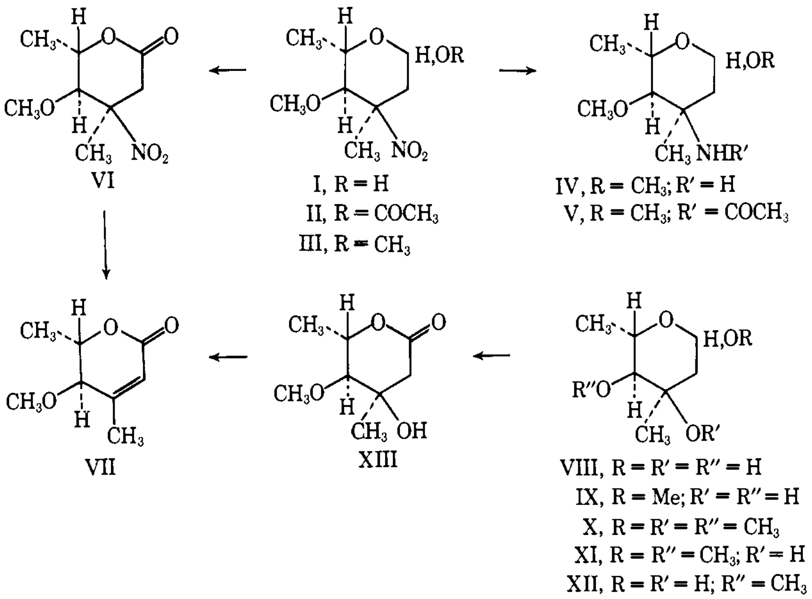

obtained chemically as follows. Evernitrose methyl glycoside (III), prepared by allowing evernitrose to react with methanolic hydrogen chloride, was catalytically hydrogenated[4] using 10% palladium on charcoal, to afford the amine IV, λ_{max} 3 μ (amino), no absorption for the nitro group. The amine was characterized as its acetyl derivative, V, $C_{11}H_{21}NO_4$; mp 114–115°, $[\alpha]D$ $-30°$; λ_{max} 3.0 (NH), 5.94 μ (amide). The nmr spectrum showed the presence of an acetamido methyl signal at δ 1.95 which is suggestive of the axial configuration of the acetamido group in V. It has been predicted[5] that the expected range for axial acetamido groups on carbon bearing methyl would be δ 1.93–1.86, compared to δ 1.87–1.78 for their equatorial counterparts. In the absence of any suitable example of an axially oriented acetamido group on a fully substituted carbon atom our assignment of configuration at C_3 is tentative.

Evernitrose (I) on oxidation with bromine water yielded a δ lactone (VI), $C_8H_{13}NO_5$; mp 63–64°, $[\alpha]D$ $-70°$; λ_{max} 5.69 (δ lactone), 6.44 μ (nitro), no hydroxyl absorption. The nmr spectrum of VI showed an AB pair of doublets centered at δ 3.10 (J = 18 cps), a secondary methyl at δ 1.50 (J = 6.5 cps), a tertiary methyl at δ 1.70, a methoxyl at δ 3.51, a one-proton doublet at δ 3.83 (J = 9 cps), and a one-proton octet at about δ 4.2. When refluxed with methanolic potassium acetate, δ lactone VI was smoothly converted to a colorless liquid (VII), $C_8H_{12}O_3$, sublimed at 40° (0.1 mm); $[\alpha]D$ $-38.6°$; $\lambda_{max}^{cyclohexane}$ 205 mμ (ϵ 11,200); λ_{max} 5.75 μ (α,β-unsaturated δ lactone), no absorption for the nitro group. The nmr spectrum showed the presence of a vinyl methyl at δ 2.10, a vinyl hydrogen at δ 5.83, a one-proton doublet at δ 3.60 (J = 7 cps), a one-proton quintet at δ 4.50 (J = 7 cps), a secondary methyl at δ 1.43 (J = 7 cps), and a methoxy at δ 3.50.

The above sequences of reactions establish the structure of evernitrose and its relative stereochemistry at C_4 and C_5.

