Periselectivity in Cycloadditions to Vinylmethylketene and Structurally Related Vinylketene Imines

Gaetano Barbaro, Arturo Battaglia,* and Patrizia Giorgianni

Istituto dei Composti del Carbonio Contenti Eteroatomi e loro Applicazioni, Consiglio Nazionale delle Ricerche, 40064 Ozzano Emilia, Italy

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The isomer distribution in cycloaddition reactions of *C*-vinylmethylketene and isoelectronic *C*-vinylketene imines, with partners of different electronic demand, has been compared. Very electrophilic reactants (TCNE, PTAD) gave, in both cases, a *unique* isomer, from a 1,4-cycloaddition involving the C–C double bond of the cumulative system (C=C=X) and the adjacent *C*-vinyl substituent. With less electrophilic substrates (azodicarboxylates, azomethines, thioketones) or electron-rich species (vinyl ethers, ynamines), several cycloadducts are obtained, arising from 1,4- and 1,2-processes.
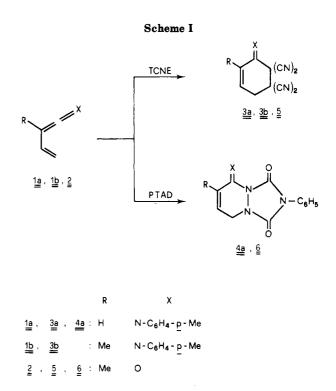
A considerable number of papers, dealing with the variable periselectivity problem in cycloaddition reactions of heterocumulenes has appeared.[1] Moreover unsaturated functions (CO, C=N, C=C), adjacent to a cumulative system, may be involved in the reaction center, increasing the number of possible isomers. Recently, a computational treatment of periselectivity, based on literature kinetic data analysis, has been developed,[2] which predicts, for a given starting material and conditions, the predominant products, among the alternate isomers of all possible thermal pericyclic processes.

However, it has been concluded that "simple rules, which might emerge for periselectivity are still elusive, owing to the enormous rate variations for pericyclic processes". This conclusion is confirmed when periselectivity changes of heterocumulene cycloadditions have to be explained. As an example our previous results,[3a–d] concerning the reactivity of ketene imine–thioketone cycloadditions, showed the formation of three different types of isomers, i.e., benzothiazines, 2-iminothietanes, and 2-iminothiacyclohexenes, depending upon stereoelectronic effects. Quite remarkably, the variations in energy activation for these three different processes lie within only few kilocalories.

This paper examines the influence of the heteroatom in the cumulene function (O or N) on the distribution of the isomers, when *C*-vinylmethylketene (2) and *C*-vinylketene imines[4] 1 cycloadd to partners of different electronic demand, and how this distribution can be affected by steric factors.

Results and Discussion

The selected partners can be classified according to their electrophilic properties: (a) highly electrophilic, such as tetracyanoethylene (TCNE) and 4-phenyl-4*H*-1,2,4-tria-

Scheme I

			R	X
1a,	**3a**,	**4a** :	H	N–C₆H₄–*p*-Me
1b,	**3b**	:	Me	N–C₆H₄–*p*-Me
2,	**5**,	**6** :	Me	O

zole-3,5-dione (PTAD); (b) electrophilic, such as diethyl azodicarboxylate (DAZD), *N*-(dicyanomethylene)anilines, thioketones, and azomethines; (c) electron-rich, as vinyl ethers and ynamines.

(a) Cycloadditions of Highly Electrophilic Partners to 1a,b and 2. TCNE and PTAD reacted with *C*-monosubstituted *N*-*p*-tolylvinylketene imine (1a) across the diene system formed by the cumulative C=C double bond and the vinyl group (1,4-C), to give the corresponding cycloadducts 3a and 4a, respectively, as the only observed reaction products (Scheme I). The same cycloaddition mode occurred with the vinylmethylketene (2),[5] to give the six-membered cycloadducts 5 and 6. An identical type of periselectivity has been reported[4] in reactions between the *C*,*C*-disubstituted *N*-*p*-tolylvinylmethylketene imine (1b) and TCNE. Therefore this cycloaddition mode (1,4-C) appears to be favored in reactions of vinylketene imines as well as ketenes with strong electrophilic partners.

(b) Cycloadditions of Electron-Poor Substrates. The reactions of vinylketene imines and ketenes with weaker electrophilic partners showed variable selectivity.
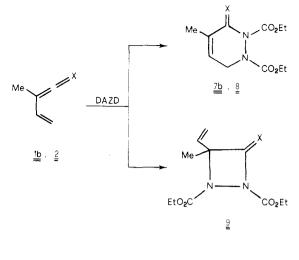
(1) Reviews on ketene imine and ketene cycloadditions can be found, for example, in: (a) Ghosez, L.; O'Donnell, M. J. In *Pericyclic Reactions*; Marchand, A. P., Lehr, E. R., Eds.; Academic: New York, 1977; Vol. II, Chapter 2. (b) Gilchrist, T. L.; Storr, R. C. In *Organic Reactions and Orbital Symmetry*; Cambridge University: Cambridge, 1979. (c) Gambarayan, N. P. *Russ. Chem. Rev. (Engl. Transl.)* 1976, *45*, 630. (d) Ulrich, H. In *Cycloaddition Reactions of Cumulenes*; Blomquist, A. T., Ed.; Academic: New York, 1967.

(2) Burnier, J. S.; Jorgensen, W. L. *J. Org. Chem.* 1984, *49*, 3001.

(3) (a) Dondoni, A.; Battaglia, A.; Giorgianni, P. *J. Org. Chem.* 1980, *45*, 3766. Dondoni, A.; Battaglia, A.; Bernardi, F.; Giorgianni, P. *Ibid.* 1980, *45*, 3773. (c) Bernardi, F.; Bottoni, A.; Battaglia, A.; Distefano, G.; Dondoni, A. *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.* 1980, *35*, 521. (d) Dondoni, A.; Battaglia, A.; Girgianni, P. *J. Org. Chem.* 1982, *47*, 3998.

(4) A previous account on the reactivity of *C*-vinylmethylketene imines can be found in: (a) Sonveaux, E.; Ghosez, L. *J. Am. Chem. Soc.* 1973, *95*, 5417. (b) See ref 1a.

(5) Attempts to react the C-monosubstituted vinylketene, generated in situ from the corresponding acyl chloride, were unsuccessful owing its istantaneous polymerization.

Scheme II

1b, **7b**   : X = N-C₆H₄-*p*-Me

2 , **8** , **9** : X = O

Scheme III

1b : R = C_6H_4-*p*-Me   **1c** : R = C_6H_2-2,4,6-Me₃

10 : R'= C_6H_5 **11** : R'= C_6H_4-*p*-Cl

			R	R'
12b	**13b**		C_6H_4-*p*-Me	C_6H_5
12c	**13c**	**14c**	C_6H_2-2.4.6-Me₃	C_6H_5
15c	**16c**		C_6H_2-2.4.6-Me₃	C_6H_4-*p*-Cl

Scheme IV

10 , **21** : R₁ = R₂ = CN

17 , **20** : R₁ = H ; R₂ = C_6H_5

While **1b** reacted with DAZD, to give the iminopyridazine **7b** in 90% yield, from 1,4-C addition, the ketene **2** afforded two isomers, viz., the pyridazinone **8** and the diazetidinone **9** in a 2.3 : 1 ratio, the second cycloadduct being formed with a 1,2-cycloaddition of DAZD across the C–C bond of the cumulenic function of **2** (1,2-C) (Scheme II). Attempts to react DAZD with **1a** were unsuccessful, due to a fast polymerization of the ketene imine. The rate of formation of **8 + 9** (ca. 3 days, CCl₄) was substantially lower with respect to **7b** under the same conditions (only a few hours).
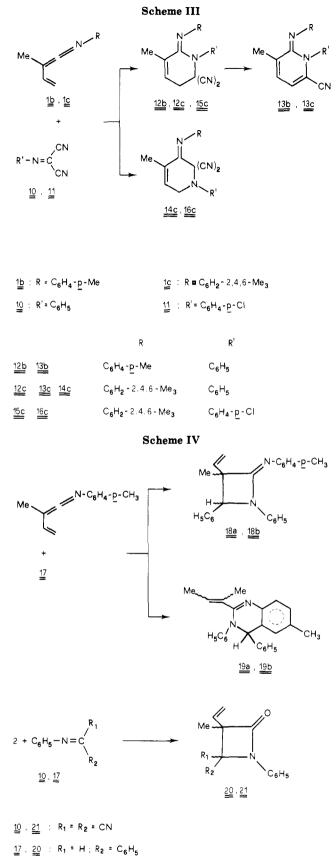
Azomethines bearing strong electron-withdrawing groups on carbon, viz., *N*-(dicyanomethylene)anilines, reacted satisfactorily with vinylketene imines. For instance, **1b** and *N*-(dicyanomethylene)aniline (**10**) gave the cycloadduct **13b** which should arise from a 1,4-C addition, leading to the undetected intermediate **12b**, followed by elimination of hydrogen cyanide (Scheme III).

