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0.5 N $NaBH_4$ in 3 N NaOH (8.0 mL, aqueous) were added and the mixture stirred for 15 min. The mercury was allowed to settle, the solution was diluted with ether, and the combined ether extracts were dried and evaporated. The crude product was purified by column chromatography to give 2.585 g (71%) of **11c**: IR (neat) 3425, 1715, 1639 cm^{-1}; NMR δ 7.07 (br s, 1 H), 3.84–3.70 (m, 3 H), 3.76 (s, 3 H), 3.71–3.39 (m, 4 H), 3.34 (s, 3 H), 1.26 (s, 3 H), 0.99 (d, 3 H, J = 8 Hz), 0.93 (d, 3 H, J = 8 Hz).

Anal. Calcd for $C_{20}H_{34}O_6$: C, 64.84; H, 9.25. Found: C, 64.66; H, 9.29.

1-Methyl-4-(1-methylethyl)-4a-[(methoxyethoxy)-methyl]-6-(hydroxymethyl)octahydronaphthalenol (12c). The ester **11c** (0.248 g, 0.669 mmol) was added to ethyl acetate (18 mL) with PtO_2 (0.035 g) and treated with H_2 (room temperature and 1 atm) for 24 h. The Pt was filtered off, and the solvent was removed to give 0.236 g of crude product. This was added to a solution of $LiAlH_4$ (0.120 g, 3.17 mmol) in dry ether (5 mL), and the solution was refluxed for 2 h. After the mixture cooled, the product was extracted with ether and water, and the ether extracts were dried and evaporated. The crude product was purified by using flash chromatography (30% ethyl acetate–hexane) to give 0.196 g (85%) of **12c**: IR (neat) 3378 cm^{-1}; NMR δ 4.96–4.60 (m, 2 H), 3.96–3.38 (m, 6 H), 3.31 (s, 3 H), 1.16 (s, 3 H), 0.88 (d, 3 H, J = 10 Hz), 0.81 (d, 3 H, J = 10 Hz).

Anal. Calcd for $C_{19}H_{36}O_5$: C, 66.24; H, 10.53. Found: C, 66.40; H, 10.31.

1-Methyl-4-(1-methylethyl)-4a-[(methoxyethoxy)-methyl]-6-methyleneoctahydro-1-naphthalenol (14a). The alcohol **12c** (0.433 g, 1.26 mmol) was added to a solution of (*o*-nitrophenyl)selenyl cyanide (0.343 g, 1.51 mmol) in THF (4.5 mL) at room temperature under N_2. Tri-*n*-butylphosphine (0.376 mL, 1.51 mmol) was added dropwise, and the reaction was stirred for 2 h. The solvent was removed under reduced pressure and purified by using flash chromatography to give 0.520 g (78%) of selenide. This was added to a solution of $NaHCO_3$ (0.95 g, 1.10 mmol) and $NaIO_4$ (0.488 g, 2.28 mmol) in methanol (17 mL) and water (3.0 mL). The solution was stirred for 90 min and then extracted with ether and $NaHCO_3$(aq). The combined ether layers were dried and evaporated. Flash chromatography (10% ethyl acetate–petroleum ether) yielded 0.229 g (56%) of **14a**: IR (neat) 3448, 3058, 1646 cm^{-1}; NMR δ 5.10–4.87 (m, 2 H), 4.76 (br s, 2 H), 3.94–3.43 (m, 4 H), 3.37 (s, 3 H), 1.24 (s, 3 H), 0.97 (d, 3 H, J = 7 Hz), 0.90 (d, 3 H, J = 7 Hz).

Anal. Calcd for $C_{19}H_{34}O_4$: C, 69.90; H, 10.50. Found: C, 70.04; H, 10.53.

(+)-Isocalamendiol (14b). The protected diol **14a** (0.085 g, 0.260 mmol) was added to dry CH_2Cl_2 (8.6 mL) at 0 °C. Then $ZnBr_2$ (0.290 g, 1.3 mmol) was added, and the reaction was stirred at 0 °C for 24 h with small additions of $ZnBr_2$ every few hours. Then concentrated aqueous NH_4OH was added, and the resulting mixture was diluted with water and extracted with ether. The combined ether extracts were dried and evaporated. Chromatography on silica gel (10% ethyl acetate–pentane) yielded 0.021 g (44%) of (+)-isocalamendiol (**14b**) as well as 0.019 g of starting material **14a**: IR (neat) 3390, 3049, 1650 cm^{-1}; NMR δ 4.87 (s, 1 H), 4.75 (s, 1 H), 1.22 (s, 3 H), 0.97 (d, 3 H, J = 8 Hz), 0.94 (d, 3 H, J = 8 Hz); $[\alpha]_D$ +17.6° (*c* 0.0128 g/mL).

Synthetic (+)-isocalamendiol (**14b**) was identical in all respects, IR and ^1H and ^{13}C NMR, with authentic (–)-isocalamendiol except in the sign of rotation, $[\alpha]_D$ –26.6° (*c* 0.0092 g/mL).

Acknowledgment. We thank Professor S. Yamamura for a sample of (–)-isocalamendiol, Glidden-Durkee for a generous sample of *trans*-piperitol, Mr. Scott Bram for technical assistance, Temple University for the award of a University Fellowship to J.F.C., and the National Science Foundation (Grant No. CHE-76-05757) for partial support.

Registry No. 1b, 40628-41-9; **2**, 4573-50-6; **3b**, 70492-73-8; **4**, 70447-85-7; **5**, 70447-86-8; **6b**, 74878-02-7; **7b**, 74923-23-2; **8b**, 74878-03-8; **9b**, 74878-04-9; **10b**, 74892-93-6; **11a**, 74878-05-0; **11b**, 74878-06-1; **11c**, 74878-07-2; **12a**, 74923-24-3; **12b**, 74957-59-8; **12c**, 74878-08-3; **13a**, 74878-09-4; **13b**, 74878-10-7; **14a**, 74878-11-8; **14b**, 74923-25-4; $MEM^+NEt_3Cl^-$, 60043-43-8.

Cyanoketenes. Mechanism of *tert*-Butylcyanoketene Cycloaddition to Aldo- and Ketoketenes

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Received May 12, 1980

tert-Butylcyanoketene cycloadds to ketene, methylketene, dimethylketene, and ethylmethylketene. The first two examples give 2-oxetanones and the last two result in cyclobutane-1,3-diones. These cycloadditions are shown to proceed by a nonconcerted dipolar mechanism involving zwitterionic intermediates. Establishment of the intermediacy of the zwitterions was accomplished by their independent generation from the thermolysis of substituted 4-azido-5-*tert*-butylcyclopentene-1,3-dione precursors. The mechanistic consequences of these cycloadditions and how they may apply to other ketene dimerizations are discussed.

