what we believe to be the first isolation of a well-characterized mixed carboxylate of a metal.

Solutions of $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$ in chloroform are unstable. Scrambling of carboxylate groups occurs and may be followed conveniently by observing the nmr spectrum *vs.* time (Figure 1). New peaks arise at δ ~2.178 and are tentatively assigned to $Be_4O(CH_3CO_2)_4(CCl_3CO_2)_2$. Interestingly, a 1:5 mole ratio mixture of $Be_4O(CCl_3CO_2)_6$ and $Be_4O(CH_3CO_2)_6$ in chloroform gave at equilibrium an nmr spectrum identical with curve D, Figure 1. In view of our observation of carboxylate scrambling, we believe that the claim of Novoselenova and Semenenko[4] for the preparation of pure acetate–monochloroacetate carboxylates simply by melting together an appropriate ratio of starting materials is untenable.

Current work is aimed at the isolation of other members in the series $Be_4O(CH_3CO_2)_x(CCl_3CO_2)_{x-6}$. By examining the rate of carboxylate scrambling for different members of the series we hope to postulate a reasonable mechanism for the scrambling reaction.

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Demonstration of Two Mechanistic Pathways in the Reaction of Dimethylketene with N-Isobutenylpyrrolidine

Sir:

Kinetic[1] and stereochemical results[2–4] are consistent with a concerted mechanism for cyclobutanone formation from ketenes and olefins or vinyl ethers. Dimethylketene combines with isobutenyldialkylamines to give cyclobutanones and 2:1 adducts[5] which proved to be γ-methylene-δ-lactones like **5**.[6] We showed recently[7] that the ratio of the 2:1 adduct **5** and the 1:1 adduct **3** from N-isobutenylpyrrolidine (**2**) is strongly dependent on the concentration of dimethylketene (**1**). The formation of **5** is best interpreted as a 1,4-dipolar cycloaddition[8,9] of the zwitterionic intermediate **4** to the carbon–carbon double bond of **1**, especially since **3** is not converted to **5** by an excess of **1**. New kinetic and competition experiments now establish that two mechanisms participate in the formation of the cyclobutanone **3**.

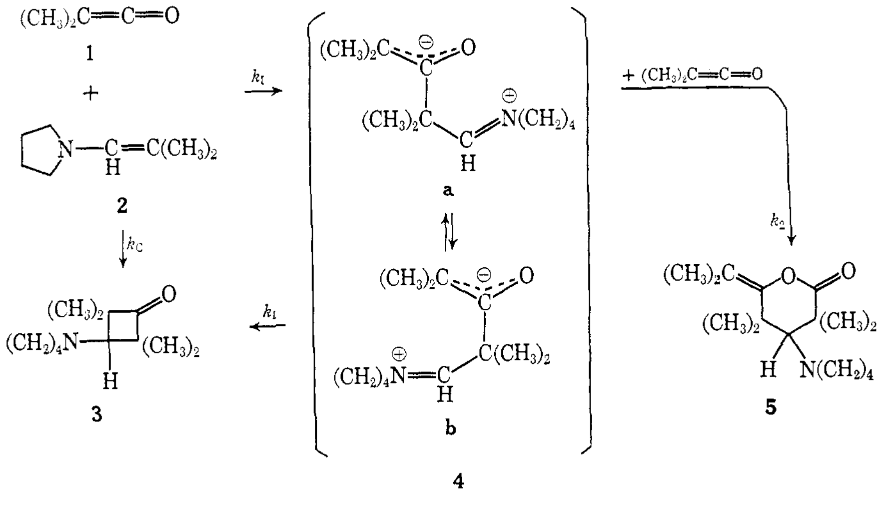

Table I. Reactions of Dimethylketene (**1**) with N-Isobutenylpyrrolidine to give **3** and **5**

