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The 1,2-diphenylethyl cation via carbene fragmentation

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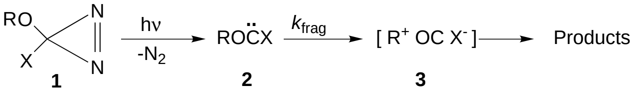
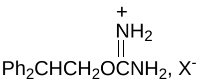
Abstract—2,2-Diphenylethoxychlorocarbene fragments with $k_{\mathrm{frag}}=2.1\times10^6$ s^{-1} in MeCN, largely with 1,2-phenyl migration and the formation of rearranged products. Related chemistry is observed for the 2,2-diphenylethyldiazonium cation. © 2001 Elsevier Science Ltd. All rights reserved.

The fragmentation of alkoxyhalocarbenes, (**2**) in Eq. (1), generates alkyl cation–halide anion ion pairs (**3**).[1] The carbenes, in turn are readily available by the photolysis (or thermolysis) of alkoxyhalodiazirines (**1**). With this methodology, we could revisit the chemistry of several pivotal cations of physical organic chemistry, including the cyclopropylmethyl[2] and cyclobutyl cations,[3] and the *exo*- and *endo*-2-norbornyl cations.[4] We have found that product distributions from ion pairs **3** resemble those obtained from analogous deaminative processes ($R^+N_2X^-$), and that the kinetics of carbene fragmentation, Eq. (1), can be measured by laser flash photolysis.[1,5] From these perspectives, we report here on the fragmentation of 2,2-diphenylethoxychlorocarbene, which features a 1,2-phenyl shift, a common motif in carbocation chemistry.



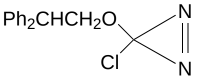
(1)

2,2-Diphenylethanol was converted to isouronium salt **4** by the reaction of 10 mmol of the alcohol with 5 mmol each of cyanamide and triflic acid in 20 ml of dry THF (25°C, 24 h).[6] Oxidation[7] of **4** with 12% aqueous NaOCl afforded diazirine **5**, which was extracted into pentane as formed, and subsequently purified by column chromatography on silica gel, eluted with cold 1:3 CH_2Cl_2/pentane. Diazirine **5** exhibited $\lambda_{\max}$ 352 nm in this solvent and $\lambda_{\max}$ 360 nm in MeCN.



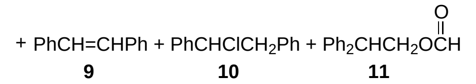
$Ph_2CHCH_2O\overset{\overset{+}{N}H_2}{\overset{\|}{C}}NH_2,\ X^-$

4



5

Photolysis of **5** in MeCN (λ >320 nm, $A_{360}=1.0$, 25°C) or in CD_2Cl_2 afforded the products shown in Eq. (2), which we attribute to 2,2-diphenylethoxychlorocarbene, **6**. Thus, 2,2-diphenylethyl chloride (**7**), 1,1-diphenylethylene (**8**), *cis*- and *trans*-stilbene (**9**), α-chlorobibenzyl (**10**), and 2,2-diphenylethyl formate (**11**) were identified by GC–MS and NMR, as well as GC and NMR spiking experiments with authentic materials.[8] Products **7**–**10** reflect prior fragmentation of carbene **6**, whereas formate **11** stems from the capture of **6** by adventitious water.[5a]



(2)

The product distributions were sensitive to the GC injector temperature: chloride **10** afforded stilbene **9** by elimination. Therefore, we determined product distributions by ^{1}H NMR integrations of crude product mixtures in $CDCl_3$ or CD_2Cl_2. Table 1 records the results for photolytic (25°C) and thermal (35°C) decompositions of diazirine **5**, as well as for the HCl-initiated decomposition of 2,2-diphenyldiazoethane (**12**).

$Ph_2CHCH{=}N_2$

12

Keywords: carbenes; diazirines; kinetics.

