

requires H-12 and H-13 to be in the positions shown, they were placed there for the final refinement cycles and for Figure 1.

Bond lengths calculated using ORFFE<sup>5</sup> are given on an ORTEP<sup>6</sup> plot in Figure 1, and bond angles are listed in Table I.

### Discussion

In the crystals under study, as has been postulated for solutions,<sup>7</sup> 10-methylisalloxazine is protonated on N-1. Other riboflavin derivatives have also been shown to be protonated at this position in the crystalline state.<sup>1</sup>

The bond lengths found for the cation are very close to those reported by Fritchie and Trus<sup>10</sup> and close to those in related structures.<sup>1a,b</sup> The long C-4-C-4a bond and the short C-4a-N-5 bond have been observed in all three of these structures.

All of the atoms except H-11 lie close to sheets of  $P_g$  symmetry parallel to the 102 plane. There are parts of six such sheets in the unit cell chosen, spaced 3.264 Å apart, starting from 408. The least squares plane calculated from the 17 nonhydrogen atoms of the cation is inclined 1.6° from the 102 plane. The standard deviation of the atoms defining the plane from the plane is only 0.053, with the deviations occurring primarily as a slight bow along the long axis of the molecule. This bow, which is quite possibly absent in solution, is probably present in the crystal to permit reasonable distances between bromide ion and N-3 in adjacent sheets [these atoms are 3.463(9) Å apart] and bromide and N-10 in adjacent sheets in the other direction [3.364(9) Å apart].

Figure 1 shows the intrasheet hydrogen bonds as dotted lines. The distances between nonhydrogen

atoms joined through hydrogen bonds are unexceptional. The values in angstroms are: N-1-O-1, 2.883 (13); O-1-O(C-4), 2.886 (10); O-1-O-2, 2.767 (11); N-3-Br, 3.433 (10); O-2-Br, 3.291 (10).

The stacking arrangement of the sheets is governed primarily by the intersheet hydrogen bond involving H-11. The formation of strong intersheet hydrogen bonds requires the water oxygens to move closer to one another [intersheet O-1-O-2 distance, 2.983 (11) Å; H-11-O-1 distance, 2.09 (8) Å], and accounts for their large deviations from the molecular plane. O-1 moves farther out of the plane than O-2, presumably to give both oxygens better tetrahedral coordination [the fourth coordination for O-2 is provided by interaction with N-10, 3.235 (10) Å away]. The bromine is sandwiched between two nitrogens with partial positive charges, N-3 and N-10, as noted above. It also serves as a hydrogen-bond acceptor for N-3 and O-2, giving it roughly square-planar coordination. An H-2 and H-4 in the same sheet are nearly close enough [2.79 (8) and 2.85 (8) Å, respectively] and at the right angle to complete an octahedral arrangement around bromide ion.

Registry No.—I, 23653-16-9.

**Acknowledgments.**—We thank G. Tollin and D. E. Fleischman of this Department for suggesting this problem and furnishing the crystals; the University of Pittsburgh Crystallography Laboratory and the Oak Ridge National Laboratory for programs; H. S. Craig and R. D. and S. H. Jay for assistance with programming; the Numerical Analysis Laboratory of the University of Arizona for computer time; and the PHS (GM-12447), Sloan Foundation (Fellowship to R. B. B.), and NSF (URP support to T. C. S.) for financial assistance.

(5) W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-306, Oak Ridge National Laboratory, 1964.

(6) C. K. Johnson, ORNL-3794.

(7) K. Dudley, A. Ehrenberg, P. Hennerich, and F. Muller, *Helv. Chim. Acta*, **47**, 1354 (1964).

## Conversion of Some Bicycloheptanols into Chlorides Using Triphenylphosphine-Carbon Tetrachloride. Stereochemistry and Mechanistic Implications

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Received August 25, 1969

The reaction of triphenylphosphine and carbon tetrachloride with *exo,exo*-2,3-dideuterio-*anti*-7-hydroxybicyclo[2.2.1]heptane affords *exo,exo*-2,3-dideuterio-*syn*-7-chlorobicyclo[2.2.1]heptane, exclusively. The isolated products from *exo,exo*-3,4-dideuterio-*exo*-2-hydroxybicyclo[3.2.0]heptane are *exo,exo*-3,4-dideuterio-*endo*-2-chlorobicyclo[3.2.0]heptane and *exo,exo*-2,3-dideuterio-*anti*-7-chlorobicyclo[2.2.1]heptane. With the aid of a comparison between the inversion found in these reactions and the predominant retention of configuration found in the products of solvolysis of the esters of the above alcohols, a tentative mechanistic rationale is presented to account for our observations.

A previous report<sup>1b</sup> has demonstrated that the reaction of triphenylphosphine and carbon tetrachloride with alcohols to give alkyl chlorides has remarkable



