drop of trifluoromethanesulfonic acid. After 25 min at 0 °C, the reaction mixture was poured into saturated sodium bicarbonate solution and extracted with dichloromethane. The combined extracts were washed with saturated sodium bicarbonate solution and water prior to drying and careful solvent removal at 0–10 °C. Column chromatography of the residue on silica gel (elution with 5% ethyl acetate in petroleum ether) gave an alcohol presumed to be **15** (3–7 mg) as a white solid: mp (unrecrystallized) 120–124 °C; IR (CCl_4, cm^{-1}) 3620, 2930, 1470; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.3 (br s, 1 H), 2.1–1.0 (series of m with clear triplet at 1.05 (J = 6 Hz)); ^{13}C NMR (C_6D_6) ppm 84.02, 58.43, 56.42, 44.67, 36.98, 35.19, 31.17, 28.42, 28.09, 27.28, 26.85, 24.06, 23.64, 11.52 (2C not observed); MS, m/e calcd (M^+) 246.1984, obsd 246.1999.

Acknowledgment. This investigation was made possible by the financial support of the National Science Foundation (Grant CHE 79-00333).

Registry No. **3**, 77973-29-6; **6**, 58461-87-3; **7**, 90047-12-4; **8**, 90047-14-6; **9**, 77180-63-3; **10**, 78037-97-5; **11**, 78037-96-4; **12** (isomer 1), 90047-13-5; **12** (isomer 2), 90129-13-8; **13**, 90047-15-7; **14**, 90047-16-8; **15**, 90047-17-9.

1-Nitrobenzotriazole–2-(Nitroimino)diazobenzene Isomerization: Formation of Triazenes by Azo Coupling with Cyclic Amines. Structure Determination and Dynamic NMR

Clarisse L. Habraken,*† Cornelis Erkelens, J. R. Mellema, and Pauline Cohen-Fernandes

The Department of Organic Chemistry, The University Leiden, Gorlaeus Laboratory, 2300 RA Leiden, The Netherlands

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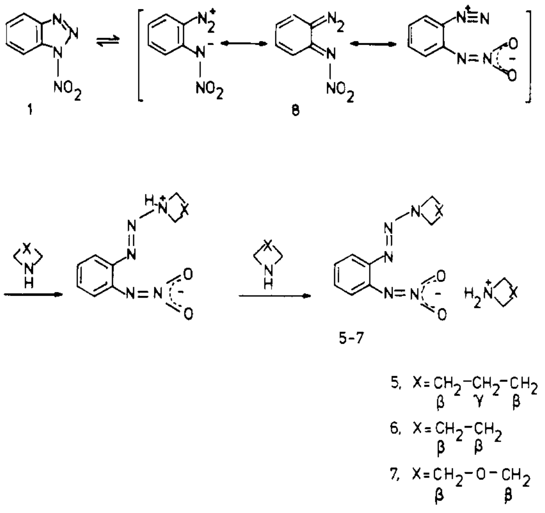
The reaction of 1-nitrobenzotriazole (1) with the cyclic amines **2–4** affording the triazenes **5–7** revealed ring opening of the 1,2,3-triazole ring of benzotriazole to the isomeric diazo compound **8** responsible for the formation of these triazenes. Crystal analysis of **5** and IR and ^1H and ^{13}C NMR spectra allowed the structure assignments for **5–7**. From a dynamic NMR study of triazene **6** restricted rotation about the single N–N bond is inferred.

N-Nitroazoles are known to undergo a variety of unexpected and novel reactions, many of which are synthetically useful and mechanistically interesting reactions. Examples of such reactions are the thermal intramolecular rearrangement of the N-nitro group to a carbon atom in the azole ring of pyrazoles,[1] 1,2,4-triazoles,[2] imidazoles, and indazoles[3] and the "cine" nucleophilic aromatic substitution of the N-nitro group by nucleophiles entering the azole ring at the adjacent carbon atom in pyrazoles,[4] 1,2,4-triazoles,[5] and indazoles.[6] Intermolecular transfer reactions of the N-nitro group are also reported.[8] This paper reports the very facile and novel reaction of N-nitrobenzotriazole (1) in acetonitrile solution with cyclic amines to give crystalline secondary alkyl ammonium salts, which are found to be triazenes. Also we present a study of the temperature-dependent ^1H and ^{13}C NMR spectra of these salts.