Introduction

Reported here is an investigation of the cycloaddition of *tert*-butylcyanoketene (TBCK) to a series of aldo- and ketoketenes.[1] It will be shown that such [2 + 2] cycloadditions proceed by a stepwise process involving zwitterionic intermediates and that these ring close to cyclobutane-1,3-diones or 2-oxetanones when generated from TBCK and, respectively, keto- or aldoketenes. This study was stimulated primarily by the fact that ketene dimerizations, in general, are fraught with ambiguities regarding the operative mechanism. Indeed, no clear unambiguous data has appeared which firmly establishes the concerted or nonconcerted nature of a ketene dimerization. Dehmlow, Stopianka and Pickardt[2] have recently shown that dimerizations of alkylphenyl- and alkylbenzylketenes give increasing amounts of *Z*-enriched cyclobutane-1,3-diones as the steric bulk of the ketene increases. In one case, isopropylphenylketene, only the *Z* isomer was observed. This enhancement of the *Z* stereoisomer is in agreement with the predictions arising from a concerted $[_{\pi}2_s + _{\pi}2_a]$ mechanism. However, the total yields of the cycloadducts are very low (3–56%) and thus mechanistic interpretations

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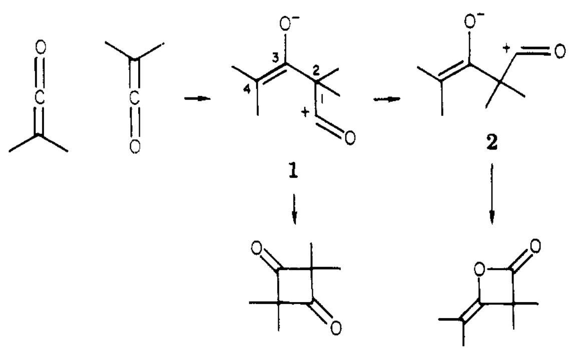
[1] A preliminary account of this work has appeared. See H. W. Moore and D. Scott Wilbur, *J. Am. Chem. Soc.*, **100**, 6523 (1978).

[2] E. V. Dehmlow, M. Stopianka, and J. Pickardt, *Liebigs Ann. Chem.*, 572 (1979).

0022-3263/80/1945-4483$01.00/0

Scheme I



based solely upon product stereochemistry are difficult. Brady and Ting[3] have observed no preference for *Z* isomer enrichment for the mixed dimerizations of certain haloketenes with nonhalogenated analogues. For example, when methylchloroketene and *tert*-butylchloroketene cycloadd to methyl-*n*-propyl- and methylisopropylketene, equal amounts of isomeric *Z*- and *E*-cyclobutane-1,3-diones result. The most definitive work is that of Huisgen and Otto[4] who have investigated the dimerization of dimethylketene to afford 2,2,4,4-tetramethylcyclobutane-1,3-dione. They observed a large negative entropy of activation (−42 eu) and a slight solvent polarity dependence on the rate of dimerization and concluded that, in this case, the reaction is concerted but that unequal bond formation must be occurring to impart some dipolar character to the transition state. Unfortunately, it is difficult to extrapolate this mechanism to account for the homodimerization of most aldoketenes since 2-oxetanones rather than cyclobutane-1,3-diones are often the observed major products. Specific examples are the dimerization of ketene itself,[5] as well as methylketene,[6] butylketene,[7] and phenylketene.[8] Mechanistic interpretations are further complicated by the observation that dione–lactone interconversion often takes place under the cycloaddition reaction conditions, particularly when the ketenes are generated from acid halides upon treatment with amines or Lewis acids.[9] In the few cases where ketoketenes have been observed to add to aldoketenes again 2-oxetanones are observed. Cases in point are the codimerization of *tert*-butylketene with methylchloro-, methylbromo-, *tert*-butyl-, chloro-, and *tert*-butylbromoketene.[3] In all of these examples the 2-oxetanones result from addition to the carbon–carbon double bond of the haloketene. Analogously, bis(trifluoromethyl)ketene adds to ketene and methylketene to give only the 2-oxetanone adducts.[10] However, when it adds to dimethylketene both cyclobutane-1,3-dione and 2-oxetanone dimers are formed, and the product ratio is dependent upon the solvent polarity. For example, in cyclohexane a high yield of dione was observed, but in the more polar solvent, ethyl acetate, a mixture of the dione and lactone resulted.

It is tempting to generalize the above results according to a nonconcerted mechanism as represented by Scheme I. That is, ketene dimerizations proceed by a zwitterionic or diradical intermediate, **1**, initially formed by a head-to-tail interaction. When sterically encumbered (ketoketenes) such intermediates ring close by C-acylation to cyclobutane-1,3-diones; in less hindered cases (aldoketene dimerizations or aldo- to ketoketene dimerizations), conformational equilibration of **1** or **2** is possible and 2-oxetanone formation effectively competes by an electronically favored O-acylation. Such an interpretation is most likely an oversimplification since, as with most general reaction types, a variety of mechanistic pathways undoubtedly exist. However, it does focus directly upon the objective of the work described in this paper. Our principal goal was to prepare zwitterions of specifically the conformation illustrated by **1**. Judicious choice of the zwitterion substituents would then allow information to be gained concerning the stereospecificity of the ring closure steps as well as conformational conversion of **1** to **2**. Successful attainment of this goal is now reported here for zwitterions **1** in which position 4 is substituted with a *tert*-butyl and a cyano group and position 2 is functionalized with alkyl groups and/or protons. The products resulting from such zwitterions compare very favorably with those obtained from an independent study of the cycloaddition of the electron-deficient *tert*-butylcyanoketene to the electron-rich analogues, ketene, methyl-, dimethyl-, and ethylmethylketene. The results obtained from these studies are consistent with the mechanism outlined in Scheme I. *Thus, for the first time, the zwitterionic intermediates proposed in a ketene to ketene cycloaddition have been independently generated, trapped, and shown to give the same products as observed in the cycloadditions themselves.*

