. M. Hornback, and J. L. Marshall, *ibid.*, **90**, 6238 (1968).

[5] The racemic mixture of tosylate **1** was used in the previous experiments[1] as well as in this work. Only one enantiomer is shown in this paper.

[6] W. L. Dilling and R. A. Plepys, *Chem. Commun.*, 417 (1969).

[7] A. I. Vogel, *J. Chem. Soc.*, 624 (1948).

[8] All new compounds gave satisfactory elemental analyses or high-resolution mass spectra, as well as satisfactory infrared, nmr, and mass spectra.

[9] All nmr spectra were run as $CDCl_3$ solutions.

Table I. Acetolysis and Formolysis of α-Deuterated *syn*-1,3-Bishomocubyl Tosylate **5**

Solvent	Temp, °C[a]	Time, hr	Per cent solvolysis[b]	Ratio **6**:**7** or **8**:**9**	Ratio **5**:**10**[c]
HOAc	120	7	~100[e]	52:48	
	120	0.67	52[f]	51:49	51:49
	100	4.75	48[g]	53:47	56:44
	68	4.75	8[h]	*i*	92:8
HCO_2H[j]	55	5	~100	49:51	
	55	0.5	44	50:50	79:21

[a] All ±1°. [b] Based on unrecovered tosylate. [c] Accuracy of nmr analyses *ca.* ±3–4%. [d] Redistilled; contains 1% acetic anhydride. [e] Material balance 89%. [f] Material balance 92%. [g] Material balance 88%. [h] Material balance 96%. [i] Amount of acetate too small to analyze. [j] 98–100% material used.

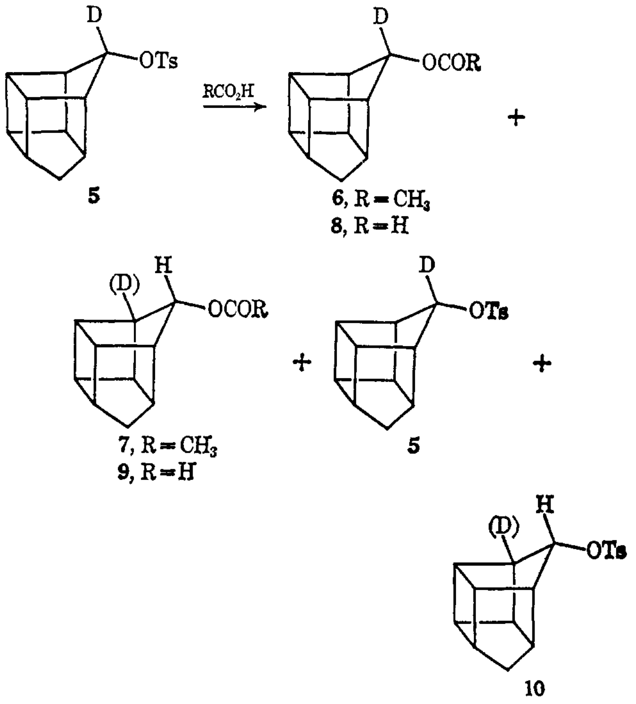
Table II. Rates of Solvolysis and Internal Return for α-Deuterated *syn*-1,3-Bishomocubyl Tosylate **5**

Solvent	Temp °C	k_2, sec^{-1}	k_1, sec^{-1}	k_1/k_2
HOAc	120[a]	2.82×10^{-4}[b]	$>7.7 \times 10^{-4}$[c]	>2.7[c]
	68	2.8×10^{-6}	8.0×10^{-6}	2.9
	55	2.3×10^{-7}[d]		
HCO_2H	55	3.6×10^{-4}	4.9×10^{-4}	1.4

[a] ±0.1°. [b] Data from ref 1. [c] Lower limit assuming maximum error, 4%, in nmr analysis. Assuming the 51:49 ratio in Table I, k_1 is 1.1×10^{-3} sec^{-1}, k_1/k_2 is 3.9. [d] Calculated from data at higher temperatures.[1]

logs of tosylate **5** (**1**), acetate **6** (**4**), and formate **8**, respectively.

The results of unbuffered acetolysis and formolysis of the deuterated tosylate **5** under various conditions are presented in Table I. The extent of rearrangement in both the product esters and recovered tosylates was determined from the area of the nmr resonance for the proton at the α position. The acetoxy methyl protons, formate proton, and tosylate aromatic protons were used as internal standards. The accuracy of the ratios of unrearranged to rearranged esters is *ca.* ±3–4%. No products other than the *syn*-1,3-bishomocubyl derivatives were detected by nmr analysis in any of the reactions shown in Table I. The esters **6** and **8** were stable to the reaction medium containing 1 equiv of *p*-toluenesulfonic acid.