[**1**], *m*	**3**, mmoles	**5**, mmoles	**3** + **5**, %	mmoles of **3** × [**1**]/ mmoles of **5**	k_1/k_2
(1) 3.594 mmoles of **2** + 20.80 mmoles of **1** in benzene; 2.85 mmoles of **3** deducted for the evaluation of k_1/k_2					
1.962	2.87	0.722	100.0	7.8	0.056
0.473	2.93	0.665	100.1	2.1	0.057
0.269	2.98	0.627	100.2	1.3	0.053
0.145	3.06	0.539	100.0	0.8	0.055
(2) 3.594 mmoles of **2** + 25.23 mmoles of **1** in acetone; 1.91 mmoles of **3** deducted for the evaluation of k_1/k_2					
2.659	2.01	1.62	101.1	3.29	0.164
0.796	2.21	1.44	101.6	1.22	0.166
0.469	2.36	1.32	102.4	0.84	0.166
0.259	2.56	1.02	99.7	0.65	0.161
(3) 3.514 mmoles of **2** + 22.37 mmoles of **1** in acetonitrile; 1.51 mmoles of **3** deducted for the evaluation of k_1/k_2					
2.033	1.81	1.70	100.0	2.14	0.36
0.432	2.43	1.15	102.2	0.91	0.36
0.268	2.66	0.83	99.8	0.85	0.37
0.144	2.95	0.57	100.3	0.74	0.36

We treated **2** with an excess of **1** in several anhydrous solvents at room temperature under nitrogen. The effect of dilution was studied by carrying out four experiments in each solvent. The ratio **2**:**1** was kept constant, but the molar concentrations differed by more than one order of magnitude. After 5 days the solvent was removed and a weighed amount of tetrachloroethane as nmr standard was added. Nmr analysis of the mixture of **3**, **5**, and tetramethylcyclobutanedione established that virtually quantitative yields of **3** + **5**

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[1] R. Huisgen, L. A. Feiler, and P. Otto, *Tetrahedron Letters*, 4485 (1968); *Chem. Ber.*, **102**, in press.

[2] R. Huisgen, L. A. Feiler, and G. Binsch, *Angew. Chem. Intern. Ed. Engl.*, **3**, 753 (1964).

[3] R. Montaigne and L. Ghosez, *Angew. Chem.*, **80**, 194 (1968).

[4] G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Letters*, 4497 (1968); R. Huisgen, L. A. Feiler, and G. Binsch, *Chem. Ber.*, **102**, in press.

[5] R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963).

[6] R. H. Hasek, P. G. Gott, and J. C. Martin, *ibid.*, **29**, 2513 (1964).

[7] P. Otto, L. A. Feiler, and R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, **9**, 737 (1968).

[8] R. Huisgen, M. Morikawa, K. Herbig, and E. Brunn, *Chem. Ber.*, **100**, 1094 (1967).

[9] Review: R. Huisgen in "Proceedings of the First International Congress of Heterocyclic Chemistry," R. N. Castle, Ed., John Wiley & Sons, Inc., New York, N. Y., 1969, in press.

Table II. Rate Constants of Concerted and Nonconcerted Reactions of N-Isobutenylpyrrolidine and Dimethylketene in Several Solvents

Solvent	E_T[a]	% concerted	k_1/k_2	k_{exptl}	k_C $\times 10^5$, l. mol^{-1} sec^{-1}	k_I
Hexane				11.9		
Cyclohexane	31.2	92.0	0.054	13.5	12.4	1.08
Toluene				83		
Benzene	34.5	79.4	0.056	113	90	23
Dioxane	36.0	70.8	0.027	170	120	50
Chlorobenzene	37.5	72.8	0.11	231	168	63
Chloroform	39.1	62.9	0.57	365	230	135
Acetone	42.2	53.1	0.17	718	382	337
Dimethylformamide				979		
Acetonitrile	46.0	43.0	0.36	1059	455	604

[a] E_T is an empirical parameter of solvent polarity: K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, *Ann. C*, **661**, 1 (1963); see also C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965).

based on **2** were obtained. If the formation of the zwitterion **4** is the only primary reaction, relation 1 should hold.

$$\frac{d[\mathbf{3}]}{d[\mathbf{5}]} = \frac{k_1}{k_2[\mathbf{1}]} = \frac{\text{mmoles of } \mathbf{3}}{\text{mmoles of } \mathbf{5}} \qquad (1)$$

As illustrated in the fifth column of Table I for three solvents, the ratios do not show the expected constancy. Only after deducting 2.85 mmoles of **3** from the yields obtained in four experiments in benzene do the residual amounts of **3** fit the competition correlation above: k_1/k_2 becomes constant. We conclude that two rate-determining primary reactions are competing. In one an intermediate is produced which can either form **3** or can be intercepted by dimethylketene to give **5**. In the other, **1** and **2** combine directly to yield **3**. The two competing primary reactions must be of the same order, very likely bimolecular. The most straightforward interpretation is the assumption of a competition between the concerted cycloaddition (k_C) and the process giving the 1,4 dipole **4** as intermediate (k_I). This leads to the conclusion that in benzene 79% of the enamine **2** reacts concertedly to give **3** while 21% goes through zwitterion **4**.

