proton gated noise decoupling with the decoupler switched off during the acquisition (this method yields a proton coupled carbon-13 spectrum with increased intensities because of the nuclear Overhauser effect), and (c) proton selective decoupling. In method c irradiation frequencies were determined from proton spectra recorded on the decoupling coil of the broadband probe used for observing carbon-13.

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Registry No. 1, 31163-70-9; 2, 110-89-4; 3, 123-75-1; 4, 110-91-8; 5, 89773-91-1; 6, 89773-93-3; 7, 89773-95-5; 8, 89773-96-6.

Supplementary Material Available: Tables 1 and 2 containing complete ^1H and ^{13}C NMR data for 5–7 and relevant reference compounds; table 3 containing temperature dependant ^{13}C and ^1H NMR data of 5–6; figure 2, variable temperature 75-MHz ^{13}C NMR spectra of 6 and figure 3, variable temperature 300-MHz ^1H spectra of 6 (5 pages). Ordering information is given on any current masthead page.

Aluminum Chloride Catalyzed Oligomerization of Ketene Imines and Incorporation of Carbon Dioxide in an Open-Chain Dimer

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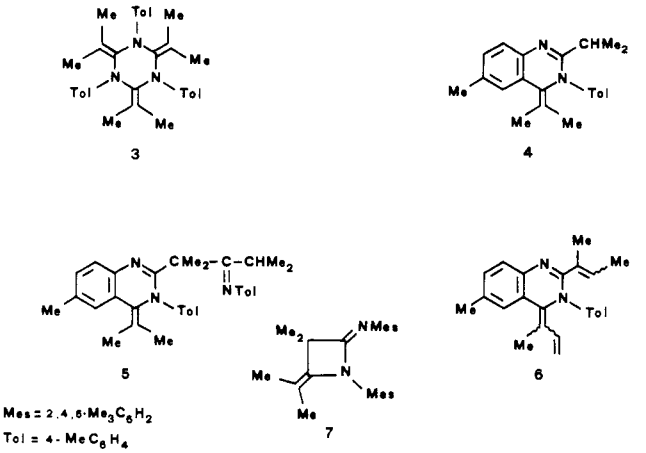
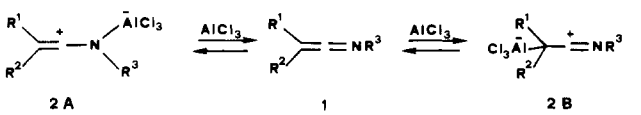
Aluminum trichloride and diethylaluminum chloride induce cyclodimerization and cyclotrimerization of three *C,C*-dimethylketene *N*-arylimines to quinazoline, azetidine, and triazine derivatives. The product distribution depends on the catalyst, the molar ratio of ketene imine to catalyst, and the substitution in the *N*-aryl group. On the other hand, *C*-methylketene *N*-mesitylimine forms an open-chain dimer, viz., an iminoketene imine which is detected by spectral means and trapped with methanol or carbon dioxide. X-ray crystallography of the latter adduct proves the 1,3-oxazin-2-one structure. The reactions occur through open-chain intermediates deriving from the attack of nitrogen, or the terminal cumulative carbon of a ketene imine molecule, at the central carbon of another molecule which is coordinated to the Lewis acid.

Ketene imines[2] 1 constitute a class of heterocumulenes that are useful intermediates in heterocyclic chemistry. Their synthetic value stems from a remarkable flexibility as cycloaddition partners since they can equally behave as the 2π-electron component[3] using one cumulative double bond or the 4π-electron component[4] using one cumulative double bond and the double bond of a substituent either on carbon or nitrogen. We have encountered this selectivity problem in the course of our studies of the thermal cycloadditions of ketene imines with thioketones[5] where

Chart I



we observed a (2 + 2) process giving a 2-iminothietane system and two (4 + 2) processes, one leading to a 4*H*-benzothiazine and the other to a thiacyclohexene system. The reactivity of ketene imines 1 is expected to be enhanced by Lewis acids, such as aluminum chlorides AlX_3 (X = Cl or alkyl) since coordination, either at nitrogen or



a, $R^1 = R^2 = Me$; $R^3 = 4\text{-}MeC_6H_4$
b, $R^1 = Me$; $R^2 = CH{=}CH_2$; $R^3 = 4\text{-}MeC_6H_4$
c, $R^1 = R^2 = Me$; $R^3 = 2,4,6\text{-}Me_3C_6H_2$
d, $R^1 = H$; $R^2 = Me$; $R^3 = 2,4,6\text{-}Me_3C_6H_2$

(1) (a) University of Ferrara. (b) Institute of Consiglio Nazionale delle Ricerche, Ozzano Emilia. (c) Centro di Diffrattometria, University of Ferrara.

(2) For reviews, see: (a) Krow, G. R. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 435. (b) Gambarayan, N. P. *Russ. Chem. Rev. (Engl. Transl.)* **1976**, *45*, 630. (c) Ghosez, L.; O'Donnell, M. J. In "Pericyclic Reactions"; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II; Chapter 2. (d) Dondoni, A. *Heterocycles* **1980**, *14*, 1547.

