

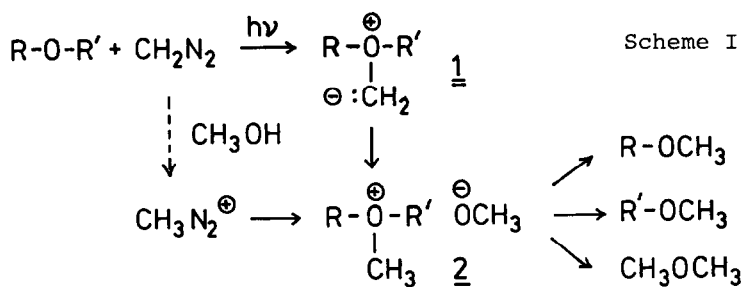
OXYGEN YLIDES - I.  
REACTIONS OF CARBENES WITH OXETANE

Klaus Friedrich, Ulrich Jansen, and Wolfgang Kirmse\*

Abteilung für Chemie der Ruhr-Universität Bochum,  
Postfach 102148, D-4630 Bochum, Federal Republic of Germany

**SUMMARY** The ylides generated from carbenes ( $:CH_2$ ,  $:CHCO_2Et$ ,  $:CHPh$ ) and oxetane in the presence of methanol undergo Stevens rearrangement and protonation competitively, yielding tetrahydrofurans and 1,3-dialkoxycyclopropanes as major products.

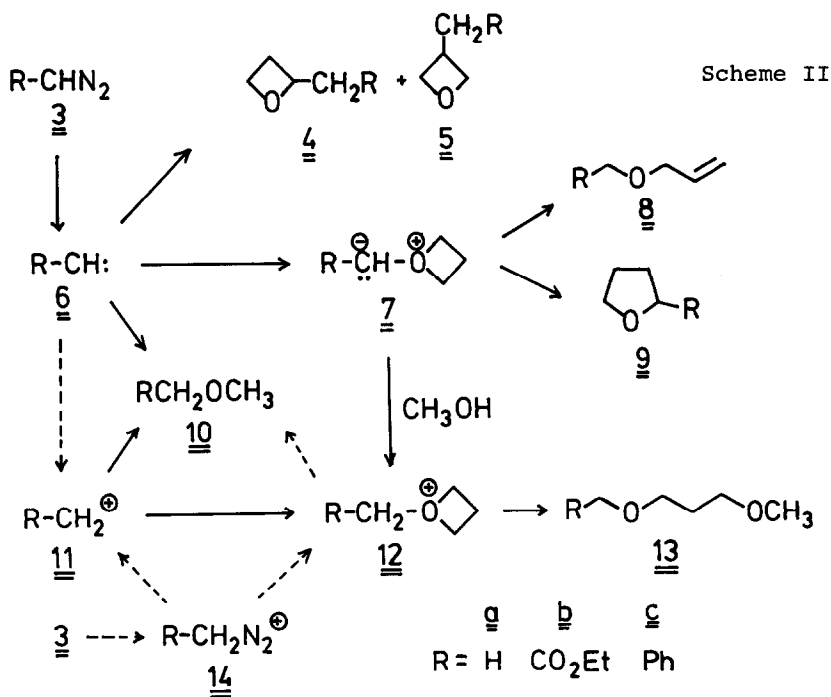
Ylide formation as a result of carbene interaction with the unshared electron pairs of heteroatoms has been extensively reviewed.<sup>1</sup> In contrast to the abundant literature on nitrogen, phosphorus, sulfur, etc., little is known about oxygen ylides. The most conclusive evidence to date for the intervention of oxonium ylides comes from the [2,3]sigmatropic rearrangements induced with allylic ethers<sup>2,3</sup> and acetals.<sup>4</sup> The CIDNP results obtained with benzylic ethers were also attributed to radical pairs derived from oxonium ylides.<sup>5</sup> Recently, Olah et al.<sup>6</sup> reinvestigated Meerwein's reaction of methylene with dialkyl ethers.<sup>7</sup> In competition with C-H insertion, about 10 % of methyl alkyl ether formation was also observed. Apparently the predominant behavior of oxonium methyllides 1 is to undergo protonation with methanol (or water) present as an impurity, rather than to undergo Stevens type rearrangement (Scheme I). A purely cationic mechanism, generating trialkyloxonium ions 2 via methanediazonium ions,<sup>8</sup> cannot be rigorously excluded.



In the course of related investigations it occurred to us that oxetane might be a useful substrate to resolve such mechanistic problems. As compared to dialkyl ethers, the oxygen of oxetane is less shielded and more amenable to carbene attack. The ring strain of oxetane-derived ylides (7) should enhance the rate of Stevens type rearrangement. Our experimental results conform to these expectations. We report here that various carbenes react with oxetane predominantly at oxygen, and that Stevens rearrangement and protonation of oxetane-derived ylides (7) occur in competition.

