СН3-СН-С	$H_2 = OCOC(CH_3)_3$	≓ CH ₃ —CH—CH₂Br
Br	30%	OCOC(CH ₃) ₃
		70%

The isomers were separated by preparative gas-liquid chromatography. 2-Bromo-1-propyl pivalate isolated from the equilibrium mixture fully retained its optical activity. This finding convincingly demonstrates that formation of a carbocation does not occur in the isomerization of (I) and that the reaction proceeds through cyclic intermediate (A) with retention of the stereochemical configuration of the starting compound.



CONCLUSIONS

In a study of the isomerization of optically active 2-bromo-1-propyl pivalate in aprotic solvents, the reaction was found to proceed with the retention of the stereochemical configuration of the starting compound. This finding indicates the formation of cyclic acyloxonium intermediate during the isomerization reaction.

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PHOTOCHEMICAL, THERMAL, AND THERMOCATALYTIC REACTIONS OF DIPHENYLDIAZOMETHANE WITH DIMETHYL THIOPHOSPHITE

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The triplet-photosensitized photolysis of diazocarbonyl compounds in dimethyl thiophosphite with benzophenone leads to the insertion of triplet carbenes into P-H bonds [1, 2]. Such insertion is not seen in the direct photolysis or thermolysis [1, 2]. This failure is apparently related to the inability of the singlet carbenes generated under these conditions to insert into P-H bonds. Hence, in accord with evidence for a rapid equilibrium between singlet and triplet diphenylcarbene [3] in the direct photolysis of a mixture of diphenyldiazomethane with dimethyl thiophosphite, we should expect the formation of the product of P-H insertion by a mechanism involving hydrogen abstraction and recombination of the radical pair [4].

Indeed, the mixture obtained from this photolysis gave 0,0-dimethyl(diphenylmethyl)thiophosphonate (I). However, in the chemically-induced ³¹P NMR spectra (CIDNP), spectra of both the direct photolysis and the benzophenone triplet-sensitized photolysis showed the

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emission of a peak assigned to product (I) (δ ³¹P 95 ppm). Tetraphenylethane (II) and the N-dimethoxythiophosphorylhydrazone of benzophenone (III) were isolated in addition to (I). Hydrazone (III) is readily formed in the dark reaction of diphenyldiazomethane with dimethyl thiophosphite at room temperature. This reaction is complete after 24 h and leads to (III) and also 0,0-dimethyl-S-(diphenylmethyl)thiophosphate (IV), formed apparently as a result of the oxidation of thiophosphite (V) upon treatment of the mixture, and tetraphenylethylene (VI).

 $\begin{array}{cccc} Ph_{2}CN_{2} & & & & & \\ & & & & & \\ \downarrow (MeO)_{2}P(S)H & & & & & \\ Ph_{2}C=N-NHP(S)(OMe)_{2} \ (III) & & & & & \\ Ph_{2}C=CPh_{2} \ (VI) & & & & & \\ + \ Ph_{2}C=CPh_{2} \ (VI) & & & & & \\ + \ Ph_{2}CHSP(OMe)_{2} \ (V) & & & & \\ & & & & & \\ \downarrow 0_{2} & & & & \\ Ph_{2}CHSP(O)(OMe)_{2} \ (IV) & & & \\ \end{array}$

The use of a heterogeneous $CuSO_4$ catalyst permitted carbenoid P-H insertion into dimethyl phosphite, while dimethyl thiophosphite passivates $CuSO_4$ [2]. On the other hand, the carbenoid insertion into the P-H bond in dimethyl thiophosphite was achieved for the first time using homogeneous cupric acetylacetonate.

 $Ph_2CN_2 + (MeO)_2P(S)H \xrightarrow[Gu(acac)_2]{80^{\circ}} Ph_2CHP(S)(OMe)_2$ (I)

EXPERIMENTAL

The ³¹P NMR spectra were taken on a ³¹P NMR spectrometer at 8 MHz. The PMR spectra were taken on a Tesla BS-5467 spectrometer with HMDS as the internal standard. The IR spectra were taken on a Specord 75 spectrometer. Accelerated chromatography [1] on silica gel L 5/40 μ m was used for the separation. The R_f values were obtained on Silufol UV-254 plates with ethyl acetate as the eluent. The sample of diphenyldiazomethane [5] was purified by recrystallization from pentane prior to use. Dimethyl thiophosphite [6] was fractionated in vacuum. The solvents were dried prior to use.