(3) Examples of (2 + 2) cycloadditions of ketene imines are the reactions with (a) nitrosobenzenes (ref 2a), (b) ketones (Singer, L. A.; Barlett, P. D. *Tetraedron Lett.* **1964**, 1887; Weidler-Kubanek, A.; Litt, M. *J. Org. Chem.* **1968**, *33*, 1844), (c) isocyanates (Naser-ud-Din, Riegl J.; Skattebøl, L. *J. Chem. Soc., Chem. Commun.* **1973**, 271), (d) azobenzenes (Barker, M. W.; Coker, M. E. *J. Heterocycl. Chem.* **1967**, *4*, 155), (e) sulphur dioxide (Dondoni A.; Giorgianni P.; Battaglia, A.; Andreetti, G. D. *J. Chem. Soc., Chem. Commun.* **1981**, 350) and (f) hydrazoic acid (L'abbé, G.; Dekerk, J.-P.; Verbruggen, A.; Toppet, S. *J. Org. Chem.* **1978**, *43*, 3042).

(4) Examples of (4 + 2) cycloadditions of ketene imines are the reactions with (a) acetylenes, cyanoalkenes, and maleic anhydride (Ghosez, L.; Sonveaux, E. *J. Am. Chem. Soc.* **1973**, *95*, 5417), (b) vinyl ethers (ref 2b), and (c) sulfur dioxide (ref 2d).

(5) Dondoni, A.; Battaglia, A.; Giorgianni, P.; Gilli, G.; Sacerdoti, M. *J. Chem. Soc., Chem. Commun.* **1977**, 43. Dondoni, A.; Battaglia, A.; Giorgianni, P. *J. Org. Chem.* **1980**, *45*, 3766. Dondoni, A.; Battaglia, A.; Bernardi, F.; Giorgianni, P. *Ibid.* **1980**, *45*, 3773. Bernardi, F.; Bottoni, A.; Battaglia, A.; Distefano, G.; Dondoni, A. *Z. Naturforsch., A* **1980**, *35*, 521. Dondoni, A.; Battaglia, A.; Giorgianni, P. *J. Org. Chem.* **1982**, *47*, 3998.

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Table I. Oligomerization of C,C-Disubstituted Ketene Imines 1a-c by Aluminum Chlorides AlX_2Cl

ketene imine (mmol)	AlX_2Cl[a] (mmol)	temp,[c] °C	rxn time	products[b] (molar ratio)	yield, %
1a (6.29)	AT (6.60)	-40	15 min	3 (35), 4 (14), 5 (15), A (7)	64
1a (6.14)	AT (3.30)	-40	15 min	3 (46), 4 (10), 5 (10), A (10)	66
1a (3.90)	DA (3.80)	rt	4 h	3 (7.4), 4 (40), A (15)	47.4
1a (5.00)	DA (0.50)	rt	18 h	4 (17.5), A (39)	17.5
1b (5.85)	DA (5.40)	rt	6 h	6 (32), A (37)	32
1c (5.60)	AT (5.80)	-20	60 min	7 (50), A (46)	50
1c (6.50)	DA (6.60)	rt	5 h	7 (54), A (15)	54

[a] AT = $AlCl_3$; DA = Et_2AlCl. [b] A is the amide derived from the hydration of the corresponding ketene imine. [c] rt = room temperature.

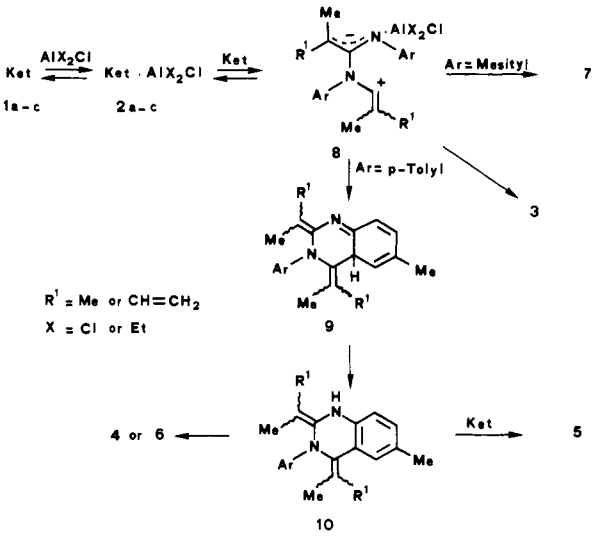
at the terminal carbon of the cumulative system,[6] should increase the electrophilic character of the central carbon as shown by structures 2A and 2B. Structure 2A corresponds to a ketene immonium system, viz., a super ketene equivalent whose reactivity in (2 + 2) cycloadditions has been widely demonstrated.[7] A report has appeared on the aluminum chloride catalyzed Friedel-Crafts reaction of a ketene imine with resorcinol.[8] We have studied the behavior of four substituted ketene imines **1a–d** in the presence of aluminum chlorides as a first approach toward their use as activated electron-acceptor partners in cycloaddition reactions and describe here the results.