Results and Discusion

The electron-rich ketene were prepared by pyrolyses of appropriate precursors and condensed at low temperature. They were then treated with a toluene solution of *tert*-butylcyanoketene (**3**)[11] and the reaction solutions allowed to warm to ambient temperature. After an appropriate period of time, the solvent was removed in vacuo and the products were purified by standard techniques. The cycloadditions of TBCK to ketene and methylketene gave the 2-oxetanones **4** and **5** in respective isolated yields of 36% and 49%. No cyclobutanedione dimers could be detected by spectral analysis (^{1}H NMR and IR) of the crude reaction product. Analogously, the ketoketenes, dimethyl- and ethylmethylketene, gave the cyclobutane-1,3-diones **6** and **7** in respective isolated yields of 38% and 44%, and no 2-oxetanone dimers were detected. The double bond stereochemistry of the single geometric isomers observed for the 2-oxetanones, **3** and **4**, was not established but is assumed to have the *E* configuration. The cyclobutane-1,3-dione **7** was formed as a mixture of *Z* and *E* isomers (Scheme II). These isomers were not separated and thus their respective stereochemistry was not established, but they were formed in a ratio of 43:57.

It was anticipated that, if these cycloadditions proceed via a nonconcerted process involving zwitterionic intermediates, such could be independently generated upon thermolysis of the corresponding 4-azido-5-*tert*-butylcyclopentene-1,3-diones. The genesis of this postulate stems from our earlier work describing the formation of analogous zwitterions upon thermolysis of appropriately substituted cyclic vinyl azides (zwittazido cleavage).[12]

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(3) W. T. Brady and P. L. Ting, *J. Org. Chem.*, **41**, 2336 (1976).

(4) R. Huisgen and P. Otto, *J. Am. Chem. Soc.*, **90**, 5342 (1968).

(5) J. R. Johnson and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **75**, 1350 (1953).

(6) J. C. Sauer, *J. Am. Chem. Soc.*, **69**, 2444 (1947); R. B. Woodward and G. Small, *ibid.*, **72**, 1297 (1950).

(7) C. D. Hurd and C. H. Blanchard, *J. Am. Chem. Soc.*, **72**, 1461 (1950).

(8) J. E. Baldwin and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 2444 (1963).

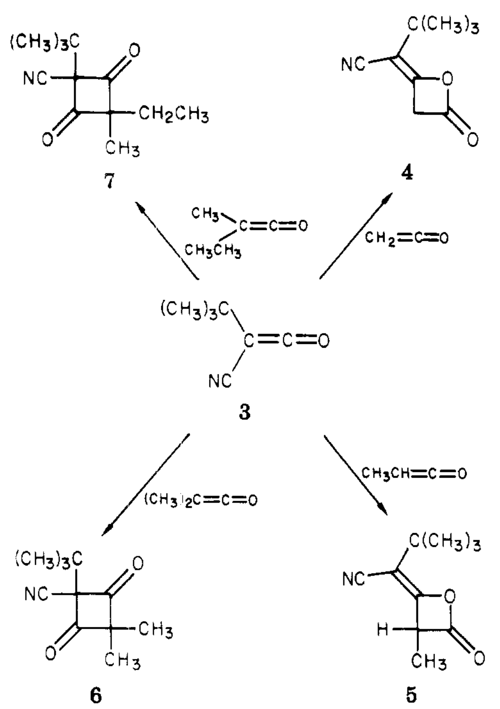
(9) D. G. Farnum, J. R. Johnson, R. E. Hess, T. B. Marshall, and B. Webster, *J. Am. Chem. Soc.*, **87**, 5191 (1965).

(10) D. C. England and C. G. Krespan, *J. Org. Chem.*, **35**, 3322 (1970).

(11) W. Weyler, Jr., W. G. Duncan, M. G. Liewen, and H. W. Moore, *Org. Synth.*, **55**, 32 (1976).

(12) H. W. Moore, *Acc. Chem. Res.*, **12**, 125 (1979).

Scheme II

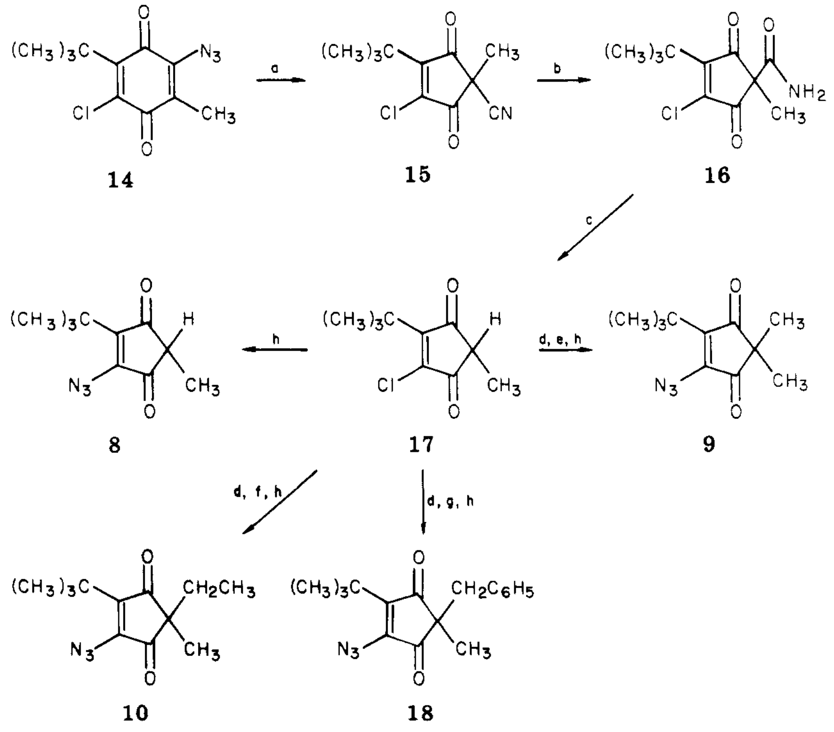


Thus, 8, 9, and 10 were prepared from 2-azido-6-*tert*-butyl-5-chloro-3-methyl-1,4-benzoquinone (14), as outlined in Scheme III, and subjected to thermolysis in benzene at 55–65 °C. Remarkably, 8 gave only the 2-oxetanone 5 (90%); 9 gave only the cyclobutane-1,3-dione 6 (80%); 10 gave only the cyclobutane-1,3-dione 7 (90%) as a 43:57 mixture of *E* and *Z* isomers, the same ratio as observed in the cycloaddition itself (Scheme IV).