On the other hand *N*-mesitylvinylmethylketene imine (**1c**) and **10** gave two regioisomeric cycloadducts, viz., **13c** and **14c** in a 1:3 ratio. In this case the initial cycloadduct **12c** could be detected in the crude reaction mixture by ¹H NMR (see Experimental Section). The same ketene imine **1c** reacted also with *N*-(dicyanomethylene)-*p*-chloroaniline (**11**), to give two regioisomeric cycloadducts **15c** and **16c** in a 6:1 ratio (CCl₄) or 15:1 ratio (C₆H₆). The former did not undergo hydrogen cyanide elimination, even under the workup conditions. From rate measurements, the reaction of ketene imine **1c** with **11** appeared to be six times faster than with **10**.
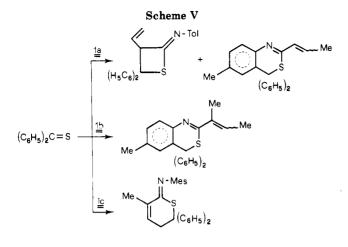
Ketene imine **1b** was unreactive toward *N*-phenylbenzaldehyde imine (**17**) in apolar media. For instance, in refluxing toluene **1b** polymerized completely, while **17** was recovered unaltered.

On the other hand a sluggish reaction occurred in a very polar solvent (CH₃CN, 55 °C, 20 days).

From this reaction four cycloadducts were isolated: the two diastereomeric 2-iminoazetidinones **18a** and **18b** in a 1:2.6 ratio, which are formed from 1,2-C cycloadditions and the two isomeric benzodiazines **19a** and **19b** in a 2.1:1 ratio, from a formal 1,4 cycloaddition involving the C=N bond of the cumulene and the C=C of the aromatic ring (1,4-N) and subsequent 1,5-hydrogen shift of the proton at C₅ (Scheme IV). The ratio of the isomers **18a + 18b/19a + 19b** was 1:4.41. In contrast, ketene **2** reacted with **17** at room temperature in apolar medium (CCl₄). A careful inspection of the crude reaction products by ¹H NMR and ¹³C NMR revealed the presence of only one of the two possible diasteroisomers of the β-lactam **20**, which was isolated in 55% yield, besides the unreacted azomethine. Finally, an identical peri- and regioselectivity was found in reaction of **2** with **10**, to give the β-lactam **21** in a very
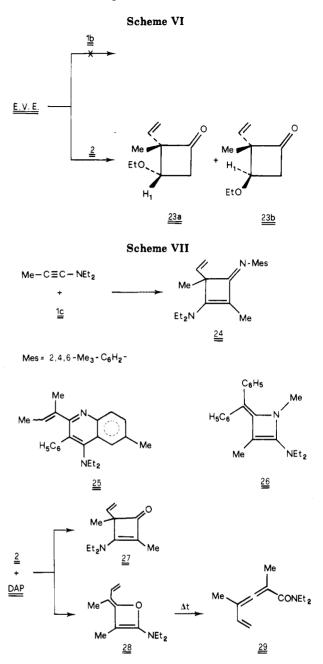
Scheme V

Tol : p-Me-C₆H₄   Mes = 2,4,6-Me₃-C₆H₂-

Scheme VI

Scheme VII

Me—C≡C—NEt₂

+

1c

Mes = 2,4,6-Me₃-C₆H₂-

poor yield (8%), due to long reaction times, associated to a preferential ketene polymerization, while no reaction was observed between 2 and the azomethine 11, the latter being recovered unaltered. These results clearly showed that substituents at the carbon of the azomethines exert an opposing effect on the reactivity and selectivity toward the two heterocumulene systems. The effect of the heteroatom in the C=C=X (X = O or NR) causes the ketene to act as the acceptor partner in the 1,2-C cycloaddition processes, independently from the electrophilicity of the azomethine, the reactivity being favored by the nucleophilicity of the latter. In contrast the ketene imine acts as donor in 1,4-C cycloadditions with electron-poor azomethines. Finally, the reduced electrophilicity of 17, causes the ketene imine **1b** to act both as donor partner in a 1,4-N cycloaddition and as acceptor in a competitive 1,2-C process.[6]

We have already reported on the selectivity of ketene imine–thioketone cycloadditions,[3a-d] which is summarized in Scheme V. We now report that ketene 2 and thiobenzophenone (TBP) give the thietanone **22** exclusively. This addition mode is preferred to the 1,4-cycloaddition processes (1,4-N and 1,4-C), as observed in structurally related C,C-disubstituted vinylmethylketene imines **1b** and **1c**, respectively. In fact the 1,2-C addition is competitive with the C-monosubstituted ketene imine **1a** only, due to a less hindered transition state and a more preferential trans conformation of its diene fragment with respect to that of **1b** and **1c**. It is worth noting that the only isomer which is not observed in reactions with thiones is the 1,2-cycloadduct involving addition across the C=X bond of C=C=X (1,2-X).

(c) Cycloadditions of Electron-Rich Substrates. No reactions of C-alkyl- and C-arylketene imines with alkoxyethylenes have been so far reported in the literature. Accordingly, ketene imine **1b** resulted unreactive toward ethyl vinyl ether (EVE).

In contrast, ketene 2 reacted satisfactorily well in the 1,2-C cycloaddition mode to give a mixture of diastereoisomers **23a** and **23b** in a 1:0.44 ratio (Scheme VI). The structure of **23b** is assigned to the minor isomer, on the basis of the ¹³C NMR deshielding δ-syn axial interaction effects of the methyl and ethoxy groups of the ring.[7] In fact the ¹³C NMR signal at δ 19.31 of the Me group of **23b**, which is in δ-syn position with respect to EtO is found at 4.41 ppm downfield with respect to that of **23a** (14.9 ppm). The selectivity observed above is identical with that of other ketenes, as dimethyl- and diphenylketene[8a,b] with

(6) The possibility to obtain 2-iminoazetidinones by using N-alkyl-instead of N-arylketene imines is under investigation. These heterocycles may constitute a new entry to β-lactams, provided the conversion of the imino into the carbonyl function is possible. This route could be alternative to that of the ketene–azomethine cycloadditions, owing to a substantial greater stability of the C=C=N function, so that a wider spectrum of substituents is available. Additionally, depending upon the basicity of the nitrogen atom of the azomethines (N-alkylazomethines) the ketene route yields more often to 2:1 cycloadducts.[1d]

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Table I. Cycloadditions of Heterocumules (C) to Unsaturated Partners (U)

U, mmol	C, mmol	product, % yield[a] (reaction type)	solvent, mL	T, °C	t, h	% yield[b]
TCNE, 3.8	1a,[c] 3.8	3a, 35 (1,4-C)	$CH_3CN:CH_2Cl_2$, 120:4	-20	17	35[d]
TCNE, 6.3	2, 6.26	5, 35 (1,4-C)	CCl_4:THF, 220:15	20	3	35[d]
PTAD, 2.7	1a, 3.40	4a, 53 (1,4-C)	CH_3CN, 175	-20	6	53[d]
PTAD, 6.6	2, 6.60	6, 72 (1,4-C)	CCl_4:THF, 100:3	20	vf	56[d]
DAZD, 4.4	1b, 4.39	7b, 94 (1,4-C)	CCl_4, 150, or CH_3CN	20	3	94
DAZD, 5.7	2, 5.70	8, 52 (1,4-C); 9, 23.4 (1,2-C)	CCl_4, 60	20	72	25[d]
10, 1.93	1b, 1.93	13b, 84 (1,4-C)	CCl_4, 25	20	100	84
10, 2.32	1c, 2.32	13c, 53 (1,4-C); 18 (1,4-C)	CCl_4, 70	30	150	56
11, 1.80	1c, 1.67	15c, 88 (1,4-C); 16c, 6 (1,4-C)	C_6H_6, 15	20	50	94
17, 4.10	1b, 4.10	18a, 4 (1,2-C); 18b, 11 (1,2-C); 19a, 45 (1,4-C); 19b, 22 (1,4-C)	CH_3CN, 25	55	480	82
17, 8.00	2, 5.82	20, 55 (1,2-C)	CCl_4, 150	20	24	55
10, 4.44	2, 4.44	21, 67 (1,2-C)	Et_2O, 90, or CH_3CN	20	48	8
TBP, 6.60	2,[e] 6.60	22, 90 (1,2-C)	CCl_4, 90	20	24	61
EVE, 65	2, 16.90	23a, 50 (1,2-C); 23b, 22 (1,2-C)	EVE, 25	20	8	72
DAP, 2.60	1c,[f] 2.6	24, 83 (1,2-C)	n-C_5H_{12}, 25	0	240	83
DAP, 9.11	2, 9.17	27, 35 (1,2-C); 29, 8 (1,2-X)	CCl_4, 160	0	3	43

[a] The yields refer to each product with respect to reacted U. [b] Crude yield. [c] With 1b, see ref 4. [d] Partial polymerization of U was unavoidable. [e] With 1a–c, see ref[3a–d]. [f] With 1b, see ref 1a.

alkoxyethylenes. Other isomers, such as oxetanes,[9] reported in the reaction of bis(trifluoromethyl)ketene with *cis*-propenyl propyl ether were not observed in our case.