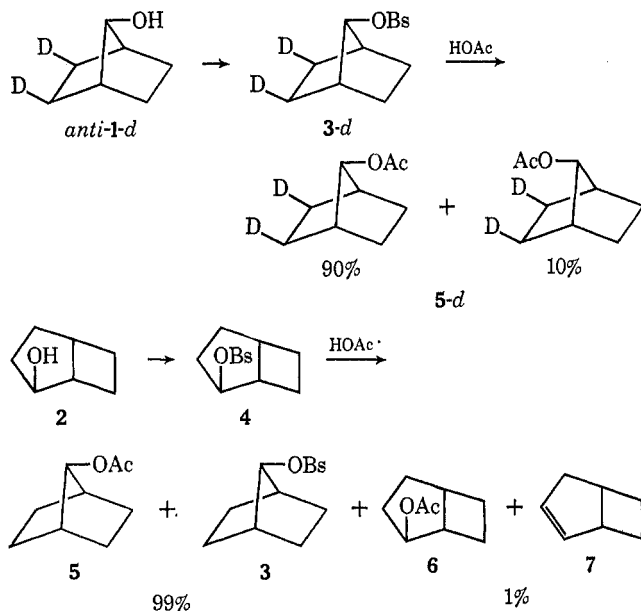
tendency for inversion, even in cases where solvolysis of the corresponding esters is largely or completely

assisted and the solvolysis products exhibit retained configurations. It is known also that such conversions occur with little or no skeletal rearrangement in those systems where  $\text{S}_{\text{N}}1$  reactions afford extensively rearranged products.<sup>1b,2</sup> To further elucidate the scope of this reaction, the course of reaction with alcohols 1 and 2 was determined.

(1) (a) To whom correspondence should be addressed: East Tennessee State University, Johnson City, Tenn. 37601. (b) R. G. Weiss and E. I. Snyder, *Chem. Commun.*, 1358 (1968).

(2) R. G. Weiss, Ph.D. Thesis, University of Connecticut, 1969; I. M. Downie, J. B. Holmes, and J. B. Lee, *Chem. Ind. (London)*, 900 (1966).

The acetolysis of **3-d** has been shown to proceed with 90% retention of configuration,<sup>3,4</sup> whereas that of **4** leads to a predominance of **5** and traces of **6** and **7**.<sup>5</sup> Both **3** and **4** share the same reaction coordinate during much of the acetolysis reaction, as has been discussed by Winstein and coworkers<sup>5</sup> and Miles.<sup>3</sup>

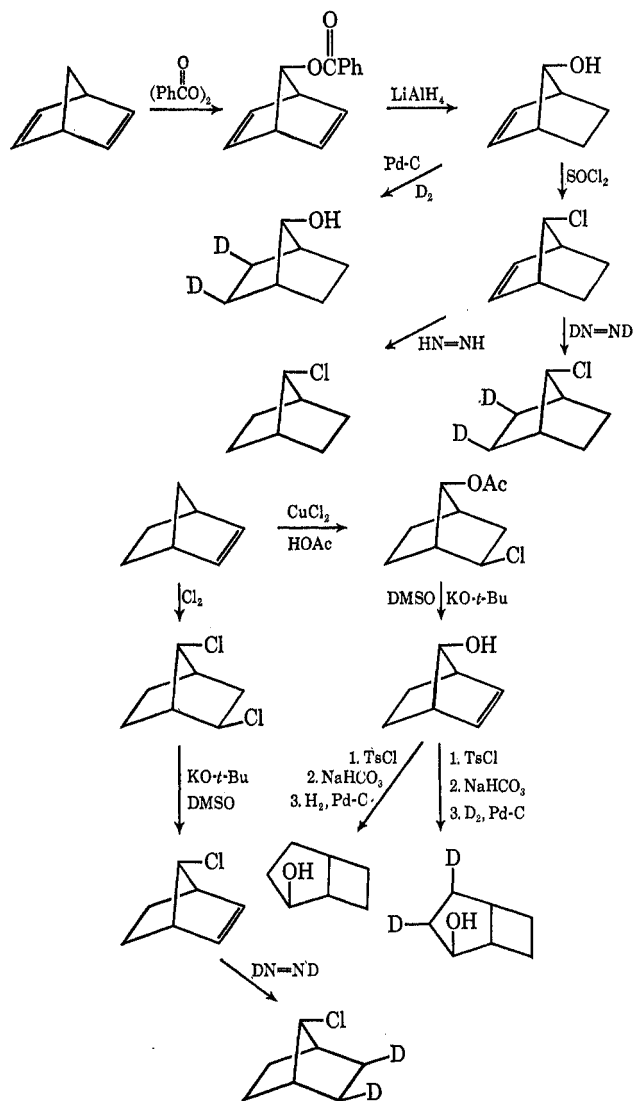


### Results

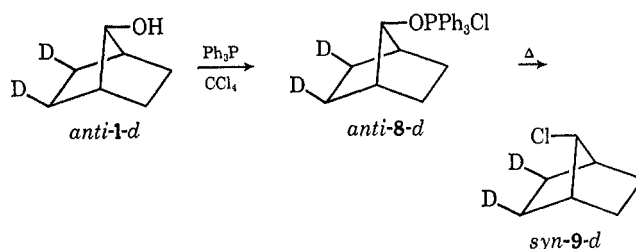
**Reactions of 1.**—Reaction of equimolar quantities of **1** and triphenylphosphine in carbon tetrachloride produces **8** as an oil which solidifies when solvent is removed. The structure of **8** was ascertained from its pyrolysis products, **9** and triphenylphosphine oxide, from its nmr spectrum,<sup>6</sup> and by analogy to work of Schaefer and Weinberg<sup>8</sup> on the Wiley<sup>9</sup> reaction. The structure of **9** was confirmed by comparison of its melting point, vpc retention time, and nmr and infrared spectra with those of an authentic sample. Consistently, 50–60% yields of **9** were obtained, although optimum reaction conditions were not sought.