Results and Discussion

Reactions of C,C-Disubstituted Ketene Imines 1a–c. After dimethylketene *N*-*p*-tolylimine (**1a**) was treated with aluminum trichloride in methylene dichloride followed by quenching the reaction mixture with aqueous sodium bicarbonate, three oligomers of **1a** (Chart I) were obtained, namely the cyclotrimer 1,3,5-hexahydrotriazine **3**, the cyclodimer 3,4-dihydroquinazoline **4**, and its side chain derivative **5**. The unreacted ketene imine **1a** was recovered in the form of its hydrated product, *N*-*p*-tolylisobutyramide. Proof of the structure of the triazine **3** stemmed from its ^1H NMR spectrum which exhibited a singlet at δ 1.47 corresponding to the protons of the six equivalent methyls on the ethylenic carbons as required by the high symmetry of the molecule, while the structure of the quinazoline **4** was supported by a strong IR band at 1580 cm^{-1} (C=N) and ^1H NMR signals at δ 1.31 (doublet) and 2.92 (septet) (J = 6.89 Hz) for the Me_2CH group and at δ 1.90 and 1.98 (singlet) for the two ethylenic methyls. The structure of **5** was established by a single-crystal X-ray analysis.[9] From a set of selected experiments (Table I), it appears that a higher molar ratio of **1a**/$AlCl_3$ favored the formation of the triazine **3** (entries 1 and 2), while the change of the Lewis acid from $AlCl_3$ to Et_2AlCl favored the dimer **4** (entry 3). Moreover, comparable amounts of the Lewis acid and **1a** were required for the formation of satisfactory amounts of oligomers (entries 1–3), while a low $AlCl_3$/**1a** ratio gave less oligomerization (entry 4).

Methylvinylketene *N*-*p*-tolylimine (**1b**) treated with Et_2AlCl underwent cyclodimerization to the corresponding quinazoline **6** (entry 5), while dimethylketene *N*-mesitylimine (**1c**) gave, with both $AlCl_3$ and Et_2AlCl (entries 6 and 7), the four-membered cyclodimer 2-iminoazetidine **7**. This exhibited consistent spectral data, namely a strong IR band at 1680 cm^{-1} (C=N), three ^1H NMR singlets at δ 1.2, 1.36 (broad), and 1.57 for the four methyls on the azetidine ring and a fragment at m/e 278 in the mass spectrum corresponding to dimesitylcarbodiimide.

Scheme I



The formation of oligomers **3-7** from ketene imines **1a-c** can be interpreted by a single Scheme I where the initial equilibrium between the free ketene imine **1** and its coordinated form **2** is followed by the attack of the nitrogen of **1** at the central carbon of **2** to give the zwitterion **8**. This cycloadds to another molecule of ketene imine **1** affording the triazine **3** or, depending upon the substitution in the Ar, undergoes an intramolecular ring closure to the azetidine **7** (Ar = mesityl) or to compound **9** (Ar = *p*-tolyl), the precursor of quinazolines **4** and **6**. The intermediate **9**, or more likely its tautomer **10**, may capture a molecule of ketene imine **1** to give the 2-(iminoalkyl)quinazoline **5**. We have observed a formally similar side reaction in the cycloaddition of thiobenzophenones to ketene imines.[5] Among the various modes of intramolecular ring closure, which in principle can take place in **8**, cyclization across the C=C bond of the *N*-aryl group appears to be the most favored process since this occurred in **1a** as well as in **1b** although the presence of the *C*-vinyl group in the latter compound offers an alternative mode of reaction. Only when inhibited by ortho methyl groups in the *N*-aryl ring, as in the case of ketene imine **1c**, does this reaction provide cyclization across the cumulative C=C. As an identical selectivity trend was observed in the cycloaddition of ketene imines with thiobenzophenones,[5] ynamines,[4a] and vinyl ethers,[4b] the tendency of C,C-disubstituted ketene *N*-arylimines to take part in cycloaddition reactions as the heterodiene partner appears general enough.

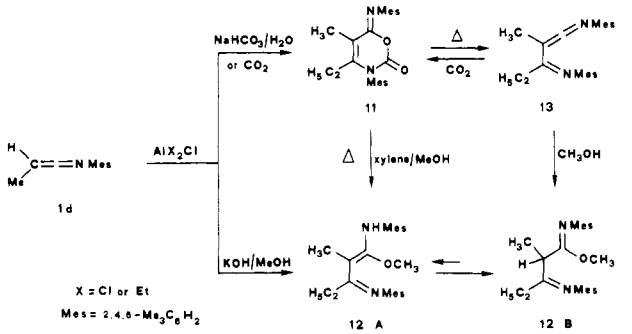
(6) According to the well-known resonance system of ketene imines,[2c,d] nitrogen and the terminal carbon of the cumulative system should bear a considerable electron density. Whilst no direct evidence has been provided, carbon has been considered the preferential site of protonation: McCarthy, D. G.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans. 2* **1980**, 579.

(7) Ghosez, L.; Marchand-Brynaert, J. *J. Am. Chem. Soc.* **1972**, *94*, 2870. Sidani, A.; Marchand-Brynaert, J; Ghosez, L. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 267. De Poortere, M.; Marchand-Brynaert, J.; Ghosez, L. *Ibid.* **1974**, *13*, 267. Marchand-Brynaert, J.; Ghosez, L. *Tetrahedron Lett.* **1974**, 377.

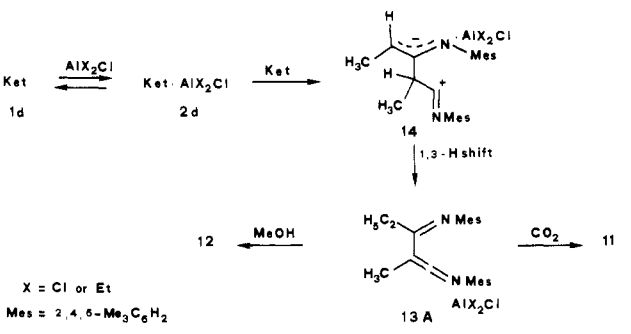
(8) Dijkstra, R.; Backer, H. J. *Recl. Trav. Chim. Pays-Bas* **1954**, *73*, 575, 695.