In order to prove the gross structure of evernitrose unequivocally and also to assign the absolute stereochemistry at C_4 and C_5, compound VII has been synthesized from mycarose[6] (VIII) in the following way. Mycarose methyl glycoside (IX) on methylation[6a] using sodium hydride and methyl iodide gave a mixture of the 3,4-di-*O*-methyl derivative X and the 3-*O*-methyl derivative XI which was separated on a silica gel column. Mycarose 1,4-dimethyl ether (XI) on hydrolysis with aqueous acid yielded XII, $C_8H_{16}O_4$; mp 134–135°, $[\alpha]D$ $-19.3° \rightarrow -81.8°$ (24 hr). Oxidation with bromine water yielded the δ lactone XIII, $C_8H_{14}O_4$; mp 118–119°; $[\alpha]D$ $-71.5°$; λ_{max} 2.80, 5.70 μ. The nmr spectrum of XIII was consistent with the assigned structure. The δ lactone XIII, when refluxed in benzene solution in the presence of a catalytic amount of *p*-toluenesulfonic acid, yielded the desired α,β-unsaturated δ lactone VII, $[\alpha]D$ $-37.5°$, which was identical (ir, uv, nmr, tlc) with the sample of the α,β-unsaturated lactone obtained from I. The synthesis of VII from mycarose (VIII) proves the gross structure of evernitrose (I) and also its absolute stereochemistry at C_4 and C_5 as 4-*O*-methyl-3-*C*-methyl-3-nitro-2,3,6-trideoxy-L-*ribo*- (or -*arabino*) hexose.

Acknowledgment. We wish to express our thanks to Mr. M. Yudis for many helpful discussions in the interpretation of the nmr spectra.

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[6] (a) D. M. Lemal, P. D. Pacht, and R. B. Woodward, *Tetrahedron*, **18**, 1275 (1962); (b) W. Hofheinz, H. Grisebach, and H. Friebolin, *ibid.*, **18**, 1265 (1962).

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Photochemical Interconversion of Cyclooctatetraene Bond Shift Isomers[1]

Sir:

The rates of bond shift in cyclooctatetraene and a number of its derivatives have been determined by nuclear magnetic resonance spectroscopy.[2] In all the

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[1] This work was supported by the National Science Foundation, Grant No. G. P. 6620.

[2] (a) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 671 (1962); (b) G. M. Whitesides and J. D. Roberts, unpublished work (*cf.* J. D. Roberts,

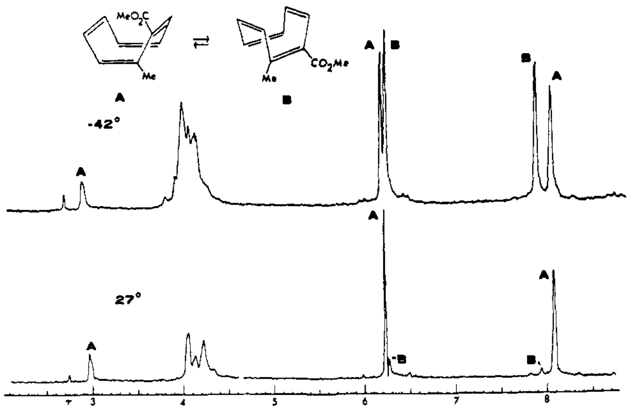

Figure 1. Nmr spectra (100 MHz) of methyl 2-methylcyclooctatetraenecarboxylate (I). The top spectrum is that of an irradiated sample of I.

compounds investigated so far the bond shifts are degenerate, and thus bond shift isomers are not possible. However, in 1,2-disubstituted cyclooctatetraenes bond shift isomers can exist. We have now studied several such compounds and have found that the two bond-shift isomers can be interconverted photochemically.

The nmr spectrum of methyl 2-methylcyclooctatetraenecarboxylate[3] (I) is shown in Figure 1. The two bond-shift isomers A and B are present in the ratio of about 17:1. The minor isomer B has its methyl bands clearly separated from those of the major isomer A. The band at τ 2.97 is attributed[2c] to the proton on C-8, adjacent to the carbomethoxy group in A. Irradiation (3500 Å) of I in $CDCl_3$ at -30 to $-50°$ for 6 hr gave a solution whose nmr spectrum (Figure 1, measured at $-42°$) showed that isomer B was now present in slightly greater amount than isomer A. This spectrum also clearly shows that B is not a bicyclic valency isomer of A since such a compound should have[4] methine bands at about τ 6.7. When the temperature was raised to $-12°$ a gradual transformation of B into A occurred until equilibrium amounts of A and B were obtained. The rate constant for the B → A transformation was about 1×10^{-3} sec^{-1}, giving $\Delta F^{\ddagger} = 18.8$ kcal/mol.

The nmr spectrum of I was also determined above room temperature in dimethyl-d_6 sulfoxide. The two ester methyl bands coalesced at about 80°, while the two ring methyl bands coalesced at about 90°. The low-field band (τ 2.97) in isomer A broadened and moved upfield with increasing temperature. At these temperatures bond shift is becoming fast on the nmr time scale. Preliminary calculations show that $\Delta F^{\ddagger} = 19.5$ kcal/mol at about 90°. This is one of the few known systems where kinetic parameters can be obtained on the same compound by both line-shape and direct equilibration methods.[5] More accurate data on this system are being obtained.

