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THE THERMAL REARRANGEMENT OF DIETHYL α-METHYLALLYL AND DIETHYL CROTYL PHOSPHITES*

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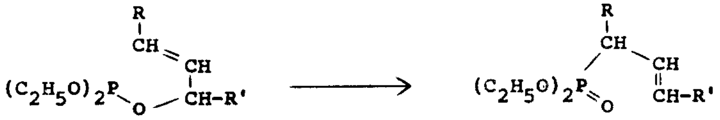
Rearrangements of diethyl α-methylallyl phosphite (I) and diethyl crotyl phosphite (II) have recently been reported by Pudovik and Aladzhyeva (1,2) to give only the products resulting from inversion of the migrating allylic groups. They accounted for the products by an intramolecular rearrangement (2) similar to the Claisen rearrangement (3):



While we have observed that the rearrangement of the α-methylallyl phosphite I gave only diethyl crotylphosphonate (III), rearrangement of the crotyl phosphite II gave the crotylphosphonate III in addition to the previously reported product (2) diethyl α-methylallylphosphonate (IV).

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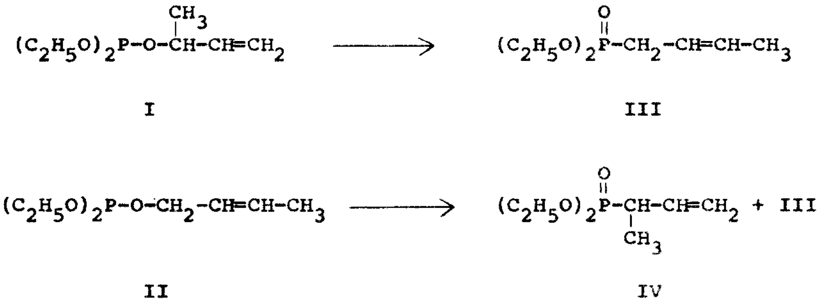

$$(C_2H_5O)_2P\text{-}O\text{-}\overset{CH_3}{\overset{|}{C}}H\text{-}CH{=}CH_2 \longrightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}\text{-}CH_2\text{-}CH{=}CH\text{-}CH_3$$

I III

$$(C_2H_5O)_2P\text{-}O\text{-}CH_2\text{-}CH{=}CH\text{-}CH_3 \longrightarrow (C_2H_5O)_2\overset{O}{\overset{\|}{P}}\text{-}\underset{CH_3}{\underset{|}{C}}H\text{-}CH{=}CH_2 + III$$

II IV

The phosphites I and II were synthesized by the reaction of diethyl phosphorochloridite with α-methylallyl alcohol and crotyl alcohol respectively, in the presence of triethylamine in ether, a method which rules out the possibility of allylic rearrangement. The crotyl phosphite was alternately synthesized by the transesterification of triethyl phosphite with crotyl alcohol.

The phosphites were rearranged neat at temperatures above 189° (Table I). Vapor phase chromatographic analysis of the rearrangement mixtures indicated that only one phosphonate, III* was formed from I while both III and IV were formed from II. The products were identified by infrared** and n.m.r. measurements.***

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*A minor peak was observed in the gas chromatogram of the rearrangement of I which was eluted at nearly the same time as IV, however, this component was subsequently identified as diethyl α-methylallyl phosphate. In a separate experiment, diethyl α-methylallyl phosphite was readily oxidized by oxygen to the phosphate in good yield at room temperature.

**The infrared spectra of I, II, III, and IV correspond to those previously reported (2).

***The n.m.r. spectra were obtained on a Varian Model A-60 spectrometer employing carbon tetrachloride as the solvent and tetramethylsilane as the internal standard.