The stereochemistry of the conversion **1**  $\rightarrow$  **9** was determined using *exo,exo*-2,3-dideuterated alcohol. The route to dideuterated alcohol *anti*-1-d (Scheme I) assures the absence of *syn*-1-d. Independent synthesis of the isomeric dideuterated chlorides *syn*- and *anti*-9-d was achieved as shown in Scheme I. Facile differenti-

SCHEME I  
SYNTHESES OF DEUTERIUM-LABELLED COMPOUNDS



ation of the *syn* and *anti* isomers of **9-d** was permitted by their distinct deuterium-decoupled nmr spectra (see Figure 1). The product from *anti*-1-d is obviously *syn*-9-d (Figure 1c). Independent control experiments showed that  $\geq 5\%$  *anti*-9-d is readily detected in a *syn-anti* mixture of chlorides **9-d**, so that reaction has proceeded with  $\geq 95\%$  inversion. When the decomposition of intermediate **8** was monitored, both its rate of disappearance and the rate of formation of **9** were roughly first order in **8**.



**Reactions of 2.**—In our hands, the method of Winstein<sup>10</sup> did not result in pure **2** despite numerous attempts. Alcohol,  $\geq 90\%$  pure by nmr, vpc, and in-

(3) F. B. Miles, *J. Amer. Chem. Soc.*, **90**, 1265 (1968).  
 (4) P. G. Gassman and J. M. Hornback, *ibid.*, **89**, 2487 (1967).  
 (5) S. Winstein, F. Gadiant, E. T. Stafford, and P. E. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).  
 (6) The nmr spectrum in either  $\text{D}_2\text{O}$  or  $\text{CDCl}_3$  showed high-field resonances clearly attributable to a 7-substituted bicyclo[3.3.1]heptane and low-field resonances in the phenyl region. Denney, Denney, and Wilson<sup>7</sup> have found  $J_{\text{POCH}} \cong 7$  cps ( $\text{CH}_2\text{Cl}_2$ ) for the pentacovalent structure i and for the ionic compounds ii and iii. In both  $\text{D}_2\text{O}$  and  $\text{CDCl}_3$ ,  $J_{\text{POCH}} \cong 7$  cps for **8**.  
 $\text{Ph}_3\text{P}(\text{OEt})_2$  (i)     $[\text{Ph}_3\text{POEt}]^+\text{BF}_4^-$  (ii)     $[\text{Bus}_2\text{POEt}]^+\text{BF}_4^-$  (iii)  
 (7) D. B. Denney, D. Z. Denney, and L. A. Wilson, *Tetrahedron Lett.*, **85** (1968).  
 (8) J. P. Schaefer and D. S. Weinberg, *J. Org. Chem.*, **30**, 2635, 2639 (1965). Compound iv was isolated and purified when **1** and bromotriphenylphosphonium bromide were mixed in triglyme. Upon pyrolysis above its melting point, iv produced triphenylphosphine oxide and 7-bromobicyclo[2.2.1]heptane. Halophosphoranes of *endo*-2-hydroxybicyclo[2.2.1]heptane and 1-hydroxybicyclo[2.2.1]heptane<sup>12</sup> have been isolated and pyrolyzed to the corresponding phosphine oxides and alkyl halides.  
 (9) G. Wiley, B. Rein, and R. Hershkowitz, *Tetrahedron Lett.*, 2509 (1964); G. Wiley, R. Hershkowitz, B. Rein, and B. Chung, *J. Amer. Chem. Soc.*, **86**, 964 (1964).  
 (10) S. Winstein and E. T. Stafford, *ibid.*, **79**, 505 (1957).

frared analyses, containing residual *exo*-2-hydroxybicyclo[3.2.0]hept-3-ene and a carbonyl-bearing compound, was used.<sup>11</sup>

Reaction of **2** with  $\text{Ph}_3\text{P}-\text{CCl}_4$  at  $65^\circ$  for short periods ( $\leq 4$  hr) followed by solvent removal leaves a white solid whose structure is inferred from previous work<sup>8,12</sup> (see above) and from its pyrolysis products (triphenylphosphine oxide, **9**, and **10**) to be a mixture of **8** and **11**. The presence of *syn*-**8-d** during the reaction of **2-d** is inferred from the observation that *anti*-**9-d** comprises at least 90% of the rearranged chloride (see Figure 1d)<sup>13</sup> and the knowledge from the previous section that decomposition of *anti*-**8-d** occurs with inversion of configuration.

The ratio of **10**:**9** obtained from the pyrolyses of the residue from **2**, triphenylphosphine, and carbon tetrachloride appears to be a function of pyrolysis temperature and duration. The results are summarized in Table I.<sup>14</sup>

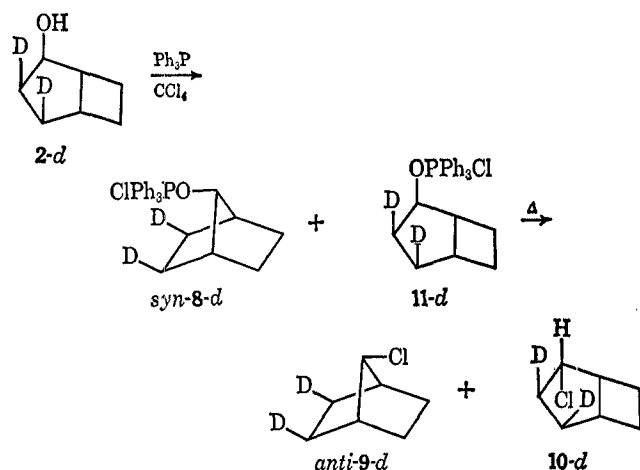


TABLE I  
REACTIONS OF **2** WITH TRIPHENYLPHOSPHINE  
AND CARBON TETRACHLORIDE

Run	Reaction time, hr	Temp, $^\circ\text{C}$	—Pyrolysis of salts—		Product ratio <sup>a</sup> 10 to <b>9</b>
			Temp, $^\circ\text{C}$	Time, min	
1	65	Ambient room			33:7.5 <sup>b</sup>
2	3.5	60–65	80–160	30	3:97 <sup>c</sup>
3	3.5	60–65	70–180	15	1:3
4	6	60			1.83:1 <sup>b</sup>
			60–135		3:8
5 <sup>d</sup>	3.5	60–65	70–180	20	13:87