The fact that these thermolyses give exactly the same products as are formed in the cycloadditions strongly suggests that these two reaction modes are intimately related. However, such results alone do not unambiguously establish that a common zwitterionic intermediate is involved since the ring contractions of 8, 9, and 10 could conceivably proceed by at least three possible pathways, i.e., (1) a concerted ring contraction, (2) fragmentation to two ketene molecules followed by their subsequent cycloaddition, (3) respective cleavage of 8, 9, and 10 to the zwitterions 11, 12, and 13 and their subsequent ring closure to products. As outlined below, this last possibility is in strict agreement with the experimental data.

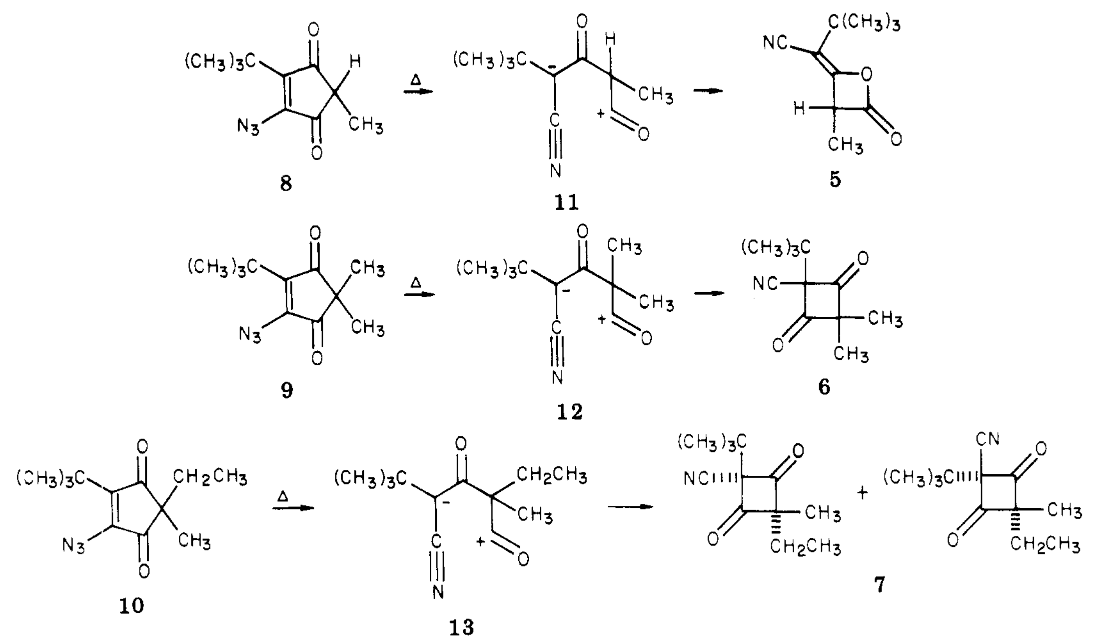
The first of the above possibilities, i.e., the concerted ring contraction, is untenable with the results. Accordingly, even though one can envisage a concerted ring contraction of 9 and 10 to, respectively, 6 and 7, such would not be possible for the conversion of 8 to the oxetanone, 5, since lactone bond formation would seemingly be impossible from a concerted process. Thus, assuming that 8, 9, and 10 all react by an analogous mechanism, a concerted ring contraction can be rejected. Further unambiguous evidence for a stepwise dipolar mechanism comes from zwitterion trapping experiments. Specifically, thermolysis of 9 in refluxing methanol gave methyl 2-cyano-3,3-dimethylbutanoate (20) and methyl 2-methylpropanoate (21) in roughly equal amounts and, significantly, the β-keto ester 19 (41%). In a control experiment the cyclobutane-1,3-dione 6 was also subjected to methanolysis under the same conditions and the exclusive product was the β-keto ester 19. However, the rate of methanolysis of 6 is appreciably slower than that observed for 9. For example, a 0.47 M solution of 9 has completely reacted after 1.5 h at 62 °C, while an analogous solution of 6 has gone to only 38% completion during the same length of time. The salient point of these data is that the β-keto ester 19 is formed upon methanolysis of 9 and that this product is not arising exclusively from methanolysis of the cyclobutane-1,3-dione 6. Thus some, if not all, of 19 must be coming from interception of the zwitterion 12. Therefore, a concerted mechanism for the conversion of 9 to 6 lacks credence. A pure ketene mechanism is also unreasonable since, if this were so, one would certainly

Scheme III[a]



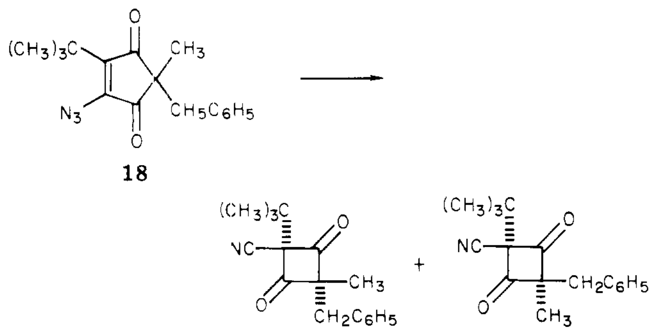
[a] a, Δ, C_6H_5Cl; b, H_2SO_4; c, HCl, DME; d, KH, THF; e, CH_3I; f, CH_3CH_2I; g, $C_6H_5CH_2Br$; h, N_3^-.