The product III was identified as a phosphonate by the strong band at 1255 $cm.^{-1}$ in its infrared spectrum, consistent with the presence of the P=O group. This band is also present in phosphates, however this possibility was ruled out by carrying out the rearrangement in a nitrogen atmosphere with essentially the same results. The structure of the allylic group was determined by n.m.r. measurements. The allylic methylene signal was present as a doublet, $J = 22$ c.p.s., (4) at 7.58 τ, which was further split by the vinylic hydrogen, with an integrated intensity of two hydrogens. This signal was also observed in the n.m.r. spectrum of diallyl allylphosphonate. The γ-methyl signal was observed as a multiplet at 8.30 τ consistent with the signal of a methyl group alpha to an olefinic double bond (5). The vinyl hydrogen signal appeared at low field with a relative intensity of two hydrogens.

The P=O group of IV was indicated by a strong band at 1255 $cm.^{-1}$ in the infrared. The resonance signal of the α-hydrogen appeared as a multiplet at 7.6 τ with an integrated intensity of one hydrogen. The vinyl hydrogens of IV appeared as a multiplet at low field, similar to the vinyl hydrogen signal of α-methylallyl alcohol, with an integrated intensity of three hydrogens. The α-methyl signal was masked by the methyl signal of the ethyl groups resulting in a complex pattern at 8.7 τ.

The data in Table I show that I rearranges much more rapidly than II and that the ratio of III to IV formed from II increases with increasing temperature and time of exposure at each temperature. No I was found in the rearrangements of

II. As little as 0.5% of I could have been easily detected by this method.

TABLE I

Rearrangement of Diethyl α-methylallyl Phosphite (I)
And Diethyl Crotyl Phosphite (II)

Compound	Temperature °C	Time hr.	Rearrangement[a] %	III %	IV %
I	189 ± 0.5	4.0[b]	77	100	--
	212 ± 1	2.0	97	100	--
II	200 ± 1	4.0[b]	19	15	85
		8.2	32	27	73
	209 ± 0.5	4.2	38	25	75
		7.9	47	37	63
	220 ± 0.5	2.0	39	30	70
		4.0	42	41	59

[a] The percentages were determined by v.p.c.

[b] same conditions as reference No. 2.

This suggested that III could have been formed by the isomerization of IV. In a separate experiment IV was heated under rearrangement conditions and found to isomerize to III. This isomerization accounted for only part of the III which was formed during the rearrangement of II. For example, at 199°, 3% of IV isomerized to III in 4.2 hr. and at 220°, 7% isomerized in 2 hr.

It has not been established whether or not the presence of II influences the rate of rearrangement of IV to III. However, there is evidence of at least some fragmentation. Small amounts of diethyl ethylphosphonate, diethyl phosphite, triethyl phosphate, and butadiene are formed in rearrangements of II. It was not possible to obtain reliable estimates of the percentage of unreacted II in the presence of these products. In separate experiments it has been observed that diethyl phosphite, diethyl ethylphosphonate and IV all enhance the formation of the "abnormal product" III from II but do not influence the isomerization of the "normal product" IV to III. Further work is in progress and will be the subject of a future communication.

It is readily seen why Pudovik and Aladzhyeva have not reported the formation of III in the rearrangement of II. Under the conditions of their rearrangement (195-200° for 4 hrs.) a total yield of 15.4% was realized. Our data (Table I) show that only 15% of the rearranged material at that temperature is III. This small amount detected by v.p.c. would have been difficult to observe by the distillation analysis used in the previous investigation (2).

REFERENCES

1. A. N. Pudovik and I. M. Aladzhyeva, Dokl. Akad. Nauk SSSR, **151**, 1110 (1963).
2. A. N. Pudovik and I. M. Aladzhyeva, Zh. Obshch. Khim., **33**, 3096 (1963).

3. S. J. Rhoads, "Molecular Rearrangements" Part I, P. de Mayo, Ed., Interscience Publishers, New York, N.Y., 1963, pp. 655-683.

4. K. D. Berlin, C. Hildebrand, A. South, D. M. Hellwega, M. Peterson, E. A. Pier, and J. G. Verkade, Tetrahedron, **20**, 323 (1964).

5. R. M. Silverstein, G. C. Bassler, "Spectrometric Identification of Organic Compounds", John Wiley and Sons, Inc., New York, N.Y., 1963, p. 84.