be simpler in the presence rather than in the absence of the quaternary ammonium salt (Table I). Ketones were obtained in good yields from other allyl alcohols, including 3-hexene-2,5-diol. No reaction occurred when 1-phenylallyl alcohol in methylene chloride was exposed to NaOH in the absence of the rhodium(I) catalyst.

A possible pathway for this reaction is outlined in Scheme I. Hydroxide ion displacement of halide from rhodium(I) species **2** would generate the rhodium hydroxide **4**. The latter can then π-complex to the unsaturated alcohol to give **5**, which on subsequent allylic hydrogen abstraction leads to the π-allyl complex **6**. Delivery of the hydride to a terminal allylic carbon affords the enol complex **7**. Decomplexation regenerates the catalyst and gives the enol of the carbonyl.

In conclusion, the two-phase reaction described above constitutes a simple, and very mild, method for the isomerization of allyl alcohols.

Experimental Section

Chlorodicarbonylrhodium(I) dimer, benzyltriethylammonium chloride, and all but one of the allyl alcohols were commercial products. We are indebted to Mr. F. Houlihan for providing generous quantities of 1-phenylallyl alcohol. Spectral data were recorded with a Unicam SP-1100 infrared spectrometer and a Varian T-60 or HA-100 proton magnetic resonance spectrometer.

General Procedure for the Isomerization of Allylic Alcohols Catalyzed by Chlorodicarbonylrhodium(I) Dimer. A mixture of the allyl alcohol (5.0 mmol) and **2** (0.1–0.2 mmol) in methylene chloride (20–25 mL), 8 M NaOH (15–20 mL), and benzyltriethylammonium chloride (if used, 1.0–2.0 mmol) was stirred at 25–30 °C for 6–18 h (reactions were usually complete in 6 h or less, but were left stirring overnight). The layers were separated, and the organic phase was washed with water, dried (Na$_2$SO$_4$ or MgSO$_4$), and then concentrated to give the carbonyl compound, which was distilled.

Facile One-Step Synthesis of Alkylphosphonothioic Dichlorides from Chloroaluminate Complexes, (RPCl$_3$)$^+$(Al$_2$Cl$_7$)$^-$

Mahabir P. Kaushik and Ramamoorthy Vaidyanathaswamy*

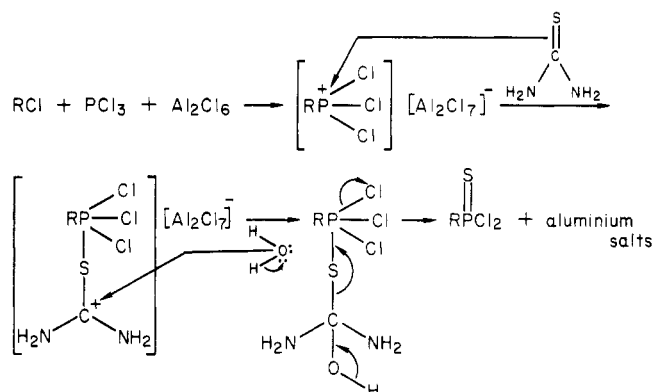*Defence Research and Development Establishment, Gwalior 474002, India*

Alkylphosphonothioic dichlorides are intermediates of importance in insecticide synthesis. Among the reported procedures,[1] only two deserve mention here as convenient laboratory methods. The high-temperature reaction of phosphorus pentasulfide with alkylphosphonic dichlorides[2]

Scheme I

invariably results in contamination by starting material while the second route makes use of less easily accessible dichlorophosphines.[3] A far more convenient procedure is reported here for the preparation of these compounds.

On hydrolysis with water, chloroaluminate (Kinnear–Perren) complexes[4] break up to yield alkylphosphonic dichlorides. Substitution of hydrogen sulfide in place of water, however, results in several side products along with the expected alkylphosphonothioic dichlorides, perhaps due to the greater nucleophilic reactivity of H$_2$S.[1c,4] In our modified method, the complex is treated with thiourea at room temperature followed by water to obtain pure alkylphosphonothioic dichloride in one step.

$$RCl + PCl_3 + Al_2Cl_6 \rightarrow (RPCl_3)^+(Al_2Cl_7)^- \xrightarrow[\text{2. water}]{\text{1. thiourea}} RP(S)Cl_2 \quad (1)$$
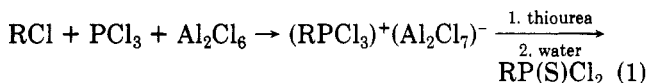
The starting alkyl halides, products, and yields are given in Table I. *n*-Butyl and 2-chloroethyl chlorides afforded rearranged products as expected from such reactions. The yields were moderate. This is probably inherent in RCl–PCl$_3$–Al$_2$Cl$_6$ complex formation[5] rather than in thiourea reaction. All alkylphosphonothioic dichlorides were characterized by comparing the boiling points and IR and NMR spectra with those of authentic samples and further confirmed by preparing diethyl derivatives.

