each of **1a** and **1b** was treated with 0.005 mol of KF in 10 ml of DMSO at 25°, only 10% of **1a** had reacted after 20 hr, but 95% of **1b** had undergone elimination.[11] The reaction also displayed significant stereoselectivity at 70°, consuming 86% of **1b**, but only 25% of **1a**, within 75 min.

Fluoride ion in solution appears to be critical to the reaction and is presumably the species engaged in attack upon substrate. Both **1a** and **1b** are stable to DMSO or KF alone under the conditions employed for elimination and were unaffected by either hot (70–90°) slurries of KCl or KI in DMSO or by hot solutions of tetrabutylammonium chloride or bromide in DMSO. Although it has been reported that tetraethylammonium fluoride generates the methylsulfinyl carbanion in DMSO,[12] we found no evidence (*via* benzophenone trapping) that KF behaves in a similar fashion.

Given the premise that fluoride ion in aprotic solvents is strongly nucleophilic toward silicon as well as toward hydrogen and carbon,[13] at least four mechanisms for elimination are, in principle, possible: (a) attack of fluoride ion at silicon in a concerted, bimolecular dechlorosilylation (E2-Si), (b) attack of fluoride ion at silicon to form the chlorovinyl carbanion followed by collapse to acetylene (E1cb-Si), (c) vicinal dehydrochlorination of substrate to trimethylsilylacetylene (**2**) followed by acid-assisted cleavage to products, and (d) geminal dehydrochlorination followed (or accompanied) by rearrangement to **2** and subsequent cleavage to products. Omitting unstable intermediates, mechanisms a and b are represented by eq 2 and mechanisms c and d by eq 3 plus 4.

$$\mathbf{1a,b} + F^- \longrightarrow \underset{\mathbf{2}}{(CH_3)_3SiC{\equiv}CH} + HF + Cl^- \qquad (3)$$

$$\mathbf{2} + HF \longrightarrow HC{\equiv}CH + (CH_3)_3SiF \qquad (4)$$

Since **2** was found to react rapidly (total consumption in 5–10 min) with anhydrous potassium bifluoride (KHF_2) in DMSO—conditions which approximate intermediate stages of c and d—to give trimethylfluorosilane and acetylene,[14] the observed absence of **2** during eliminations of either **1a** or **1b** is mechanistically inconclusive. As a result of indirect evidence, however, we tend at the present time to favor an E2-Si process (a) in which anti dechlorosilylation is more facile than syn elimination.[15] Only a few proven examples of an E1cb-H mechanism have been reported in the vinylic series, and all involve carbanions stabilized by resonance[16] or inductive[17] effects of α substituents. Heterolytic rupture of the carbon–silicon bond in either **1a** or **1b** (mechanism b) would generate a chlorovinyl carbanion lacking such stabilization. Pathway c, proceeding by way of vicinal dehydrochlorination as the rate-determining step, would require that syn, rather than anti, dehydrochlorination be faster. The reverse is instead true for analogous substrates not containing silicon.[16] Finally, vinyl chloride was found to be inert to KF in DMSO under conditions (100°, 4.5 hr) which serve to completely convert **1a** or **1b** to products, evidence which mitigates against pathways c and d.[18]

We are currently investigating the nature of this and similar eliminations from the standpoints of substrate type and reaction conditions.[19]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. PRF 4535-AC1, 3), for support of this work.

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[11] Eliminations were followed by glpc (10-ft SE-30 column) using the internal standard method.

[12] J. Hayami, N. Ono, and A. Kaji, *Tetrahedron Lett.*, 1385 (1968).

[13] A. J. Parker, *Advan. Org. Chem.*, **5**, 1 (1965).

[14] Trimethylsilylacetylene is easily cleaved by KF in the presence in a proton donor: C. S. Kraihanzel and J. F. Poist, *J. Organometal. Chem.*, **8**, 239 (1967). We found **2** to be stable to KF in DMSO for at least 120 hr at 25°.

[15] A preference for anti dechlorometalation is also indicated for some other β-chlorovinyl metalloids. See A. N. Nesmeyanov, A. E. Borisov, and I. S. Savel'eva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 286 (1968); C. L. Hewett, *J. Chem. Soc.*, 1203 (1948).