(9) The details of the X-ray crystallographic determination of **5** and **11** as well as the molecular parameters can be obtained from V.B.

Scheme II



Scheme III



Reactions of Methylketene *N*-Mesitylimine (1d). The reactivity of ketene imine **1d** does not fit the reaction Scheme I. Treatment of **1d** with aluminum chlorides $AlCl_3$ and Et_2AlCl in methylene dichloride followed by quenching of the reaction mixture with aqueous sodium bicarbonate gave, in modest yield (ca. 40%), the 1,3-oxazin-2-one derivative **11** (Scheme II), together with a mixture of unseparable polymers of **1d** and *N*-mesitylpropionamide. The yield of **11** increased to 53% by bubbling carbon dioxide into the reaction mixture before the workup. The 1,3-oxazinone **11**, which can be regarded as an adduct between 2 mol of ketene imine **1d** and 1 mol of carbon dioxide, showed consistent spectral characteristics, namely an IR band at 1770 cm^{-1} for the O–CO group, ^1H NMR resonances at δ 0.9 and 2.12 for the C_2H_5, and peaks at m/e 390 for M^+ and 346 for $M^+ - CO_2$ in the mass spectrum. Moreover, the structure of **11** was confirmed by a single-crystal X-ray analysis.[9] On the other hand, quenching the **1d**–$AlCl_3$ reaction mixture with potassium hydroxide in methanol gave a tarry material and a low yield of an adduct **12** from 2 mol of ketene imine **1d** and 1 mol of methanol (mass spectrum, m/e 378 for M^+ and 347 for M^+ – OMe). Since the NMR spectra of **12** indicated the presence of the CHMe group (doublet at δ 1.4 and quartet at δ 3.5, J = 7.0 Hz) and two nonequivalent C=N groups (δ 171.9 and 161.9), the tautomer B is preferred over A, under the circumstances used to collect this data. A few simple reactions shed some light on the structural relation between compounds **11** and **12** as well as on their formation. The oxazinone **11** in refluxing xylene containing 10% methanol gave **12** in almost quantitative yield, whereas when heated neat at 190 °C for a few minutes, **11** was transformed into an oil which exhibited an intense IR band at 2020 cm^{-1} and a peak at m/e 346 in the mass spectrum. After standing 1 h at room temperature, the oil lost the above spectral features and was transformed into a tarry material. When the oil was immediately treated with excess methanol, compound **12** was obtained. When left under slight pressure of dry carbon dioxide, the oil gave the oxazinone **11**. The *C*-imino ketene imine **13** can be reasonably assumed to be the intermediate involved in these reactions as well as in the formation of **11** and **12** from **1d**. The dimerization of **1d** to **13** (Scheme III) can occur by attack of the terminal cumulative carbon of **1d** at the central carbon of its coordinated form **2d**. The resulting zwitterion **14**, which is inhibited toward ring closure and/or intermolecular reactions by the presence of the mesityl groups, rearranges by a 1,3-proton shift to the coordinated *C*-imino ketene imine **13A** which, as observed in the above control experiments, adds carbon dioxide[10] and methanol to form products **11** and **12**, respectively. The reactivity of **1d** through its cumulative terminal carbon, instead of nitrogen, as suggested for ketene imines **1a–c** (Scheme I), may reasonably be attributed to the low steric hindrance at the monosubstituted carbon[5] together with its nucleophilic character indicated by the chemical[2] and spectroscopic evidence[11] and theoretical considerations.[2]

This suggests that, unlike the case of protonation,[6] the site of the nucleophilic activity of the ketene imine (C or N) may be controlled not only by electronic effects, but also by steric effects. Steric effects, in fact, are important in other cycloaddition reactions of ketene imines.[5]

The incorporation of carbon dioxide into a ketene imine dimer to give the six-membered ring heterocycle **11** merits a short comment. The above observations suggest a hetero Diels-Alder process between the *C*-imino ketene imine **13** acting as a diene[12] with carbon dioxide as the dienophile. This constitutes a case of a (4 + 2) cycloaddition with carbon dioxide which contrasts with the current belief on the inertness of this compound toward this kind of process.[13] Moreover, this reaction provides a new example of the ability of heterocumulenes bearing an unsaturated functionality to act as 4π-electron systems in cycloaddition reactions.[4a,5,14]

Experimental Section

Melting and boiling points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-100 instrument and chemical shifts are given as δ values in parts per million from Me_4Si. IR spectra were recorded on a Perkin-Elmer 297 spectrometer and low-resolution mass spectra were recorded at an ionizing voltage of 70 eV. All solvents were purified by the usual methods before their use. Diethylaluminum chloride was purchased as a 25% solution in *n*-hexane. Ketene imines **1a–c** were prepared as described[15] and showed consistent physical and spectroscopic characteristcs.

Methylketene *N*-mesitylimine (1d), which has been hitherto unreported, was prepared as follows. To a stirred solution of potassium *tert*-butoxide (29.5 mmol) in 250 mL of THF was added at 0 °C an equivalent amount of *N*-mesitylacetimidoyl chloride[16] in 15 mL of the same solvent. After 10 min the solvent was concentrated in vacuo at room temperature and the residue treated with 150 mL of *n*-pentane. After filtration to remove the material precipitated and evaporation of the solvent, the oily residue was

(10) This was formed from sodium bicarbonate used as a quencher. The use of carefully dried carbon dioxide and solvent in the control experiment of **13** to **11** safely excludes the bicarbonate ion and demonstrates that carbon dioxide itself is the actual reagent of the cyclization.

