Table I. Preparation of Alkylphosphonothioic Dichlorides

no.	RCl/RBr used	R in $RP(S)Cl_2$	% yield	bp, °C	lit. bp, °C	type deriv prepared
1	C_2H_5Cl	C_2H_5	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*-C_4H_9Cl	*sec*-C_4H_9	54	80–82 (8 mm)	80 (8 mm)[7]	diethyl
4	$C_6H_5CH_2Cl$	$C_6H_5CH_2$	45	115 (4 mm)	112 (1 mm)[8]	diethyl
5	cyclohexyl chloride	cyclohexyl	43	78 (2 mm)	76–77 (2 mm)[8]	diethyl
6	$ClCH_2CH_2Cl$	$ClCH_2CH_2$ (73%), CH_3CHCl (27%)	43	85–92 (10 mm)	*b*	none
7	$BrCH_2CH_2Br$	$BrCH_2CH_2$	35	95–97 (10 mm)	*c*	none
8	$CH_2=CHCH_2Cl$	$CH_2=CHCH_2$	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 PCl_3 and Al_2Cl_6. [b] Compounds obtained as mixture of these two isomers, analyzed by ^1H NMR. Reported boiling points are 92 °C (10 mm) for $ClCH_2CH_2P(S)Cl_2$ and 84 °C (13 mm)[9] for $CH_3CHClP(S)Cl_2$. [c] An authentic sample was prepared by conversion of the corresponding phosphonic dichloride with P_2S_5 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, CH_3, 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, OCH_2), 1.75 (m, 1 H, CH), 1.0–1.4 (m, 12 H), the last absorption has a triplet (CH_3CH_2) at δ 1.30 merged with the low-field portion of the doublet of doublets (CH_3CH). The high-field portion of the same was centered at δ 1.03.

Registry No. $(RPCl_3)^+(Al_2Cl_7)^-$ (R = C_2H_5), 73178-62-8; $(RPCl_3)^+(Al_2Cl_7)^-$ (R = *i*-Pr), 73178-64-0; $(RPCl_3)^+(Al_2Cl_7)^-$ (R = C_4H_9), 73178-65-1; $(RPCl_3)^+(Al_2Cl_7)^-$ (R = $C_6H_5CH_2$), 73178-67-3; $(RPCl_3)^+(Al_2Cl_7)^-$ (R = cyclohexyl), 73178-68-4; $(RPCl_3)^+(Al_2Cl_7)^-$ (R = $ClCH_2CH_2$), 73178-26-4; $(RPCl_3)^+(Al_2Cl_7)^-$ (R = $BrCH_2CH_2$), 73178-28-6; $(RPCl_3)^+(Al_2Cl_7)^-$ (R = $CH_2{=}CHCH_2$), 73178-30-0; $RP(S)Cl_2$ (R = C_2H_5), 993-43-1; $RP(S)Cl_2$ (R = *i*-Pr), 1498-60-8; $RP(S)Cl_2$ (R = *sec*-C_4H_9), 4653-41-2; $RP(S)Cl_2$ (R = $C_6H_5CH_2$), 6588-19-8; $RP(S)Cl_2$ (R = cyclohexyl), 1498-63-1; $RP(S)Cl_2$ (R = $ClCH_2CH_2$), 20428-20-0; $RP(S)Cl_2$ (R = CH_3CHCl), 22789-36-2; $RP(S)Cl_2$ (R = $BrCH_2CH_2$), 73178-31-1; $RP(S)Cl_2$ (R = $CH_2{=}CHCH_2$), 1498-61-9; C_2H_5Cl, 75-00-3; *i*-PrCl, 75-29-6; C_4H_9Cl, 109-69-3; $C_6H_5CH_2Cl$, 100-44-7; cyclohexyl chloride, 542-18-7; $ClCH_2CH_2Cl$, 107-06-2; $BrCH_2CH_2Br$, 106-93-4; $CH_2{=}CHCH_2Cl$, 107-05-1; $RP(S)(OC_2H_5)_2$ (R = C_2H_5), 2455-45-0; $RP(S)(OC_2H_5)_2$ (R = *i*-Pr), 52038-87-6; $RP(S)(OC_2H_5)_2$ (R = *sec*-C_4H_9), 73178-32-2; $RP(S)(OC_2H_5)_2$ (R = $C_6H_5CH_2$), 73178-33-3; $RP(S)(OC_2H_5)_2$ (R = cyclohexyl), 73178-34-4; aluminum chloride, 27893-52-3; phosphorus trichloride, 7719-12-2.