Scheme I



Results and Discussion

Ring–Chain Isomerism. Addition of piperidine (2), pyrrolidine (3), or morpholine (4) at room temperature to a solution of 1-nitrobenzotriazole (1) in acetonitrile results in the precipitation of the crystalline compounds **5–7** in very high yields. Each of these products, according to elemental analysis, consisted of one molecule of **1** and two molecules of the respective cyclic amines **2–4**. ^1H NMR spectral analysis revealed two signals in the region of the α-methylene protons. The low-field shift of one of the signals, a striking feature of the NMR spectra of these compounds, was initially interpreted only to indicate that one of the cyclic amines is in the protonated form (however see below). The signals of the aromatic protons, however, were shifted approximately 0.5 ppm to higher external field as compared to those of 1-nitrobenzotriazole (1). A

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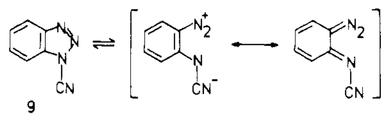
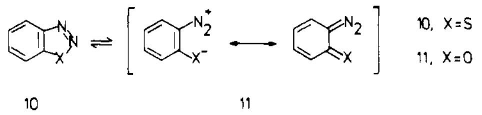
Scheme II



Scheme III



prominent feature in the IR spectra of **5**–**7** is the absence of the characteristic vibrations of the nitro group in *N*-nitroazoles. In addition, the IR spectra determined in KBr disks show bands around 2500 cm^{-1} indicating strong N-H-X (X = N or O) hydrogen bonds (vide infra). Ultimately, X-ray diffraction[16] revealed the structure of the product of the reaction of **1** with piperidine (**2**) (see Scheme I) to be the piperidinium salt **5**. On the basis of similar spectral properties we conclude that the structures of all three compounds **5**–**7** are 1-(*N*-hydroxylato-2-*NNO*-azoxyphenyl)triazenes. This rather surprising reactivity of **1** can be explained most simply by inferring an equilibrium of **1** with the isomeric α-diazo 1-nitroimine **8** as result of a ring opening of the 1,2,3-triazole ring. In the presence of nucleophiles such as a cyclic amine, this open chain isomer **8** then is trapped by attack on the diazo group. Subsequently, a second molecule of the amine now reacting as a base affords the piperidinium salt **5** (see scheme I). Eventually, crystallization forces this ring–chain equilibrium to the right resulting in the observed high yields of **5**–**7**.

Ring opening of benzotriazoles[9,10] (or triazoles)[11] without loss of nitrogen is a rare phenomenon. To our knowledge only one example of a ring–chain equilibrium of a benzotriazole with the isomeric α-diazo imines is recorded. Hermes and Marsh[10] describe that colorless crystalline 1-cyanobenzotriazole (**9**) in polar solvents or on melting shows reversible thermochromic behavior. Without having chemical evidence, ring opening to the α-diazo *N*-cyanoimine, the authors argued, might be an intriguing explanation for these color changes (scheme II). Our findings, described here for 1-nitrobenzotriazole (**1**) definitely establish the existence of an open chain α-diazo imine compound in equilibrium with 1,2,3-benzotriazole.

Apparently, **1** occupies a position between the 1,2,3-benzothiadiazoles (**10**), thought to be principally cyclized structures, and α-diazo oxides **11**, considered to exist only in the open ring diazo state[12,13] (Scheme III). Further support for the cyclic structure of **10** is found in the report[14] that whereas the α-diazo oxides **11** undergo direct coupling with alkaline β-naphthol **10** does not. With X stable enough and the X–N bond weak enough, an open form will be favored. For X = N–R, the ring is normally closed, but with R having the proper electron-withdrawing capacity, the open form becomes stabilized. Evidently, a nitro group fulfills this condition and in solution **1** is in equilibrium with the α-diaza N-nitroimine **8**. The deep red color observed when a solution of **1** was poured into an alkaline solution of β-naphthol provided an additional proof for the presence of diazo compound **8**.[15]

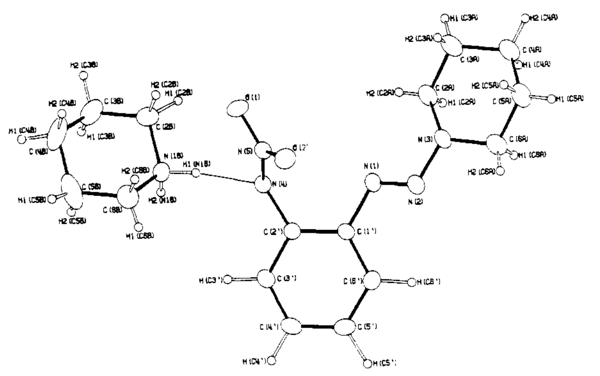


Figure 1. Stereochemistry and atomic labeling of **5**, i.e., A for the piperidine ring attached to the azo group, B for the hydrogen-bonded piperidinium ring, and C for the aromatic ring.