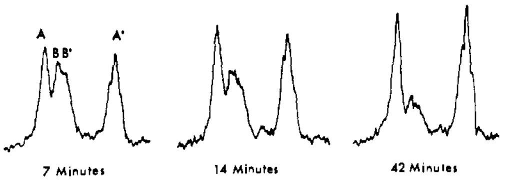

Figure 2. Variation with time of the ring methyl bands (100 MHz) of a sample of II irradiated at -30 to $-50°$. The times indicated are the elapsed times after warming to $-5°$. The assignment of the low-field band as A and the high-field band as A′ is arbitrary.

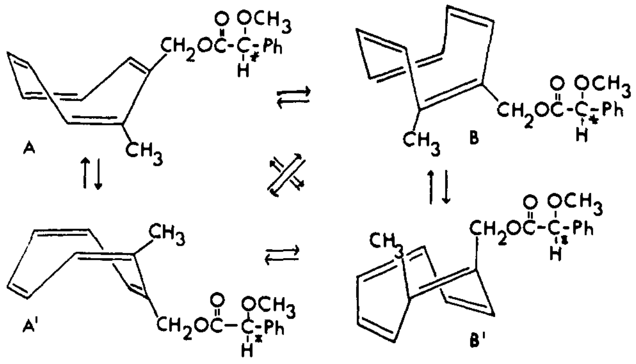

Figure 3. General kinetic scheme for ring inversion and bond shift in II.

The nmr spectrum of 2-methylcyclooctatetraenylmethyl O-methylmandelate (II)[6,7] shows two resolved ring methyl bands (τ 8.27 and 8.38) because of the presence of diastereomers A and A′ of the predominant bond shift state. There are also minor amounts (about 15% total) of the bond shift isomers B and B′ which give rise to virtually superposed methyl bands at τ 8.32. Only one methoxyl band was observed, and the methylene and methine proton bands were overlapped and very complex.

The ring methyl bands of A and A′ coalesce to a single line at 70° (60 MHz) because of rapid ring inversion. However, they do not coalesce with the methyl bands of B and B′ because at this temperature bond shift is slow on the nmr time scale.

When II was irradiated in $CDCl_3$ in the manner previously described for I, approximately equal amounts of isomers A and A′ and B and B′ were obtained, as shown by the nmr spectrum. When the solution was warmed to $-5°$, the BB′ bands gradually decreased while the A and A′ bands increased in intensity (Figure 2).[8]

Since the transition state for bond shift is expected to be planar,[2] or nearly so, the rate constants for A → B and A → B′ should be virtually identical. We are at present studying this system in more detail.

A general kinetic scheme for ring inversion and bond shift in II is shown in Figure 3. The vertical arrows represent ring inversion and the horizontal and diagonal

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J. Vsuenoe Chem., 7, 367 (1962); (c) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Am. Chem. Soc.*, **86**, 3576 (1964); D. E. Gwynn, G. M. Whitesides, and J. D. Roberts, *ibid.*, **87**, 2862 (1965); (e) J. F. M. Oth, R. Merenyi, Th. Martini, and G. Schröder, *Tetrahedron Letters*, 3087 (1966); (f) J. Stothers, personal communication.

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(7) II was obtained as an oil from *l*-O-methylmandelyl chloride and 2-(hydroxymethyl)methylcyclooctatetraene.[3] It was purified by chromatography on silica gel and showed a correct mass spectrum (molecular ion at *m/e* 296).

(8) The chemical shift of the BB′ ring-methyl bands had a marked temperature dependence, so that at $-42°$ these bands were superposed on the ring-methyl band of A.

arrows represent bond shifts. Of the 12 potentially different rate constants (arrows), only nine are independent of one another. In more symmetrical cyclooctatetraenes the kinetic scheme becomes simpler; this point will be discussed in a full paper.