<sup>a</sup> Ratios were determined by direct comparison of vpc peak weights. <sup>b</sup> Ratio of **10** to **9** present in the reaction solvent prior to pyrolysis of the residue. <sup>c</sup> Deuterated substrate, **2-d**. <sup>d</sup> Contained a third, unidentified product.

The stereochemistry of the catalytic deuteration of *exo*-2-hydroxybicyclo[3.2.0]hept-3-ene is not known.

(11) The role of the impurities during reaction of **2-d** is not known. Although they are not expected to alter the product stereochemistry, they may have influenced the ratio of *anti*-**9-d** to **10-d**.

(12) D. B. Denney and R. R. DiLeone, *J. Amer. Chem. Soc.*, **84**, 4737 (1962).

(13) Control experiments showed that 10% *syn* **9-d** is detected in a *syn-anti* mixture of chlorides **9-d**.

(14) The results from reaction of **2** with  $\text{Ph}_3\text{P}-\text{CCl}_4$  at  $\leq 65^\circ$  over extended times are puzzling. Although rearranged chloride, **9**, is formed, other experiments suggest that the oxyphosphorane **8** is thermally stable under these conditions. If both statements above are valid, then the sequence **2**  $\rightarrow$  **8**  $\rightarrow$  **9** cannot be correct, at least at these temperatures. We note that the absolute yields of **9** formed under these conditions is small, and that we have insufficient data to resolve this point at present.

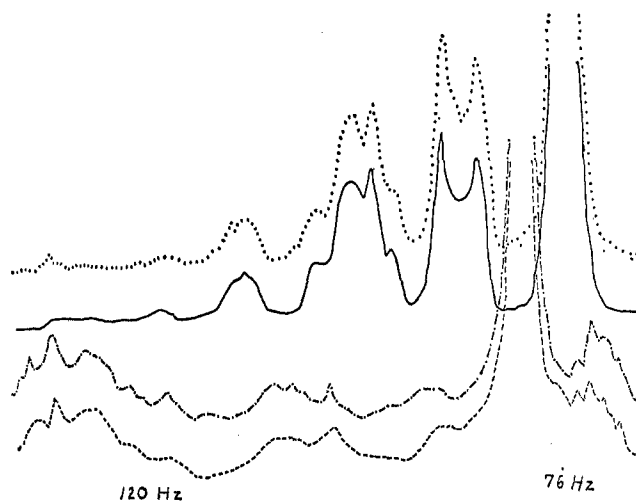
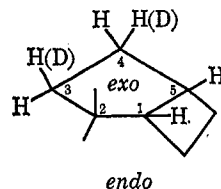


Figure 1.—Nmr spectra of *exo,exo*-2,3-dideuterio-*syn*-7-chloro[2.2.1]heptane (....), chloride from *exo,exo*-2,3-dideuterio-*anti*-7-hydroxybicyclo[2.2.1]heptane (—), *exo,exo*-2,3-dideuterio-*anti*-7-chlorobicyclo[2.2.1]heptane (---), and chloride from *exo,exo*-3,4-dideuterio-*exo*-2-hydroxybicyclo[3.2.0]heptane (----).

By analogy to the deuteration of bicyclo[2.2.1]heptene<sup>15</sup> and from comparison of the nmr spectra of deuterated and undeuterated **2** (see below), the deuteriums are assigned as 3,4-*exo* in **2-d**.

Chloride products from runs 3 and 5 were isolated by vpc. The compound of shorter retention time in run 3 was identified as **9** by comparison of its vpc retention time, melting point, mass spectrum, and nmr spectrum with those of an authentic sample. The compound of shorter retention time of run 5 was identified similarly as *anti*-**9-d**.<sup>13</sup> The longer retention time compounds of runs 3 and 5 were **10** and **10-d**, respectively. Although the mass spectra of **10** and **10-d** are nearly identical with those of **9** and *anti*-**9-d**, their infrared spectra and vpc retention times are distinctly different. The high-field portions of the nmr spectra are characteristic of a 2-substituted bicyclo[3.2.0]heptane skeleton.

The couplings of the low-field 2-proton resonances serve to determine the stereochemistry of **10**. (The arguments for the chlorides apply to the alcohols as well.) Molecular models of *endo* and *exo* 2-substituted bicyclo[3.2.0]heptanes show that the 1-bridgehead proton is geometrically disposed to couple very strongly with an *exo* 2 proton but very weakly with an *endo* 3 proton. Owing to ring puckering an *exo* 3 proton couples weakly with both *exo* and *endo* 2 protons and an *endo* 3 proton couples strongly with both *exo* and *endo* 2 protons. Therefore, an *endo* 2 proton (substituent