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Table 1. Product distributions from diazirine **5** and diazoalkane **12**[a]

Run	Subst.	Cond.	% **7**	% **8**	% *tr*-**9**	% *cis*-**9**	% **10**	% **11**	Rearr.[b]
1[c,d]	**5**	*hν*, MeCN	1.2	1.9	34.7	8.5	38.0	4.0	6
2[c,e]	**5**	*hν*, CD_2Cl_2	2.2	1.2	38.9	5.5	38.7	3.7	24
3[f]	**5**	Δ, CD_2Cl_2	0.9	0.6	43.2	2.2	41.9	–	58
4[c,g]	**5**	*hν*, CD_2Cl_2	17.3	3.3	24.1	4.8	36.2	14.5	3.2
5[c]	**12**	HCl, MeCN	12.6	3.8	56.8	–	26.9	–	5.1
6[c,g]	**12**	HCl, MeCN	9.2	8.9	48.3	0.8	32.7	–	4.5

[a] NMR integration is relative to $PhCH_2CH(Ph)Cl$ of product **10**. Results are averages of two experiments.

[b] The extent of rearrangement is taken as (**9**+**10**)/(**7**+**8**).

[c] At 25°C.

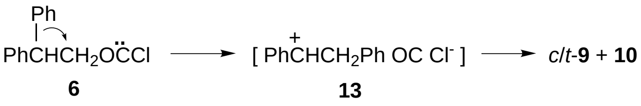
[d] 11.7% of an unknown product was also present.

[e] 9.8% of an unknown product was present.

[f] At 35°C for 12 h; 11.2% of unknown was present.

[g] tetra-*n*-Butylammonium chloride (2.52 M) was present.

When 2,2-dipenylethoxychlorocarbene (**6**) is generated photochemically (runs 1 and 2) or thermally (run 3) from diazirine **5**, carbene fragmentation very largely occurs with 1,2-Ph migration, affording products **9** and **10** which derive from the 1,2-diphenylethyl cation; cf. Eq. (3). The rearranged cation, as part of ion pair **13**, can give either the stilbenes (**9**) by proton loss (probably to Cl^-), or α-chlorobibenzyl (**10**) by cation/anion collapse.

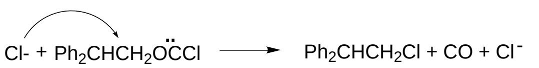


$$\underset{\mathbf{6}}{\overset{\text{Ph}}{\text{PhCH}}\text{CH}_2\text{O}\ddot{\text{C}}\text{Cl}} \longrightarrow \underset{\mathbf{13}}{[\,\overset{+}{\text{PhCH}}\text{CH}_2\text{Ph OC Cl}^-\,]} \longrightarrow c/t\text{-}\mathbf{9} + \mathbf{10} \qquad (3)$$

We imagine that the fragmentation of **6**→**13** is concerted with phenyl migration, as depicted in Eq. (3), and in harmony with the fragmentations of neopentyloxychlorocarbene and 1-(adamantyl)methoxychlorocarbene which also mainly afford rearranged products (derived from the *t*-amyl or homoadamantyl cations, respectively).[5a,9,10]

Very little product of runs 1–3 can be attributed to the unrearranged primary 2,2-diphenyl-1-ethyl cation ($Ph_2CHCH_2^+$). Indeed, products **7** and **8** might arise from chloride or HCl attack directly on carbene **6**, or loss of H^+ concerted with the fragmentation. Avoidance of primary cation formation is also suggested by the relatively high rate constant observed for the fragmentation of **6**.

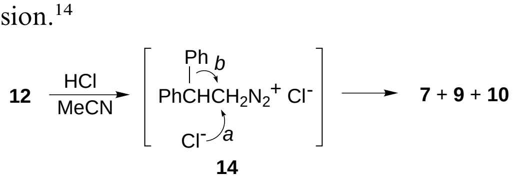
When the carbene is generated in the presence of 2.5 M added chloride, we observe a significant increase in the yield of unrearranged primary chloride **7** (Table 1, run 4). The extent of rearrangment [expressed as (**9**+**10**)/(**7**+**8**)] decreases from 24 (run 2) to 3.2 (run 4); cf. Table 1. We attribute this to fragmenting S_N2 attack of Cl^- on the carbene, Eq. (4), competitive with the phenyl migration fragmentation process of Eq. (3).[11] The 'bimolecular' fragmentation mechanism has been shown to govern the fragmentations of *n*-BuOCCl and *i*-BuOCCl.[5b] In these cases, as in the present example, the intermediacy of a primary alkyl cation is avoided.



$$\text{Cl}^- + \text{Ph}_2\text{CHCH}_2\text{O}\ddot{\text{C}}\text{Cl} \longrightarrow \text{Ph}_2\text{CHCH}_2\text{Cl} + \text{CO} + \text{Cl}^- \qquad (4)$$

To further the analogy[1] between carbene fragmentation and dediazoniation reactions,[12] we examined the HCl-catalysed decomposition of diazoalkane **12**[13] in MeCN saturated with gaseous HCl (3.5 M HCl). Reaction of HCl with **12** generates 2,2-diphenylethyldiazonium chloride ($Ph_2CHCH_2N_2^+Cl^-$, **14**); decomposition of **14** then affords **7**, **8**, *trans*-**9**, and **10**; cf. Table 1, run 5.