Direct Photolysis of Diphenyldiazomethane in Dimethyl Thiophosphite. A sample of 19.4 g (154 mmoles) dimethyl thiophosphite was added to 3 g (15.4 mmoles), placed into a Pyrex ampul, flushed with argon for 15 min, sealed, and irradiated with a high-pressure DRL-1000 lamp at 10°C for 6 h. Dimethyl thiophosphite was removed in vacuum. The residue was dissolved in 1:1 benzene-hexane and maintained at -15°C. White crystals were filtered off and recrystallized from benzene to give 0.54 g (21.0%) tetraphenylethane (II), mp 209-211°C [8]. PMR spectrum in CCl₄ (δ , ppm): 4.73 s (2H, CHPh), 6.96 s (20H, Ph). The filtrate was twice chromatographed on 17 × 2-cm columns initially with 250 ml 1:19 ethyl acetatehexane and 400 ml 1:5.6 ethyl acetate-hexane and, then, with 300 ml 1:4 ethyl acetatehexane for individual fractions to give 0.48 g (10.6%) (I), mp 76-78°C (from cyclohexane), R_F 0.77. PMR spectrum in CCl₄ (δ , ppm, J_{PH}, Hz): 3.52 d (6H, CH₃OP, ³J_{PH} = 13), 4.52 d (1H, CHP, ³J_{PH} = 24), 7.09-7.55 m (10H, Ph). δ ³¹P 95 ppm (CCl₄). Found: C, 61.51; H, 6.06; P, 10.75%. Calculated for $C_{15}H_{17}O_2PS$: C, 61.63; H, 5.76; P, 10.60%. The yield of (III) was 0.28 g (5.7%), mp 75-77°C (from cyclohexane), R_f 0.70. PMR spectrum in CCl₄ (δ , ppm, J_{PH}, Hz): 3.75 d (6H, CH₃OP, ³J_{PH} = 14), 6.45 d (1H, NHP, ²J_{PH} = 34), 7.1-7.59 m (10H, Ph). δ ³¹P 65 ppm (CC1₄). IR spectrum in vaseline mull (ν, cm⁻¹): 660 (P=S), 1020 (P-O), 1170 (C-O), 3340 (N-H). Found: C, 56.53; H, 5.29; N, 8.24; P, 10.03%. Calculated for C₁₅H₁₇N₂O₂PS: C, 56.24; H, 5.35; N, 8.74; P, 9.67%.

<u>Reaction of Diphenyldiazomethane with Dimethyl Thiophosphite.</u> A sample of 6.2 g (49 mmoles) dimethyl thiophosphite was added to 0.94 (4.9 mmoles) Ph_2CN_2 and maintained for 22 h. A total of 45.3 ml (42%) nitrogen was released. Pentane was added and the mixture was maintained at -15°C to give a white crystalline precipitate of 0.13 g (16.0%) tetraphenylethylene, mp 222-226°C [7], which was filtered off. PMR spectrum in CCl₄ (δ , ppm): 6.97 s (Ph). Dimethyl thiophosphate was removed from the filtrate in vacuum. Then, 5:1 pentane-CCl₄ was added and the mixture was maintained at -15°C to give 0.20 g (12.7%) (III). The residue was subjected to chromatography on a 22 × 2-cm column using 1:19 ethyl

acetate-hexane as the eluent (300 ml) to give 0.02 g (1.3%) (III) and 1:4 ethyl acetate-hexane as the eluent (300 ml) to give 0.16 g (10.6%) (IV) as an oil, n_D^{20} 1.5795 [8], R_f 0.34, δ^{31} P 26 ppm (CCl₄). PMR spectrum in CCl₄ (δ , ppm, J_{PH}, Hz): 3.49 d (6H, CH₃OP, ³J_{PH} = 13), 5.55 d (1H, CHSP, ³J_{HP} = 11), 7.02-7.40 m (10H, Ph). IR spectrum, neat (ν , cm⁻¹): 550 (P-S-C), 750-810, 1000-1010 (P-O), 1170 (C-O), 1250 (P-O).

<u>Thermocatalytic Decomposition of Diphenyldiazomethane in Dimethyl Thiophosphite</u>. A sample of 1 g (5.2 mmoles) Ph_2CN_2 in 15 ml benzene was added dropwise to a mixture of 3.38 g (27 mmoles) dimethyl thiophosphite, 15 ml benzene, and 0.1 g (0.38 mmole) $Cu(acac)_2$ at reflux over 2.5 h and then, the mixture was heated at reflux for 1 h, cooled, and passed through a 10 × 2-cm column packed with silica gel L 100/160 µm, additionally eluting with 100 ml benzene. The removal of benzene and dimethyl thiophosphite in vacuum gave 0.89 g (59%) (I), mp 76-78°C (from cyclohexane), $\delta^{31}P$ ppm (CC1₄).

CONCLUSIONS

The direct photolysis of diphenyldiazomethane in dimethyl thiophosphite gave the product of P-H insertion. The thermal reaction leads to the N-dimethoxythiophosphorylhydrazone of benzophenone and 0,0-dimethyl S-(diphenylmethyl) thiophosphate. Carbenoid P-H insertion occurred in the thermocatalytic decomposition.

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