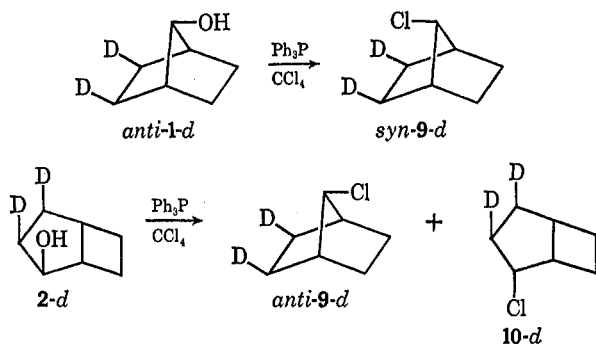
*exo*) should exhibit an AX, and an *exo* 2 proton (substituent *endo*) should exhibit an ABX pattern, where it is assumed that the weak couplings are much less than the major couplings (first-order analysis). Consistent

(15) B. Franzus, W. C. Baird, Jr., and J. H. SurrIDGE, *J. Org. Chem.*, **33**, 1288 (1968).

with this interpretation, doublets are observed for the 2 protons of **2** and **2-d**, whereas rough quartets are observed for the comparable protons of **10** and **10-d**.

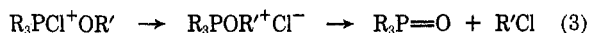
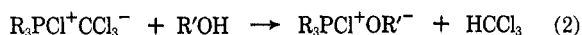
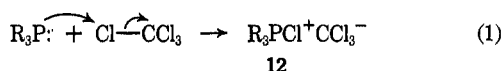
### Discussion

Reaction of neither **1** nor **2** with triphenylphosphine and carbon tetrachloride exhibit  $S_N1$  characteristics. Solvolyses products of *anti*-**3-d** are formed with 80–90% retention of configuration;<sup>3,4</sup> solvolysis products of **4** are predominantly rearranged (7-norbornyl), presumably with substituent *syn* to C-3–C-4 of **4**, but the unrearranged portion is of retained configuration exclusively.<sup>5</sup> In contrast, we find that *anti*-**1-d** is converted into *syn*-**9-d** exclusively and **2-d** yields *anti*-**9-d** and inverted unrearranged **10-d**.

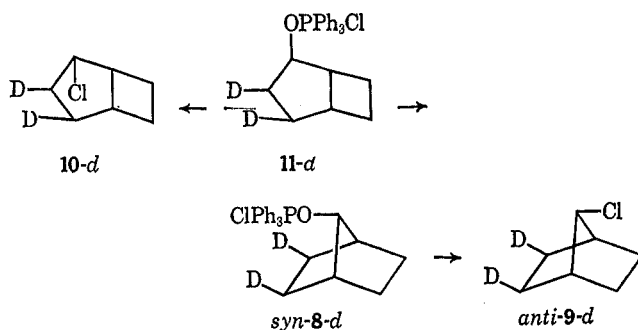


Nonsolvolytic displacement reactions at the 7 position of norbornanes are difficult and to our knowledge the only other such reaction where the stereochemistry has been determined<sup>16</sup> also proceeds with inversion.

As has been shown by Downie, Lee, and Matough<sup>17</sup> and by Ried and Appel,<sup>18</sup> phosphines attack carbon tetrachloride at chlorine, forming a chlorophosphonium trichloromethide salt, **12**, which reacts with alcohols as shown below.



That [3.2.0] and [2.2.1] products are obtained from **2-d** indicates that **11-d** decomposes by two pathways. The easiest way for us to explain the formation of *anti*-**9-d** is by internal return to *syn*-**8-d** followed by its decomposition to *anti*-**9-d**. The energy of activation



for internal return must be comparable with that for formation of **10-d** since both products are formed in similar amounts.

But the existence of a cationoid intermediate poses the dilemma that it should collapse by front-side attack, in analogy to the work of Miles<sup>3</sup> and Gassman,<sup>4</sup> whereas the experimental results show that under 10% of the chloride is formed by this route. This means that either the ion pair formed,  $\text{R}^+\text{OPPh}_3\text{Cl}^-$ , is so "tight" that it does not react with external nucleophile or that nucleophilic species are absent. Since added external nucleophile (cyanide) does not compete with chlorine in the homogeneous decomposition of the 2-phenylethoxyphosphorane,<sup>19</sup> there is some evidence supporting the former contention. Similarly pyrolysis of an admixture of **8** and sodium cyanide affords only chloride.

The observed propensity for inversion accords with a modified  $S_N2$  reaction (eq 3). However, it must be recognized that under reaction conditions (pyrolysis for **1** and **2**, carbon tetrachloride solution for other alcohols) chloride ion, if present, must be part of a quite tight ion pair,  $\text{R}^+\text{OPPh}_3^+\text{Cl}^-$ . (Note the distinction between this ion pair and that, discussed above, resulting from C–O heterolysis.) That external nucleophiles do not compete with chloride in decomposition of the oxyphosphoranes such as **8**, and that (admittedly rough) kinetic data point to a first-order decomposition of oxyphosphorane, requires product formation either *via* a tight ion pair or an intramolecular covalent decomposition. On this basis we suggest that a reasonable reaction mechanism involves intramolecular, reasonably concerted decomposition of the oxyphosphoranes **8** and **11**. An activated complex in which P–Cl and C–O bond cleavage are concerted with C–Cl and P=O bond formation affords the high energy of the latter bond as an effective driving force which is probably responsible for the relative facility with which reaction occurs.