In Scheme I, a plausible explanation for the formation of phosphonothioic dichloride is offered. The key step of the reaction is the attack of nucleophilic sulfur on phosphorus followed by reaction of water with this new complex. Elimination of urea affords the required product.[6]

Experimental Section

IR spectra were recorded on a Perkin-Elmer 577 instrument as neat liquid. ^{1}H NMR spectra in CCl$_4$ solutions were obtained with a Perkin-Elmer R–32 instrument with Me$_4$Si as internal standard. GC analyses were performed on a Varian Aerograph Model 2868 using an OV-17 column. TLC plates, 20 cm × 5 cm, were of silica gel. All alkyl halides were commercial products and were used after distillation. Thiourea (BDH) was dried at 110 °C for 5 h prior to use. Anhydrous aluminum chloride and phosphorus trichloride were commercial products and were used as such. The preparations of isopropylphosphonothioic dichloride and its diethyl derivative serve as typical procedures and are given below.

(1) (a) M. Fild and R. Schmutzler in "Organic Phosphorus Compounds", Vol. 4, G. M. Kosolapoff and L. Maier, Eds., Wiley-Interscience, New York, 1972, Chapter 9; (b) B. Nagy and M. Nadasy, *Nehezvegyip. Kut. Intez. Kozl.*, 5, 103 (1975); *Chem. Abstr.*, 84, 5069 (1976); (c) E. A. Perren and A. M. Kinnear, British Patent 740 444; *Chem. Abstr.*, 50, 13985f (1956).

(2) L. Maier, *Helv. Chim. Acta*, 48, 133 (1965).

(3) L. Maier, *Helv. Chim. Acta*, 46, 2026 (1963).

(4) A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 3437 (1952).

(5) (a) L. Maier, *Helv. Chim. Acta*, 52, 1337 (1969), for example, obtained only a 38% yield of 2-chloroethylphosphonic dichloride as compared to the originally reported yield of 58%;[4] (b) G. M. Kosolapoff in "Friedel–Crafts and Related Reactions", Vol. IV, G. A. Olah, Ed., Interscience, New York, 1965, Chapter 51, p 231.

(6) We thank one of the referees for modifying the mechanism suggested earlier by us.

Table I. Preparation of Alkylphosphonothioic Dichlorides

no.	RCl/RBr used	R in RP(S)Cl₂	% yield	bp, °C	lit. bp, °C	type deriv prepared
1	C₂H₅Cl	C₂H₅	32^a	62 (15 mm)	62 (14 mm)[7]	diethyl
2	*i*-PrCl	*i*-Pr	53	70 (12 mm)	70 (12 mm)[7]	diethyl
3	*n*-C₄H₉Cl	*sec*-C₄H₉	54	80–82 (8 mm)	80 (8 mm)[7]	diethyl
4	C₆H₅CH₂Cl	C₆H₅CH₂	45	115 (4 mm)	112 (1 mm)[8]	diethyl
5	cyclohexyl chloride	cyclohexyl	43	78 (2 mm)	76–77 (2 mm)[8]	diethyl
6	ClCH₂CH₂Cl	ClCH₂CH₂ (73%), CH₃CHCl (27%)	43	85–92 (10 mm)	b	none
7	BrCH₂CH₂Br	BrCH₂CH₂	35	95–97 (10 mm)	c	none
8	CH₂=CHCH₂Cl	CH₂=CHCH₂	27	80 (20 mm)	80 (20 mm)[7]	none

^{a} Before the addition of thiourea, the required aluminium chloride complex was obtained by passing ethyl chloride into dichloromethane containing PCl₃ and Al₂Cl₆. ^{b} Compounds obtained as mixture of these two isomers, analyzed by ¹H NMR. Reported boiling points are 92 °C (10 mm) for ClCH₂CH₂P(S)Cl₂ and 84 °C (13 mm)[9] for CH₃CHClP(S)Cl₂. ^{c} An authentic sample was prepared by conversion of the corresponding phosphonic dichloride with P₂S₅ and was compared by use of TLC and NMR and IR spectra.