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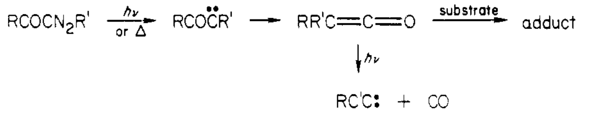
(7) Reference 1, p 205.
(8) Reference 1, p 206.
(9) Reference 1, p 204.

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, CO_2, 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



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

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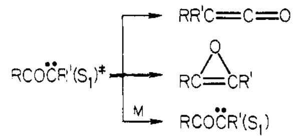
(1) W. Kirmse, "Carbene Chemistry", Academic Press, New York, 1971.
(2) A. M. Trozzolo and S. R. Fahrenholtz, "Abstracts of Papers", 151st National Meeting of the American Chemical Society, Pittsburgh, PA, 1966, K.23; A. M. Trozzolo, *Acc. Chem. Res.*, 1, 329 (1968); H. Murai, M. Torres, and O. P. Strausz, 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).

0022-3263/80/1945-2271$01.00/0

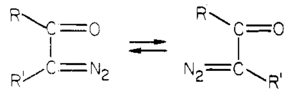
for these species, and the T_0–S_1 separation is relatively small, of the order of 25 kcal mol^{-1} for $HCO\ddot{C}H$. Over a decade ago, experiments with ^{13}C-labeled substrates provided indirect but compelling evidence to the effect that $4n$-π antiaromatic oxirene is an intermediate in the photolytic and high-temperature thermal decomposition of α-diazo ketones, α-diazo esters, and ketenes.[5] Oxirene can only be formed from vibrationally excited singlet-state ketocarbenes and this reaction occurs in parallel and in competition with the ketocarbene–ketene rearrangement and with vibrational relaxation:



S_1 ketocarbenes subsequently isomerize to ketene or can undergo intersystem crossing to the ground (T_0) state, the chemical reactivity of which is distinctly different. The structural and kinetic factors determining the relative rates of these interconversions, together with the results of ab initio calculations, have been reviewed recently.[6]

Matrix-isolation techniques for the detection and characterization of unstable intermediates have met with great success, most recently with the synthesis of thiirene and several substituted thiirenes from the photolysis of argon matrix isolated 1,2,3-thiadiazoles and vinylene trithiocarbonates.[7] As expected, substituents exert a stabilizing effect on the thiirene ring and bis(trifluoromethyl)thiirene is the most stable of all the thiirenes examined to date.

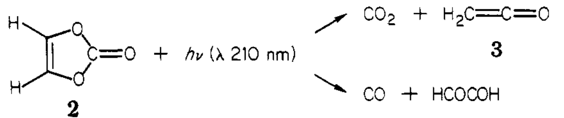
Argon matrix isolated α-diazoacetaldehyde yielded only ketene upon photolysis[8] and no transient spectrum was observed, in agreement with the predicted[9] small kinetic stability of oxirene with respect to ring opening. On the other hand, as was shown to be the case for thiirene, it is possible that substituents will exert a stabilizing effect and that suitably substituted oxirenes may be matrix isolated at 8 K. The most obvious precursors, however, α-diazo ketones, are known to exist as an equilibrium mixture of the two cis and trans configurations **1a** and **1b**, respectively, and whereas the cis configuration is the most stable for α-diazoacetaldehyde, increasing substitution will likely favor the trans configuration[10] thus, adding the activation energy of isomerization to the energy barrier for oxirene formation.



1a **1b**

In vinylene carbonates and thioxocarbonates, the cis conformation is fixed, and we were interested in investigating the possibility that photochemical extrusion of the stable molecules CO_2 and COS might generate ketocarbenes, which may or may not subsequently isomerize to oxirene. Our preliminary experiments, which will now be described, strongly indicate that the above compounds are indeed novel precursors to the Wolff rearrangement and may constitute a new methodology for the synthesis and characterization of hitherto unknown ketenes.

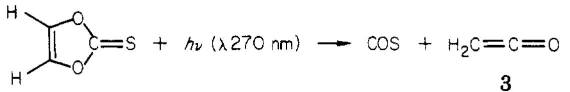
Argon-matrix (8 K) photolysis of vinylene carbonate **2**



2 **3** **4**

at λ = 210 nm resulted in the formation of CO, CO_2, ketene **3**, and glyoxal **4**, identified in the IR spectrum of the photolysate by comparison with known spectra.[11,12] Clearly, two primary processes take place simultaneously: cheletropic extrusion of CO, also encountered in the photolysis of dithiocarbonates,[13] yielding glyoxal **4**, and elimination of CO_2 to yield ketene, probably via an intermediate ketocarbene, with the former process being favored. Elimination of CO and CO_2 from the thermolysis of *o*-phenylene carbonate has also been reported,[14] although in this case CO_2 elimination is favored by an estimated ratio of 3:1.