Scheme IV

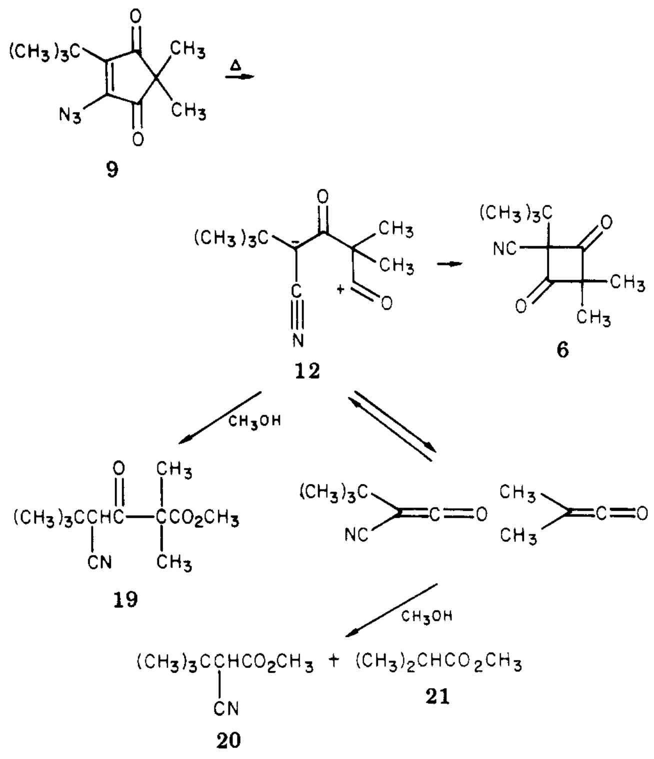


expect methanolysis of **9** to give only the esters **20** and **21** which are, in fact, the only products detected when a mixture of TBCK and dimethylketene at −78 °C is treated with methanol. Yet the major product observed from the methanolysis of **9** is the β-keto ester **19**. That leaves as the most reasonable alternative a mechanism in which the azidocyclopentene-1,3-dione, **9**, cleaves to the zwitterion **12** and this partitions between ring closure to **6** and equilibration with TBCK and dimethylketene. When the thermolysis of **9** is accomplished in methanol, the zwitterion **12** is trapped to give **19** and the respective ketenes give **20** and **21** (Scheme V). Finally, since the cycloadditions of TBCK to methyl-, dimethyl-, and ethylmethylketene give exactly the same products as the thermolyses of respectively, **8**, **9**, and **10**, both processes must involve common zwitterionic intermediates.

It is noteworthy to reemphasize the fact that the thermolysis of **10**, as well as the cycloaddition of TBCK to ethylmethylketene, gave a nearly equal mixture (43:57) of the *E* and *Z* isomers of the cyclobutane-1,3-dione **7**. This nonstereospecificity in the zwitterion ring-closure step was further documented by investigating the thermolysis of 4-azido-2-benzyl-5-*tert*-butyl-2-methylcyclopentene-1,3-dione (**18**) which also gave a mixture (46:54) of the *E* and *Z* isomers of **22**. This lack of stereospecificity is to be compared with the previously mentioned work of Dehmlow, Stopianka, and Pickardt[2] who observed that homodimerization of ketoketenes gave progressively enhanced amounts of the *Z*-cyclobutane-1,3-dione stereoisomers as the steric bulk of the ketene substituents was increased. Such an observation is, of course, anticipated for a concerted $[_\pi 2_s + {}_\pi 2_a]$ cycloaddition, but, again, the low yields reported for these reactions make such an interpretation suspect.

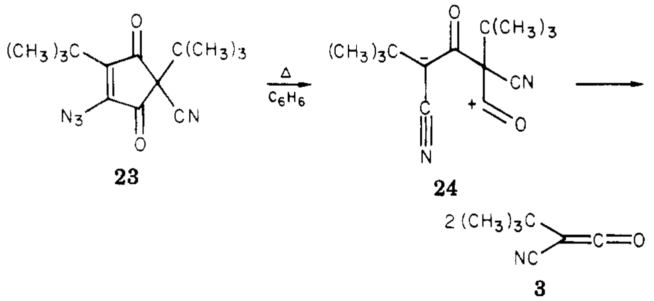


Scheme V

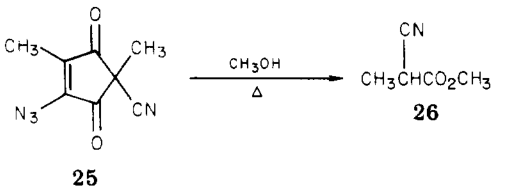


The nonstereospecificity of the ring contractions of **10** and **18** also provides a precedent suggesting a nonconcerted mechanism for Brady and Ting's[3] observed cycloadditions of sterically differentiated methylchloro- and *tert*-butylchloroketenes to methyl-*n*-propyl- and methylisopropylketenes which also resulted in equal amounts of *Z*- and *E*-cyclobutane-1,3-dione.

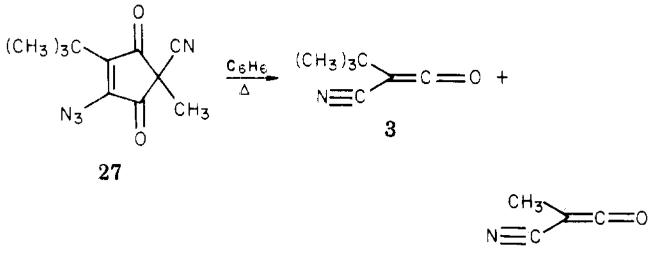
Clearly, the data presented here establish a dipolar mechanism for the codimerization of TBCK to electron-rich analogues. What about cyanoketene homodimerizations? Do they undergo facile self-dimerization, and, if so, is a zwitterionic intermediate involved? The 4-azidocyclopentene-1,3-dione thermolyses, as reported here, provide a very useful method for seeking answers to these questions. That is, thermolysis of appropriately substituted 2-cyano-4-azidocyclopentene-1,3-diones should give the corresponding zwitterions that would result if two cyanoketenes were to interact by a dipolar mechanism. Such intermediates could then either ring close to ketene dimers or fragment to 2 equiv of cyanoketene. This latter fragmentation appears to be the exclusive pathway. For example, thermolysis of **23** in refluxing benzene has previously been shown to give nearly a quantitative yield of TBCK and no detectable amounts of dimeric products.[11] Thermolysis of the methyl analogue **25** in anhydrous benzene gave a complex unidentifiable mixture of products. However, when the thermolysis was accomplished in methanol, only methyl 2-cyanopropionate (**26**) was formed.[11] No trapped zwitterion products or ketene dimers could be detected. Analogously, thermolysis of **27** in anhydrous benzene gave only TBCK and methylcyanoketene (**28**). Thus it appears that zwitterions such as **24** are destabilized by the additional cyano substituent and rapidly cleave to ketenes rather than ring close to ketene dimers or be intercepted by methanolysis.