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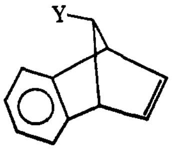
Bridged Polycyclic Compounds. LII. Retention of Configuration in Acetolysis of Epimeric 7-Chlorobenzonorbornadienes[1]

Sir:

Although there has been considerable interest in the solvolysis of homoallylic or homobenzylic systems and in the stereochemistry of such processes,[2] there appears to be no case described in the literature where both members of a set of epimers solvolyze with retention of configuration. Instead, even in those cases where participation by an apparently suitably disposed π-electron system could occur in both epimers,[2,3] solvolysis of one epimer occurs with retention of structure and configuration and that of the other with Wagner–Meerwein rearrangement. It appeared important to us to correct this deficiency, and our results are described in this and in the following communication.[4]

At the time we began our work, *syn*- and *anti*-7-substituted benzonorbornadienes (**1** and **2**) appeared to offer likely compounds for such a study, as a variety of *anti* compounds **2** had been described and had been shown to solvolyze with retention of configuration,[5–9] and it was also well established that participation by a double bond (as measured by rate enhancement) is substantially greater than that by a benzene ring.[5]



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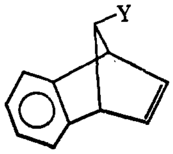

2

anti-7-Chlorobenzonorbornadiene (**2**-Cl) has already been described.[10] *syn*-7-Chlorobenzonorbornadiene (**1**-Cl), the first representative of the class of *syn*-7-substituted benzonorbornadienes, was obtained in an over-all yield of 70% from *exo*-5-acetoxy-*syn*-7-chlorobenzonorbornene[10] by converting the latter *via* the corresponding alcohol (transesterification in methanol with concentrated hydrochloric acid) to the *p*-bromobenzenesulfonate (standard procedure with *p*-bromobenzenesulfonyl chloride in pyridine). The latter gave **1**-Cl, mp 59–59.5°, in 90% yield upon treatment with potassium *t*-butoxide in hexamethylphosphoramide for 12 hr at 0°.

As anticipated, acetolyses of **1**-Cl and **2**-Cl proceed with complete retention of configuration at 81.9° in glacial acetic acid containing 1 vol % of acetic anhydride and 1 equiv of potassium acetate. **2**-Cl solvolyzed under these conditions with a first-order rate constant of 3×10^{-8} sec^{-1} cleanly to **2**-OAc, mp 56–57° (we estimate that vpc analysis would have shown 0.2% of other products). The rate of acetolysis of **1**-Cl is faster by a factor of 10^3, not including accelerative effects of added potassium acetate,[11] and yields **1**-OAc, mp 56–57°, with **2**-OAc mmp <25°, as the only detectable product. The configurations of these products was established by their nmr spectra,[12] which show clear evidence for either the presence or the absence of a long-range coupling[13,14] of 0.8 to 0.9 Hz between the vinylic protons and the bridge proton oriented *anti* to them (as in **2**) and thus establish the orientation of the 7 substituent. In *syn*-7-substituted benzonorbornadienes (**1**) the vinylic protons and the bridge proton give rise to clean triplets.

Our results clearly demonstrate the absence of any Wagner–Meerwein rearrangement in the acetolysis of either **1**-Cl or **2**-Cl. Homobenzylic or homoallylic stabilization is apparently sufficiently large so that the driving force for rearrangement to a benzylic cation as is seen in dihydro-**1**-OBs[9] is not of any consequence. The relative rates for the epimers suggest that the cation derived from **1**-Cl is of considerably greater stability. In spite of this, no epimeric acetate has been detected in the acetolysis of **2**-Cl, *i.e.*, there is no indication of leakage to products of the more stable carbonium ion system. The results observed are those we had anticipated when beginning this research, and in particular are consistent with recent nmr studies on the 7-norbornadienyl cation.[15,16] These studies showed that 7-norbornadienyl cation is unsymmetrical and that the energy barrier to interconversion to its mirror image is about 20 kcal/mol. Our results show simply that the epimers of the 7-benzonorbornadienyl cation are separated by an energy barrier great enough that coordination with acetic acid occurs much more rapidly than interconversion.

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(1) Previous paper in this series: S. J. Cristol and W. Y. Lim, *J. Org. Chem.*, in press.

(2) For leading references see: S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, **85**, 2875 (1963).

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(11) Potassium acetate was found to exert a substantial first-order accelerative effect on the rate of acetolysis of **1**-Cl but not on that of **2**-Cl. The rate for **1**-Cl was determined in the absence of potassium acetate and obtained as the initial rate ($k = 3 \times 10^{-5}$ sec^{-1}) from a rate plot indicative of approach of equilibrium. The equilibrium between **1**-Cl and **1**-OAc and hydrogen chloride could be reached readily from either direction. With an initial **1**-Cl concentration of 0.026 *M*, the equilibrium mixture contained 40% **1**-Cl and 60% **1**-OAc. Note that this latter experiment shows that the displacement goes in both directions with clean retention. The salt effects and the reactivities compared with analogs will be discussed in a later communication.

(12) Determined in carbon tetrachloride solution on a Varian A-60-A nmr spectrometer.

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