

mechanism is further supported by a similar result in an analogous system,¹³ and by the demonstration that the Ramberg-Bäcklund reaction is successful with 1-bromo- or 1-chloro-8-thiabicyclo[3.2.1]octane,^{14,15} where a double inversion mechanism is possible but a double retention mechanism is excluded for steric reasons.

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is not excluded by the data but seems highly unlikely for reasons given earlier.¹³

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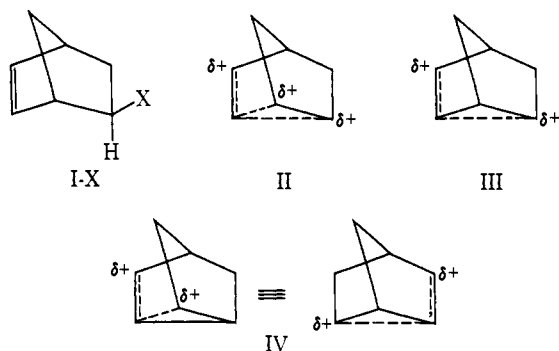
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Temperature Effects in the Acetolysis of *exo*-Dehydro-2-norbornyl Brosylate¹

Sir:

In 1955, Roberts and coworkers² reported that from the acetolysis of *exo*-dehydro-2-norbornyl-2,3-¹⁴C₂ brosylate (I-2,3-¹⁴C-OBs), there was a 38% rearrangement of the isotopic label from C-2,3 to C-1,4-7 in the resulting *exo*-dehydro-2-norbornyl acetate (I-x-¹⁴C-OAc) (the major product was nortricycyl acetate). Since the intervention of a symmetrical intermediate such as II would give rise to 50% rearrangement, it was proposed that the unsymmetrical homoallylic cation III was formed first, and that some of this ion was trapped by solvent before it isomerized to its enantiomer IV, or to the symmetrical ion II. However, Cristol and coworkers³



have recently found that the acetolysis of *exo*-dehydro-2-norbornyl-3-*exo-d* brosylate (I-3-*d*-OBs) gave a product I-x-*d*-OAc, the mass spectral analysis of which indicated an essentially 50% rearrangement of the D label from C-3 to C-7. It was suggested that this isotopic distribution was the result of the involvement of symmetrical ion II or rapidly equilibrating ions III and IV. It has also been stated in a literature survey⁴

(1) Supported by a grant from the National Research Council of Canada.

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(3) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, *ibid.*, **88**, 3087 (1966).

that the unsymmetrical distribution of the label reported by Roberts and coworkers² "appears to be definitely incorrect." In an attempt to clarify the apparent discrepancy between the results obtained from I-2,3-¹⁴C-OBs and I-3-*d*-OBs, we have studied the acetolysis of *exo*-dehydro-2-norbornyl-2-*d* brosylate (I-2-*d*-OBs), and analyzed the unsaturated product, I-x-*d*-OAc, by nmr and by mass spectrometry using Cristol's method.⁵

I-2-*d*-OBs was prepared in a manner analogous to the preparation of *exo*-2-norbornyl-2-*d* brosylate.⁶ Dehydronorcamphor was reduced with LiAlD₄ to give a 9:1 mixture of *endo*:*exo* dehydro-2-norborneol-2-*d* and then converted to the mixed brosylates. Selective solvolysis in aqueous acetone removed the *exo* isomer, and treatment of the pure *endo*-brosylate with (CH₃)₄N⁺OAc⁻ in dry acetone gave I-2-*d*-OAc, which was reduced with LiAlH₄ and then converted to the desired I-2-*d*-OBs.

Initially, the acetolysis was carried out with 0.48 M I-2-*d*-OBs in the presence of 10% excess KOAc at 45° for 1 hr (Roberts' conditions) or with 0.24 M I-2-*d*-OBs in the presence of a tenfold excess of NaOAc at 24° for 11 hr (similar to one set of Cristol's conditions, with the exception that Cristol used a less concentrated solution of the brosylate). The I-x-*d*-OAc produced was separated from the nortricycyl acetate by preparative vpc (25% Carbowax 20 M on Chromosorb P at 150°). Mass spectral analysis of the I-x-*d*-OAc based on the formation of the cyclopentadiene cation as described by Cristol and coworkers⁵ gave the per cent rearrangement of the D label from C-2,3 to C-1,4-7. Similarly, from the nmr spectrum of the I-x-*d*-OAc, the H absorption at C-2 gave another measure of the extent of rearrangement of the D label from C-2 to the rest of the carbon positions. The results, given in Table I, show that the previously reported data of Roberts² and Cristol³ were both substantially correct.

The different extents of isotopic scrambling observed by Roberts and by Cristol, and confirmed by the present work, apparently must be due to some difference in experimental conditions. The experiments reported by Cristol³ included some variations in brosylate concentration, amount of NaOAc added, and reaction time, and all these experiments gave about 50% rearrangement. However, Cristol's data were obtained from reactions at 24° (except for one experiment at 28°), while Roberts used a reaction temperature of 45°. This temperature difference thus appeared to be a probable factor in determining the difference in the per cent rearrangements observed. In order to confirm that the reaction temperature does influence the extent of isotopic scrambling, the acetolysis of I-2-*d*-OBs was also carried out at 65 and 14° (the lowest practical temperature without freezing the reaction mixture). The results are included in Table I.

From the changes in appearance of the C-2 absorption in the nmr spectra of samples of brosylate recovered after partial acetolysis of I-3-*d*-OBs, Cristol³ concluded that there was internal return from ion pairs to

(4) B. Capon, M. J. Perkins, and C. W. Rees, "Organic Reaction Mechanisms, 1966," Interscience Publishers, New York, N. Y., 1967, p 25.

