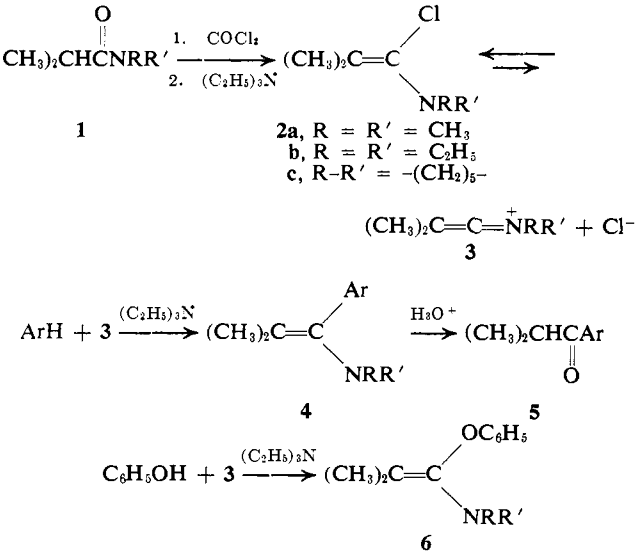
Table I. Reaction of α-Chloroenamines (2) with Aromatics

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]



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.

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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.

Jacqueline Marchand-Brynaert, Léon Ghosez*
Laboratoire de Chimie Organique de Synthèse
Université de Louvain, 3000 Louvain, Belgium

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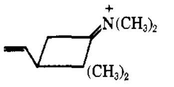
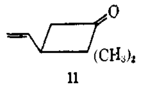
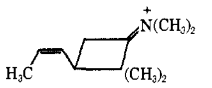
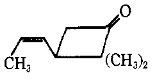
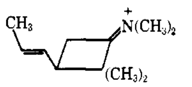
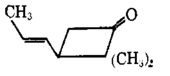
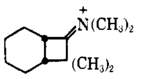
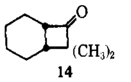
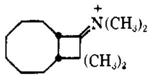
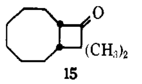
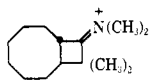
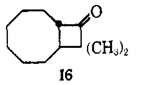
Cycloadditions of Keteneimmonium Cations to Olefins and Dienes. A New Synthesis of Four-Membered Rings

Sir:

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

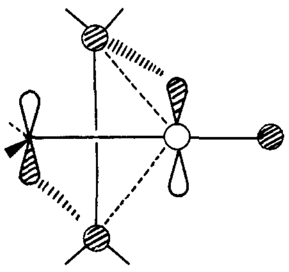
(1) For pertinent discussions and references, see: R. Huisgen, L. A. Feiler, and P. Otto, *Chem. Ber.*, **102**, 3444 (1969); R. Huisgen, L. A. Feiler, and G. Binsch, *ibid.*, **102**, 3460 (1969); L. Ghosez, R. Montaigne, A. Roussel, H. Vanlierde, and P. Mollet, *Tetrahedron*, **27**, 615 (1971); W.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

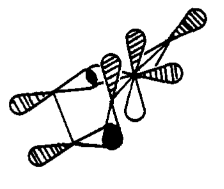
Table I. Reaction of 1-Chloro-*N*,*N*,2-trimethylpropenylamine with Olefins and Dienes in the Presence of $AgBF_4$

	Adducts			Cyclobutanones		
Olefins	Structure[a]	Yields,[b] %	Ir ($CHCl_3$), cm^{-1}	Structure	Yields,[c] %	Ir (CCl_4), cm^{-1}
Butadiene	 **5**	84	1730 1060	 **11**	86	1788
cis-Piperylene	 **6**	85	1730 1060	 **12**	93	1785
trans-Piperylene	 **7**	82	1730 1060 970	 **13**	89	1783
Cyclohexene	 **8**	83	1718 1060	 **14**	89	1770
cis-Cyclooctene	 **9**	86	1715 1060	 **15**	88[d]	1775
trans-Cyclooctene	 **10**	85	1715 1060	 **16**	87[d]	1773

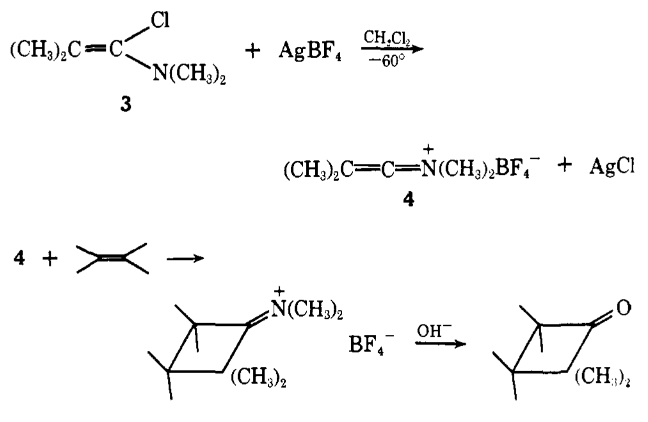
[a] Isolated as tetrafluoroborate salts. [b] Recrystallized from chloroform–ether. [c] The hydrolysis was effected on the crude cyclobutaneimmonium salt. [d] Vpc analysis on the crude reaction mixture showed *ca.* 4% of the corresponding epimer.