(11) Firl, J.; Runge, W.; Hartmann, W.; Utikal, H.-P. *Chem. Lett.* **1975**, 51.

(12) The reactivity of **13** generated by thermolysis of **11** with various dienophiles is under investigation in our laboratory.

(13) Ruden, R. A.; Bonjouklian, R. *J. Am. Chem. Soc.* **1975**, *97*, 6892. Aumann, R.; Ring, H.; Kruger, C.; Goddard, R.; *Chem. Ber.* **1979**, *112*, 3644.

(14) Dondoni, A.; Kniezo, L.; Medici, A. *J. Org. Chem.* **1982**, *47*, 3994.

(15) Stevens, C. L.; French, J. C. *J. Am. Chem. Soc.* **1954**, *76*, 4398. Dondoni, A.; Battaglia, A.; Giorgianni, P. *J. Org. Chem.* **1980**, *45*, 3766. Sonveaux, E.; Ghosez, L. *J. Am. Chem. Soc.* **1973**, *95*, 5417.

(16) The title compound was prepared from equimolar amounts of the corresponding amide and PCl_5,[15] bp 58 °C (0.02 mmHg).

distilled under vacuo to give 13.9 mmol (47%) of **1d**: bp 55–58 °C (0.02 mmHg); IR (CCl_4) 2010 cm^{-1} (C=C=N); ^1H NMR ($CDCl_3$) δ 1.67 (d, 3 H, Me, J_{H-Me} = 7.0 Hz), 2.27 (s, 9 H, 3 Me), 3.61 (q, 1 H, J_{H-Me} = 7.0 Hz), 6.84 (s, 2 H, aromatic); MS, *m/e* 173 (M^+), 158, 119.

Reactions of Ketene Imines 1. General Procedure. To a stirred slurry of $AlCl_3$ or a solution of Et_2AlCl in CH_2Cl_2 at ca. −70 °C (acetone/CO_2 bath), in a teflon rubber closed flask previously purged with argon, was introduced an amount of the selected ketene imine **1a–d** by a syringe. The bath temperature was raised to the proper value for the time required. The progress of the reaction was followed by pouring aliquots of the reaction solution into aqueous $NaHCO_3$, extracting the quenched reaction with CH_2Cl_2, and measuring the IR peak of the ketene imine at ca. 2010 cm^{-1}. As soon as all the ketene imine had reacted, the mixture was poured into aqueous $NaHCO_3$, unless otherwise stated. After removing the aluminum hydroxide by filtration, the organic phase was washed with water, dried with $CaCl_2$, and the solvent evaporated. The products were separated by column chromatography.

Reaction of Dimethylketene *N*-*p*-Tolylimine (1a). A. With $AlCl_3$. Ketene imine **1a** (6.14 mmol) was treated with $AlCl_3$ (3.3 mmol) in CH_2Cl_2 (120 mL) at −40 °C for 15 min. Chromatography (silica, 10:1 pentane/ethyl acetate) gave the triazine **3** (0.943 mmol, 46%), the quinazolines **5** (0.21 mmol, 10%) and **4** (0.31 mmol, 10%), and *N*-*p*-tolylisobutyramide (0.56 mmol, 9%). Under the same conditions, the reaction of **1a** (6.29 mmol) with 1 molar equivalent of $AlCl_3$ (6.6 mmol) gave **3** (0.73 mmol, 35%), **5** (0.31 mmol, 15%), **4** (0.44 mmol, 14%), and the amide (0.45 mmol, 7.2%).

B. With Et_2AlCl. Ketene imine **1a** (3.9 mmol) in an Et_2AlCl (3.8 mmol) solution (CH_2Cl_2, 150 mL) at room temperature for 4 h gave the triazine **3** (0.096 mmol, 7.4%), the quinazoline **4** (0.79 mmol, 40%), and the amide (0.059 mmol, 15%) (overall yield 64.4%). A mixture of **1a** (5.04 mmol) and Et_2AlCl (0.5 mmol) in CH_2Cl_2 (130 mL) after 18 h at room temperature showed by IR at 2010 cm^{-1} that the amount of the ketene imine had decreased to 2.16 mmol corresponding to 43% of the starting material. Chromatography gave the quinazoline **5** (0.44 mmol, 17.5%) and the amide (1.98 mmol, 39%).

2,4,6-Triisopropylidene-1,3,5-tri-*p*-tolylhexahydro-1,3,5-triazine (3): mp 190–192 °C (from ethyl ether/pentane); IR(CCl_4) 3000, 2910, 2860, 1680, 1640, 1510, 1330 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (s, 18 H, 6 Me), 2.23 (s, 9 H, 3 Me), 6.77–7.07 (m, 12 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 19.35 (Me), 20.55 (Me), 113.96 (C), 117.36 (CH, aromatic), 129.08 (CH, aromatic), 133.58 (C), 143.89 (C); MS, *m/e* 477 (M^+), 159, 133. Anal. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.06; H, 8.21; N, 8.73.