(Diethylamino)propyne (DAP) reacted with ketene imine 1c to give the corresponding cyclobutene derivative 24 in 85% yield, from 1,2-C addition. Quite interestingly the literature reports both the formation of a quinoline derivative 25, from 1,4-N cycloaddition of (diethylamino)phenylacetylene and 1b,[1a] and the formation of a 1,2-cycloadduct, viz., the azete derivative 26 from 1,2-N addition of DAP to the C=N bod of N-methyldiphenylketene imine[10] (Scheme VII). This suggests that steric and electronic effects compete for the isomer distribution, the 1,4-C addition being the only unfavored reaction. In each case, however, presence of 2:1 adducts, indicating a possible formation of dipolar intermediates, was detected in the mass spectrum.

(Diethylamino)propyne also reacted with ketene 2, to give a mixture of the cyclobutenone 27 and the vinylallene 29. The latter should arise from undetected oxirene 28. A similar mixture of isomers have been reported to be formed from diphenyl- and dimethylketene with (diethylamino)phenylacetylene.[11]

Conclusions

The experimental conditions of the reactions, together with the isomer distribution of the cycloadducts obtained, are collected in Table I. A complete rationalization of the results is difficult, due to the competition of several conflicting parameters (steric, electronic, medium polarity, conformational, etc.) and the extremely low differences in activation energy involved. On this basis only sophisticated ab initio MO approaches could be useful for predictive purposes. In our opinion more detailed experimental results are needed, to explore the whole potentiality of each extended conjugated heterocumulene for the synthesis of heterocycles. Notwithstanding these following qualitative aspects, common to both C-vinylketenes and -ketene imines, clearly emerge: (a) the 1,4-C cycloaddition is favored when electrophilic partners, as TCNE and PTAD, were added. In these cases a *unique* isomer was found. This can be explained in MO perturbational terms, through the presence of only one dominant interaction, i.e., HOMO(cumulene)–LUMO(substrate). In these cases the

higher charge density is located at the terminal carbon of the vinyl group, forming a dienic fragment with the C=C of the cumulene. With less electrophilic substrates, as azodicarboxylates, (dicyanomethylene)anilines, and thioketones, the interaction, involving HOMO(substrate)–LUMO or N–LUMO(cumulene) compete for the isomer distributions, favoring the 1,2-C cycloaddition on the central C=C. In these cases, the role of a favorable secondary interaction of the Π system of the substrate with the low-lying $\Pi^*_{C=O}$ or the $\Pi^*_{C=N}$ of the cumulene is emphasized in all perturbational treatments.[12a–d] This causes bonding to develop at the central carbon of the cumulene function in the early stage of the reaction and the subsequent ring closure at the terminal carbon of the C=C=X, rather than at the heteroatom O or N. Owing to a substantial energy stabilization of $\Pi^*_{C=O}$ with respect to $\Pi^*_{C=N}$, the 1,2-C addition is preferred in ketenes rather than in ketene imines. These observations are supported by the change of selectivity, accompanied by inversion of the substituent effect on the reactivity, in the 1,2-C addition of 2 and the 1,4-C addition of ketene imines vs. the same azomethines (Scheme III). As the electrophilicity of the partners decreases, the interaction favoring the 1,4-C addition become less important and it is totally ruled out with electron-rich reagents (vinyl ethers, ynamines). In these cases other cycloaddition modes (1,4-N, 1,2-X), probably through dipolar intermediates, compete for the isomer distribution. With the most nucleophilic partner (ynamine), substantial amounts of the 1,2-X cycloadducts, involving addition across the C=X bond of the cumulenes are isolated. A similar behavior to that of ynamines has been reported in reactions of vinyl ethers and electrophilic activated N-phenylbis(trifluoromethyl)ketene imine,[1c] leading to a quinoline derivative from a hetero 1,4-N cycloaddition, while the more nucleophilic ketene acetals react with the same ketene imine to give an azetidine derivative through a 1,2-cycloaddition across C=N (1,2-N). Finally, this cycloaddition mode appears to be favored also by increasing the electrophilicity of the cumulene. In fact, while dimethyl- and diphenylketene react with vinyl ethers, across the C=C (1,2-C) bond of the cumulative function exclusively,[8a,b] the bis(trifluoromethyl)ketene gives a mixture of a cyclobutanone (1,2-C), linear ketone, and an oxetane through addition across the C=O of the ketene

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(1,2-X).[9] Beside the question of the mechanism of these reactions (concerted and/or polar) it appears that on increasing the electrophilicity of the cumulene or the nucleophilicity of the partners, the 1,2-X addition is favored.

Finally the importance of the role of the solvents on the reactivity of polar cycloadditions[13] is clearly shown in the case of the cycloaddition reaction of **1b** and *N*-phenylbenzaldehyde imine. Actually, only in a very polar solvent, as CH$_3$CN, a sluggish reaction occurred, whereas in such apolar media, as C$_6$H$_6$ or CCl$_4$, no reaction at all could be observed.

Experimental Section

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on 90-MHz Varian EM 390 and Varian CFT-80 spectrometers, and chemical shifts were given as δ values in parts per million from Me$_4$Si. IR spectra were determined on a Perkin-Elmer 257 grating spectrometer. Low-resolution mass spectra were recorded at an ionizing voltage of 70 eV on a Varian spectrometer. Analytical TLC was done on E. Merck silica gel plates, whereas column chromatography used E. Merck silica gel 60 (70–230) mesh or E. Merck aluminium oxide active 90 (70–230) mesh). Melting points were uncorrected. All solvents were purified before use.[14]

Starting Materials. (Diethylamino)propyne, ethyl vinyl ether, diethyl azodicarboxylate, tetracyanoethylene, 4-phenyl-4*H*-1,2,4-triazole-3,5-dione were available from Aldrich. Thiobenzophenone,[3a] ketene imines **1b** and **1c**,[3a–d] and (dicyanomethylene)anilines[15] were prepared according to the literature. Ketene imine **1a**[3d] was generated in CH$_2$Cl$_2$ (40 °C, 1 h), from the corresponding amide and an equimolar amount of triphenylphosphine and bromine and a 15 molar excess of triethylamine. Vinylmethylketene (**2**) was generated in the selected solvent, from the corresponding acyl chloride[16] and an equimolar amount of triethylamine (IR (CCl$_4$) 2120 cm^{-1}).

Both **1a** and **2** suddenly polymerized when their isolation in a neat state was attempted, while they showed a substantial greater stability when in solution. For this reason ketene imine **1a** was purified as follows; the solvent was evaporated under vacuo at ca. –10 °C to a few milliliters, and 60 mL of *n*-pentane was added. After standing 1 h at –20 °C, the solution was filtered from triphenylphosphine oxide and unreacted amide, the solvent was evaporated at –10 °C to a few milliliters, and the crude oily residue was redissolved in the proper solvent: IR (CCl$_4$) 2010 cm^{-1}. For this reason the presence of traces of triethylamine were unavoidable, causing a partial polymerization of very electrophilic PTAD and TCNE, when they were added to a solution of **1a**.

Such polymerizations were avoided in reactions with ketene **2** by using a slight defect (2–3%) of the theoretical amount of triethylamine. With ketene imine **1a** and ketene **2** yields were calculated from the starting amide and acyl chloride, respectively.

Details on each reaction and the characteristics of the products are given below.

Reaction with TCNE. (A) With Ketene Imine 1a. The ketene imine **1a**, generated from the corresponding amide (0.67 g, 3.83 mmol), was dissolved in CH$_3$CN (120 mL) at –80 °C, and TCNE (0.48 g, 3.75 mmol) in 4 mL of CH$_2$Cl$_2$ was added. After storage at –20 °C for 17 h, the solution was filtered from some polymeric material, the solvent evaporated, and the residue extracted six times with a total amount of 200 mL of anhydrous ethyl ether at room temperature There was obtained 0.38 g (1.33 mmol, 35%) of **3a**, still contaminated by ca. 5–10% of polymeric material.

