Tetrahedron Letters No.25, pp. 3013-3016, 1968. Pergamon Press. Printed in Great Britain.

REARRANGEMENT OF ALLYL PHOSPHINITES AND OPTICAL STABILITY OF ALLYL PHOSPHINE OXIDES

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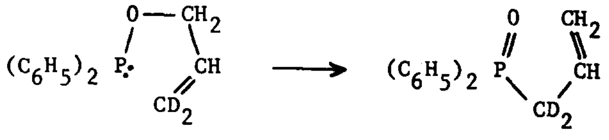
(Received in USA 15 March 1968; received in UK for publication 25 March 1968)

It has been shown that the thermal rearrangement of allyl sulfenates to allyl sulfoxides and the thermal racemization of allyl sulfoxides are intimately related events which may be regarded as different aspects of the same process (1). We now report results of a study aimed at investigating related reactions in the analogous phosphorus system.

It has long been known that allyl phosphinites undergo thermal rearrangement to allyl phosphine oxides (2,3), and it has been suggested that this process is intramolecular since cinnamyl diphenylphosphinite gives 1-phenylallyldiphenylphosphine oxide and 1-phenylallyldiphenylphosphinite gives cinnamyldiphenylphosphine oxide in up to 65% yields (3). However, it has been reported (4) that, although α-methylallyl diethyl phosphite rearranges thermally with complete inversion of the allyl group to give diethyl crotylphosphonate, crotyl diethyl phosphite rearranges with loss of specificity to give a mixture of isomers containing up to ca. 40% of diethyl crotylphosphonate. Since the isomers in the phosphinite → phosphine oxide rearrangement (3) had not been quantitatively accounted for, we examined the specificity of this reaction by heating allyl-3,3-$\underline{d}_2$ diphenylphosphinite (I), prepared from 90% isotopically pure allyl-3,3-$\underline{d}_2$ alcohol (5) and chlorodiphenylphosphine, in benzene at 100° (sealed tube under argon). Comparison of the integrated intensity of the residual methylene n.m.r. signal ($CDCl_3$) at δ 3.15 in the product of rearrangement (II) with that of the residual vinylic methylene signal at δ 5.27 in the starting alcohol indicated that the rearrangement proceeds with complete (> 95%) specificity.



I

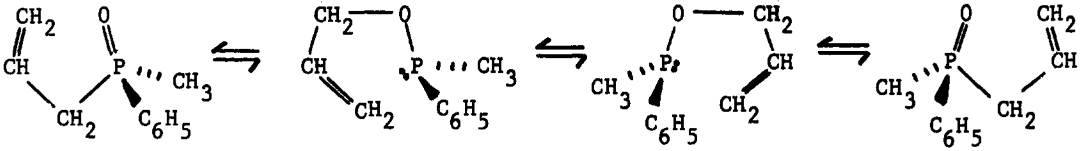
II

This conclusion was independently confirmed by internal comparison of the integrated intensity of the vinylic methylene multiplet (2 H) in II at δ ca. 5.2 with that of the vinyl multiplet (1 H) at δ ca. 5.8 and that of the phenyl multiplet (10 H) at δ 7.6. Furthermore, the rearrangement of α-methylallyl diphenylphosphinite and crotyl diphenylphosphinite under the same conditions gives crotyldiphenylphosphine oxide and α-methylallyldiphenylphosphine oxide, respectively, with > 99% specificity as judged by n.m.r. and v.p.c. evidence.

The kinetics of the rearrangement of allyl diphenylphosphinite (III) in benzene were followed by the sealed tube (under argon) method: at periodic intervals, tubes were withdrawn from the thermostated bath, the unreacted III was quenched by mercuric oxide oxidation (6) to allyl diphenylphosphinate (IV), and the mixture of IV and allyldiphenylphosphine oxide (V) was analyzed by v.p.c. (On a 4 ft. XE-60 10% Silicone (nitrile) on Chromosorb W column at 230°, helium flow rate 140 ml/min., IV and V had retention times of 8 and 15 min., respectively). Control experiments established that neither IV nor V were present prior to inception of the kinetic runs: a tube heated for 10 half-lives gave > 99% of V, and oxidation of a sample prior to heating gave only IV (no V). The rearrangement of III follows first-order kinetics; $\underline{k} \times 10^5$ (sec^{-1}) = 5.32 (at 89.9°), 12.7 (at 99.9°), and 29.2 (at 109.7°), whence $\Delta H^{\ddagger}$ 23 kcal./mole and $\Delta S^{\ddagger}$ - 14 e.u. The low $\Delta H^{\ddagger}$ value is consistent with a concerted mechanism in which the energy lost in breaking the carbon-oxygen bond in III is compensated for in part by the energy gained in forming the new carbon-phosphorus bond in V. The negative entropy term is consistent with the loss of degrees of freedom in the cyclic transition state.