(5) S. J. Cristol, R. A. Sanchez, and T. C. Morrill, *J. Org. Chem.*, **31**, 2738 (1966).

(6) C. C. Lee and E. W. C. Wong, *J. Amer. Chem. Soc.*, **86**, 2752 (1964).

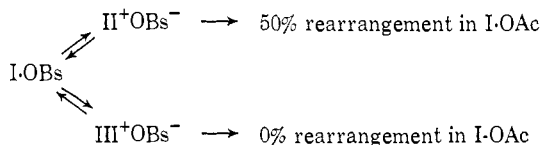
Table I. Percentage Rearrangement of Isotopic Label from C-2,3 to C-1,4-7 in the *exo*-Dehydro-2-norbornyl-*x-d* Acetate (I-*x-d*-OAc) from the Acetolysis of *exo*-Dehydro-2-norbornyl-2-*d* Brosylate (I-2-*d*-OBs) under Various Conditions

Experimental conditions	% rearrangement		
	Present results Ms	Nmr ^a	Previous results
0.48 M I-2- <i>d</i> -OBs, 1.1 equiv of KOAc, 45°, 1 hr	35	33	38 ^b
0.24 M I-2- <i>d</i> -OBs, 10 equiv of NaOAc, 24°, 11 hr	50	46	49.0; 47.5 ^c
0.48 M I-2- <i>d</i> -OBs, 1.1 equiv of KOAc, 65°, 1 hr	43	43	
0.48 M I-2- <i>d</i> -OBs, 1.1 equiv of KOAc, 14°, 8 days	51	50	

^a The nmr data gave the per cent rearrangement from C-2 to C-1,3-7. ^b From acetolysis of I-2,3-¹⁴C-OBs, ref 2. The acetolysis of *endo*-dehydro-2-norbornyl-2-*d* brosylate at reflux temperature for 48 and 96 hr gave, respectively, 27 and 29% rearrangement, in substantial agreement with the 30% rearrangement reported in ref 2 for the acetolysis of *endo*-dehydro-2-norbornyl-2,3-¹⁴C₂ brosylate at reflux temperature for 48 hr. ^c From acetolysis of I-3-*d*-OBs, ref 3.

scrambled brosylate. This conclusion has been confirmed in the present work. The H absorption at C-2 in the nmr spectra of the brosylate recovered after acetolysis of 0.48 M I-2-*d*-OBs in the presence of 10% excess KOAc at 25° for 30, 60, and 90 min, respectively, showed 10, 15, and 19% rearrangement of the D label from C-2 to C-1,3-7.

The temperature effects on the extents of rearrangement (Table I) may be rationalized by assuming that in the formation of the I-OAc product, competitive reactions involving two ion pairs could occur. At the



lower temperatures of 14 or 24°, the I-OAc could arise only from an ion pair, the cationic part of which would be symmetrical such as II, giving rise to 50% rearrangement. At higher temperatures, formation of ion pair III⁺OBs⁻ became competitive, with the homoallylic cation III leading to isotopically unrearranged I-OAc. The net I-OAc product from both II and III would show less than 50% rearrangement. Concurrently, internal returns would produce isotopically scrambled I-OBs which could subsequently solvolyze and contribute to the overall scrambling. When the reaction was carried out at 65° instead of 45°, there could be more extensive equilibrations between I-OBs and II⁺OBs⁻ via internal returns; thus the overall rearrangement in the I-OAc was greater at 65° than at 45°. The present results could not eliminate the possibility that at 45 and 65°, interconversion between II⁺OBs⁻ and III⁺OBs⁻ might take place in conjunction with their competitive formation; such consecutive transformations between unsymmetrical and symmetrical ions have originally been suggested by Roberts.² The present data and the results of Cristols,³ however, indicate that at 14 or 24°,

the I-OAc product from the acetolysis of I-OBs arose essentially only from a symmetrical cationic intermediate; the formation of unsymmetrical ion III apparently was too slow to compete at these temperatures.

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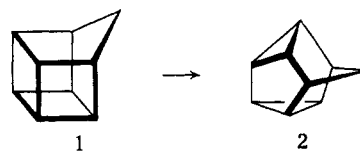
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Silver Ion Catalyzed Rearrangements of Strained σ Bonds. Application to the Homocubyl and 1,1'-Bishomocubyl Systems

Sir:

The correlation of orbital symmetry conservation with the concertedness of many thermal and photochemical reactions has enjoyed outstanding recent success.¹ Despite these developments, surprisingly little is known about the capability of heavy metal ions to affect the molecular orbitals of reactants in a fashion which causes an otherwise forbidden bond reorganization to become allowed.² We now describe a remarkably facile skeletal isomerization of homocubane and 1,1'-bishomocubane derivatives which occurs uniquely in the presence of a heavy metal ion (e.g., Ag⁺).

When dilute CDCl₃ or acetone-*d*₆ solutions of homocubane (1), mp 104–105°,³ are treated with catalytic amounts of silver fluoroborate, the hydrocarbon is converted quantitatively to pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (2), mp 87–88°,⁴ within 1 day at 25° (nmr analysis and isolation). In the absence of silver ion,

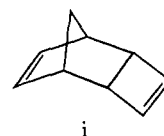


1 is stable to 240°.³ Since the rearrangement of 1 to 2 is the formal result of a symmetry disallowed $\sigma_{2a} + \sigma_{2a}$ electrocyclic reaction, the indicated geometric changes (3) are expected to be associated with a high

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