The reaction has been analyzed[2] by Woodward and Hoffmann as a $({}_{\pi}2_s + {}_{\pi}2_a)$ cycloaddition of a C=C double bond to a modified vinyl cation (transition state **1**) where the place of the vacant p orbital is taken by the exceptionally low-lying unoccupied $\pi_{C=O}{}^*$ orbital of the ketene molecule. Alternatively,[3] the reaction can be explained in terms of a "Hückel" or "aromatic" transition state **2** isoconjugated with that in a Diels–Alder reaction. In both analyses the crucial role of the carbonyl group in the (2 + 2) addition of ketenes must be emphasized to offer a rationalization to the long-time puzzling observation that, in contrast with ketenes, allenes give only Diels–Alder adducts with conjugated dienes.[4] It is thus expected that replacing the carbonyl group in the ketene molecule by an immonium function should give a cumulene which is better tailored to play the role of antarafacial component in $({}_{\pi}2_s + {}_{\pi}2_a)$ cycloadditions; we have found indeed that tetramethylketeneimmonium fluoroborate cycloadds to olefins and dienes with exceptional ease, opening a new and potentially useful route for the synthesis of four-membered rings.


1


2

1-Chloro-*N*,*N*,2-trimethylpropenylamine (**3**), an exceptionally reactive chloride,[5] is an obvious source of **4**: addition of silver tetrafluoroborate to an equivalent amount of **3** in CH_2Cl_2 at −60° gave instantaneously a quantitative precipitation of silver chloride. **4** was allowed to react *in situ* with an olefin or diene. A typical experiment consisted of adding 1 g



$$(CH_3)_2C{=}C\begin{smallmatrix}Cl\\ N(CH_3)_2\end{smallmatrix} + AgBF_4 \xrightarrow[-60°]{CH_2Cl_2} (CH_3)_2C{=}C{=}\overset{+}{N}(CH_3)_2BF_4^- + AgCl$$

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(2) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969.

(3) H. E. Zimmermann, *Accounts Chem. Res.*, **4**, 272 (1971); M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971).

(4) Review: H. Fischer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, London, 1964.

(5) L. Ghosez, B. Haveaux, and H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **8**, 454 (1969); M. Rens and L. Ghosez, *Tetrahedron Lett.*, 3765 (1970); H. Weingarten, *J. Org. Chem.*, **35**, 3970 (1970); J. Marchand-Brynaert and L. Ghosez, *J. Amer. Chem. Soc.*, **94**, 2869 (1972).

of **3** to a solution of 1.46 g of $AgBF_4$ and 1 ml of cyclohexene in 10 ml of dry CH_2Cl_2 at −60° and slowly warming the mixture to room temperature (no cycloaddition occurred at −60°). After filtration of AgCl (1.1 g, *ca.* 100%) and evaporation of the solvent, a residue was obtained which contained essentially the adduct **8** (>90%) contaminated with *N*,*N*-dimethylisobutyramide (<10%). Recrystallization from chloroform–ether gave pure **8** in 83% yields. The cycloadducts obtained with various olefins and dienes are summarized in Table I. They have been characterized by ir and nmr spectroscopy. The structures were confirmed by hydrolysis of the adducts to the corresponding cyclobutanones.

Several characteristic features of these cycloadditions should be mentioned: (1) Reactions with conjugated dienes give only the (2 + 2) cycloadducts; no Diels–Alder adducts are observed. Thorough examination of the crude reaction mixtures showed that *N*,*N*-dimethylisobutyramide was the sole side product of the reaction, resulting probably from the hydrolysis of unreacted **4** during work-up. (2) With *cis*- or *trans*-piperylene, the addition occurred at the less-substituted double bond (**6** and **7**) in the same manner as the corresponding reactions with ketenes.[6] (3) *cis*- and *trans*-cyclooctenes reacted stereospecifically, giving isomeric adducts (**9** and **10**, respectively). They showed distinct ir and nmr spectra. However, the configurational assignments were more readily made on the corresponding ketones. *cis*-10,10-Dimethylbicyclo[6.2.0]decan-9-one (**15**) obtained from the hydrolysis of **9** showed indeed the two net ir absorptions at 1462 and 1450 cm^{-1} which appear to be typical for an eight-membered ring cis fused to three- or four-membered rings.[7] The protons of the *gem*-dimethyl groups gave two singlets (δ 1.23 and 0.93). On the other hand, *trans*-10,10-dimethylbicyclo[6.2.0]decan-9-one (**16**) obtained from the hydrolysis of **10** showed only one signal for the six methyl protons at δ 1.08. Finally, **15** and **16** were compared with authentic samples prepared from the (ketene + olefin) reactions.[8] For both cycloadditions the degree of intercontamination was checked by hydrolyzing the crude salts **9** or **10** under controlled conditions[9] and examining the resulting mixtures by vpc; less than 5% intercontamination was observed. These data appear fully consistent with the mechanistic hypothesis of a $({}_{\pi}2_{s} + {}_{\pi}2_{a})$ concerted cycloaddition.