Analogous sets of experiments bring to light a pronounced solvent dependence (Table II). The path through the zwitterion (k_I), only 8% in cyclohexane, gains importance with rising solvent polarity and reaches 57% in acetonitrile. Log (k_I/k_C), evaluated from the percentages of the competing primary reactions, gives a moderately good correlation with E_T[10] (Figure 1).

We have measured the over-all rate of the reaction $\mathbf{1} + \mathbf{2}$ (*i.e.*, $k_{\text{exptl}} = k_C + k_I$) photometrically in the same solvents. The second-order k_{exptl} values (Table II) are corrected for the much smaller rate of dimerization of **1**.[11] The correlation of log k_{exptl} with E_T (Figure 1) is more qualitatively than quantitatively obeyed. The reaction is 79 times faster in acetonitrile than in cyclohexane.

The over-all constant k_{exptl} allows a separation into the partial rate factors of the concerted addition (k_C) and the formation of zwitterion **4** (k_I). Table II reveals that k_I depends to a much higher extent on solvent polarity than k_C. In acetonitrile the 1,4 dipole **4** is produced 560 times faster than in cyclohexane, while the same solvent change accelerates the concerted pathway (transition state with partial charges[1]) only 36-fold.

On first glance it is surprising that k_1/k_2, the ratio of rate constants starting from the zwitterion **4**, is <1 (Table II). We suggest that the zwitterion **4** is primarily formed in the rotameric state **a** with lowest coulombic potential. The ring closure to **3** must be preceded by a rotation of **4a** to **4b** which has a higher coulombic potential; this slows down the rate of ring closure. That k_1/k_2 increases from 0.054 to 0.57 with rising solvent polarity is in accord with this explanation.

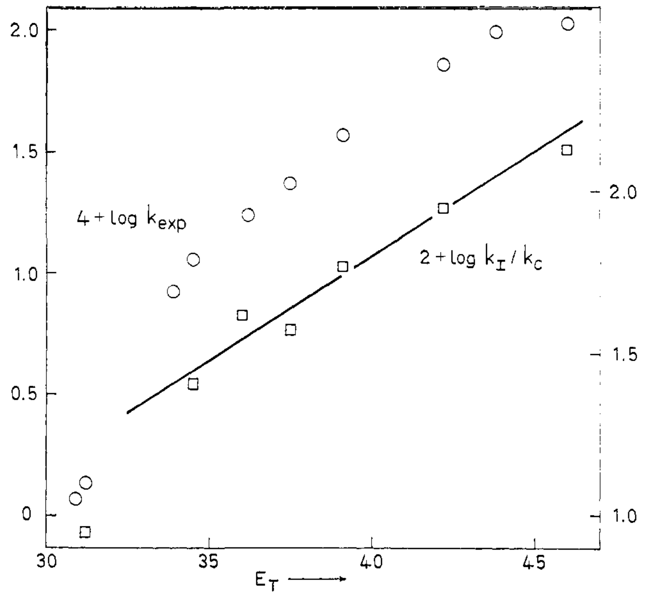

Figure 1. Kinetics of the reaction of N-isobutenylpyrrolidine with dimethylketene. Correlation of log (k_I/k_C) and log k_{exptl} with solvent polarity E_T[10] (see Table II, footnote *a*).

It is significant to note that in the reaction of dimethylketene with *enamines* the two-step process through the zwitterion competes with the concerted mechanism. The addition of ketenes to *vinyl ethers* seems not to involve the two-step process at all. There is superior stabilization of the formal charges in the zwitterion **4**.

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(10) See Table II, footnote *a*.

(11) R. Huisgen and P. Otto, *J. Am. Chem. Soc.*, **90**, 5342 (1968).