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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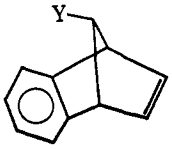
Received September 9, 1968

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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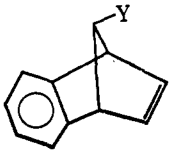

2

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).

(3) C. H. DePuy, I. A. Ogawa, and J. C. McDaniels, *ibid.*, **82**, 2397 (1960).

(4) S. J. Cristol and G. W. Nachtigall, *ibid.*, **90**, 7133 (1968).

(5) P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960).

(6) H. Tanida, *ibid.*, **85**, 1703 (1963).

(7) H. Tanida, T. Tsuji, and H. Ishitobi, *ibid.*, **86**, 4904 (1964).

(8) H. Tanida and H. Ishitobi, *ibid.*, **88**, 3663 (1966).

(9) H. Tanida, Y. Hata, S. I. Ikegami, and H. Ishitobi, *ibid.*, **89**, 2928 (1967).

(10) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3727 (1967).

(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.

(13) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3738 (1967).

(14) M. E. Brennan and M. A. Battiste, *ibid.*, **33**, 324 (1968).

(15) P. R. Story, *J. Amer. Chem. Soc.*, **84**, 4876 (1962).

(16) M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, **89**, 6353, 6354 (1967).

Sciences. All new compounds had satisfactory elemental analyses (Galbraith Laboratories, Inc.).

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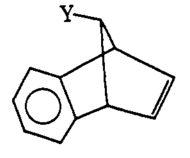
Bridged Polycyclic Compounds. LIII. Solvolyses of the Epimeric 7-Chlorobenzonorbornadienes and 5,12-Diphenyl-6,11-dihydro-6,11-(chloromethano)naphthacenes[1]

Sir:

The previous communication[1] showed that the cations formed by ionization of *syn*-7-chlorobenzonorbornadiene (**1**-Cl) and the *anti* epimer (**2**-Cl) are different and are not interconverted (or lost by Wagner–Meerwein rearrangement) during acetolysis. Instead **1**-Cl gives **1**-OAc cleanly and **2**-Cl gives **2**-OAc. These results are consistent with the formulation of the intermediate cations as **3** and **4** from **1** and **2**, respectively. Formulations **3** and **4** are derivative of others suggested for analogous species.[2]



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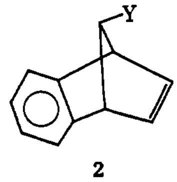

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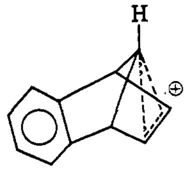

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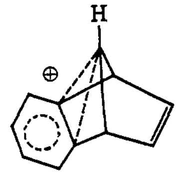

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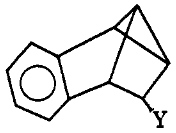
However, just as with the analogous *anti*-7-dehydronorbornyl and 7-norbornadienyl cations,[3-8] tricyclo[4.1.0.0^{4,7}]heptane derivatives are capturable with the cation which we have represented as **3**, although not from its presumed epimer **4**. Thus, treatment of **1**-Cl with 4 *M* sodium methoxide in methanol leads to substantial amounts of **5**-OCH$_3$, along with **1**-OCH$_3$. **5**-OCH$_3$ rearranges completely under acid conditions to **1**-OCH$_3$. The formation of **5**-OCH$_3$ from **1**-Cl raises the same question regarding our work that had been raised earlier[3,9] regarding the 7-norbornadienyl and *anti*-7-dehydronorbornyl cations, namely, that the ion resulting from **1** is a pair of rapidly equilibrating tricyclic ions, *viz.*, **6** and its enantiomorph. Here it might be assumed that **6** leads by direct coordination with nucleophiles to **5** or by geitonodesmic[10] reaction to **1** products, although the argument given by Winstein and his coworkers[7,8,11] against this suggestion seems equally well applicable to our case.