Finally, the synthetic utility of the reaction should be emphasized; it is indeed suggested that tetraalkyl-substituted keteneimmonium ions should be superior to the corresponding ketenes for the building of four-membered rings by (2 + 2) cycloadditions. The conditions are very mild, the yields are excellent, and the starting material is cheap and readily available. Clearly more synthetic uses of these reactions have to be expected; our more recent studies on the cycloadditions of keteneimmonium ions to other substrates such as acetylenes or imines will be reported later.

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Jacqueline Marchand-Brynaert, Léon Ghosez*
Laboratoire de Chimie Organique de Synthèse
Université de Louvain, 3000 Louvain, Belgium

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(6) J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, **30**, 4175 (1965); R. Huisgen and P. Otto, *Chem. Ber.*, **102**, 3475 (1969).

(7) R. Montaigne and L. Ghosez, *Angew. Chem., Int. Ed. Engl.*, **7**, 221 (1968).

(8) A. P. Krapcho and J. H. Lasser, *J. Org. Chem.*, **31**, 2030 (1966).

(9) The hydrolysis has been shown to cause epimerization of the salts **9** or **10**. Short reaction times and buffered solutions were used to prevent isomerization. However, it is highly probable that the small amount of intercontamination still resulted from the hydrolysis.

Characterization of the Triplet State of Aromatic Esters. Electron Spin Resonance Spectrum of the Triplet State of Substituted Methyl Benzoates[1]

Sir:

In comparison with the many, extensively studied photochemical reactions of aldehydes and ketones, the carboxyl carbonyl of esters is, in general, much less reactive and has received correspondingly little attention. Since many of the reactions of the carbonyl group are known to involve the n,π^* excited state, the lack of reactivity of the carboxyl carbonyl has been taken as an indication that in these molecules the lowest states have π,π^* character. Such generalizations are being challenged with increasing frequency and, in fact, two groups of workers have recently reported efficient photochemical reactions from the triplet state of some benzoate esters and the character of the lowest excited triplet state of these molecules was opened to question.[2,3] We report here electron spin resonance and phosphorescence emission spectral data (Table I) which characterize the lowest triplet state of the benzoate esters studied as π,π^* (that is, a perturbed $^3B_{1u}$ state of benzene). The zero-field splitting parameter (D) indicates that a considerable spin density is distributed onto the carboxyl group and thus the carboxyl carbonyl oxygen should have some radical reactivity. The results also give an indication of two other correlations: (1) there is a relationship between the zero-field splitting parameter (D) and the triplet energy (E_T); (2) the zero-field splitting parameters vary with substitution in a way which may indicate differing contributions of the diallyl radical and paraquinoidal structures of the triplet (*vide infra*).

The phosphorescence emission of all the esters studied (with the exception of dimethyl phthalate where interaction of the adjacent carboxyl groups offers a plausible explanation for anomalous behavior) had

(1) Contribution No. 28 from the Photochemistry Unit.

(2) Alkyl benzoate esters undergo the Norrish type II cleavage with very low quantum yield.[3] The suggestion has been made that the inefficiency is due mainly to reversal of the hydrogen-transfer step.[3a] This seems untenable with the expected behavior of the 1,4 diradical; alternatively, vibronic coupling of the carboxyl group with the γ-hydrogen[4] should be considered.

(3) (a) J. A. Barltrop and J. D. Coyle, *J. Chem. Soc. B*, 251 (1971); (b) M. Day and D. M. Wiles, *Can. J. Chem.*, **49**, 2916 (1971); (c) H. Morrison, R. Brainard, and D. Richardson, *Chem. Commun.*, 1653 (1968).

(4) A. Heller, *Mol. Photochem.*, **1**, 257 (1969).

(5) Benzoate esters substituted with electron-withdrawing groups (Table I; **2**, **4**, **5**, **7**, and **8**) undergo photocycloaddition to 1,1-diphenylethylene.[6a] The authors first proposed a mechanism involving the n,π^* triplet state of the ester.[6a] This was later withdrawn in favor of an exciplex pathway[6b] which is consistent with the results reported here.

(6) (a) Y. Shigemitsu, H. Nakai, and Y. Odaira, *Tetrahedron*, **25**, 3039 (1969); (b) Y. Shigemitsu, Y. Katsuhara, and Y. Odaira, *Tetrahedron Lett.*, 2887 (1971).