5

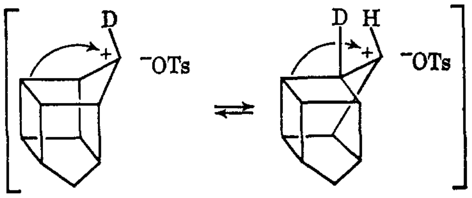
6, R = CH_3
8, R = H

7, R = CH_3
9, R = H

5

10

The 50:50 distribution, within experimental error, of unrearranged and rearranged acetates and formates is consistent with the intermediacy of a symmetrical bridged ion **2** or its equivalent of equilibrating classical ion pairs **11**.[10] However, due to the relatively rapid internal return in acetic acid (see below), a symmetrical intermediate(s) is not demanded. A rapid prior equilibration of tosylates **5** and **10** followed by a slower acetolysis which does not involve skeletal rearrangement as in **3** could be accommodated by the experimental results.[11] The formolysis results cannot be explained in this manner and demand a symmetrical intermediate(s).



11

Approximate rate constants for solvolysis (k_2) and internal return (k_1)[12] are presented in Table II. The

$$\begin{tikzcd} 5 \arrow[r, "k_2"] \arrow[d, shift right, "k_1"'] & 6 + 7 \text{ or } 8 + 9 \\ 10 \arrow[u, shift right, "k_1\ \text{RCO}_2\text{H}"'] \arrow[ur, "k_2"'] & \end{tikzcd}$$

ratio of rate constants for formolysis to acetolysis of *ca.* 1600 at 55° and the ratios of internal return to solvolysis (k_1/k_2) in both acetic and formic acids are comparable to those reported for related processes.[13]

[10] Secondary deuterium isotope effects were assumed to be negligible within our experimental error.

[11] The result at 100° may indicate incomplete scrambling of the recovered tosylate. However this result is only slightly outside the experimental error for a 50:50 mixture. Reaction variables were not explored thoroughly to find conditions where the acetate could be shown to be completely scrambled while the recovered tosylate was not completely scrambled.

[12] The internal return rate constant (k_1) was calculated from the equation $k_1 = \frac{1}{2}[(\ln x)/t - k_2]$ where x is the difference between [**5**] and [**10**] expressed as mole fractions of the total reaction products, t is the time, and k_2 is the solvolytic rate constant.

[13] (a) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1127 (1952); (b) S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952); (c) S. Winstein, M. Brown, K. C. Schreiber, and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952); (d) S. Winstein and D. Trifan, *ibid.*, **74**, 1155 (1952); (e) S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952); (f) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

Acknowledgment. The authors wish to thank Dr. E. C. Steiner, Professor M. Stiles, and Professor J. C. Martin for numerous helpful comments.

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Received March 27, 1969

Trapping of Hydrogen and Deuterium Atoms Produced by the Photolysis of Hydrogen Iodide in 3-Methylpentane-d_{14}[1]

Sir:

Photolysis of HI in 3-methylpentane (3MP) glass at 77°K produces hot hydrogen atoms, which abstract hydrogen from the matrix to form C_6H_{13} radicals,[2–4] and thermal H atoms which add to olefins present as dilute solutes.[3] The quantum yield[4] of thermal atoms, which is *ca.* 0.8 in liquid 3MP at 300°K, drops to *ca.* 0.1 at 77°K, as a result of increasing geminate recombination. Using esr detection, we have sought to determine whether thermal H atoms can be produced by photolysis of HI in 3MP glass at temperatures below 77°K, and, if so, whether there are conditions under which they can be trapped. The work was initiated to assist in determining[5] whether the absence of esr signals for H atoms in γ-irradiated solid hydrocarbons means that such atoms are not produced, or simply that they are not trapped.

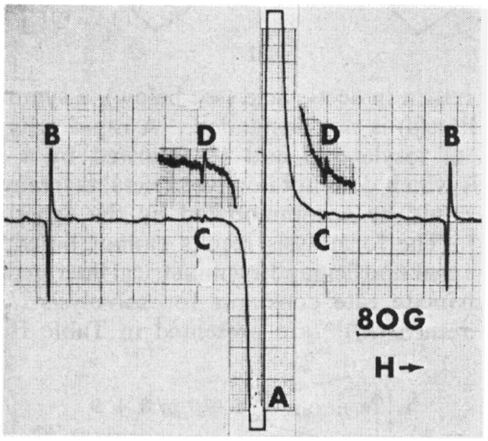

Figure 1. Esr spectrum produced by photolys is of HI in perdeuterated 3-methylpentane at 27°K, showing lines due to the C_6D_{13} radical (A), ^1H (B), and ^2H (C). The inserts (D) show the ^2H lines recorded at a fivefold higher amplifier gain. The microwave power was 3.9 mW.