23 **24** **3**



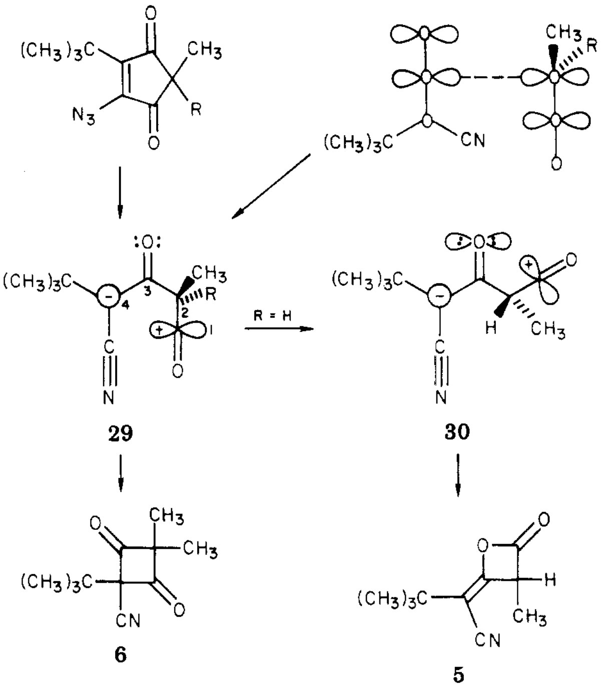
25 **26**



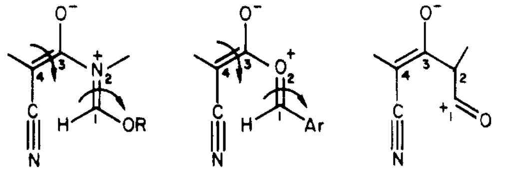
27 **3** **28**

The data presented here for the cycloadditions of TBCK to aldo- and ketoketenes suggest still an additional significant feature of the cycloaddition mechanism; namely, the two ketenes undergo initial bond formation from a head-to-tail orientation to give the zwitterion represented by conformer **29** (Scheme VI). *Such an interpretation is possible, since **29** would be exactly the expected conformer to arise directly when the zwitterion is independently generated from the azidocyclopentenedione precursors.* Direct ring closure of **29** (R = CH_3) to **6** would involve the orthogonal enolate anion and acyl cation orbitals. This ring closure apparently experiences very little steric influence from the substituents at positions 2 and 4 of the zwitterion since a nearly equal mixture of *Z* and *E* isomers is observed for the ring closures of **29** (R = CH_2CH_3 or $CH_2C_6H_5$). However, there is a pronounced steric effect on conformational equilibrium of the zwitterion as a function of the substituents at position 2. That is, when R = H rapid rotation to conformer **30** is allowed, and subsequent ring closure to the 2-oxetanone **5** may be a most facile process since it now involves a carbonyl nonbonding electron pair in an orbital which is not orthogonal to the acyl cation orbital. Indeed, 2-oxetanone formation would be expected to be the kinetically favored route on electronic grounds but can compete sterically with cyclobutane-1,3-dione formation only when one of the ketene components is an aldoketene or ketene itself.

Scheme VI



Finally, a few brief comments on the stereospecificity and mode of ring closures of 1,4-dipolar intermediates related to **29** are in order. A variety of such intermediates have now been generated via the thermolyses of appropriately substituted cyclic vinyl azides.[12] For example, 4-azido-2-pyrrolinones cleave to **31**, 4-azido-2(5*H*)-furanones give **32**, and, as shown here, 4-azidocyclopentene-1,3-diones give **29**. The first two, **31** and **32**, must



31 **32** **29**

assume the indicated planar geometry due to the delocalization of the nonbonding electron pair on the heteroatom at position 2 into the adjacent cationic center. In addition, this electron pair would impart some double bond character to the bond between positions 2 and 3. As a result, conformational rigidity is dictated, and products, respectively, β-lactams[13] and β-lactones,[14] arise stereospecifically by a conrotatory ring closure. As mentioned, zwitterions of type **29**, lacking the heteroatom at position

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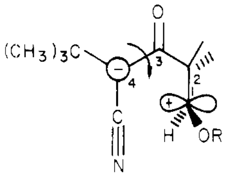
[13] H. W. Moore, L. Hernandez, and R. Chambers, *J. Am. Chem. Soc.*, **100**, 2245 (1978).

[14] H. W. Moore, F. Mercer, D. Kunert, and P. Albaugh, *J. Am. Chem. Soc.*, 101, 5435 (1979).

2, ring close nonstereospecifically to cyclobutane-1,3-diones when substituted with two different alkyl groups at position 2. Release of steric strain by substitution of a proton for one of these alkyl groups allows rotation around the C_2–C_3 bond and 2-oxetanone formation is observed. A most interesting class of zwitterions, for comparison to the above, would be those arising from 4-azido-3-alkoxycyclopenteneones, e.g., **33**. Here the initially formed zwitterion would have the enolate anion and carbocation orbitals orthogonally arranged just as in **29**. However, unlike **29**, position 1 now carries two different substituents and thus allows an additional stereochemical probe of the ring closure and conformational equilibration. Indeed, zwitterion **33** is exactly that which would be proposed from orbital correspondence analysis in maximum symmetry (OCAMS) to arise from the cyloaddition of *tert*-butylcyanoketene and an enol ether.[15] This theory further predicts the ring closure to be stereospecific as indicated by the depicted rotation, i.e., cyano rotating by the smaller substituent at C-1 to ultimately give the contrathermodynamic cyclobutanone. Results of our work in this series will be reported subsequently.



33

Conclusions

In conclusion, we emphasize the significant points resulting from this study. (1) For the first time the zwitterions formed from the interaction of a ketene with a ketene have been independently generated and shown to give the same products as the cycloaddition itself. (2) The initially formed zwitterion is one which results from a head-to-tail interaction of the two ketenes. The fact that these ring close to cyclobutane-1,3-diones or 2-oxetanones and that the choice is dependent upon the steric size of the substituents on the cationic half of the zwitterion is suggestive of a general mechanism to account for ketoketene as well as aldoketene dimerizations. (3) The fact that zwitterions are formed in the thermolysis of **8**, **9**, **10**, and **18** further establishes the predictive power of the zwittazido cleavage reaction. (4) These results suggest a potentially general mechanistic probe for the investigation of the cycloadditions of a variety of cyano-substituted compounds since suitably substituted cyclic vinyl azides can be viewed as precursors to possible cyano-substituted zwitterionic intermediates in [2 + 2], [3 + 2], and [4 + 2] cycloadditions.

Experimental Section

General Comments. ^1H NMR spectra were recorded on either a Varian EM-360 or a Brucker WH-90 spectrometer, employing tetramethylsilane as an internal standard; the chemical shifts are reported in parts per million. Infrared data was obtained on a Perkin-Elmer 283 IR spectrophotometer. Only those absorptions which are characteristic of typical functional groups are reported. Mass spectra were obtained from a Finnigan 1015 or a Hewlett-Packard 5983H spectrometer. Elemental analyses were performed by Robertson Laboratory, Florham Park, NJ. Melting points were determined with a Thomas-Hoover capillary melting-point apparatus and were uncorrected unless otherwise specified.