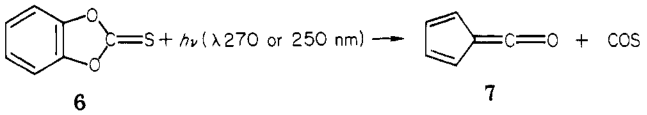
Upon thio substitution, the absorption maximum is shifted to longer wavelengths (270 nm) and elimination of COS ($\Delta H_f = -32.80$ kcal/mol)[15] should be the only observable process since $\Delta H_f = +60$ kcal/mol[16] for CS elimination. As expected, photolysis of vinylene thioxocarbonate **5** at 270 nm resulted in the exclusive formation of COS and ketene **3**, basically in 100% yield. No other bands were detected in the IR spectrum of the photolysate.



5 **3**

Flow pyrolysis of **5** at 820 °C using argon as the carrier and condensation of the pyrolysate at 8 K in an IR cell also resulted in the exclusive formation of COS and ketene **3**.

Similarly, photolysis of argon matrix isolated *o*-phenylene thioxocarbonate **6** at λ = 270 nm resulted in the formation of COS and cyclopentadienylidene ketene **7**, identified by its IR absorptions at 2133 (vs), 2130 (s), 1445 (m), 1325 (m), 898 (m), 578 (w), and 520 (w) cm^{-1}. Cyclopentadienylidene ketene has been generated by the pyrolysis of *o*-phenylene carbonate[15,17] and various other precursors[17,18] and also by the reaction of cyclopentadienylidene with a CO matrix.[19] Except for the



6 **7**

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high-frequency IR bands reported by Baird et al.[19] (which are in agreement with ours), however, the IR spectrum of 7 has not been reported. Photolysis of **6** under the same conditions but at λ = 250 nm, where COS absorbs, yielded the same products, but the time required to achieve complete photolysis was shorter.

Flow pyrolysis of **6** at 660 °C under the same conditions as described for **5** also resulted in the formation of COS and ketene **7**.

These results indicate that COS elimination from vinylene thioxocarbonates and Wolff rearrangement of the ketocarbene intermediate to ketene is probably a general process in both photolysis and pyrolysis, thus paralleling the behavior of α-diazo ketones. The advantages of using these precursors are that they are easily prepared[20,21] and can be stored in large quantities (in contrast to α-diazoacetaldehyde and *o*-diazophenol) and, under matrix-isolation conditions, it appears that **5** and **6** undergo complete conversion to COS + ketene, without interfering side reactions. Thus vinylene thioxocarbonates are ideal precursors for the synthesis and characterization of novel ketenes and, since the primary fragment is very likely a ketocarbene, photolysis and thermolysis of these compounds constitute a new methodology for mechanistic studies of the Wolff rearrangement.

No transient spectra which could be attributed to oxirene or benzoxirene were detected upon photolysis of **5** or **6**. This result was not unexpected since oxirene was not detected in the 8 K photolysis of α-diazoacetaldehyde[8] and, in fact, is predicted to be kinetically only marginally stable.[9] Also, the solution-phase photolysis of various ^{13}C-labeled annelated α-diazo ketones[22] did not yield scrambled products, presumably because the hypothetical oxirene intermediate is further destabilized by a prohibitively high ring-strain energy. As mentioned above, however, the conformation of thioxocarbonates is favorable to the generation of oxirenes, especially under matrix conditions, and we intend to examine the photolysis of variously substituted source compounds in our efforts to isolate a stable oxirene. ESR experiments are currently under way to ascertain whether ketocarbenes are formed in photolysis.

Acknowledgment. We thank the National Science and Engineering Council of Canada for financial support and Dr. E. M. Lown for helpful discussions.

Registry No. 2, 872-36-6; **3**, 463-51-4; **5**, 37635-87-3; **6**, 2231-05-2; **7**, 4727-22-4.