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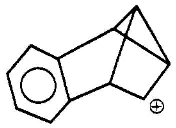

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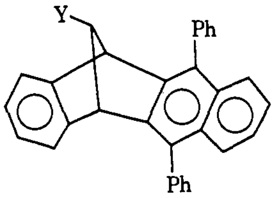

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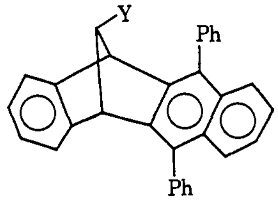

8

In view of the Brown–Deno objections and the peculiar kinetics observed[1] in the acetolysis of **1**-Cl (but not of **2**-Cl), we decided that it was worthwhile to study the acetolysis of an epimeric homobenzylic system where both participating π systems were aromatic rings. It has been shown[12] that 7-dibenzonorbornadienyl *p*-bromobenzenesulfonate solvolyzes without rearrangement, so that substituted analogs seemed likely prospects for stereochemical study. **2**-Cl was a particularly resistant dienophile, but use of 1,3-diphenylisobenzofuran[13] as a diene under conditions (benzene solution; 120–155° for up to 300 hr) which gave Diels–Alder addition followed by dehydration led to **7**-Cl, mp 309–310°, from **1**-Cl, and **8**-Cl, mp 194–195°, from **2**-Cl.

Compounds **7**-Cl and **8**-Cl were subjected to silver ion assisted acetolysis at 150–155° in glacial acetic acid containing 1.2 equiv of silver acetate. In 56 hr the reactions proceeded to the extent of 20% in the case of **7**-Cl and to the extent of 75% in the case of **8**-Cl, indicating that the compound with the *anti* benzene ring solvolyzes about six times faster than its epimer. The configurations at the 7 position of the chlorides **7** and **8** are known from their modes of formation. Their nmr spectra[14] show a two-proton doublet for the bridgehead protons and a one-proton triplet for the bridge proton ($J \sim 1.7$ Hz in each case). The bridge-proton triplet for **7**-Cl occurs at τ 5.42 while that for **8**-Cl occurs at τ 5.70, indicating a greater shielding power of the fused benzene ring over that of the fused diphenylnaphthalene system. Consequently, the same relative chemical shift order may be expected for the bridge protons of the acetates **7** and **8**, but for their acetoxy methyl groups the shielding effect should be in the opposite order. This is what is observed. The acetate **7** has its H-7 triplet at τ 4.78 and its methyl resonance at τ 8.22, while for the **8**-OAc the H-7 triplet occurs at τ 4.96 and the methyl singlet at τ 8.15. It is noteworthy that the relative shielding power of the fused aromatic moieties, supposedly an indication of the strengths of the induced ring currents and therefore a possible measure of electron availability, correlates

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(1) Previous paper in this series: S. J. Cristol and G. W. Nachtigall, *J. Amer. Chem. Soc.*, **90**, 7132 (1968).

(2) See footnotes 5–9, 15, and 16 in ref 1.

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

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

(5) H. Tanida and Y. Hata, *J. Org. Chem.*, **30**, 977 (1965).

(6) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **88**, 864 (1966).

(7) A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966).

(8) M. Brookhart, A. Diaz, and S. Winstein, *ibid.*, **88**, 3135 (1966).

(9) N. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

(10) S. J. Cristol, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Amer. Chem. Soc.*, **87**, 2879 (1965).

(11) M. Brookhart, R. K. Lustgarten, and S. Winstein, *ibid.*, **89**, 6352 (1967).

(12) J. Meinwald and E. G. Miller, *Tetrahedron Letters*, 253 (1961).

(13) M. S. Newman, *J. Org. Chem.*, **26**, 2630 (1961); M. P. Cava and F. M. Scheel, *ibid.*, **32**, 1304 (1967).

(14) Spectra for compounds 7 and 8 were determined in deuteriochloroform solution on a Varian A-60-A nmr spectrometer.