1,1,2,2-Tetracyano-3-(p-tolylimino)cyclohex-4-ene (3a): mp 162–169 °C (from ethyl ether, –20 °C); IR (Nujol) 2260 (vw), 1655, 1640, 1510 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 1.93–2.08 (m, 2 H, CH$_2$), 2.07

(s, 3 H, Me), 4.80–5.06 (m, 1 H of CH=CHCH$_2$, $J_{CH=CH}$ = 10.65 Hz, J_{CHCH_2} = 4.0 Hz), 5.60–5.82 (m, 1 H of *H*C=CHCH$_2$, J_{HCH_2} = 1.9 Hz), 6.47–6.93 (q, 4 H, arom); ^{13}C NMR (CDCl$_3$) δ 21.03 (Me), 33.39 (CH$_2$), 40.14 (C), 47.82 (C), 108.47 (b, 2 C of 2 CN), 109.82 (b, 2 C of 2 CN), 119.98 (CH), 120.66 (2 CH), 129.97 (2 CH), 133.12 (CH), 137.38 (C), 143.61 (C), 147.50 (C); mass spectrum, *m/e* 285 (M$^+$), 258, 233, 193, 179, 157.

(B) With Vinylmethylketene (2). The ketene (0.513 g, 6.26 mmol) was generated in CCl$_4$ (220 mL) at 0 °C with an equimolar amount of Et$_3$N. After 5 min, the triethylamine chloridate was filtered, and TCNE (0.79 g, 6.26 mmol) in 15 mL of THF was added at –30 °C. The temperature was raised at 20 °C, and after 3 h, the solvent was evaporated. The residue, recrystallized from ethyl ether at –20 °C, yielded 0.425 g (2.15 mmol, 35%) of **5**.

4-Methyl-1,1,2,2-tetracyano-4-cyclohexen-3-one (5): mp 103–107 °C dec; ^{1}H NMR (CD$_3$COCD$_3$) δ 2.02–2.11 (br, 3 H, Me), 3.89–4.01 (br, 2 H of CH$_2$, J_{CHCH_2} = 4.5 Hz), 7.30–7.45 (br, 1 H); ^{13}C NMR (CD$_3$COCD$_3$) δ 14.4 (Me), 30.53 (CH$_2$), 40.1 (C), 48.0 (C), 106.64 (br, 2 C of 2 CN), 109.17 (br, 2 C of 2 CN), 131.92 (C), 142.84 (CH), 173.74 (C); IR (Nujol) 2260, 2230, 1720 cm^{-1}; mass spectrum, *m/e* [absence of M$^+$] 128, 82, 54.

Reactions of 4-Phenyl-4*H*-1,2,4-triazole-3,5-dione. (A) With Ketene Imine 1a. To a solution (CH$_3$CN, 150 mL) of the dione (0.48 g, 2.70 mmol) at –50 °C was quickly added a solution (CH$_3$CN, 25 mL) of **1a** (from 0.60 g, 3.40 mmol of the amide). After 1 h the temperature bath was raised to –20 °C and left for 6 h. After removal of the solvent in vacuo, ^{1}H NMR inspection of the crude (CDCl$_3$) revealed the presence of the 1:1 adduct together with a consistent amount of polymeric material from PTAD. A flash chromatography of the residue on a 5 cm high column (SiO$_2$; ethyl acetate–CH$_2$Cl$_2$, 2.5:12.5) afforded a relatively enriched fraction (ca. 65%) of **4a** (0.73g, 1.43 mmol, 53%).

2-Phenyl-8-(p-tolylimino)-4,5,8,9-tetrahydrotriazolo[1,2-a]pyridazine-1,3-dione (4a): ^{1}H NMR (CDCl$_3$) δ 2.36 (s, 3 H, Me), 4.37–4.50 (m, 2 H, CH$_2$), 6.17–6.53 (m, 2 H of CH=CH, $J_{CH=CH}$ = 10.5 Hz), 6.67–7.27 (q, 4 H of C$_6$H$_4$), 7.33–7.67 (arom H's of NC$_6$H$_5$ and of polymeric PTAD); mass spectrum, *m/e* 332 (M$^+$), 185.

(B) With Ketene 2. The ketene **2** (0.545 g, 6.64 mmol) was generated as described in CCl$_4$ (100 mL). After filtration of the triethylamine chloridate, the dione (1.16 g, 6.60 mmol), dissolved into a few milliliters of THF, was added at 20 °C. An instantaneous formation of a white solid was observed. Filtration afforded 0.95 g (3.69 mmol) of pure **6**, while the filtrate revealed the presence of 0.245 g (1.45 mmol) of unreacted PTAD. Yield of **6**, with respect to reacted PTAD, was 72%.

2-Phenyl-7-methyl-4,5,8,9-tetrahydrotriazolo[1,2-a]pyridazine-1,3,8-trione (6): mp 185–187 °C (from CH$_2$Cl$_2$-*n*-pentane); IR (Nujol) 3080, 1750, 1500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.98–2.09 (br, 3 H, Me), 4.47–4.59 (m, 2 H, CH$_2$), 6.64–6.79 (m, 1 H of C*H*CH$_2$), 7.53 (s, 5 H, arom); ^{13}C NMR (CDCl$_3$) δ 15.83 (Me), 42.66 (CH$_2$), 125.75 (2 CH), 128.29 (C), 128.72 (CH), 129.26 (2 CH), 130.29 (C), 133.32 (CH), 145.16 (C), 157.45 (C); mass spectrum, *m/e* 257 (M$^+$), 138, 82. Anal. Calcd for C$_{13}$H$_{11}$N$_3$O$_3$: C, 60.70; H, 4.31; N, 16.33. Found: C, 60.62; H, 4.29; N, 16.39.

Reactions with Diethyl Azodicarboxylate. (A) With Ketene Imine 1b. The carboxylate (0.76 g, 4.39 mmol) reacted with **1b** (0.751 g, 4.39 mmol) in CCl$_4$ (150 mL) at room temperature. After 3 h the reaction was complete. Elution of the reaction residue on column chromatography (SiO$_2$; CH$_2$Cl$_2$-*n*-pentane, 2:1) yielded **7b** (1.43 g, 4.41 mmol, 94%). The same result was obtained with CH$_3$CN (150 mL) as solvent.

4-Methyl-1,2-bis(ethoxycarbonyl)-3-(p-tolylimino)-1,2,3,6-tetrahydropyridazine (7b): mp 137–139 °C (from CH$_2$Cl$_2$-*n*-pentane); IR (CCl$_4$, CS$_2$) 3030, 2990, 1730, 1650 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.80–1.00 (t, 3 H, Me of OC$_2$H$_5$, $J_{CH_2CH_3}$ = 10.5 Hz), 1.27–1.47 (t, 3 H, Me of OC$_2$H$_5$, $J_{CH_2CH_3}$ = 10.5 Hz), 2.0–2.13 (m, 3 H, Me of HC=CCH$_3$, J_{HCH_3} = 1.5 Hz), 2.35 (s, 3 H, Me), 3.77–4.10 (m, 1 H of CH$_2$), 3.77–4.00 (q, 2 H, CH$_2$ of C$_2$H$_5$), 4.17–4.40 (q, 2 H, CH$_2$ of C$_2$H$_5$), 4.43–4.76 (m, 1 H of CH$_2$, J_{HH} = 19.2 Hz), 6.17–6.37 (m, 1 H of *H*CCH$_2$, J_{CHCH} = 5.5 Hz), 6.97–7.43 (q, 4 H, arom); ^{13}C NMR (CDCl$_3$) δ 13.83 (Me), 14.53 (Me), 18.34 (Me), 21.00 (Me), 44.05 (CH$_2$), 62.81 (CH$_2$), 63.13 (CH$_2$), 122.10 (2 CH), 128.98 (2 CH), 130.34 (CH), 132.26 (C), 134.46 (C), 143.66 (C), 144.85 (C), 152.07 (C), 155.00 (C); mass spectrum, *m/e* 345 (M$^+$), 300, 272, 244, 228, 199, 171. Anal. Calcd

(13) Further examples concerning the role of polar solvents can be found also in ref 4 and 10.

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for $C_{18}H_{23}N_3O_4$: C, 62.59; H, 6.71; N, 12.17. Found: C, 62.70; H, 6.67; N, 12.12.