The observed inversion places some rigid requirements on the reaction profile. If in nonpolar media we are dealing with pentavalent phosphorus as a trigonal bipyramid, then the most stable arrangement is one where both oxygen and chlorine are apical.<sup>20</sup> Product can not be formed directly from this conformer by a unimolecular decomposition unless ionic chloride wanders around the periphery in a tight ion pair, in which case one deals with a tetrahedral phosphorus as a cation. The operational distinction between a trigonal bipyramidal oxyphosphorane and a tight ion pair with tetrahedral phosphorous may even vanish. Alternatively, either apical oxygen or chlorine may be converted into the equatorial conformer by pseudorotation.<sup>21</sup> The feasibility of product formation from the latter conformer is suggested by inspection of models, which indicate that chlorine is some 2.0–2.5 Å from the carbon being substituted. If one requires that chlorine attack colinearly with oxygen to effect *inversion*, spatial requirements become too severe for reaction to occur directly from a trigonal bipyramid.

(19) R. G. Weiss and E. I. Snyder, submitted for publication.

(16) J. T. Lumb and G. H. Whitham, *Chem. Commun.*, 400 (1966). We thank a referee for calling this to our attention.

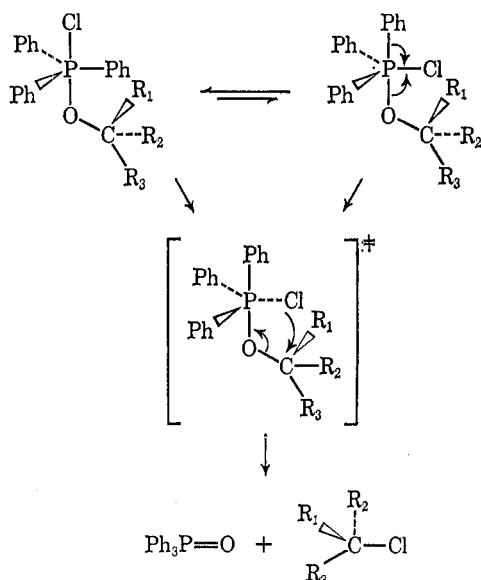
(17) I. M. Downie, J. B. Lee, and M. F. S. Matough, *ibid.*, 1350 (1968).

(18) W. Ried and H. Appel, *Justus Liebigs Ann. Chem.*, **679**, 51 (1964).

(20) E. Muettterties and R. Schunn, *Quart. Rev. (London)*, **20**, 245 (1966). The more electronegative substituents on a trigonal bipyramidal phosphorus atom assume the apical positions at equilibrium.

(21) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

It seems reasonable that P-Cl bond cleavage precedes somewhat C-O bond cleavage in a very tight ion pair.



This rationale is not without its difficulties. In particular, we fail to understand why a concerted, four-center decomposition with retention of configuration fails to occur. Models suggest that the latter is sterically less severe than an inversion process, and analogs of this process are known.<sup>22</sup> Nor do we understand the reluctance toward sufficient C-O bond cleavage to give a cation which behaves as do more typical cations. Thus neopentyl alcohol affords no rearranged products, and the neopentyl chloride is formed with inversion.<sup>19</sup> Even cyclopropyl alcohol reacts to give, in part, unrearranged cyclopropyl chloride.<sup>19</sup> It must be recognized explicitly that the mechanistic hypothesis presented has not yet been subjected to rigorous mechanistic tests and remains speculative at present.

### Experimental Section

Boiling and melting points (sealed capillary) are uncorrected. Infrared spectra were taken on a Perkin-Elmer Infracord spectrophotometer. Nmr spectra were recorded on a Varian Associates A-60 spectrometer using an NMR Specialties HD-60A decoupler when appropriate. Vpc analyses were performed on a Wilkens Aerograph chromatograph using the following columns (0.25 in. o.d.): column A, 15-ft 20% Ucon HB5100 on 40/60 Chromosorb W; column B, 10-ft 10% DC550 on 80/100 Chromosorb W, HMDS; column C, 10-ft 10% *p*-cresyl phosphate on 80/100 Chromosorb W, HMDS. Triphenylphosphine (Carlisle Chemical Co.) was recrystallized from cyclohexane-isopropyl alcohol and melted in a dry atmosphere prior to use. Carbon tetrachloride was stored over phosphorus pentoxide.

**anti-7-Hydroxybicyclo[2.2.1]heptene (anti-13).**—The method of Tanida and Tsuji<sup>23</sup> was used to prepare 7-benzoyloxybicyclo[2.2.1]heptadiene. Reduction with lithium aluminum hydride in ether<sup>24</sup> yielded *anti-13* containing 11% benzyl alcohol as determined by vpc analysis (A, 130°).

**exo,exo-2,3-Dideuterio-anti-7-hydroxybicyclo[2.2.1]heptane (anti-1-d).**—A solution of 2.3 g of crude *anti-13*, 0.25 g of Pd-C, and 50 ml of absolute methanol was shaken for 1 hr in a Paar bottle under 30 psi of deuterium gas.<sup>15</sup> The mixture was filtered through diatomaceous earth and the solvent was distilled. The residue was sublimed at 85° (1 mm) to yield 2.0 g of *anti-1-d*, mp 154–156.5°.

*Anal.*<sup>25</sup> Calcd for C<sub>7</sub>H<sub>10</sub>D<sub>2</sub>O: 16.66 atom % excess. Found: 16.60 atom % excess or 1.99 D per molecule.

**syn-7-Hydroxybicyclo[2.4.1]heptene (syn-13),** mp 80–86°, was prepared according to Baird.<sup>26</sup>

**7-Hydroxybicyclo[2.2.1]heptane (1).**—Reduction of *syn-13* over 10% Pd-C (0.58 mol %) at 20 psi of hydrogen afforded 1, mp 146–150° (lit.<sup>27</sup> mp 152–153°), after recrystallization from pentane and sublimation at 90° (1 atm).