Comparison of runs 5 and 1 shows that the diazonium ion decomposition produces more unrearranged chloride (**7**), more *trans*-stilbene (**9**), and less rearranged chloride (**10**) than does the carbene fragmentation. The overall extent of rearrangement (defined above) is only ~5 in run 5, but reaches 26 in run 1. Chloride ion attack at the α-carbon of the diazonium chloride ion pair **14** (competitive with 1,2-phenyl migration) must be responsible for the enhanced yield of **7**; Eq. (5), paths *a* versus *b*. Other decompositions of primary alkyldiazonium ions, for example the acetolysis of the chiral butanediazonium-α-*d* cation, occur bimolecularly with inversion.[14]



$$\mathbf{12} \xrightarrow[\text{MeCN}]{\text{HCl}} \underset{\mathbf{14}}{\left[\underset{\text{Cl}^-\,a}{\overset{\text{Ph}\,b}{\text{PhCH}}}\text{CH}_2\text{N}_2^+\,\text{Cl}^-\right]} \longrightarrow \mathbf{7+9+10} \qquad (5)$$

Curiously, the formation of **7** from **14** is not subject to enhancement by added chloride (Table 1, run 6), whereas the opposite holds for carbene fragmentation (runs 2 and 4). This probably reflects the substantial excess of HCl already present in the MeCN solvent for the decomposition of **12** and **14**.

The product-based evidence suggests that both carbene **6** and diazonium ion **14** decompose by composits of bimolecular attacks at their α-carbon atoms and 1,2-phenyl migrations that are (weakly) concerted with CO or N_2 expulsion. In related solvolytic processes, such as the 75–100°C acetolysis of 2,2-diphenylethyl tosylate,[15] phenyl participation leads to solvolytic rate enhancement and to the rearranged product, *trans*-stilbene.[16] The phenyl participation which accompanies expulsion of the tosylate leaving group is sufficient to exclude competing mechanisms that would afford unrearranged products. In the decompositions of **6** or **14**, however, the activation energies for the loss of CO or N_2 are so low that displacements at the α-carbon are able to compete with phenyl migration.

Rate constants for the fragmentations of **6** in MeCN or dichloroethane (DCE) were determined by laser flash photolysis (LFP)[17] using the pyridine visualisation method.[18] LFP at 351 nm and 25°C of diazirine **5** in MeCN ($A_{360}=1.0$) in the presence of pyridine afforded a UV absorption due to the formation of a carbene–pyridine *N*-ylide (monitored at 436 nm in MeCN and 428 nm in DCE). A correlation of the apparent rate constants for ylide formation, k_{obs} ($3.0–8.7\times10^6$ s^{-1}) versus [pyridine] (0.41–3.3 M) was linear (eight points, $r=0.997$) with a slope of 2.1×10^6 M^{-1} s^{-1}, which represents the rate constant for ylide formation. The *Y*-intercept was 2.2×10^6 s^{-1}, which is the sum of the rate constants for all processes that destroy the carbene when [pyridine]=0. We take 2.2×10^6 s^{-1} as a good estimate of k_{frag}, the rate constant for the fragmentation of $Ph_2CHCH_2\ddot{O}CCl$.