Structure and ^{1}H and ^{13}C NMR Studies. The structure of one molecular unit of piperidinium 1-(*N*-hydroxylato-2-*NNO*-azoxyphenyl)-3,3-pentamethylenetriazene (**5**) is depicted in Figure 1 together with the labeling system.[16] All intramolecular distances in the compound are as expected. The piperidine rings A and B are in the chair form, whereas the aromatic ring C is planar. The plane of the benzene ring is virtually in the same plane as the N—N═N group (torsion angle 1.4°) and the azo group is in the trans configuration in agreement with X-ray diffraction analysis and ^{13}C NMR studies of 1-phenyl-3,3-dialkyltriazenes by Lunazzi et al.[18] Also **5** has similar bond distances for the N—N═N group, i.e., 1.35 Å for the single bond and 1.25 Å for the double bond. The least square plane of the piperidine ring A is tilted 21° with respect to the plane of the benzene ring and therefore the conformation of these two rings and the azo group is coplanar rather than perpendicular (see Figure 1). The plane of the NO_2 group, on the contrary, is tilted by 62.3° with respect to the plane of the benzene ring.

Apart from the fact that the crystal structure proves the formation of the triazene unit, by addition of the piperidine group to the ring-opened nitrotriazole, an interesting interionic hydrogen bonding is observed. One of the N-H groups of the piperidinium cation is strongly hydrogen

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(15) We are currently engaged in the investigation of azo compounds synthesized from **1**.

(16) We thank Drs. S. Gorter of the Department of Crystallography, The University Leiden, Gorlaeus Laboratories, Leiden, The Netherlands, for the permission to present these data of the crystal structure analysis of **5**, which will be published elsewhere.

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bonded to the N(4) atom of the N–NO_2 group. The other N–H group is hydrogen bonded in a bifurcated manner to the oxygen atoms of the NO_2^- group in the underlying unit cell. The two short N(1B)···O(1,2) (2.93, 2.95 Å) distances and the N(1B)···N(4) (2.91 Å) distance in the solid state agree nicely with the observed N–H stretching vibrations at 2340, 2430, 2530, and 2750 cm^{-1}, observed in the IR spectrum.[16,17]

As already pointed out a striking feature of the ^1H NMR spectra of **5**–**7** is the presence of two different resonances for the α-methylene protons (for **5** δ 2.97–3.01 and 3.71–3.73, for **6** δ 3.18–3.22 and 3.75, for **7** δ 2.86–2.90 and 3.84–3.91). Similar large downfield shifts of the α-methylene protons have been reported for the simple *N*-phenylazo analogues of **5**–**7**.[19] Therefore the lower of the two resonances of the α-methylene protons in **5**-**7** are assigned to the α-protons H-α(A) in the ring attached to the azo group (see Scheme I).

The 75-MHz ^{13}C NMR of **5**–**7** revealed in the aliphatic region two kinds of α- as well as β- and γ-carbon atoms. For the α-carbon atoms two signals at approximately 45 and 48 ppm were found for all three compounds **5**–**7** (48.27 and 44.86 ppm for **5**, 48.60 and 45.40 ppm for **6**, 48.49 and 45.82 ppm for **7**).

A detailed study of compound **6** was carried out. Selective irradiation of H-α(A), 3.75 ppm instead of the usual broadband decoupling, afforded the assignment of C-α(A) at 48.60 ppm for the ring attached to the azo group. Double resonance experiments established the correlation between the signals at 3.75 ppm and 2.33 ppm. The signal at 2.33 ppm was assigned to the β-methylene protons in ring A (H-β(A)) (Figure 1) and selective irradiation at 2.33 ppm gave the assignment of C-β(A) at 23.71 ppm.