2-Azido-6-*tert*-butyl-3-methyl-1,4-benzoquinone (14). To 25 g (0.118 mol) of 2-*tert*-butyl-6-chloro-5-methyl-1,4-benzoquinone[16] in 800 mL of MeOH was added 15 g (0.231 mol) of NaN_3 in 50 mL of H_2O. After 1.5 h the orange reaction mixture was diluted to 2 L with ice–water, resulting in the precipitation of bright orange solid, 22.9 g (89.2%), mp 41–42 °C dec. Recrystallization of a small sample from aqueous MeOH gave an analytical sample: mp 41.5–42.5 °C dec; IR (Nujol) 2115, 1668, 1650, 1593 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.63 (s, 1 H), 1.88 (s, 3 H), 1.27 (s, 9 H); mass spectrum, *m/e* 219 (1.5%), 191 (9.4%), 176 (35%), 148 (100%).

Anal. Calcd for $C_{11}H_{13}N_3O_2$: C, 60.26; H, 5.98. Found: C, 59.95; H, 6.14.

4-*tert*-Butyl-2-cyano-2-methylcyclopent-4-ene-1,3-dione (15). A solution of 20 g (0.091 mol) of **14** in 150 mL of anhydrous chlorobenzene was maintained at 120 °C for 2 h. The solvent was removed and the residue triturated with pentanes (200 mL) to give 13.2 g (75.7%) of a yellow-brown solid, mp 87–88 °C. An analytical sample was obtained by recrystallization from ether/pentane to yield yellow needles: mp 88–89 °C (lit.[17] mp 85.2–86.5 °C); IR (Nujol) 2248, 1757, 1712, 1598 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.05 (s, 1 H), 1.60 (s, 3 H), 1.33 (s, 9 H); mass spectrum, *m/e* 191 (21.9%), 176 (49.1%), 148 (100%), 41 (26.6%).

2-Amido-4-*tert*-butyl-5-chloro-2-methylcyclopent-4-ene-1,3-dione (16). To 80 mL of concentrated H_2SO_4 was aded 10.0 g (44.3 mmol) of 4-*tert*-butyl-5-chloro-2-cyano-2-methylcyclopent-4-ene-1,3-dione. The light yellow solution was stirred for 2 h and poured onto ice to give a tacky yellow material which subsequently solidified. The aqueous acid mixture was extracted with $CHCl_3$ and the organic layer was then washed with H_2O, dried with $MgSO_4$, and evaporated to yield a light yellow solid. This solid was dissolved in a minimum amount of hot $CHCl_3$ and triturated with pentanes. The resulting precipitate was collected and washed with pentanes to yield 10.04 g (93.0%) of very pale yellow square plates, mp 117–119 °C.

An analytical sample was prepared by several recrystallizations from aqueous EtOH to yield very faint yellow flakes: mp 118.5–120.5 °C; IR (Nujol) 3400, 3317, 3252, 3203 (amide), 1759, 1712, 1668 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.20 (br, 2 H), 1.60 (s, 3 H), 1.53 (s, 9 H); mass spectrum, *m/e* 243 (2.1%), 245 (0.7%), 209 (12.6%), 208 (100%), 185 (16.9%).

Anal. Calcd for $C_{11}H_{14}ClNO_3$: C, 53.99; H, 6.18; Cl, 14.49; N, 5.72. Found: C, 54.16; H, 5.91; Cl, 14.27; N, 5.76.

4-*tert*-Butyl-5-chloro-2-methylcyclopent-4-ene-1,3-dione (17). To a solution of 60 mL of concentrated HCl in 40 mL of dimethoxyethane was added 10.0 g (41.0 mmol) of 2-amido-4-*tert*-butyl-5-chloro-2-methylcyclopent-4-ene-1,3-dione (**16**). The reaction solution was heated to reflux for 2 h, allowed to cool to room temperature, and then poured into ice–water. The resulting light yellow solid was collected and dried to give 8.12 g (98.7%), mp 47–48.5 °C. Recrystallization from aqeuous EtOH yielded pale yellow needles: mp 47–48.5 °C; IR (Nujol) 1767 and 1712 (C=O), 1569 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.73 (q, 1 H, J = 7 Hz), 1.83 (s, 9 H), 1.22 (d, 3 H, J = 7 Hz); mass spectrum, *m/e* 200 (83.4%), 202 (26.5%), 185 (100%), 187 (31.8%), 158 (65.8%), 160 (21.8%), 129 (56.5%). Anal. Calcd for $C_{10}H_{13}ClO_2$: C, 59.86; H, 6.53. Found: C, 60.12; H, 6.62.

4-*tert*-Butyl-5-chloro-2,2-dimethylcyclopent-4-ene-1,3-dione. A solution of 1.0 g (5.0 mmol) of 4-*tert*-butyl-5-chloro-2-methylcyclopent-4-ene-1,3-dione (**17**) dissolved in 10 mL of freshly distilled anhydrous THF was added (5 min) to a suspension of 2.0 g of a 20% oil suspension of KH (0.4 g of KH, 10 mmol) in 50 mL of anhydrous THF. The solution was stirred for an additional 5 min to ensure complete reaction. To the deep red solution was added 0.7 mL (11.2 mmol) of methyl iodide. The reaction solution color changed from deep red to a faint brown in 5 min. The solution was allowed to stir for an additional 10 min and then 1 mL of acetic acid in 10 mL of THF was added slowly, followed by 2 mL of undiluted acetic acid and finally 5 mL of MeOH. Evaporation of the solvent yielded a residue as

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[15] E. A. Halevi, *Helv. Chim. Acta.*, **58**, 2136 (1975); E. A. Halevi, *Angew. Chem., Int. Ed. Engl.*, **15**, 593 (1976); D. Becker and N. C. Brodsky, *J. Chem. Soc., Chem. Commun.*, 237 (1978).

[16] L. Forman and W. Sears, *J. Am. Chem. Soc.*, **76**, 4977 (1954).

[17] H. Muller and H. Lande, *J. Prakt. Chem.*, **4**, 69 (1956).

a white solid in a yellow oil. The residue was extracted with CHCl$_3$, dried with MgSO$_4$, filtered, and concentrated to yield a yellow-green oil. This oil was eluted on a short silica column (5 × 15 cm) with pentanes and then with a 1:1 mixture of chloroform/pentanes to yield 0.94 g (87.9%) of a light yellow solid, mp 56.5–59 °C. Purification of the sample was accomplished by recrystallization from pentanes (−30 °C) to yield light yellow-green plates, mp 60.5–61.8 °C.