2-Isopropyl-3-*p*-tolyl-4-isopropylidene-6-methyl-3,4-dihydroquinazoline (4): oil; IR (CCl_4) 3020, 2970, 2930, 2870, 1580, 1485, 1387, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (d, 6 H, 2 Me), 1.9 (s, 3 H, Me), 1.98 (s, 3 H, Me), 2.25 (s, 3 H, Me), 2.33 (s, 3 H, Me), 2.93 (septet, 1 H, J_{H-CH_3} = 6.89 Hz), 6.73–7.35 (m, 7 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.64 (Me), 21.23 (Me), 32.46 (CH), 123.74, 123.98, 125.59, 126.42, 127.76, 128.31, 129.47, 130.95, 133.68 (C), 134.14 (C), 141.29 (C), 141.81 (C), 166.55 (C); MS, *m/e* 318 (M^+), 303, 227, 200; Anal. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.02; H, 8.25; N, 8.76.

2-(1,1,3-Trimethyl-2-(*p*-tolylimino)butyl)-3-*p*-tolyl-4-isopropylidene-6-methyl-3,4-dihydroquinazoline (5): mp 134–136 °C (from ethyl ether/pentane); IR (CCl_4) 3030, 2980, 2930, 2870, 1675, 1510, 1470, 1225 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.97 (d, 6 H, 2 Me, J_{H-CH_3} = 7.35 Hz), 1.53 (s, 6 H, 2 Me), 2.0 (s, 3 H, 1 Me), 2.20–2.40 (b, 12 H, 4 Me), 3.1 (septet, 1 H), 6.6–7.43 (m, 11 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 20.05 (Me), 20.74 (Me), 21.37 (Me), 21.42 (Me), 22.11 (Me), 22.25 (Me), 25.91 (Me), 34.71 (CH), 54.66 (C), 118.62 (CH), 122.53 (CH), 124.14 (CH), 125.33, 127.3, 128.35, 128.50, 129.51, 130.45, 131.63 (C), 132.1 (C), 133.9 (C), 135.15 (C), 140.7 (C), 143.31 (C), 148.65 (C), 166.67 (C), 177.75 (C); MS, *m/e* 477 (M^+), 462, 318, 159. Anal. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.90; H, 8.19; N, 8.76.

Reaction of Methylvinylketene *N*-*p*-Tolylimine (1b). A solution of ketene imine **1b** (5.85 mmol) in CH_2Cl_2 (120 mL) was treated with Et_2AlCl (5.40 mmol) at room temperature for 6 h. Chromatography of the residue (SiO_2, 14:2 pentane/ethyl acetate) afforded the quinazoline **6** (1.00 mmol, 32.2%) and amide CH_2=CHMeCONHTolyl (2.06 mmol, 37%).

2-(2-Buten-2-yl)-3-*p*-tolyl-4-(methylvinylmethylidene)-6-methyl-3,4-dihydroquinazoline (6): oil; IR (CCl_4) 3090, 3030, 2920, 2860, 1640, 1510, 1480, 1280 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (d, 3 H, 1 Me, J_{H-CH_3} = 8.0 Hz), 2.06–2.25 (b, 9 H, 3 Me), 2.30 (s, 3 H, 1 Me), 5.18–5.7 (m, 2 H, CH=C*H*$_2$), 6.6–7.5 (m, 9 H); MS, *m/e* 342 (M^+), 327, 251. Anal. Calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.24; H, 7.68; N, 8.14.

Reaction of Dimethylketene *N*-Mesitylimine (1c). A. With $AlCl_3$. Ketene imine **1c** (5.61 mmol) and an $AlCl_3$ (5.86 mmol) slurry (CH_2Cl_2, 150 mL) at −20 °C for 1 h, followed by workup and chromatography of the residue (SiO_2, 19:1 pentane/ethyl acetate then 12:3 CH_2Cl_2/ethyl acetate) gave the azetidine **7** (1.46 mmol, 50%) and the amide $Me_2CHCONH$mesityl (2.58 mmol, 46%).

B. With Et_2AlCl. Ketene imine **1c** (6.52 mmol) in a CH_2Cl_2 (150 mL) solution of Et_2AlCl (6.58 mmol) at room temperature for 5 h afforded **7** (1.76 mmol, 54%) and the amide (1 mmol, 15%).

2-(Mesitylimino)-3,3-dimethyl-4-isopropylidene-*N*-mesitylazetidine (7): mp 111–114 °C (from pentane/ethyl ether, −70 °C); IR (CCl_4, C_2Cl_4, CS_2) 3010, 2960, 2910, 2850, 1760, 1680, 1480, 1160, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (s, 3 H, 1 Me), 1.36 (s, 6 H, 2 Me), 1.57 (s, 3 H, 1 Me), 2.17 (s, 6 H, 2 Me), 2.20 (s, 3 H, 1 Me), 2.27 (s, 3 H, 1 Me), 2.36 (s, 6 H, 2 Me), 6.73 (s, 2 H, aromatic), 6.9 (s, 2 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 16.01 (Me), 17.87 (Me), 18.04 (Me), 18.76 (Me), 20.71 (Me), 21.07 (Me), 21.42 (Me), 52.30 (C), 96.32 (C), 128.09 (CH), 128.48 (C), 128.81 (CH), 130.92 (C), 131.55 (C), 136.8 (C), 137.82 (C), 140.77 (C), 143.11 (C), 159.7 (C); MS, *m/e* 374 (M^+), 278, 215, 187. Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15; N, 7.48. Found: C, 83.41; H, 9.19; N, 7.45.

Reaction of Methylketene *N*-Mesitylimine (1d). A. With $AlCl_3$. (a) Ketene imine **1d** (5.9 mmol) was treated with a slurry of $AlCl_3$ (7.35 mmol) in 120 mL of CH_2Cl_2 at −30 °C for 3 h. After quenching with 10% aqueous $NaHCO_3$ (200 mL) and chromatography workup (SiO_2, 12:2 pentane/ethyl acetate) the oxazinone **11** (1.24 mmol, 38%) and isopropyl-*N*-mesitylamide (2.20 mmol, 37%) were obtained.

