however, convenient representations: D. J. Darensbourg and A. H. Graves, *Inorg. Chem.*, **18**, 1257 (1979).

(17) This substitution can readily be effected through efficient removal of CO as it is evolved during the substitution process.

Gerard R. Dobson,* Khalil J. Asali
Department of Chemistry, North Texas State University
Denton, Texas 76203

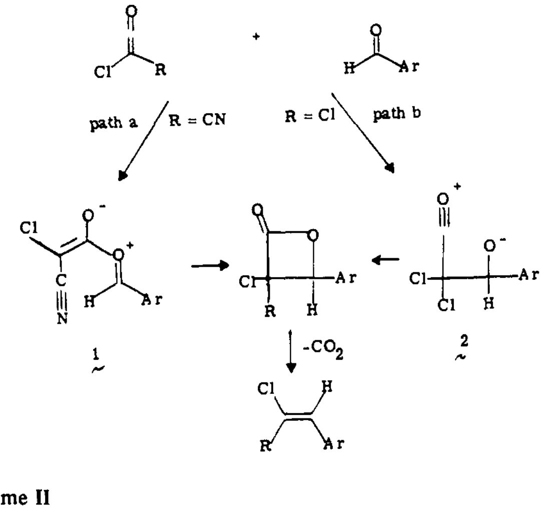
Received February 9, 1979

Cyanoketenes. Cycloadditions of Halocyanoketenes to Benzaldehydes

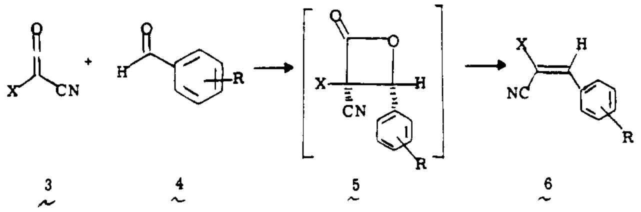
Sir:

Reported here is an investigation of the reaction of halocyanoketenes[1] with aromatic aldehydes to give exclusively the *E* isomer of 1-halo-1-cyano-2-phenylethenes (**6a–m**). As anticipated, the penultimate precursors to these alkenes are the corresponding β-lactones (**5a–m**) formed by the cycloaddition of the ketene to the aldehyde carbonyl group; these β-lactones then suffer stereospecific decarboxylation under the reaction conditions to give the alkenes. Even though this stereoselective conversion of an aldehyde into an alkene is of synthetic note, it does not constitute the most significant aspect of this work. Most important is the fact that the initial cycloaddition is a nonconcerted dipolar process in which the cyanoketene uniquely functions as an electrophile and the aldehyde as the nucleophile (zwitterion **1**, Scheme I). To our knowledge, such an observation is without precedent since all other ketene-aldehyde cycloadditions for which mechanistic data has been reported suggests nucleophilic character to the ketene and electrophilic character to the aldehyde (zwitterion **2**, Scheme I).[2] Scheme I summarizes the mechanistic rationale for the work outlined here using chloro- (or bromo-) cyanoketene (path a) and compares it to results recently reported by Krabbenhoft[2e] for an analogous study with dichloroketene (path b).

Scheme I



Scheme II



The halocyanoketene cycloadditions were accomplished by generating the cyanoketenes from 4-azido-3-halo-5-methoxy-2(5*H*)-furanone in refluxing benzene in the presence of 1 equiv of the aldehyde. The reactions were complete within 5 hr to give only the *E* isomers of 1-halo-1-cyano-2-phenylethene, **6a–m**, as isolable products (Scheme II and Table I).[4] The reaction conditions preempted isolation of the β-lactones **5a–m**. However, in one case, **5l**, this product was detected by monitoring the reaction with IR and ^{1}H NMR spectroscopy; the former showed the formation and subsequent disappearance of the characteristic β-lactone carbonyl absorption at 1860 cm^{-1} and the latter showed the transient absorption of the methine proton in **5l** at δ 5.99. The indicated *E* stereochemistry of the β-lactones is assumed since the thermally induced decarboxylation of β-lactones is known to proceed with retention of stereochemistry.[5]

The structures of the alkenes **6a–m** are based upon spectral and analytical data, and, additionally, in one case, **6h**, upon an independent synthesis involving antarafacial addition of bromine to (*E*)-1-cyano-2-phenylethene followed by antarafacial (E_2) dehydrobromination. This transformation gives a product which is identical in all respects to the product obtained by the cycloaddition of bromocyanoketene to benzaldehyde, i.e., **6h**. Thus, the stereochemistry of **6h** can be reasonably concluded to be *E*, and, by implication, analogous stereochemistry for the other alkenes are assigned.