**exo,exo-2,3-Dideuterio-anti-7-chlorobicyclo[2.2.1]heptane (anti-9-d).**—*anti-7*-Chlorobicyclo[2.2.1]heptane was prepared from *anti-13* by the method of Tanida and Hata.<sup>28</sup> A 6.7-g (0.105 mol) portion of acetic acid-*d*<sub>4</sub> (Stohler, 99.5% D) in 5 ml of methyl alcohol-*d* was slowly dripped into an ice-cooled, mechanically stirred mixture of the above olefin (2.06 g, 0.016 mol) and potassium azodicarboxylate<sup>29</sup> (9.3 g, 0.048 mol) in 20 ml of methanol-*d*. Stirring was continued overnight at room temperature. The mixture was diluted with water and extracted with pentane (three 25-ml portions). The combined organic phases were washed with water, dried (MgSO<sub>4</sub>), and distilled, bp 40°. The residue, 1.4 g (66%), was sublimed five times at 35–60° (1 atm) to yield *anti-9-d*,<sup>30</sup> mp 46–47°.

*Anal.* Calcd for C<sub>7</sub>H<sub>9</sub>D<sub>2</sub>Cl: 18.18 atom % excess. Found: 17.05 atom % excess or 1.87 D per molecule.

An undeuterated sample, 9, was prepared in an analogous fashion. Analyses by vpc (column A, 120°) of purified samples of 9 and *anti-9-d* showed no impurity.

**exo,exo-2,3-Dideuterio-syn-7-chlorobicyclo[2.2.1]heptane (syn-9-d).**—*syn,exo-2,7*-Dichlorobicyclo[2.2.1]heptane (14.3 g, 0.0867 mol), prepared according to Roberts, Johnson, and Carboni,<sup>31</sup> was stirred in a closed flask for 3.5 days with potassium *t*-butoxide (14.3 g, 0.13 mol) in 50 ml of dry dimethyl sulfoxide. The solution was diluted with water and extracted with pentane (four 75-ml portions). The combined pentane extracts were washed with water, dried (MgSO<sub>4</sub>), and distilled. By nmr and vpc (column B, 105°) analyses, the cut with a boiling point of 50° (16 mm) [lit. bp 45° (16 mm)], yield 10.7 g (96%), was >99% *syn-7*-chlorobicyclo[2.2.1]heptane. Reduction with potassium azodicarboxylate as described above yielded, after sublimations at 75° (77 mm) and 75° (1 atm), *syn-9-d* (61%).

*Anal.* Calcd for C<sub>7</sub>H<sub>9</sub>D<sub>2</sub>Cl: 18.18 atom % excess. Found: 16.20 atom % excess or 1.78 D per molecule.

**exo,exo-3,4-Dideuterio-*exo-2*-hydroxybicyclo[3.2.0]heptane (2-d).**—*exo-2*-Hydroxybicyclo[3.2.0]hept-3-ene, prepared by the method of Winstein and Stafford,<sup>32</sup> was reduced in absolute methanol using 5% Pd-C (0.13 mol %) under 20 psig of deuterium gas. The product, 2-*d*, was a viscous liquid.

*Anal.* Calcd for C<sub>7</sub>H<sub>10</sub>D<sub>2</sub>O: 16.66 atom % excess. Found: 14.60 atom % excess or 1.75 D per molecule.

An undeuterated sample of 2 was prepared in an analogous manner. By nmr and vpc (column C, 100°) analyses, the only noted impurity in 2 and 2-*d* was unreduced *exo-2*-hydroxybicyclo[3.2.0]hept-3-ene (<5%). In our hands, the purity of 2 and 2-*d* was not improved by repeated distillation, sublimation, and recrystallization.

**Reactions of Triphenylphosphine, Carbon Tetrachloride, and Alcohols. A. With *anti-1-d*.**—A solution of *anti-1-d* (1.14 g, 0.01 mol) and triphenylphosphine (2.88 g, 0.011 mol) in 6 ml of carbon tetrachloride was stirred in a closed flask for 24 hr at room temperature. Solvent was distilled at ≤35° (30 mm) in a dry atmosphere. The residue was heated slowly at 16 mm pressure to 175°. The distillate collected in a Dry Ice trap (1.15 g) was sublimed and eluted on a 1.5-g Florisil column first with pentane and then with methanol. Pentane was carefully distilled and the residue obtained was sublimed at 55–70° to give *syn-9-d* mp 43–45°.

*Anal.* Calcd for C<sub>7</sub>H<sub>9</sub>D<sub>2</sub>Cl: 18.18 atom % excess. Found: 17.90 atom % excess or 1.97 D per molecule. Distillation of the methanolic fraction left a solid whose nmr spectrum was that of *anti-1-d*.

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In a similar fashion, 1 was allowed to react to yield 9 (53%), mp 41–44°.

When the dried phosphonium salt 8 was heated in chloroform at 60° for 45 hr, no chloride 9 resulted.

**B. With 2-d.**—A solution of 2-d (1.14 g, 0.01 mol) and triphenylphosphine (2.88 g, 0.011 mol) in 6 ml of carbon tetrachloride was stirred in a dry atmosphere at 60–65° for 3.5 hr. The solvent was removed at 1 mm. By vpc analysis (column C, 100°), the distillate collected by slowly heating the residue to 180° (1 mm) contained a 13.3:86 ratio of 10-d to anti-9-d. Pure samples of anti-9-d and 10-d were collected by vpc (column C, 65°).