In combination, the values of the activation parameters and the specificity of the rearrangement of the label (7) provide unimpeachable evidence for a cyclic, concerted, intramolecular allylic shift which is completely analogous to the allylic sulfenate → sulfoxide rearrangement (1). However, the high energy barrier ($\Delta G^{\ddagger}$ 29 kcal./mole) for the rearrangement of III to V is in contradistinction to the ease of rearrangement of allyl p-toluenesulfenate (VI) to allyl p-tolyl sulfoxide (VII): whereas III → V requires temperatures near 1C

VI → VII proceeds rapidly even at 0° (1). The contrast between these barriers is also reflected in the further observation that (*R*)-allylmethylphenylphosphine oxide (VIII) (9) suffers no loss in optical purity when heated at 200° in *o*-xylene for 12 hours, whereas VII is readily racemized at temperatures near 50° (1). By analogy with the mechanism of racemization of VII (1), the first step in the racemization of VIII would be rearrangement to allyl (*S*)-methylphenylphosphinite (IX). From the principle of microscopic reversibility and the likelihood that the ground state of VIII lies *ca.* 10-20 kcal./mole below that of IX (11), it follows that the barrier to rearrangement of VIII to IX is *ca.* 40-50 kcal./mole, *i.e.* of a magnitude sufficient to prevent conversion of VIII to IX at a measurable rate under the stated conditions. Racemization of VIII additionally requires conversion of IX into its mirror image, IX', followed by allylic rearrangement of IX' to VIII', the mirror image of VIII. If the magnitude of the barrier to pyramidal inversion implicit in IX ⇄ IX' is no greater than 30 kcal./mole (12), the above estimate of the barrier to rearrangement is also an upper limit for the barrier to racemization, VIII ⇄ VIII' (13).



VIII IX IX' VIII'

Acknowledgment:

This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-67. One of us (A.W.H.) thanks the National Science Foundation for a postdoctoral fellowship.

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7. In contrast to the facile rearrangement of III, allyl-3,3-d_2 diphenylphosphinate suffers no loss of identity, *i.e.* no label scrambling, when heated at 210° in *o*-xylene for 12 hours. This result is comparable to the stability of allyl carboxylates toward cyclic rearrangement (8).
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9. This compound, prepared by reaction of allylmagnesium bromide with menthyl (*S*)-methylphenylphosphinate (10), had m.p. 74-76°, $[\alpha]_D + 21^\circ$ (methanol); anal. calcd. for $C_{10}H_{13}OP$: C, 66.66; H, 7.27; P, 17.19, found: C, 66.34; H, 7.12; P, 16.95. The n.m.r. spectrum was consistent with the assigned structure and featured a doubled doublet ($J_{PCH} = 15.5$ Hz; $J_{vic} = 7$ Hz) at δ 2.78 (methylene) and a doublet (J = 12.6 Hz) at δ 1.70 (methyl).
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11. R.F. Hudson, *Structure and Mechanism in Organo-Phosphorus Chemistry*, Academic Press, New York, 1965, p. 124. This quantity thus stands for the thermodynamic driving force (1) of the rearrangement of III to V.
12. By analogy with the pyramidal inversion of phosphines; *cf.* L. Horner and H. Winkler, *Tetrahedron Letters*, 461 (1964); J.B. Lambert and D.C. Mueller, *J.Amer.Chem.Soc.* **88**, 3669 (1966).
13. We note, incidentally, that in contrast to benzyl *p*-tolyl sulfoxide, which racemizes at temperatures near 130° by a homolytic scission-recombination mechanism (1), (*R*)-benzylmethylphenylphosphine oxide (10) is optically stable when heated in *o*-xylene at 200° for 21 hours.