The mechanism of these cycloadditions was established to involve a zwitterionic intermediate such as **1** rather than **2** by the following data. (1) Chlorocyanoketene did not react with the electron-deficient carbonyl of chloral. Many other ketenes, including dichloroketene, are known to cycloadd to this aldehyde.[2e] (2) The product yields (Scheme I) observed in the cycloadditions of the halocyanoketenes to the benzaldehydes

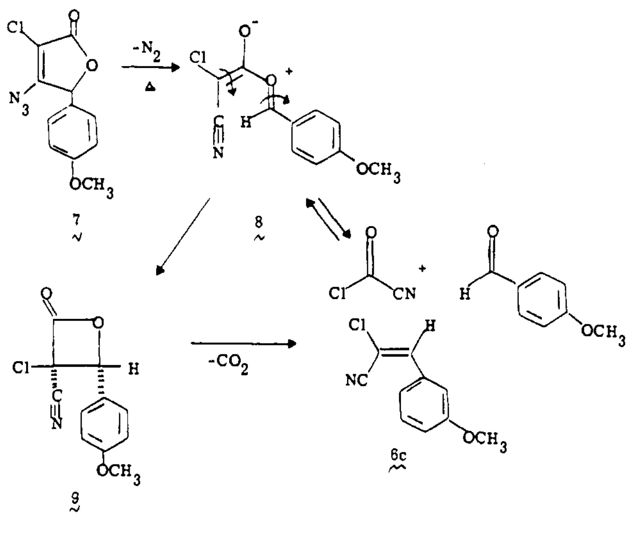
Table I

compd	X	R	yield, %	mp, °C	^{13}C NMR, δ(CDCl$_3$) C_2	C_1	^{1}H NMR, δ(CDCl$_3$), vinyl H	IR, C≡N
6a	Cl	2,4-(OCH$_3$)$_2$	92	92-94	140.0	97.0	7.67	2210
6b	Cl	4-N(CH$_3$)$_2$	78	58-60	145.5	93.4	7.16	2202
6c	Cl	4-OCH$_3$	73	53-55	144.9	97.3	7.26	2208
6d	Br	4-OCH$_3$	79	66-67	148.5	81.3	7.50	2201
6e	Cl	4-OCOCH$_3$	61	81-82	144.2	100.2	7.34	2208
6f	Br	4-OCOCH$_3$	51	84-85	152.8	84.7	7.72	2198
6g	Cl	H	61	oil	145.3	100.4	7.30	2215
6h	Br	H	48	oil	148.9	84.3	7.60	2203
6i	Cl	4-CH$_3$	54	oil	145.3	99.2	7.30	2218
6j	Cl	4-Cl	32	51-52	144.0	101.1	7.33	2217
6k	Br	4-Cl	27	oil	147.6	85.3	7.50	2203
6l	Cl	4-NO$_2$	8[a]	85-86	148.8	104.7	7.48	2221
6m	Br	4-NO$_2$	<5[b]					

[a] In order to achieve an 8% yield, the ratio of ketene to aldehyde was 2:1. [b] Estimated yield of unisolated product based upon ^{1}H NMR analysis.

© 1979 American Chemical Society

Scheme III



increase as the electron density of the aldehyde carbonyl increases. The opposite trend in product yields was reported by Krabbenhoft[4e] in his analogous study with dichloroketene. (3) The relative rates of the chlorocyanoketene cycloadditions parallel the product yields. For example, generation of chlorocyanoketene in the presence of 1 equiv each of 2,4-dimethoxy- and 4-methoxybenzaldehyde gave a **6a**:**6c** product ratio of 20:1 after 35% conversion, thus indicating that the ketene reacts at least 20 times faster with the more electron-rich aldehyde.

An interesting set of experiments which unambiguously establishes zwitterion **1** as an intermediate in these cycloadditions was accomplished; specifically, the zwitterion was independently generated and its products favorably compared with those obtained in the cycloaddition itself. Based upon our previously reported work on the *zwittazido cleavage* reaction,[7] one would anticipate the thermolysis of 4-azido-3-chloro-5-(4-methoxyphenyl)-2(5*H*)-furanone (**7**)[8] to give zwitterion **8** (Scheme III), the same as that proposed in the cycloaddition of chlorocyanoketene to 4-methoxybenzaldehyde. Indeed, when **7** was subjected to thermolysis in refluxing benzene, an 80% yield of **6c** was realized. Even though a number of mechanisms can be envisaged for the conversion of **7** into **6c**, the zwitterionic mechanism is the most reasonable. Central to such a claim are the following experimental observations. When the furanone **7** was decomposed, as described above, except that 1 equiv of 2,4-dimethoxybenzaldehyde was added, a ratio of 7:1 for **6a**:**6c** was realized after 35% conversion. The fact that both **6a** and **6c** are formed rules out a concerted ring contraction for **7**. A pure ketene mechanism, i.e., one in which **7** exclusively fragments to chlorocyanoketene and 4-methoxybenzaldehyde and these fragments then cycloadd, can also be rejected. That is, if such a mechanism were operative, the **6a**:**6c** ratio should be much greater than the observed 7:1. For example, as shown earlier, the relative rate of cycloaddition of chlorocyanoketene to 2,4-dimethoxybenzaldehyde compared with that of the 4-methoxy analogue is at least 20:1. During the time period for the 35% decomposition of **7** in the above competition experiment, the concentration of the externally added and more reactive 2,4-dimethoxybenzaldehyde would be much greater than that of the internally generated 4-methoxybenzaldehyde. This, coupled with the above-mentioned relative rate differences, would dictate the ratio of **6a**:**6c** to be even greater than 20:1 during this early phase of the reaction. The fact that the observed ratio was 7:1 suggests the most logical interpretation of these data; the azidobutenolide **7** cleaves to the zwitterion **8** and this then partitions between conrotatory ring closure to **9** and equilibration with chlorocyanoketene and 4-methoxybenzaldehyde.