(b) Ketene imine **1d** (8.67 mmol) was treated with an excess of $AlCl_3$ (10.2 mmol) in CH_2Cl_2 (180 mL) under an atmosphere of CO_2 at −30 °C for 1 h. After quenching with 10% aqueous $NaHCO_3$ (200 mL) and chromatography (see above) **11** (2.3 mmol, 53%) and the amide (0.76 mmol, 9%) were obtained.

(c) **Ketene** imine **1d** (3.14 mmol) and $AlCl_3$ (3.1 mmol) in 60 mL of CH_2Cl_2 at −30 °C for 3 h, followed by quenching with a solution of KOH (8 mmol) in 100 mL of MeOH, and evaporation of the solvent gave an oil. This, on treating with ethyl ether and 80 mL of pentane, gave 0.36 g of a solid material whose mass spectrum showed predominant peaks at *m/e* 519 and 173 (3 M^+ and 1 M^+ of **1d**, respectively). Column chromatography of the residue (silica, CH_2Cl_2) gave **12** (0.53 mmol, 33%).

B. With Et_2AlCl. Ketene imine **1d** (5.4 mmol) was treated with a solution of Et_2AlCl (5.8 mmol) in 200 mL of CH_2Cl_2 at −30 °C for 4 h. After quenching with 10% aqueous $NaHCO_3$, chromatography (see above) gave the oxazinone **11** (0.5 mmol, 18.4%).

***N*-Mesityl-4-ethyl-5-methyl-6-(mesitylimino)-3,6-dihydro-2*H*-1,3-oxazin-2-one (11)**: mp 161–162 °C (from ethyl ether/pentane); IR (CCl_4) 3020, 2980, 2920, 2860, 1770, 1667, 1488, 1405, 1337, 1304 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 (t, 3 H, 1 Me, $J_{CH_2CH_3}$ = 7.5 Hz), 2–2.25 (m, 2 H, 1 CH_2), 2.13 (b, 6 H, 2 Me), 2.16 (b, 6 H, 2 Me), 2.17 (b, 3 H, 1 Me), 2.24 (b, 3 H, 1 Me), 2.30 (b, 3 H, 1 Me), 6.87 (b, 2 H, aromatic), 7.00 (b, 2 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 11.74 (Me), 12.73 (Me), 17.73 (Me), 18.18 (Me), 20.7 (Me), 21.03 (Me), 22.35 (CH_2), 104.77 (C), 127.22 (C), 128.31 (CH), 129.63 (CH), 132.04 (C), 132.21 (C), 135.92 (C), 139.15 (C), 141.17 (C), 147.05 (C), 147.32 (C), 147.99 (C); MS, *m/e* 390 (M^+), 346, 331, 173. Anal. Calcd for $C_{25}H_{30}N_2O_2$: C, 76.89; H, 7.74; N, 7.17. Found: C, 76.82; H, 7.66; N, 7.22.

1-Methoxy-2-methyl-1,3-bis(*N*-mesitylimino)pentane (12): mp 97–99 °C (from pentane, acetone/CO_2 bath); ^1H NMR ($CDCl_3$) δ 0.69 (t, 3 H, 1 Me, $J_{CH_2CH_3}$ = 7.81 Hz), 1.40 (d, 3 H, 1 Me, J_{H-CH_3} = 7.0 Hz), 1.92 (s, 3 H), 2.00 (s, 3 H, 1 Me), 2.03 (q, 2 H, CH_2), 2.14 (s, 6 H, 2 Me, 2.27 (s, 6 H, 2 Me), 3.5 (q, 1 H), 3.9 (s, 3 H, OMe), 6.83 (s, 2 H, aromatic), 6.87 (s, 2 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 10.42 (Me), 15.00 (Me), 17.72 (Me), 17.85 (Me), 18.34 (Me), 20.73 (Me), 26.16 (CH_2), 42.51 (CH), 53.43 (OMe), 124.98

(C), 125.59 (C), 127.3 (C), 127.41 (C), 128.46 (CH), 128.54 (CH), 128.79 (CH), 131.6 (C), 131.81 (C), 142.43 (C), 145.46 (C), 161.93 (C, C=N), 172.93 (C, C=N); MS, m/e 378 (M^+), 347, 363, 205; IR (CCl_4) 2980, 2940, 1660 cm^{-1}; Anal. Calcd for $C_{25}H_{34}N_2O$: C, 79.32; H, 9.05; N, 7.40. Found: C, 79.39; H, 9.00; N, 7.44.

Reactions of the Oxazinone (11). A. Pyrolysis and Addition of CO_2 or Methanol. The compound 11 (0.2 g, 0.51 mmol) was heated in an oil bath at 190–195 °C for 2 min under gentle suction. After the completition of CO_2 evolution, the oily residue was quickly frozen at 0 °C. Its mass spectrum revealed an intense peak at m/e 346 (2 M^+ of **1d**) and the complete disappearance of the peak at 390 (M^+ of 11); IR (CCl_4) showed an intense band at 2010 cm^{-1} (C=C=N), while the bands at 1770 and 1667 cm^{-1} of 11 were absent. The crude residue (0.15 g), dissolved in CH_2Cl_2 (50 mL), was bubbled with dry (H_2SO_4, silica) CO_2 for 40 min. The IR spectrum (CCl_4) of the reaction mixture revealed the absence of the band at 2010 cm^{-1} and the appearance of the bands at 1770 and 1667 cm^{-1} of 11. Evaporation of the solvent and chromatography of the residue (SiO_2, CH_2Cl_2) gave the oxazinone 11 (0.050 g, 0.128 mmol, 25%). In another experiment, using the same amount of 11, the oil from pyroylis was dissolved in 5 mL of MeOH and the solution refluxed for 1 h. Evaporation of the solvent and chromatography (SiO_2, CH_2Cl_2) gave 12 (0.07 g, 0.185 mmol, 36.3%).