Diazomethane (3a), ethyl diazoacetate (3b), and phenyldiazomethane (3c) were photolyzed in oxetane and in oxetane-methanol mixtures (medium-pressure mercury arc, pyrex vessel). The products were separated by GC and identified by their spectra, by comparison with authentic samples, and/or by independent synthesis (Table). Even with methylene C-H insertion accounts for less than half of the products. The  $\alpha:\beta$  ratio (corrected for the number of hydrogens) is 1.7, somewhat higher than that found for tetrahydrofuran (1.3).<sup>9</sup> The more selective carbenes 6b,c strongly favor electrophilic attack at oxygen over C-H insertion, which occurs almost exclusively at the  $\alpha$  position. The oxetane-derived ylides 7 undergo ring expansion (Stevens rearrangement) to give tetrahydrofurans 9 in competition with intramolecular  $\beta$ -elimination, yielding allyl ethers 8. The 9:8 ratio increases in the order 7a,b,c. Delocalization of electrons from the ylidic carbon, as in 7b,c, would be expected to retard  $\beta$ -elimination and to facilitate the Stevens rearrangement (radical-pair mechanism).<sup>10</sup>

Additional products are formed in oxetane-methanol mixtures. Some of them are trivial as they arise by C-H and O-H insertions of the carbenes with methanol. Methylene (6a) yielded ethanol and dimethyl ether; ethoxycarbonyl-



carbene (6b) gave essentially the product pattern previously reported for the photolysis of ethyl diazoacetate in methanol.<sup>11</sup> The most important product of these reactions is 13, incorporating carbene, oxetane, and methanol. The formation of 13 in relative yields up to 50 % (Table) is reasonably attributed to nucleophilic substitution of the oxonium ion 12. 1-Methyltetrahydrofuranium ion (the homolog of 12a) has been reported to react with nucleophiles predominantly by ring opening<sup>12</sup>; analogous behavior of 12 should be expected.

Table. Product Distributions from Photolyses of Diazo Compounds in Oxetane and Oxetane-Methanol<sup>a)</sup>

	<u>4</u>	<u>5</u>	<u>8</u>	<u>9</u>	<u>13</u>	$\frac{\underline{8}+\underline{9}+\underline{13}}{\underline{4}+\underline{5}}$	% <sup>b)</sup>
CH <sub>2</sub> N <sub>2</sub> ( <u>3a</u> )							
Oxetane, neat	36.9	10.8	13.2	39.1		1.1	
Oxetane-MeOH (1:1) <sup>c)</sup>	37.2	13.6	8.3	22.5	18.4	1.0	70 <sup>d)</sup>
N <sub>2</sub> CHCO <sub>2</sub> Et ( <u>3b</u> )							
Oxetane, neat	17.5	tr	12.2	70.3		4.7	
Oxetane-MeOH (3:1)	18.2	tr	6.3	23.6	51.9	4.5	54
(1:1)	21.0	tr	6.1	22.7	50.2	3.8	29 <sup>e)</sup>
PhCHN <sub>2</sub> ( <u>3c</u> )							
Oxetane, neat	9.7	-	12.2	78.1		9.3	
Oxetane-MeOH (1.5:1)	7.1	-	8.7	43.8	40.4	13.1	57 <sup>f)</sup>
Oxetane-MeOH (1:1)	6.3	-	7.9	34.7	51.1	14.9	44

a) Oxetane-derived products normalized to 100 %

b) Relative yield of oxetane-derived products

c) v:v, molar ratio 0.62

d) Methanol-derived products were MeOMe (15.5 %) and EtOH (14.8 %). The estimate of the volatile dimethylether may be too low.

e) Methyl methoxyacetate (3 %), methyl ethoxyacetate (20 %), ethyl methoxyacetate (40 %), and ethyl β-hydroxypropionate (8 %) were formed by reaction of 3b with methanol.

f) Benzyl methyl ether (10c) was the only additional product.

An obvious route to oxonium ions 12 is protonation of ylides 7. Alternatively, oxetane might be alkylated by carbocations 11 or by diazonium ions 14.<sup>8</sup> Although the diazo compounds 3 used in this study were sufficiently stable in oxetane-methanol in the dark, protonation of photoexcited states 3<sup>\*</sup> or of carbenes 6 is conceivable. The alternative mechanisms may be distinguished on the basis of product ratios. Protonation of ylide 7 does not affect the fraction of C-H insertion products (4 and 5); 13 is formed at the expense of 8 and 9. In contrast, protonation of diazo compound 3 or of carbene 6 generates (additional) 13 by an ylide-independent path. Exclusive operation of the cationic route via 11 and (or) 14 should give identical (8+9):(4+5) ratios in the presence and absence of methanol. Our data (Table) clearly exclude this case. A significant contribution of the cationic mechanism to the formation of 13 should be revealed by an increase in (8+9+13):(4+5) ratios with added methanol. We observe slightly decreasing ratios for methylene (6a) and ethoxycarbonylcarbene (6b),<sup>13</sup> but slightly increasing ratios for phenylcarbene (6c) (Table). Consequently, there is no reason to assume protonation prior to the ylide stage, except for the case of phenylcarbene. The behavior of phenylcarbene in alkene-methanol mixtures also suggests the intervention of benzyl cations (11c).<sup>14</sup>

In conclusion, oxetane-derived ylides 7 have been shown to undergo protonation by methanol in competition with 1,2-carbon shifts (Stevens rearrangement) and intramolecular β-elimination. The influence of charge-stabilizing

groups (Ph, CO<sub>2</sub>Et) on the relative rates is small. More dramatic structural effects are currently under investigation with ylides derived from cyclopropylidenes and alkenylidenes.

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13. Decreasing (8+9+13):(4+5) ratios are attributed to competing reactions of the oxonium ions 12. Nucleophilic displacement may give minor amounts of 10, indistinguishable from the O-H insertion product of 6. No search for oligomers, resulting from 12 and oxetane,<sup>8</sup> has been made in the present study.
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