Isopropylphosphonothioic Dichloride. To a slurry of anhydrous aluminum chloride (53.2 g, 0.4 mol) and phosphorus trichloride (27.4 g, 0.2 mol) in dichloromethane (200 mL) was introduced dropwise isopropyl chloride (15.7 g, 0.2 mol) at 20–25 °C. After completion of the addition, the solution was stirred for 0.5 h more. To this was added powdered thiourea (30.4 g, 0.4 mol) in small portions, maintaining the temperature between 20 and 25 °C. The solution was further stirred for 0.5 h, diluted with fresh dichloromethane (200 mL), and cooled to –20 °C. Water was added in small portions with vigorous shaking. After about 65 mL of water was added, aluminum salts suddenly coagulated, leaving a clear supernatant solution. This was filtered, the solvent was removed, and the residue was distilled to give a colorless liquid: 18.8 g (53.0%); bp 70 °C (12 mm) [lit.[7] bp 70 °C (12 mm)]; the IR showed $\nu_{P=S}$ at 730 cm⁻¹ and no peak corresponding to $\nu_{P=O}$ in the 1200–1300-cm⁻¹ region; ¹H NMR δ 2.75 (m, 1 H, CH), 1.45 (dd, 6 H, CH₃, J_{PH} = 31 Hz, J_{HH} = 7 Hz). Both IR and NMR spectra were identical with those of an authentic sample.

Diethyl Isopropylphosphonothioate. Sodium ethoxide was made from sodium (2.3 g, 0.1 mol) and ethanol (80 mL). To this was added isopropylphosphonothioic dichloride (8.8 g, 0.05 mol) dropwise. The reaction took place instantaneously. Water was added, and the contents were extracted with petroleum ether (bp 40–60 °C). After removal of the solvent, there was obtained a liquid: 4.9 g (50%); bp 75 °C (5 mm). This was homogenous on TLC and GC, with identical R_f and retention time, respectively, with an authentic sample: IR, $\nu_{P=S}$ at 775 cm⁻¹; ¹H NMR δ 4.05 (m, 4 H, OCH₂), 1.75 (m, 1 H, CH), 1.0–1.4 (m, 12 H), the last absorption has a triplet (CH₃CH₂) at δ 1.30 merged with the low-field portion of the doublet of doublets (CH₃CH). The high-field portion of the same was centered at δ 1.03.

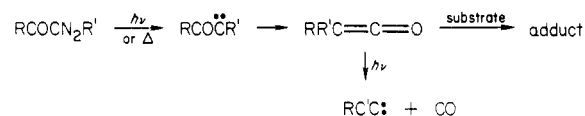(7) Reference 1, p 205.
(8) Reference 1, p 206.
(9) Reference 1, p 204.

Communications

Photolysis of Vinylene Thioxocarbonates: A New Source of Ketocarbenes

Summary: Photolysis (λ = 210 nm) of argon matrix isolated vinylene carbonate resulted in the formation of CO, CO₂, ketene, and glyoxal via two simultaneous primary processes. Under similar conditions vinylene and *o*-phenylene thioxocarbonate yield COS and ketene and cyclopentadienylidene ketene, respectively. No transient spectra attributable to oxirene or benzoxirene were observed. Flow pyrolysis of these compounds resulted in smooth conversions to the corresponding ketenes. It is concluded that vinylene thioxocarbonates are novel source compounds for the synthesis of ketenes and for mechanistic studies of the Wolff rearrangement.

Sir: The Wolff rearrangement of α-diazo ketones has been the subject of extensive studies, but until recently the major emphasis was on the synthetic and mechanistic aspects of the addition reaction of the product ketenes with various substrates. For many years, the overall reaction was assumed[1] to be

$$RCOCN_2R' \xrightarrow[\text{or } \Delta]{h\nu} R\ddot{C}O\ddot{C}R' \longrightarrow RR'C\!\!=\!\!C\!\!=\!\!O \xrightarrow{\text{substrate}} \text{adduct}$$
$$\downarrow h\nu$$
$$RC'C: + CO$$

and the intermediacy of ketocarbenes in these systems was confirmed by the observation of ESR signals compatible with triplet-state ketocarbene carriers generated upon low-temperature photolysis of the parent α-diazo ketones.[2] Ab initio MO calculations[3,4] predict a triplet ground state

(1) W. Kirmse, "Carbene Chemistry", Academic Press, New York, 1971.
(2) A. M. Trozzolo and S. R. Fahrenholtz, "Abstracts of Papers", 151st National Meeting of the American Chemical Society, Pittsburgh, PA, 1966, K.23; A. M. Trozzolo, *Acc. Chem. Res.*, 1, 329 (1968); H. Murai, M. Torres, and O. P. Strausz, to be published.
(3) R. K. Gosavi and O. P. Strausz, to be published.
(4) N. C. Baird and K. F. Taylor, *J. Am. Chem. Soc.*, **100**, 1333 (1978).