[16] G. Modena, *Accounts Chem. Res.*, **4**, 73 (1971).

[17] S. I. Miller, and W. G. Lee, *J. Amer. Chem. Soc.*, **81**, 6313 (1959).

[18] J. T. Maynard, *J. Org. Chem.*, **28**, 112 (1963), has reported that vinyl chloride affords acetylene in indefinite yield upon treatment with KF in *N*-methyl-2-pyrrolidone at 200°.

[19] Preliminary results indicate that tetraethylammonium fluoride and metal alkoxides are potent reagents for such eliminations when employed in homogeneous solutions of aprotic solvents.

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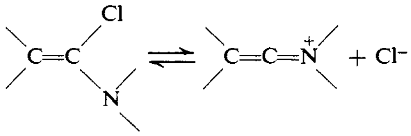
Received December 27, 1971

Electrophilic Aminoalkenylation of Aromatics with α-Chloroenamines

Sir:

The simultaneous presence of an electron-donating substituent and a good leaving group on a sp^2 carbon atom has been shown[1] to confer versatile chemical behavior to the readily available alkyl- or aryl-substituted α-chloroenamines.



Like enamines they react at the β-carbon atom with various electrophilic reagents.[1,2] Furthermore, in contrast to ordinary vinylic halides, they show a remarkably high reactivity toward nucleophilic reagents.[1,3] The nucleophilic substitutions are accelerated by the addition of silver ions[4,5] and considerably retarded (or suppressed) by the presence of electron-withdrawing substituents in the β position.[5] These results are best explained by a prior ionization to a keteneimmonium chloride followed by attack of the nucleophile.

We wish now to report that alkyl-substituted α-chloroenamines react readily with electron-rich aromatics in electrophilic substitutions, *without the need of an acid catalyst.* The α-chloroenamines **2a–c** were obtained

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[1] L. Ghosez, B. Haveaux, and H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **6**, 454 (1969).

[2] T.-F. Lin, unpublished results.

[3] M. Rens and L. Ghosez, *Tetrahedron Lett.*, 3765 (1970).

[4] (a) The addition of silver tetrafluoroborate to alkyl-substituted α-chloroenamines at −60° gives the keteneimmonium salts and silver chloride. J. Marchand-Brynaert and L. Ghosez, *J. Amer. Chem. Soc.*, **94**, 2870 (1972). (b) Recently, H. Weingarten, *J. Org. Chem.*, **35**, 3970 (1970), described the pmr spectrum of tetramethylketeneimmonium hexafluorophosphate.

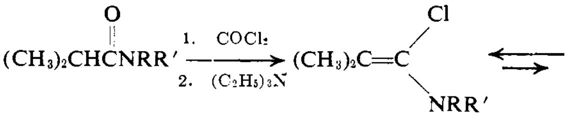
[5] B. Haveaux, M. Rens, and J. Marchand-Brynaert, unpublished results.

Table I. Reaction of α-Chloroenamines (**2**) with Aromatics

Aromatic (*M*)	**2** (*M*)	$[(C_2H_5)_3N]$, *M*	Solvent	Temp, °C	Reaction time, hr	R	R′	Product (% yield[a])
Furan (3.0)	**2a** (1.13)	1.5	Acetonitrile	Reflux	24	CH_3	CH_3	2-Isobutyrylfuran (83)
Furan (3.0)	**2b** (0.93)	1.5	Acetonitrile	Reflux	24	C_2H_5	C_2H_5	2-Isobutyrylfuran (85)
Furan (3.0)	**2c** (0.86)	1.5	Acetonitrile	Reflux	24	$-(CH_2)_5-$		2-Isobutyrylfuran (85)
Pyrrole (0.75)	**2a** (0.375)	0.5	Ether	20	6	CH_3	CH_3	2-Isobutyrylpyrrole (94)
Pyrrole (0.75)	**2b** (0.310)	0.5	Ether	20	6	C_2H_5	C_2H_5	2-Isobutyrylpyrrole (94.7)
Pyrrole (0.75)	**2a** (0.285)	0.5	Ether	20	6	$-(CH_2)_5-$		2-Isobutyrylpyrrole (94.3)
N,*N*-Dimethylaniline (1.13)	**2a** (1.13)	1.5	Acetonitrile	Reflux	24	CH_3	CH_3	*p*-*N*,*N*-Dimethylaminoisobutyrophenone (89)
Anisole (0.75)	**2a** (0.75)	1	Acetonitrile	Reflux	50	CH_3	CH_3	(0)
Phenol (0.50)	**2a** (0.50)	0.66	Ether	20	4	CH_3	CH_3	(0[b])