A repetition of these experiments led to $k_{\mathrm{frag}}=1.9\times10^6$ s^{-1}, so that the average $k_{\mathrm{frag}}=(2.05\pm0.15)\times10^6$ s^{-1}. Similarly, k_{frag} was determined in DCE; two sets of experiments gave $k_{\mathrm{frag}}=(4.6\pm0.4)\times10^5$ s^{-1}. The fragmentation appears to be ~4.4 times slower in the less polar solvent, DCE.[19]

A surprisingly good Arrhenius correlation was obtained between $\ln k_{\mathrm{frag}}$ and $1/T$ for the fragmentation of **6** in MeCN studied between 231 and 294 K (seven points, $r=0.97$). We obtained $E_a=1.5$ kcal mol^{-1}, $\ln A=18.2$ s^{-1}, and $\Delta S^*=-24$ e.u. (298 K). The remarkably low E_a underscores the concerted nature of the **6**→**13** fragmentation, Eq. (3); it is hard to believe that a primary cation ($Ph_2CHCH_2^+$) could be formed at such a low energetic cost, even by fragmentation of **6**.[20] Negative activation entropies, which may reflect solvent restriction during these polar fragmentations, have been previously noted. For example, the fragmentation of 1-adamantylmethoxychlorocarbene, largely to the homoadamantyl cation, had $E_a=3.6$ kcal mol^{-1}, $\Delta S^*=-18$ e.u. (298 K).[5c] The more negative ΔS^* attending the fragmentation of **6** may signal additional rotational restrictions connected with phenyl participation.

In summary, 2,2-diphenylethoxychlorocarbene fragments with $k_{\mathrm{frag}}=2.1\times10^6$ s^{-1} ($E_a=1.5$ kcal mol^{-1}, $\Delta S^*=-24$ e.u.) in MeCN, largely with 1,2-phenyl migration to ion pair **13**, from which rearranged products (stilbene, α-chlorobibenzyl) form. Small quantities of unrearranged fragmentation products (2,2-diphenylethyl chloride, 1,1-diphenylethene) also form, probably directly from the carbene; fragmentation to the unrearranged 2,2-diphenyl-1-ethyl cation is unlikely. Similar chemistry is found for the 2,2-diphenylethyldiazonium chloride ion pair (**14**). The low activation energies of the carbene fragmentation (or dediazoniation) reactions make possible competitive displacement reactions that afford at least some unrearranged products, in contrast to the solvolysis of 2,2-diphenylethyl tosylate ($\Delta H^*=27.1$ kcal mol^{-1})[15a] where phenyl partcipation strongly dominates, and only rearranged products form.[15]

Acknowledgements

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9. (a) 1,2-Hydride shift concerted with fragmentation of **6** would give Ph_2C^+Me. No Ph_2CClMe corresponding to this cation was observed (δ 2.30 in $CDCl_3$),[9b] although some **8** could have been formed by proton loss from the cation; (b) Strazzolini, P.; Giumanini, A. G.; Verardo, G. *Tetrahedron* **1994**, *50*, 217.
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11. The increase of **7** comes largely at the expense of *trans*-stilbene, which decreases from 38.9% in run 2 to 24.1% in run 4. The enhanced yield of formate **11** in run 4 probably reflects adventitious water introduced with the chloride salt.

12. For a contemporary review of aliphatic dediazoniation, see: Zollinger, H. *Diazo Chemistry II*; Weinheim: VCH, 1995; Chapter 7.
13. 2,2-Diphenyldiazoethane was prepared by the method of Hellerman, L.; Cohn, M. L.; Hoen, R. E. *J. Am. Chem. Soc*. **1928**, *50*, 1716 with some modifications. 2,2-Diphenylethylamine was converted to the urethan with ethyl chloroformate; the urethan was nitrosated with $NaNO_2$ in $HOAc–Ac_2O$ at 0°C; and the *N*-nitrosourethan was treated with NaOEt/EtOH (−2 to −10°C, 3 h), affording diazoalkane **12** (65%). Red, crystalline **12**, was freed of ethanol under vacuum at −10°C, and exhibited $\nu_{N2} = 2059$ cm^{-1}; ^{1}H NMR (δ, DMSO-d_6) 7.20–7.35 (m, 10H, 2Ph), 4.95 (d, $J = 7$ Hz, 1H, CH), 4.02 (d, $J = 7$ Hz, 1H, CH).
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16. With substituted 2,2-diarylethyl tosylates, added acetate ion leads to (rearranged) 1,2-diarylethyl acetates and stilbenes.[15d]
17. See Ref. 5b for a description of our LFP system.
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19. $\varepsilon_{MeCN} = 35.6$; $\varepsilon_{DCE} = 10.7$.
20. k_{frag} is also ‘high,’ consistent with concerted fragmentation, e.g. k_{frag} for $PhCH_2OCCl$ is $0.7–1.3\times10^6$ s^{-1}.