(B) With Vinylmethylketene (2). The ketene was generated from the chloride (0.671 g, 5.70 mmol) in CCl_4 (60 mL). After 10 min the chloridate was filtered, and 0.987 g (5.67 mmol) of diethyl azodicarboxylate (DAZD) was added to a solution of 2 and left at 20 °C for 3 days. Evaporation of the solvent and chromatographic workup of the residue (SiO_2, CH_2Cl_2) yielded in order the unreacted DAZD (0.661 g, 3.80 mmol), 9 (0.112 g, 0.438 mmol, 23.4% with respect to reacted DAZD), 8 (0.25 g, 0.976 mmol, 52.2%); 9/8 = 1/2.27.

4-Methyl-1,2-bis(ethoxycarbonyl)-1,2,3,6-tetrahydro-pyridazin-3-one (8): oil; IR (film) 1750 cm⁻¹; ¹H NMR ($CDCl_3$) δ 1.17-1.40 (t, 3 H, Me of OC_2H_5, $J_{CH_2CH_3}$ = 7.2 Hz), 1.25-1.48 (t, 3 H, Me of OC_2H_5, $J_{CH_2CH_3}$ = 7.2 Hz), 1.89-2.0 (m, 3 H, Me of HC=CCH_3, J_{HCH_3} = 1.80 Hz), 4.04-4.32 (q, 2 H, CH_2 of OC_2H_5), 4.20-4.47 (q, 2 H, CH_2 of OC_2H_5), 4.04-4.30 (m, 2 H of HCCH_2), 6.57-6.73 (m, 1 H of $HCCH_2$, J_{CHCH} = 3.8 Hz); ¹³C NMR ($CDCl_3$) δ 14.02 (M), 14.12 (Me), 15.91 (Me), 45.28 (CH_2), 63.23 (OCH_2), 63.39 (OCH_2), 131.12 (C), 137.93 (CH), 150.84 (C), 155.54 (C), 162.1 (C); mass spectrum, m/e 256 (M)⁺, 211, 183, 125, 101, 82. Anal. Calcd for $C_{11}H_{16}N_2O_5$: C, 51.56; H, 6.29; N, 10.93. Found: C, 51.64; H, 6.25; N, 10.83.

1,2-Bis(ethoxycarbonyl)-4-methyl-4-vinyl-1,2-diazetidin-3-one (9): oil; IR (film) 1845, 1780-1750 cm⁻¹; ¹H NMR ($CDCl_3$) δ 1.23-1.43 (t, 3 H, Me of OC_2H_5, $J_{CH_2CH_3}$ = 7.5 Hz), 1.30-1.50 (t, 3 H, Me of OC_2H_5, $J_{CH_2CH_3}$ = 7.5 Hz), 1.73 (s, 3 H, Me), 4.17-4.47 (q, 2 H, CH_2 of OC_2H_5), 4.25-4.55 (q, 2 H of OC_2H_5), 5.37-6.17 (m, 3 H, vinyl); ¹³C NMR ($CDCl_3$) δ 14.10 (Me), 14.23 (Me), 19.11 (Me), 63.32 (CH_2), 64.04 (CH_2), 84.55 (C), 119.82 (CH_2), 131.27 (CH), 148.09 (C), 157.6 (C), 164.37 (C); mass spectrum, m/e 256 (M)⁺, 227, 183, 174. Anal. Calcd for $C_{11}H_{16}N_2O_5$: C, 51.56; H, 6.29; N, 10.93. Found: C, 51.48; H, 6.24; N, 11.00.

Reactions of Azomethines 10, 11, and 17. (A) With Ketene Imines 1b and 1c. The selected ketene imine was reacted with the proper azomethine in the proper solvent. As soon as the ketene imine disappeared, workup of the reaction mixture through column chromatography (SiO_2; ethyl acetate-*n*-pentane, 3:12) afforded the reaction products.

(a) Ketene imine **1b** (0.33g, 1.93 mmol) was reacted with *N*-(dicyanomethylene)aniline (**10**) (0.30g, 1.93 mmol) in CCl_4 (25 mL) for 4 days at room temperature. After disappearance of the reagents a column chromatography of the reaction residue gave 0.53 g (1.63 mmol, 84%) of **13b**.

1-Phenyl-2-cyano-5-methyl-6-(*p*-tolylimino)-1,6-dihydro-pyridine (13b): mp 157-159 °C (from CHCl₃); IR (CCl_4, CS_2, C_2Cl_4) 2225, 1645, 1600 cm⁻¹; ¹H NMR (C_6D_6) δ 1.72-1.80 (br, 3 H, Me of HC=CCH_3, J_{HCH_3} = 1.2 Hz), 2.10 (s, 3 H, Me), 5.68-5.80 (d, 1 H, of CHCH=CCN, J_{CHCH} = 7.0 Hz), 5.91-6.03 (d, 1 H of $CHCH$=CCN), 6.37-6.88 (q, 4 H, arom of C_6H_4), 6.95 (s, 5 H, arom); ¹³C NMR ($CDCl_3$) δ 20.63 (Me), 21.78 (Me), 113.91 (CH), 120.32 (2 CH and C), 128.59 (2 CH), 128.80 (2 CH), 129.29 (2 CH), 129.96 (CH), 131.25 (CH), 137.37 (C), 140.74 (C), 147.38 (C); mass spectrum, m/e 299 (M⁺), 206, 181. Anal. Calcd for $C_{20}H_{17}N_3$: C, 80.24; H, 5.72; N, 14.04. Found: C, 80.12; H, 5.67; N, 14.10.

(b) Ketene imine **1c** (0.46 g, 2.32 mmol) was reacted with **10** (0.36 g, 2.32 mmol) in CCl_4 (70 mL) for 6 days at 30 °C. An ¹H NMR ($CDCl_3$) spectrum of the crude revealed the presence of both **12c** and **14c**.

1-Phenyl-2,2-dicyano-5-methyl-6-(mesitylimino)-1,2,3,6-tetrahydropyridine (12c): ¹H NMR ($CDCl_3$) δ 1.85 (s, 6 H, 2 Me), 2.05 (s, 3 H, Me), 1.80-2.0 (m, 3 H, Me), 2.9-3.1 (br, 2 H, CHCH_2), 6.0-6.2 (br, 1 H, CHCH_2), 6.33-6.5 (br, 2 H, arom).

Elution on column chromatography gave in order unreacted **10** (0.07 g, 0.45 mmol) and the following.

2,2-Dicyano-4-methyl-1-phenyl-3-(mesitylimino)-1,2,3,6-tetrahydropyridine (14c): 0.12 g, 0.34 mmol, 18% (with respect to reacted **10**); mp 126-128 °C (from ethyl ether-*n*-pentane); IR (CCl_4, CS_2) 2260 (vw), 2225 (vw), 1740, 1660 cm⁻¹; ¹H NMR ($CDCl_3$) δ 1.35-1.47 (br, 3 H, Me), 2.09 (s, 6 H, 2 Me), 2.26 (s, 3 H, Me), 3.9-4.1 (br, 2 H, CH_2), 6.2-6.4 (br, 1 H of CH_2CH=CMe), 6.77-6.90 (br, 2 H, arom), 7.53-7.60 (br, 5 H, arom); ¹³C NMR ($CDCl_3$) δ 17.93 (2 Me), 19.5 (Me), 20.7 (Me), 50.94 (CH_2), 71.80 (C), 111.62 (C of CN), 124.77 (2 C), 125.89 (2 CH), 128.14 (C), 128.31 (3 CH), 129.78 (2 CH), 133.37 (C), 136.67 (CH), 143.66 (C), 145.81 (C); mass spectrum, m/e 354 (M⁺), 328, 199, 155.

1-Phenyl-2-cyano-5-methyl-6-(mesitylimino)-1,6-dihydro-pyridine (13c): 0.34 g, 0.97 mmol, 53%; mp 158-160 °C (from CH_2Cl_2-*n*-pentane); IR (CCl_4, C_2Cl_4, CS_2) 2234 (strong), 1650, 1610, 1600 cm⁻¹; ¹H NMR ($CDCl_3$) δ 1.72-1.78 (br, 3 H, Me), 1.93 (s, 6 H, 2 Me), 2.13 (s, 3 H, Me), 6.22-6.37 (d, 1 H of HCCH=CCN, J_{CHCH} = 7.2 Hz), 6.47-6.67 (br, 1 H of HCCH and 2 H arom), 7.13-7.47 (m, 5 H, arom); ¹³C NMR ($CDCl_3$) δ 18.51 (2 Me), 20.55 (Me), 20.86 (Me), 113.09 (CH), 113.32 (C of CN), 120.19 (C), 126.67 (2 C), 127.57 (2 CH), 128.25 (2 CH), 129.01 (CH), 129.28 (2 CH), 130.06 (C), 131.03 (CH), 136.14 (C), 140.43 (C), 145.55 (C) 147.37 (C); mass spectrum, m/e 327 (M⁺), 312, 223, 149. Anal. Calcd for $C_{22}H_{21}N_3$: C, 80.65; H, 6.46; N, 12.83. Found: C, 80.29; H, 6.51; N, 12.89.