In conclusion, we summarize the significant results to come from this study. (1) Chloro- and bromocyanoketene, unlike other ketenes which have been studied, cycloadd to aryl aldehydes in such a fashion as to impart electrophilic character to the ketene component. (2) The intermediacy of zwitterions such as **1** in the cyanoketene cycloadditions was established, in part, by the previously unprecedented independent generation of one such zwitterion (**8**). (3) From a purely synthetic perspective, these cycloadditions provide a convenient and stereoselective route to (*E*)-1-halo-1-cyano-2-arylethenes.

Acknowledgment. The authors thank the National Science Foundation (CHE-78-02103) and the National Cancer Institute (CA 11890) for financial support of this work.

References and Notes

(1) D. M. Kunert, R. Chambers, F. Mercer, L. Hernandez, Jr., and H. W. Moore, *Tetrahedron Lett.*, 929 (1978).

(2) (a) The mechanism of these cycloadditions has not been unambiguously established, i.e., concerted vs. dipolar. However, in either case the ketene behaves as the nucleophilic component. For representative studies, see W. T. Brady and L. Smith, *J. Org. Chem.*, **36**, 1637 (1971); (b) D. Borrman and R. Wegler, *Chem. Ber.*, **99**, 1245 (1966); (c) D. Borrman and R. Wegler, *ibid.*, **102**, 64 (1969); (d) D. Borrman and R. Wegler, *ibid.*, **100**, 1575 (1967); (e) H. O. Krabbenhoft, *J. Org. Chem.*, **43**, 1305 (1978).

(3) H. W. Moore, L. Hernandez, Jr., and A. Sing, *J. Am. Chem. Soc.*, **98**, 3228 (1976).

(4) ^{13}C NMR and ^{1}H NMR of the crude reaction products show no absorptions corresponding to the *Z* isomers.

(5) W. Adams, J. Baeza, and J. C. Liu, *J. Am. Chem. Soc.*, **94**, 2000 (1972); D. S. Noyes and E. H. Banitt, *J. Org. Chem.*, **31**, 4043 (1966).

(6) The product ratio was determined by ^{1}H NMR analysis of the reaction as a function of time. The percent conversion refers to the percent of disappearance of the ketene precursor at the time the product ratio was measured—approximately 1 h.

(7) H. W. Moore, *Acc. Chem. Res.*, **12**, 125 (1979).

(8) This oil was prepared in 47% yield by treating an ethanolic solution of 3,4-dichloro-5-(4-methoxyphenyl)-2(5*H*)-furanone with NaN$_3$. The dichloride is a known compound: S. Jung, L. Jung, and P. Cordier, *C.R. Acad. Sci., Ser. C*, **262**, 1793 (1966).

Harold W. Moore,* Frank Mercer
Donna Kunert, Pamela Albaugh
Department of Chemistry, University of California
Irvine, California 92717

Received December 14, 1978

Preparation and Catalytic Properties of Polymer- and Silica-Supported Bimetallic Clusters

Sir:

Bimetallic transition metal clusters hold promise as selective catalysts, offering pairs of neighboring metal centers which, in contrast to those on alloy surfaces, are structurally unique. Supported clusters may be regarded as models of and precursors of bimetallic ("alloy") crystallites on supports, the catalysts used industrially in re-forming of petroleum distillates.[1] We report here preparation of the first supported bimetallic clusters and a demonstration of their catalytic activity.[2] Anchoring of clusters to supports offers the familiar advantages of solid catalysts (ease of separation from reaction products and minimized corrosion) and the prospective advantage of stabilization of coordinatively unsaturated species, which in solution might form aggregated and/or mononuclear species.

We have begun a systematic study of the catalytic behavior of supported bimetallic clusters, using clusters with similar structural units to determine the effects of changes in the metal framework on the catalytic activity. Several bimetallic and monometallic clusters have been attached to phosphine-functionalized poly(styrene-divinylbenzene) and silica by li-

© 1979 American Chemical Society