The similarity of the ^{13}C NMR spectral properties of **5** and **7** to those of **6** proves that in all three compounds the chemical shifts of the α-methylene carbon atoms, C-α(A), are at approximately 48 ppm. Consequently, the signals at approximately 45 ppm are the resonances of the α-methylene carbons of the second aliphatic ring, C-α(B), in **5**–**7**.

The ^{13}C as well as the ^1H NMR spectrum of **6** recorded at ambient temperatures showed some conspicuous line broadening of the specific peaks at 48.60 (C-α (A)), 23.71 (C-β(A)), and 3.75 ppm (H-α(A)). In order to investigate the origin of this line broadening, spectra were recorded at decreasing temperatures down to 220 K. The 220 K spectra clearly represent the slow exchange limits of coalescing spin systems. In this way, two ^{13}C signals and one ^1H signal were followed and their coalescence temperatures (T_c) were estimated to be 283 K for C-α(A), 253 K for C-β(A), and 265 K for H-α(A). From these values a $\Delta G^{\ddagger}_{c}$ of 52.7 kJ/mol (12.6 kcal/mol) is found.[20]

The nonequivalence of the α- and β-carbon atoms as well as the α-methylene protons in **6** apparently results from the restricted rotation of the pyrrolidine ring about the single N–N bond. Lunazzi et al.[18] have reported the rotational barriers about the N–N bond for a number of 1,1-dialkyl-3-aryltriazenes including some containing a piperidine ring. The observed $\Delta G^{\ddagger}$ value falls well in the range of free energies of activation reported by them for the rotational barriers of triazenes. Similar values were reported for barriers of rotation about the N–C amide bond in 1-acetyl- and 1-carbomethoxypiperidine as well as in 1-acetyl- and 1-benzoylmorpholine.[21]

Finally, in a low-temperature experiment we investigated at 240 K the split carbon signals of **6** at 46.41 (triplet) and 51.15 (triplet) ppm with the split α-hydrogen signals at 3.57 and 3.94 ppm. Selective irradiation at 3.94 ppm gave a singlet at 51.15 and a triplet at 46.41 ppm whereas irradiation at 3.57 ppm gave a triplet at 51.15 and a singlet at 46.41 ppm showing that the two magnetically equivalent protons are bonded to the same carbon atom. Of the three dynamic processes possible, (a) rotation about the N–N single bond, (b) ring reversal, and (c) nitrogen inversion, the nitrogen inversion barrier should be below the range detectable by ^1H and ^{13}C dynamic NMR.[21,22]

The final observation that the two magnetically equivalent protons belong to the same α-methylene group, indicating that ring reversal still occurs at the temperatures used, consequently strongly suggests that the dynamic process involved concerns restricted rotation about the single N–N bond. To our knowledge, this is the first example of the observation of rotation about a single N–N bond in the case of a pyrrolidine ring.

Experimental Section

IR spectra (KBr) were recorded on a Beckman IR-10 instrument. Melting points are uncorrected. Elemental analyses were performed by W. J. Buis (TNO Laboratory of Organic Chemistry, Utrecht, Netherlands). Solvents were reagent grade and were used without further purification. The cyclic amines **2**–**4** were dried over sodium hydroxide. Nitrobenzotriazole **1** was prepared as has been described previously.[3]

General Procedure for the Synthesis of Compounds 5–7. To a solution of 5 mmol of **1** in 5 mL of acetonitrile at room temperature was added 10–15 mmol of the cyclic amine **2**–**4**. The products readily started to crystallize and after 15 min to 2.5 h the crystals were collected on a Buchner funnel, washed with acetonitrile, and dried. Yields varied from 68–90% and no attempts were made to optimize the yields.

Piperidinium 1-(*N*-hydroxylato-2-*NNO*-azoxyphenyl)-3,3-pentamethylenetriazine 5: beige crystals (from ethanol) or off white powdery crystals (from benzene); mp 133–134 °C dec; IR 1090 (N–N), 1300, 1320, 1353, 1440, 1480 (azoxy and N=N), 2320–2360, 2430, 2530, 2730–2770, 2830–2860, 2950 cm^{-1} (N–H–N and N–H–O). Anal. ($C_{16}H_{26}O_2N_6$) Calcd: C, 57.46; H, 7.84; N, 25.13. Found: C, 57.40; H, 7.86; N, 24.96.