In initial tests 0.1 mole % HI was photolyzed in perdeuterated 3-methylpentane (3MP-d_{14}), with 0.3 mole % isobutylene (iB) present to serve as a detector for thermal H atoms (by forming t-C_4H_9 radicals observable by esr). 3MP-d_{14} rather than 3MP-h_{14} was used as the matrix because the outer lines of the t-C_4H_9 spectrum (~150 G) are free of overlap with the C_6D_{13} spectrum (~50 G), whereas the C_6H_{13} signal (produced by hydrogen abstraction by hot H) would give interference. Degassed samples were photolyzed in 3-mm i.d. Suprasil tubes in a Varian V-4531 esr cavity using a quartz-jacketed AH4 medium-pressure mercury lamp (with and without a Vycor filter) focused on the sample by a quartz lens. The techniques of purification, measurement, and temperature control by cold helium gas are discussed elsewhere.[2,3,5,6]

Photolysis of the 3MP-d_{14}–HI–iB mixture for 2.5 min at temperatures below 77°K produced both C_6D_{13} and t-C_4H_9 radicals. We therefore photolyzed 3MP-d_{14} containing 0.1 mole % HI without iB. Pronounced lines of the H doublet appeared after 60 sec of photolysis, or less, at all temperatures tested from 20 to 50°K. On further photolysis the two outer lines of the ^2H triplet appeared, the central line being obscured by the C_6D_{13} signal (Figure 1). We attribute the ^1H doublet to the trapping of thermal H atoms produced from HI photolysis and the ^2H lines to trapping of thermal D atoms produced by displacement of D atoms from C_6D_{14} by hot H atoms or by photolysis of DI formed by disproportionation between an I atom and a radical with which it is caged ($C_6D_{13} + I \rightarrow C_6D_{12} + DI$). The radical is formed by attack by the hot H partner split off from the I by photolysis of HI. Decay kinetics of radicals offer strong evidence for such caging.[2]

At 30°K the lines of the ^1H doublet grew continuously during a 10-min photolysis, but at a decreasing rate. Initial decay of the ^1H signal in a sample which received a 30-sec photolysis was about 50% in 1 min, becoming progressively slower thereafter. Initial decay following longer illuminations was slower, indicating a higher fraction of more strongly trapped atoms. When a sample photolyzed at 30°K was raised to successively higher temperatures, a relatively rapid initial decay followed by much slower decay occurred at each temperature.

Photolysis of HI in 3MP-h_{14}, under conditions identical with those used with the 3MP-d_{14} matrix, shows no evidence of the ^1H doublet. This indicates either that 3MP-h_{14} is incapable of trapping ^1H, in contrast to the ability of 3MP-d_{14} to trap both ^1H and ^2H, or that the protiated matrix reduces the escape of thermal H atoms formed from the primary photolytic process more than does the deuterated matrix (by increasing the probability of the hot reaction or of geminate recombination). There is an analogy for such an effect in the slow decay of trapped free radicals in deuterated as compared to protiated matrices at 77°K.[2] Both experimental observations and activation energy considerations exclude the possibility that the latter decay occurs by hydrogen abstraction from the matrix.[2]

Despite the above evidence that D atoms can be trapped and observed in 3MP-d_{14}, no D atom signal appears during the growth of C_6D_{13} radicals produced by the self-radiolysis of tritiated 3MP-d_{14}[7] at 30–50°K in the esr cavity, or during γ radiolysis at 4°K.[5] Likewise no H atoms are produced during γ radiolysis of a variety of other hydrocarbons at 4°K, except CH_4.[8]

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(1) This work has been supported in part by U. S. Atomic Energy Commission Contract AT(11-1)-1715 and by the W. F. Vilas Trust of the University of Wisconsin.

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(3) S. Aditya and J. E. Willard, *J. Amer. Chem. Soc.*, **88,** 229 (1966).

(4) J. R. Nash, R. R. Williams, and W. H. Hamill, *ibid.*, **82,** 5974 (1960).

(5) D. Timm and J. E. Willard, *J. Phys. Chem.*, in press.

(6) D. Timm and J. E. Willard, *Rev. Sci. Instr.*, in press.

(7) Prepared by Dr. Mervyn Long of our laboratory.

(8) Trapped H atoms produced in CH_4 at 4°K by radiolysis have previously been observed by (a) B. Smaller and M. S. Matheson, *J. Chem. Phys.*, **28,** 1169 (1958); (b) D. W. Brown, R. E. Florin, and L. A. Wahl, *J. Phys., Chem.*, **66,** 2602 (1962); (c) W. Gordy and R. Morehouse, *Phys. Rev.*, **151,** 207 (1966).