Similar reactions of 2 were conducted. Ratios of 10 to 9 varied from 3:97 for residue pyrolyzed at 160° (30 min) to 1:18: for pyrolysis at 60° (6 hr in carbon tetrachloride). The maximum yield for purified 9 and 10 in any run was 19% (30% crude).

**Isomerization Experiment of 10 and 9.**—A solution of 0.1 g of 9 and 10, 0.1 g of triphenylphosphine, and 0.1 g of triphenylphosphine oxide in 0.2 ml of chloroform was heated to 150° during 5 min. The ratios of 10 to 9 measured by vpc (column C, 100°) before and after heating were 1.0:3.0 and 1.0:3.1, respectively.

**Kinetically Followed Decomposition of 8.**—Crude 8 was prepared by stirring a solution of 1 (0.85 g, 7.6 mmol) and triphenylphosphine (2.15 g, 8.2 mmol) in 7 ml of carbon tetrachloride at 65° for 3.5 hr. Solvent was removed *in vacuo* and the residue

was twice shaken up in chloroform and precipitated with anhydrous ether. After being dried *in vacuo* over phosphorus pentoxide, 8 was dissolved in deuteriochloroform (1% TMS) and sealed in two nmr tubes. The tubes were heated at 120 ± 3° and the decomposition of 8 and appearance of 9 were monitored periodically by recording the nmr spectrum and integrating the signals of the 7 proton of 8 (4.82 ppm) and of 9 (3.94 ppm). Experimental plots of log [8] *vs.* time and log ([9]<sub>∞</sub> - [9]) *vs.* time were constructed. Both gave roughly straight-line slopes: for decomposition of 8,  $k \cong 7.7 \times 10^{-6} \text{ sec}^{-1}$ ; for formation of 9,  $k \cong 8.2 \times 10^{-6} \text{ sec}^{-1}$ .

**Registry No.**—Triphenylphosphine, 603-35-0; carbon tetrachloride, 56-23-5; anti-1-d, 23667-07-4; 2-d, 23667-08-5; 9, 765-80-0; anti-9-d, 23667-10-9; syn-9-d, 23754-34-9; 13, 13118-70-2.

**Acknowledgment.**—This work was made possible through support from the National Science Foundation and Petroleum Research Fund. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support.

## Vinylogous Imides. II. Ultraviolet Spectra and the Application of Woodward's Rules<sup>1,2</sup>

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Received July 7, 1969

The ultraviolet spectra of a variety of  $\beta$ -amino  $\alpha,\beta$ -unsaturated carbonyl compounds and their N-alkyl and N-acyl derivatives were examined with due regard for chromophore stereochemistry. Included in this study were 37 vinylogous amides,  $-\text{NC}=\text{CC}(\text{O})-$ ; 26 vinylogous imides,  $-(\text{O})\text{CNC}=\text{CC}(\text{O})-$ ; 13 vinylogous urethans,  $-\text{NC}=\text{CCOOR}$ ; and 2 vinylogous ureas,  $-\text{NC}=\text{CC}(\text{O})\text{N}-$ . Analysis of the relative locations of the  $\pi \rightarrow \pi^*$  transitions gave substituent increments of +75  $\mu$  for *cis*- $\beta$ -amino, +65  $\mu$  for *trans*- $\beta$ -amino, +10  $\mu$  for  $\beta$ -N-alkyl, -10  $\mu$  for  $\beta$ -N-acetyl, and +6  $\mu$  for  $\beta$ -N-benzoyl. These substituent constants can be used to distinguish between *cis*- and *trans*-vinylogous imides, and also to reinforce stereochemical assignments for vinylogous amides and urethans based upon their molar extinction coefficients.

Empirical rules for correlating the structure of an  $\alpha,\beta$ -unsaturated ketone with the ultraviolet (uv) absorption maximum of its  $\pi \rightarrow \pi^*$  transition were first enunciated by Woodward<sup>4</sup> in 1941. Subsequently these rules were expanded to include the corresponding aldehydes,<sup>5</sup> acids, and esters,<sup>6</sup> and the effect of ring size on band positions for  $\alpha,\beta$ -unsaturated carbonyl compounds in general.<sup>7</sup> Considerable study has also been devoted to the bathochromic effects of various substituents. In 1959 Fieser and Fieser<sup>8</sup> modified slightly the solvent corrections initially applied by Woodward.<sup>4</sup> As spectral information accumulated, the results, including substituent shifts, have been published<sup>8,9</sup> periodically in tabular form to facilitate their application.

The availability of vinylogous amides,  $\beta$ -amino  $\alpha,\beta$ -unsaturated ketones,  $-\text{NC}=\text{CC}(\text{O})-$ , and imides,  $\beta$ -amido  $\alpha,\beta$ -unsaturated ketones,  $-(\text{O})\text{CN}=\text{CC}(\text{O})-$ , of known structure and stereochemistry from a previous project<sup>1</sup> prompted us to investigate their uv spectral properties. Although a substituent increment of +95  $\mu$  for a  $\beta$ -dialkylamino group ( $-\text{NR}_2$ ) of a vinylogous amide was reported<sup>10</sup> in 1946, the compounds included in this study were limited in both number and scope. In addition the relationship of stereochemistry to substituent shift has not been thoroughly investigated for this system. Planar structures I–IV<sup>11</sup> allow maximum resonance stabilization. In the case of form II intramolecular hydrogen bonding of  $-\text{NH}$  to carbonyl oxygen is also possible.

Examination of the literature revealed the existence of spectral data for related compounds such as vinylo-

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