Pyrrolidinium 1-(*N*-hydroxylato-2-*NNO*-azoxyphenyl)-3,3-tetramethylenetriazine 6: off white crystals (from ethanol); mp 135–138 °C; IR 1012 (N–N), 1310, 1345, 1375, 1450, 1470 (azoxy and N=N), 2320–2360, 2460, 2530, 2590, 2720–2760, 2880, 2920, 2980 (N–H–N and N–H–O). Anal. ($C_{14}H_{22}O_2N_6$) Calcd: C, 54.88; H, 7.24; N, 27.43. Found: C, 54.99; H, 7.25; N, 27.40.

Morpholinium 1-(*N*-hydroxylato-2-*NNO*-azoxyphenyl)-3,3-oxydiethylenetriazene 7: off white crystals (from ethanol); mp 137–139 °C dec; IR 1010, 1105, 1120 (N–N?), 1305, 1315, 1350, 1365, 1435, 1480 (azoxy and N=N), 2320–2380, 2490–2500, 2740, 2860, 2985 cm^{-1} (N–H–N and N–H–O). Anal. ($C_{14}H_{22}O_3N_6$) Calcd: C, 49.69; H, 6.55; N, 24.84. Found: C, 49.76; H, 6.70; N, 24.95.

NMR Spectra. High-resolution NMR spectra were recorded on a Bruker WM-300 spectrometer operating in the Fourier transform mode and equipped with a B-VT 1000 variable temperature unit. Data accumulation and processing were carried out on an Aspect-2000 computer. Proton spectra were recorded at 300 MHz using a spectral window of 3000 Hz at 16K data points. Carbon-13 spectra were measured at 75 MHz using a spectral window of 18000 Hz at 16K data points. The latter spectra were zero filled up to 64K data points before Fourier transformation in order to obtain a satisfactory digital resolution. Various techniques were employed to assign the carbon-13 spectra at low and high temperatures: (a) proton noise decoupling, (b)

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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.

Acknowledgment. We are grateful to Prof. Dr. J. Reedijk for his stimulating interest in this study and to Prof. Dr. C. Altona and Dr. G. Verschoor for useful comments and discussions. The help of S. Amadio in preparing the English manuscript is gratefully acknowledged. It is a pleasure to C. L. H. to thank Professor C. W. Rees for very helpful suggestions and for his encouragement in this work.

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 ^{1}H and ^{13}C NMR data for 5–7 and relevant reference compounds; table 3 containing temperature dependant ^{13}C and ^{1}H NMR data of 5–6; figure 2, variable temperature 75-MHz ^{13}C NMR spectra of 6 and figure 3, variable temperature 300-MHz ^{1}H 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

Alessandro Dondoni,*[1a] Gaetano Barbaro,[1b] Arturo Battaglia,*[1b] Valerio Bertolasi,[1c] and Patrizia Giorgianni[1b]

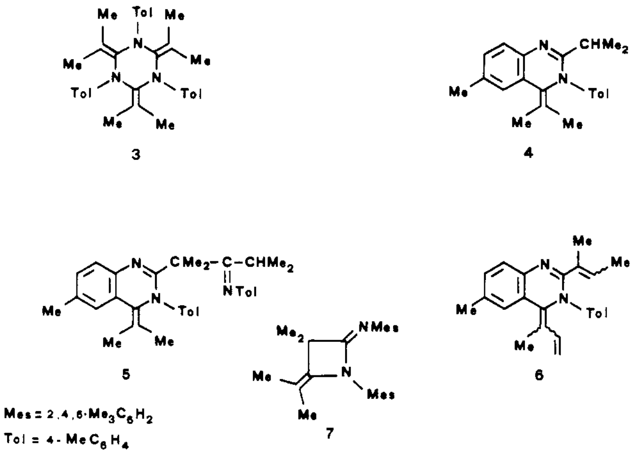
Laboratorio di Chimica Organica, Facoltà di Scienze, Università, Ferrara, Italy, Istituto dei Composti del Carbonio contenenti Eteroatomi del C.N.R., Ozzano Emilia, Italy, and Centro di Strutturistica Diffrattometrica, Università, Ferrara, Italy

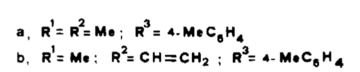
Received September 27, 1983

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 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

Chart I





2 A 1 2 B

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, $R^1 = H$; $R^2 = Me$; $R^3 = 2,4,6\text{-}Me_3C_6H_2$

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

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(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).

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