(c) Ketene imine **1c** (0.33 g, 1.67 mmol) was reacted with *N*-(dicyanomethylene)-*p*-chloroaniline (**11**) (0.342 g, 1.80 mmol) in benzene (15 mL) for 2 days and yielded in order the following.

1-(*p*-Chlorophenyl)-2,2-dicyano-3-(mesitylimino)-4-meth-yl-1,2,3,6-tetrahydropyridine (16c): 0.038 g, 0.10 mmol, 6.2% [along with slightly impure (ca. 5-10%) **11**]; mp 149-155 °C (from benzene); IR (CCl_4) 2260 (vw), 2215 (vw), 1730, 1660 cm⁻¹; ¹H NMR ($CDCl_3$) δ 1.38-1.5 (br, 3 H, Me), 2.08 (s, 6 H, 2 Me), 2.28 (s, 3 H, Me), 3.85-4.05 (m, 2 H of HC=CH_2), 6.22-6.37 (br, 1 H, of HC=CH_2), 6.82-6.87 (br, 2 H, arom), 7.48 (s, 4 H, arom); mass spectrum, m/e 388 (M⁺), 344.

2,2-Dicyano-6-(mesitylimino)-5-methyl-1-(*p*-chlorophe-nyl)-1,2,3,6-tetrahydropyridine (15c): 0.57 g, 1.47 mmol, 88%; mp 148-150 °C (from benzene); IR (CCl_4) 2235 (vw), 1635, 1493 cm⁻¹; ¹H NMR ($CDCl_3$) δ 1.89 (s, 6 H, 2 Me), 1.90-2.03 (br, 3 H, Me of HC=CMe), 2.12 (s, 3 H, Me), 3.10-3.30 (br, 2 H, of CHCH_2), 6.10-6.32 (br, 1 H of HCCH_2), 6.53-6.58 (br, 2 H, arom), 7.17 (s, 4 H, arom); ¹³C NMR ($CDCl_3$) δ 18.08 (2 Me), 19.36 (Me), 20.32 (Me), 35.24 (CH_2), 55.26 (C), 113.08 (2 C), 124.19 (CH, br), 125.2 (2 C), 127.76 (2 CH), 129.0 (2 CH), 129.8 (2 CH), 131.67 (C), 134.86 (C), 135.70 (C br), 138.77 (C), 142.95 (C), 146.31 (C); mass spectrum, m/e 388 (M⁺), 373. Anal. Calcd for $C_{23}H_{21}N_4Cl$: C, 71.03; H, 5.44; N, 14.41; Cl, 9.12. Found: C, 71.21; H, 5.38; N, 14.47.

In a separate experience **1c** (0.061 g, 0.31 mmol) was reacted with **11** (0.06 g, 0.31 mmol) in CCl_4 (1 mL). After 8 days at 35 °C, an isomer distribution of **11d/11d'** = 6.1 was found.

(d) Ketene imine **1b** (0.70 g, 4.10 mmol) was reacted with *N*-phenylbenzaldehyde imine (**17**) (0.75 g, 4.10 mmol) in CH_3CN (25 mL) at 55 °C for 20 days. After the disappearance of the reagents, column chromatography (silica, benzene) allowed the separation of periisomers **18a,b** from **19a,b**. Each diastereomeric mixture was resolved by chromatography (silica; ethyl acetate-*n*-pentane, 3:12). Obtained in order were the following.

2-(*p*-Tolylimino)-3-methyl-3-vinyl-4-phenyl-*N*-phenyl-azetidine (18a): oil; 0.07 g (0.17 mmol), 4.1%; ¹H NMR ($CDCl_3$) δ 0.83 (s, 3 H, Me), 2.27 (s, 3 H, Me), 4.93-5.2 (m, 2 H of H_2C=CH), 5.06 (s, 1 H of HCN), 6.0-6.37 (m, 1 H of H_2C=CH), 6.77-7.1 (m, 4 H, arom of C_6H_4), 7.13-7.63 (m, 10 H, arom); mass spectrum, m/e 352 (M⁺), 208, 181, 171; IR (CCl_4) 1698 cm⁻¹.

18b: oil; 0.16 g (0.455 mmol), 11%; IR (CCl_4) 1692 cm⁻¹; ¹H NMR ($CDCl_3$) δ 1.63 (s, 3 H, Me), 2.38 (s, 3 H, Me), 4.73-5.20 (m, 2 H of H_2C=CH), 5.0 (s, 1 H of HCN), 5.37-5.73 (m, 1 H of H_2C=CH), 6.8-7.1 (m, 4 H arom of C_6H_4), 7.12-7.63 (m, 10 H, arom); ¹³C NMR ($CDCl_3$) δ 20.80 (Me), 21.11 (Me), 57.74 (C), 69.99 (CH), 116.14 (CH_2), 116.99 (2 CH), 122.12 (CH), 122.51 (2 CH), 126.88 (2 CH), 127.88 (CH), 128.51 (2 CH), 128.76 (4 CH), 131.89 (C), 136.00 (C), 136.76 (CH), 140.19 (C), 144.52 (C), 157.16 (C); mass spectrum, m/e 352 (M⁺), 208, 181, 171. Anal. Calcd for $C_{25}H_{24}N_2$: C, 85.19; H, 6.86; N, 7.95. Found: C, 85.45; H, 6.81; N, 7.92.

2-(2-Buten-2-yl)-3,4-diphenyl-6-methyl-3,4-dihydro-quinazoline (19a): oil; 0.65 g (1.85 mmol), 44.7%; IR (C_2Cl_4) 1570 cm⁻¹; ¹H NMR ($CDCl_3$) δ 1.59 (d, 3 H, Me, J_{HCH_3} = 7.5 Hz), 1.62-1.69 (br, 3 H, Me), 2.20 (s, 3 H, Me), 5.62 (s, 1 H), 6.26 (q, 1 H, J_{HCH_3} = 7.5 Hz), 6.72-6.80 (br, 1 H, arom), 6.93-7.70 (m. 1 H, arom); ¹³C NMR ($CDCl_3$) δ 14.03 (Me), 14.25 (Me), 21.03 (Me), 65.96 (CH), 124.02 (2 CH), 124.70 (CH), 124.75 (CH), 125.91 (2 CH), 126.22 (CH, C), 127.78 (CH), 128.63 (2 CH), 128.88 (CH), 129.01 (2 CH), 132.24 (CH), 133.27 (C), 134.98 (C), 138.64 (C), 144.99 (C), 146.45 (C), 157.44 (C); mass spectrum, m/e 352 (M⁺), 275. Anal. Calcd for $C_{25}H_{24}N_2$: C, 85.19; H, 6.86; N, 7.95. Found: C, 85.24; H, 6.81; N, 8.00.

19b: oil; 0.32 g (0.91 mmol), 22%; IR (C$_2$Cl$_4$) 1570 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.60–1.73 (br, 3 H, Me), 1.73 (d, 3 H, J_{HCH_3} = 7.7 Hz), 2.20 (s, 3 H, Me), 5.42 (q, 1 H, J_{HCH_3} = 7.7 Hz), 5.64 (s, 1 H), 6.63–6.73 (br, 1 H, arom), 6.93–7.50 (m, 12 H, arom); mass spectrum, m/e 352 (M$^+$), 275; ^{13}C NMR (CDCl$_3$) δ 15.48 (Me), 21.03 (Me), 21.78 (Me), 66.46 (CH), 124.87 (CH), 125.36 (C), 126.06 (2 CH), 126.46 (CH), 126.51 (CH), 126.95 (2 CH), 128.01 (CH), 128.62 (2 CH), 128.91 (2 CH), 129.04 (CH), 132.96 (C), 135.04 (C), 138.48 (C), 144.52 (C), 145.00 (C), 155.47 (C).

(B) With Vinylmethylketene (2). (a) The ketene **2**, generated from the acyl chloride (0.69 g, 5.82 mmol), in 150 mL of CCl$_4$, and filtered from the chloridate, was reacted with *N*-phenylbenz-aldehyde imine (**17**) (0.808 g, 8.0 mmol) for 1 day at room tem-perature. ^{1}H NMR inspection of the crude, after evaporation of the solvent, showed the presence, together with unreacted **17**, of only one of the two possible diastereoisomers of the azetidinone **21**, which was isolated from column chromatography (SiO$_2$, CH$_2$Cl$_2$), while **17** hydrolyzed to the corresponding benzaldehyde and aniline.