B. Reaction of 11 with Methanol. Compound 11 (0.2 g, 0.59 mmol) was heated in a refluxing mixture of xylene (110 mL) and methanol (10 mL). The disappearance of 11 was monitored by IR at 1770 cm^{-1} on samples withdrawn at intervals. After compound 11 had totally disappeared, the solvent was evaporated and the oily residue was chromatographed (SiO_2, CH_2Cl_2) to give compound 12 (0.47 mmol, 78%).

Registry No. 1a, 18779-86-7; 1b, 42463-98-9; 1c, 74331-60-5; 1d, 89827-16-7; 3, 89827-17-8; 4, 52223-07-1; 5, 89827-18-9; 6, 89848-02-2; 7, 89827-19-0; 11, 89827-20-3; 12, 89827-21-4; $AlCl_3$, 7446-70-0; Et_2AlCl, 96-10-6.

N- vs. O-Acylation of 1,2-Diazetidin-3-one: 4,5-Dihydro-1,3-oxadiazin-6-ones by Ring Enlargement

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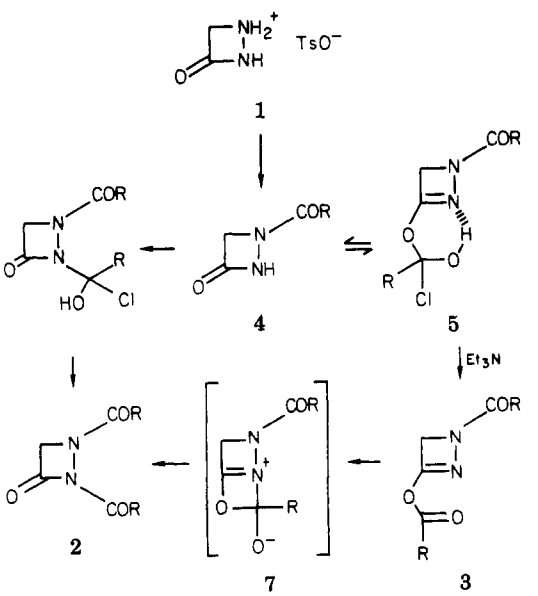
Treatment of 1,2-diazetidin-3-one with acid chlorides in the presence of 2,6-lutidine led to 1,2-diacyl-1,2-diazetidin-3-ones (N,N-diacylation), while the use of triethylamine as base gave 1-acyl-3-(acyloxy)-1,4-dihydro-1,2-diazetes (N,O-diacylation). Several 1-benzhydryl-2-acyl-1,2-diazetidin-3-ones were found to rearrange smoothly upon treatment with ethyl chloroformate to give 2-substituted 4-benzhydryl-4,5-dihydro-1,3,4-oxadiazin-6-ones.

We are currently engaged in a program aimed at the synthesis of highly strained aza analogues of the β-lactam antibiotics, starting from the readily accessible 3-oxo-1,2-diazetidinium tosylate (1).[1] We report in this paper some surprising results obtained from attempts to introduce acyl and aroyl substituents at N-1 and/or N-2.

It is well-known that azetidin-2-ones (β-lactams) unsubstituted on nitrogen readily polymerize in base in the presence of a catalytic amount of an acylating agent.[2] This sensitivity is shared by 1,2-diazetidin-3-one. All attempts to effect monoacylation of 1 under a wide variety of reaction conditions led only to a colorless solid of indefinite melting point that was clearly polymeric in nature. By contrast, however, treatment of a stirred suspension of 1 with 2 equiv of benzoyl chloride and 3 equiv of 2,6-lutidine in methylene chloride at −78 °C led to the formation in modest yield of 1,2-dibenzoyl-1,2-diazetidin-3-one (**2a**), which is characterized by IR carbonyl absorption bands at 1810, 1667, and 1652 cm^{-1}.[3] Under the same reaction conditions, 1 could be reacted with 4-anisoyl chloride, 4-nitrobenzoyl chloride, and cyclohexanecarbonyl chloride to give the respective 1,2-diacyl derivatives **2b–d** (Scheme I). Since only polymeric materials were isolated from attempts to effect diacylation with less electrophilic reagents (i.e., benzyl chloroformate, acetic anhydride), we

Scheme I



a, R = C_6H_5; b, R = $C_6H_4OCH_3$-4; c, R = $C_6H_4NO_2$-4; d, R =  ; e, R = $C(CH_3)_3$

(1) Taylor, E. C.; Haley, N. F.; Clemens, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 7743.

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(3) In our preliminary communication on this work the structure of this product was incorrectly assigned: Taylor, E. C.; Davies, H. M. L.; Clemens, R. J.; Yanagisawa, H.; Haley, N. F. *J. Am. Chem. Soc.* **1981**, *103*, 7660.

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