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Received November 21, 1979

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gem-Difluoroallyllithium: Improved Synthesis Brings Improved Applicability

Summary: The action of *n*-butyllithium in hexane on $CF_2BrCH{=}CH_2/CF_2{=}CHCH_2Br$ (5:2 to 20:1 mixture) in 5:1:1 THF/Et_2O/pentane at −95 °C generates *gem*-difluoroallyllithium which may be trapped, generally in good yield, by an in situ procedure using triorganochlorosilanes ($R_3SiCF_2CH{=}CH_2$) and aldehydes and ketones ($RR'C(OH)CF_2CH{=}CH_2$).

Sir: gem-Difluoroallyllithium (I) is of interest as a reagent which allows the introduction of a functional fluorinated substituent into organic and organometallic compounds. We have generated this reagent at low temperature by the transmetalation procedure (eq 1).[1] The reagent is not

$$Me_3SnCH_2CH{=}CF_2 + n\text{-}C_4H_9Li \xrightarrow[THF]{-95\ ^\circ C} \underset{I}{Li[CF_2CHCH_2]} + n\text{-}C_4H_9SnMe_3 \quad (1)$$

stable in solution even at −95 °C and cannot be preformed prior to its reaction with the desired substrate. Its reactions with chlorosilanes were carried out by the in situ procedure: slow addition of n-C_4H_9Li solution to a mixture of $Me_3SnCH_2CH{=}CF_2$ and the chlorosilane, so that the reagent is trapped as it is formed. The addition of $Li[CF_2CHCH_2]$ to the C=O of 3-pentanone by the in situ procedure was not successful since the rate of *n*-butyllithium addition to the ketone is faster than its rate of displacement of the difluoroallyl substituent from tin. Addition of $Li[CF_2CHCH_2]$ to the C=O bond of 3-pentanone to give $(C_2H_5)_2C(OH)CF_2CH{=}CH_2$ (75% yield) was achieved by the method of alternate, incremental additions.[1] However, this procedure is tedious and cumbersome and not well adapted to larger scale application.

In view of these difficulties with $Li[CF_2CHCH_2]$/carbonyl reactions and also because of the difficult, multistep preparative route to $Me_3SnCH_2CH{=}CF_2$, the $Li[CF_2CHCH_2]$ precursor,[1] we sought an alternative method of generating *gem*-difluoroallyllithium.

The benzoyl peroxide induced addition of dibromodifluoromethane to ethylene in an autoclave at 80 °C was reported by Tarrant and Lovelace[2] to give $CF_2BrCH_2CH_2Br$. The single example of this reaction which was described[2] involved a runaway exotherm with consequent loss of most of the contents of the autoclave through the rupture disk, but we have used this reaction repeatedly without mishap. In a typical example, the yield of $CF_2BrCH_2CH_2Br$ was 76%, based on unrecovered CF_2Br_2, which had been used in excess. Treatment of $CF_2BrCH_2CH_2Br$ with aqueous KOH at 115-130 °C gave a 5:2 mixture (by NMR) of $CF_2BrCH{=}CH_2$ and $CF_2{=}CHCH_2Br$ in 74% yield. Slow distillation of this product mixture gave a distillate with an isomer ratio which had been increased to ca. 20:1. Either isomer mixture serves well as a precursor for *gem*-difluoroallyllithium (eq 2).[3] In

$$CF_2BrCH{=}CH_2 + n\text{-}C_4H_9Li \xrightarrow{-95\ ^\circ C} Li[CF_2CHCH_2] + n\text{-}C_4H_9Li \quad (2)$$

situ reactions with chlorosilanes gave moderate to good yields of 1,1-difluoroallylsilanes. In one such reaction, when 15 mmol of *n*-butyllithium in hexane was added slowly to a mixture of 19 mmol of 20:1 $CF_2BrCH{=}CH_2/CF_2{=}CHCH_2Br$ and 30 mmol of $PhMe_2SiCl$ in 5:1:1 (by volume) THF/Et_2O/pentane at −95 °C (under nitrogen, with stirring for 60 min at −95 °C), $PhMe_2SiCF_2CH{=}CH_2$[1] was produced in 71% yield. Also prepared in this manner were $Et_3SiCF_2CH{=}CH_2$ (51%), n-$Pr_3SiCF_2CH{=}CH_2$ (50%), and $Me_3SiCF_2CH{=}CH_2$ (89%). In the case of the

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[3] In writing eq 2 we have assumed that it is $CF_2BrCH{=}CH_2$, not its isomer, which leads to $Li[CF_2CHCH_2]$, in analogy to RLi/polyhalomethane vs. RLi/allylic halide reactions. This question, however, will be investigated in future experiments.

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