3-Methyl-4-phenyl-3-vinyl-*N*-phenylazetidin-2-one (20): 0.85 g, 3.23 mmol, 52%; mp 105–108 °C (from ethyl ether–*n*-pentane); IR (CCl$_4$) 1770 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.63 (s, 3 H, Me), 4.85 (s, 1 H of H*C*N), 4.89–5.07 (m, 1 H of C*H*=CH$_2$), 5.16–5.47 (m, 2 H of CH=C*H$_2$*), 6.88–7.5 (m, 10 H arom); ^{13}C NMR (CDCl$_3$) δ 20.69 (Me), 61.62 (C), 67.13 (CH), 117.09 (CH$_2$), 117.24 (2 CH) 123.74 (CH) 126.87 (2 CH), 128.07 (CH), 128.54 (2 CH), 128.90 (2 CH), 134.12 (CH), 134.94 (C), 137.65 (C), 168.60 (C); mass spectrum, m/e 263 (M$^+$), 181, 144, 119, 82. Anal. Calcd for C$_{18}$H$_{17}$NO: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.01; H, 6.46; N, 5.38.

(b) The ketene **2** (0.364 g, 4.44 mmol) was reacted with the azomethine **10** (0.688 g, 4.44 mmol) in ethyl ether (90 mL). After 2 days, workup of the reaction mixture through column chro-matography (SiO$_2$, benzene) yielded the unreacted **10** (0.61g, 3.93 mmol) and the lactam **21** (0.08 g, 0.34 mmol, 7.7%). The same reaction in CH$_3$CN gave **21** in 8.1%.

2,2-Dicyano-3-methyl-3-vinyl-*N*-phenylazetidin-4-one (21): oil; IR (film) 2255 (vw), 1790, 1600, 1500 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.87 (s, 3 H, Me), 5.55–5.82 (m, 2 H, of HC=C*H$_2$*), 5.97–6.30 (m, 1 H of *H*C=CH$_2$), 7.23–7.65 (m, 5 H, arom); ^{13}C NMR (CDCl$_3$) δ 18.11 (Me), 52.53 (C), 69.54 (C), 110.65 (2 C), 117.20 (2 CH), 122.60 (CH$_2$), 126.69 (CH), 129.83 (2 CH), 130.3 (CH), 134.24 (C), 163.14 (C); mass spectrum, m/e 237 (M$^+$), 119, 82. Anal. Calcd for C$_{14}$H$_{11}$N$_3$O: C, 70.87; H, 4.67; N, 17.71. Found: C, 70.98; H, 4.73; N, 17.65.

Reaction of Thiobenzophenone and Vinylmethylketene (2). The ketene was generated in situ by dropping a solution of the acyl chloride (0.77 g, 6.60 mmol) in an equimolar solution of triethylamine and the thione (1.30 g, 6.60 mmol) in 90 mL of CCl$_4$ at 0 °C in 10 h. After 1 day an IR inspection of the reaction mixture at ν_{CCO} 2120 cm^{-1} revealed that the ketene **2** had totally disappeared, while the amount of unreacted thione (0.546 g, 2.76 mmol) was measured by its absorbance on a UV spectrum [λ_{max} 600 nm (ϵ 205)]. Evaporation of the solvent, followed by column chromatography (SiO$_2$; *n*-pentane–benzene, 2:1) afforded **22**.

3-Methyl-3-vinyl-4,4-diphenylthietan-2-one (22): 1.12 g, 4.0 mmol, 90%, on reacted thioketone; oil; IR (CCl$_4$) 1770 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.30 (s, 3 H, Me), 4.97–5.47 (m, 2 H of HC=C*H$_2$*), 5.63–6.0 (m, 1 H of *H*C=CH$_2$), 7.07–7.5 (m, 10 H, arom); ^{13}C NMR (CDCl$_3$) δ 22.96 (Me), 63.42 (C), 81.62 (C), 115.83 (CH$_2$), 127.11 (CH), 127.40 (CH), 127.6 (2 CH), 127.97 (2 CH), 129.11 (2 CH), 129.64 (2 CH), 137.73 (CH), 140.21 (C), 141.97 (C), 194.73 (C); mass spectrum, m/e 280 (M$^+$), 220 (M$^+$ – COS), 198, 82. Anal. Calcd for C$_{18}$H$_{16}$OS: C, 77.11; H, 5.75; S, 11.44. Found: C, 77.29; H, 5.71; S, 11.49.

Reaction of Ethyl Vinyl Ether and Ketene 2. The acyl chloride (2.0 g, 16.9 mmol) was dropped into a solution of equimolar amount of triethylamine in 25 mL of ethyl vinyl ether at room temperature in 8 h. Workup of the reaction mixture and elution on column chromatography (SiO$_2$; *n*-pentane–ethyl ether, 18:2) yielded the cyclobutanones **23a** and **23b** (1.3 g, 8.44 mmol, 50%, and 0.57 g, 3.71 mmol, 22%, respectively).

***anti*-2-Methyl-2-vinyl-3-ethoxycyclobutanone (23a)**: oil; IR (CCl$_4$) 1795 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.15–1.4 (t, 3 H of OC$_2$H$_5$, $J_{CH_2CH_3}$ = 6.9 Hz), 1.29 (s, 3 H, Me), 3.08–3.25 (m, 2 H of HCC*H$_2$*, J_{cis} = J_{trans} = 6.45 Hz, J_{HH} = 3.30 Hz), 3.4–3.7 (q, 2 H, CH$_2$ of OC$_2$H$_5$), 4.05–4.23 (t, 1 H of *H*CCH$_2$), 5.03–5.3 (m, 2 H of HC<< dbdC*H$_2$*), 5.75–6.1 (m, 1 H of *H*C=CH$_2$); ^{13}C NMR (CDCl$_3$) δ 14.9 (2 Me), 49.96 (CH$_2$), 65.56 (OCH$_2$), 69.68 (C), 72.1 (CH), 114.4 (CH), 137.5 (CH), 209.1 (C); mass spectrum, m/e 154 (M$^+$), 125, 82.

***syn*-2-Methyl-2-vinyl-3-ethoxycyclobutanone (23b)**: oil; IR (CCl$_4$) 1795 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.13–1.38 (t, 3 H, OCH$_2$C*H$_3$*, $J_{CH_2CH_3}$ = 7.0 Hz), 1.32 (s, 3 H, Me), 3.12–3.3 (m, 2 H of HCC*H$_2$*, J_{cis} = J_{trans} = 6.42 Hz, J_{HH} = 2.1 Hz) 3.38–3.68 (q, 2 H, CH$_2$ of OC$_2$H$_5$), 3.85–4.05 (t, 1 H of *H*CCH$_2$), 5.08–5.28 (m, 2 H of HC=C*H$_2$*), 5.95–6.32 (m, 1 H of *H*C=CH$_2$); ^{13}C NMR (CDCl$_3$) δ 15.01 (Me), 19.31 (Me), 50.81 (CH$_2$), 65.51 (OCH$_2$), 69.51 (C), 74.41 (CH), 116.0 (CH$_2$), 133.11 (CH), 208.41 (C); mass spectrum, m/e 154 (M$^+$), 112, 82.

Reactions of (Diethylamino)propyne. (A) With Ketene Imine 1c. The ketene imine **1c** (0.515g, 2.59 mmol) was reacted with the ynamine (0.288g, 2.59 mmol) in 25 mL of pentane at 0 °C for 10 days. ^{1}H NMR inspection of the crude revealed the presence of the 1:1 adduct **24** in 83% yield. Additionally its mass spectrum revealed the presence of a peak at m/e 421 (M$^+$ of a 2:1 adduct formed by two molecules of ynamine and one of **1c**). The reaction mixture, dissolved in 100 mL of ethyl ether, was treated with gaseous hydrogen chloride at 0 °C for 1 min. The organic layer was extracted five times with a total amount of 120 mL of water, and the organic phase was discarded. The aqueous solution was neutralized with sodium hydrogen carbonate, con-centrated in vacuo to a few milliliters and extracted with CH$_2$Cl$_2$. The organic phase, dried over CaCl$_2$ (anhydrous) and evaporated, left the hydrated form of **24** quantitatively: oil; IR (film) 2850–2300, 1560 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.23 (s, 3 H, Me), 1.17–1.5 (br, 6 H, 2 Me of N(C$_2$H$_5$)$_2$), 1.90 (s, 3 H, Me), 2.18 (s, 3 H, Me), 2.26 (s, 6 H, 2 Me), 3.2–3.7 (br, 5 H, 2 CH$_2$ and 1 H), 5.27–5.5 (m, 2 H of HC=C*H$_2$*), 6.1–6.5 (m, 1 H of *H*C=CH$_2$), 6.85 (s, 2 H, arom), 10.0–14.0 (br); ^{13}C NMR (CDCl$_3$) δ 7.98 (Me), 13.14 (Me), 13.88 (Me), 17.62 (Me), 17.79 (Me), 19.08 (Me), 20.66 (Me), 43.27 (CH$_2$), 45.2 (CH$_2$), 56.69 (C), 101.2 (C), 118.3 (CH$_2$), 128.42 (2 CH), 131.3 (C), 134.68 (C), 134.83 (C), 136.4 (CH), 137.53 (C), 170.78 (C), 171.55 (C).