[a] Pure products after hydrolysis; the remaining material was the corresponding *N*,*N*-dialkylisobutyramide resulting from the hydrolysis of unreacted **2a–c**; the enamines **4** could also be isolated in comparable yields. [b] Product **6** was formed instead (97%); see ref 1.

in 50–80% yields from the reaction of phosgene with the appropriate *N*,*N*-dialkylisobutyramide (**1**) followed by elimination of HCl with triethylamine.[6]

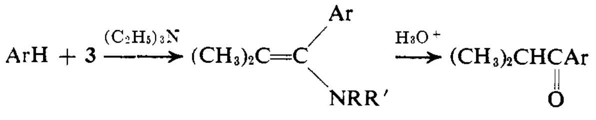


1

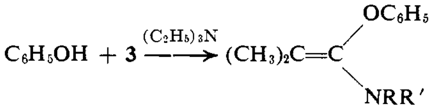
2a, R = R′ = CH_3
b, R = R′ = C_2H_5
c, R-R′ = $-(CH_2)_5-$

$$(CH_3)_2C{=}C{=}\overset{+}{N}RR' + Cl^-$$

3



4 **5**



6

In marked contrast to ordinary alkenyl halides, **2a–c** reacted readily with furan, pyrrole, or *N*,*N*-dimethylaniline in the presence of triethylamine to yield aminoalkenylation products in high yields (Table I). Spectral data (mass, ir, and pmr) firmly supported the assigned structures of all products; they were further confirmed by hydrolysis in aqueous HCl to the corresponding ketones **5** which could be obtained independently from the acylation of the corresponding aromatics with isobutyryl chloride or anhydride in the presence of a Lewis acid ($AlCl_3$ or BF_3).

The aminoalkenylation reactions follow the typical pattern of electrophilic aromatic substitution: (1) orientation; with pyrrole and furan, aminoalkenylation occurred exclusively at the 2 position, whereas *N*,*N*-dimethylaniline gave the para-substituted product; (2) relative reactivities; furan and dimethylaniline required prolonged heating in refluxing acetonitrile whereas pyrrole reacted rapidly even at room temperature (violently in the absence of solvent). It is worth noting that phenol also reacted rapidly but gave exclusively an *O*-aminoalkenylation product. Anisole was completely unreactive toward **2a–c**. From the data now available it seems reasonable to propose that the initial step of the reaction is the formation of the strongly electrophilic keteneimmonium cation[7] which then attacks the aromatic substrate.

This approach allows for the specific and direct introduction of enamine functional groups into aromatic molecules having nucleophilic carbon centers from readily available starting material and under mild conditions. The convenience of the method suggests a variety of synthetic applications. Initial studies indicate that the reaction can be extended to nucleophilic olefins or enolizable ketones. These results will be presented later.

Acknowledgment. The authors are grateful to the Institut pour l'encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture for a research fellowship (J. Marchand-Brynaert) and the Fonds de la Recherche Fondamentale Collective for financial support.

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(6) **2a** was identical with the product isolated by H. Weingarten (see ref 4b) from α-methylpropenylidenebisdimethylamine and dichlorophenylphosphine. **2b** and **2c** have been described earlier.

(7) A prior displacement of a chloride by triethylamine has been excluded by a control experiment.

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Received February 7, 1972

Cycloadditions of Keteneimmonium Cations to Olefins and Dienes. A New Synthesis of Four-Membered Rings

Sir:

The thermal cycloadditions of ketenes to weakly polar olefins and dienes have been shown to be concerted processes in most cases.[1]

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(1) For pertinent discussions and references, see: R. Huisgen, L. A. Feiler, and P. Otto, *Chem. Ber.*, **102**, 3444 (1969); R. Huisgen, L. A. Feiler, and G. Binsch, *ibid.*, **102**, 3460 (1969); L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971); W. T. Brady, *Synthesis*, 415 (1971).