Elution of the hydrated form on Al$_2$O$_3$ (ethyl acetate) gave **24** quantitatively. In another experiment ketene imine **1c** (0.06 g, 0.3 mmol) was reacted with (diethylamino)propyne (0.032 g, 0.30 mmol) in CDCl$_3$ (1 mL) at 25 °C for 2 days. Elution of the crude reaction mixture (Al$_2$O$_3$, ethyl acetate) gave **24**.

2-(Mesitylimino)-3,4-dimethyl-3-vinyl-1-(diethylamino)-cyclobutene (24): 0.08 g, 87%; oil; IR (film) 1593, 1485 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.15 (t, 6 H, 2 Me, $J_{CH_2CH_3}$ = 7.3 Hz), 1.18 (s, 3 H, Me), 1.57 (s, 3 H, Me), 2.03–2.15 (br, 6 H, 2 Me), 2.23 (s, 3 H, Me), 3.23 (q, 4 H, 2 CH$_2$ of N(C$_2$H$_5$)$_2$), 5.08–5.43 (m, 2 H of HC=C*H$_2$*), 5.9–6.3 (m, 1 H of *H*C=CH$_2$), 6.66–6.8 (br, 2 H, arom); ^{13}C NMR (CDCl$_3$) δ 8.34 (Me), 13.09 (2 Me), 13.87 (Me), 17.16 (2 Me), 19.86 (Me), 42.09 (2 CH$_2$), 57.44 (C), 101.4 (C), 114.16 (CH$_2$), 126.65 (2 CH), 127.73 (2 C), 129.66 (C), 139.95 (CH), 145.21 (C), 163.28 (C), 163.63 (C); mass spectrum, m/e 310 (M$^+$), 295, 281, 239, 199.

(B) With Vinylmethylketene (2). The ketene, generated from the corresponding acyl chloride (1.086 g, 9.17 mmol) and an equimolar amount of triethylamine at 0 °C in CCl$_4$ (160 mL), was reacted, after filtration of the chloridate, with the ynamine (1.01 g, 9.11 mmol). After disappearance of the ketene (ca. 3 h), monitored by IR, and evaporation of the solvent, the residue was chromatographed (SiO$_2$; ethyl ether–*n*-pentane, 3:12). The fol-lowing were obtained in order.

2,4-Dimethyl-*N*,*N*-diethyl-2,3,5-hexatrienamide (29): 0.14 g, 0.726 mmol, 8%; oil; IR (film) 1960 (w, C=C=C), 1630 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.14 (t, 6 H, 2 Me, $J_{CH_2CH_3}$ = 7.2 Hz), 1.87 (s, 3 H, Me), 1.97 (s, 3 H, Me), 3.48 (q, 4 H, 2 CH$_2$), 5.00–5.33 (m, 2 H of HC=C*H$_2$*), 6.17–6.56 (m, 1 H of *H*C=CH$_2$); ^{13}C NMR (CDCl$_3$) δ 12.63–14.20 (br, 2 Me of N(C$_2$H$_5$)$_2$), 14.2 (Me), 17.49 (Me), 38.54–43.2 (br, 2 CH$_2$ of N(C$_2$H$_5$)$_2$), 95.29 (C), 101.18 (C), 113.55 (CH$_2$), 134.26 (CH), 167.2 (C), 204.39 (C); mass spectrum, m/e 193 (M$^+$), 178, 164, 121, 100, 93.

3-(Diethylamino)-2,4-dimethyl-4-vinyl-2-cyclobuten-1-one
(27): 0.62 g, 3.21 mmol, 35.4%; oil; IR (film) 1750, 1585 cm^{-1};
^{1}H NMR (CDCl$_3$) δ 1.20 (t, 3 H, Me, $J_{CH_2CH_3}$ = 7.8 Hz), 1.27 (t,
3 H, Me, $J_{CH_2CH_3}$ = 7.8 Hz), 1.43 (s, 3 H, Me), 1.73 (s, 3 H, Me),
3.36 (q, 2 H, CH$_2$), 3.44 (q, 2 H, CH$_2$), 5.0–5.33 (m, 2 H of
H_2C=CH), 5.78–6.17 (m, 1 H of H$_2$C=CH); ^{13}C NMR (CDCl$_3$)
δ 7.09 (2 Me), 13.75 (Me), 16.92 (Me), 42.68 (CH$_2$), 44.47 (CH$_2$),
64.03 (C), 105.84 (C), 115.48 (CH$_2$), 139.08 (CH), 170.78 (C), 187.70
(C); mass spectrum, *m/e* 193 (M$^+$), 178, 121, 111, 82. Anal. Calcd
for C$_{12}$H$_{19}$NO: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.69; H,
9.96; N, 7.21.

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HZSM-5-Catalyzed Isomerization of Alkylanilines[†]

F. J. Weigert

*Central Research & Development Department, Experimental Station, E. I. du Pont de Nemours & Company,
Wilmington, Delaware 19898*

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Zeolite HZSM-5 catalyzes the equilibration of toluidines and ethylanilines by an intramolecular 1,2-shift
mechanism. The three xylidines with the 1,2,4-substitution pattern are also interconverted by this catalyst. Larger
methylanilines are neither formed nor consumed by the catalyst.

HZSM-5 has been a popular catalyst for the isomeriza-
tion of substituted toluenes.[1] It has extremely strong acid
sites, and its intermediate-size pores resist coke formation
better than the larger pore faujasites. The three-dimen-
sional pore structure is less resistant to blockage than the
one-dimensional pore structure of mordenites. Industrial
processes using solid acids cause much less corrosion than
processing using more traditional Lewis acids such as AlCl$_3$.
Xylene equilibration using HZSM-5 is practiced on a large
scale to prepare the para isomer as a polyester interme-
diate.[2]

Though less important commercially, reports on the
isomerization of other substituted toluenes with HZSM-5,
such as chlorotoluenes,[3] cresols,[4] and toluonitriles,[5] have
appeared; but at the time this work was begun, toluidine
isomerization had not been reported. Patents describing
work overlapping ours[6] have appeared.[7]

Under more severe conditions, HZSM-5 has been re-
ported to isomerize aniline and phenylenediamines to
methylpyridines and aminopicolines.[8,9]

We present here a study of the HZSM-5-catalyzed
isomerization of alkylanilines.

Results

A mixture of each toluidine in aniline was passed over
HZSM-5. We could only feed liquids to our reactor, so as
to keep the reaction conditions as similar as possible, all
reagents were fed in aniline as solvent. The toluidine
isomer profile from pure *o*-toluidine as the starting ma-
terial was the same as for the solution of *o*-toluidine in
aniline. Dealkylation and transalkylation do not occur
except under the most severe conditions. No methyl-
pyridine was detected in these experiments, which were
run under conditions much milder than previous work.[8,9]

Table I. Equilibrium Compositions for Alkylanilines

	o	*m*	*p*
xylenes[a]	23	53	24
toluidines	31	52	17
ethylanilines	24	57	19
dimethylanilines[b]	23	26	51

[a] Reference 12, 600 K. [b] Orientations of methyls: 3,4; 2,4; 2,5.

The toluidine isomer distribution of the reaction prod-
ucts is shown in Figure 1 as a composition diagram. Each
vertex represents a pure isomer, each edge a binary mix-
ture, and a point inside represents a ternary mixture.
There is one unique equilibrium point in the interior of
such a triangle. The advantages of such a coordinate
system have been described previously.[10]

Each symbol represents a separate experiment in which
the independent variables were contact time, partial
pressure, aniline/toluidine ratio, and temperature. A single
variable, severity, suffices to explain the progress of the
reaction as can be seen by the narrow band of the data
points from each starting isomer. A similar plot for the
ethylanilines is given in Figure 2. The equilibria deter-

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