An analytical sample was prepared by sublimation at 55 °C (1 torr) to yield a yellow-green solid: mp 61.5–63 °C; IR (Nujol) 1752 and 1711 (C=O), 1568 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.41 (s, 9 H), 1.15 (s, 6 H); mass spectrum, *m/e* 214 (76.3%), 216 (24.0%), 201 (54.5%), 199 (100%), 174 (21.5%), 173 (25.5%), 172 (61.6%), 171 (47.5%), 144 (36.3%), 129 (36.7%), 41 (23%).

Anal. Calcd for C$_{11}$C$_{15}$ClO$_2$: C, 61.54; H, 7.04. Found: C, 61.85; H, 6.94.

4-*tert*-Butyl-5-chloro-2-ethyl-2-methylcyclopent-4-ene-1,3-dione. A solution of 1.0 g (5.0 mmol) of 4-*tert*-butyl-5-chloro-2-methylcyclopent-4-ene-1,3-dione (**17**) dissolved in 10 mL of freshly distilled anhydrous THF was added to a suspension of KH in 50 mL of anhydrous THF over a 5-min period. To the deep red solution was added 1.6 mL (19.5 mmol) of ethyl iodide in one portion. The solution was stirred at room temperature for 2 h. During this time the color changed from deep red to light brown. The product was isolated as described above to yield 0.90 g (78.9%) of a yellow-green oil.

The oil was further purified by Kugelrohr distillation at 35–40 °C (0.25 torr) to yield 0.81 g (71.1%) of a light yellow-green oil: IR (neat) 1755 and 1708 (C=O), 1569 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.68 (q, 2 H, J = 7 Hz), 1.40 (s, 9 H), 1.10 (s, 3 H), 0.69 (t, 3 H, J = 7 Hz); mass spectrum, *m/e* 228 (7.5%), 230 (2.5%), 213 (13.0%), 186 (11.2%), 149 (45.6%), 129 (36.7%), 69 (100%).

Anal. Calcd for C$_{12}$H$_{17}$ClO$_2$: C, 63.02; H, 7.48. Found: C, 63.32; H, 7.58.

2-Benzyl-4-*tert*-butyl-5-chloro-2-methylcyclopent-4-ene-1,3-dione. A solution of 1.0 (5.0 mmol) of 4-*tert*-butyl-5-chloro-2-methylcyclopent-4-ene-1,3-dione (**17**) dissolved in 10 mL of freshly distilled anhydrous THF was added to a suspension of 2.0 g of KH in 50 mL of anhydrous THF. To the deep red solution was added 0.75 mL (6.3 mmol) of benzyl bromide. The solution was stirred at room temperature for 30 min, during which time the solution became a light yellow-brown color. The product was isolated as described above to yield 1.02 g (70.3%) of a light yellow-green oil which solidified upon standing, mp 53–54 °C.

An analytical sample was prepared by sublimation at 60–65 °C (0.05 torr) to yield yellow-green cubes: mp 54–55 °C; IR (Nujol) 1748 and 1702 (C=O), 1563 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.2 (br m, 5 H), 2.96 (s, 2 H), 1.23 (s, 3 H), 1.18 (s, 9 H); mass spectrum, *m/e* 290 (4.1%), 292 (1.4%), 275 (4.6%), 277 (1.5%), 262 (2.8%), 206 (2.5%), 198 (2.1%), 91 (100%).

Anal. Calcd for C$_{17}$H$_{19}$ClO$_2$: C, 70.22; H, 6.59. Found: C, 70.11; H, 6.75.

4-Chloro-2-cyano-2,5-dimethylcyclopent-4-ene-1,3-dione. A solution of 14.80 g (69.9 mmol) of 2-azido-6-chloro-3,5-dimethyl-1,4-benzoquinone[13] dissolved in 100 mL of dry chlorobenzene was heated to reflux for 1 h. The reaction solution was allowed to cool and the chlorobenzene was removed to yield a dark colored solid. Purification of the crude reaction product was accomplished by column chromatography on silica gel. Elution with a 1:1 solution of chloroform/pentanes yielded 8.84 g (68.8%) of slightly off white needles, mp 96.5–97.5 °C.

An analytical sample was prepared by recrystallization from chloroform/pentanes to yield white needles: mp 96.8–97.5 °C; IR (Nujol) 2240 (CN), 1762 and 1707 (C=O), 1612 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.20 (s, 3 H), 1.63 (s, 3 H); mass spectrum, *m/e* 183 (98.2%), 185 (30.8%) 141 (13.7%), 127 (27.0%), 120 (45.3%), 104 (23.3%), 102 (73.0%), 92 (45.2%), 81 (65.0%), 74 (71.7%), 67 (100%).

Anal. Calcd for C$_8$H$_6$ClNO$_2$: C, 52.34; H, 3.29. Found: C, 52.21; H, 3.47.

4-Azido-5-*tert*-butyl-2-cyano-2-methylcyclopent-4-ene-1,3-dione (27). To 1.0 g (4.4 mmol) of 4-*tert*-butyl-5-chloro-2-cyano-2-methylcyclopent-4-ene-1,3-dione dissolved in 30 mL of THF was added 0.50 g (7.7 mmol) of NaN$_3$. A couple of drops of water was added, and the solution was protected from light and stirred with slight cooling. The solvent was then removed and the residue extracted with CHCl$_3$, dried over MgSO$_4$, filtered, and evaporated to yield 1.0 g (97%) of a light yellow oil. This oil showed no contaminants by ^{1}H NMR or TLC (1:1 chloroform/pentane) and was not purified further: IR (neat) 2240 (CN), 2130 (N$_3$), 1758 and 1708 (C=O), 1573 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.58 (s, 3 H), 1.22 (s, 9 H); mass spectrum, *m/e* no parent, 205 (1.2%), 124 (9.9%), 123 (49.3%), 108 (100%), 81 (33.0%), 80 (22.1%), 57 (42.1%), 53 (50%).

4-Azido-5-*tert*-butyl-2-methylcyclopent-4-ene-1,3-dione (8). To 1.0 g (50 mmol) of 4-*tert*-butyl-5-chloro-2-methylcyclopent-4-ene-1,3-dione in 25 mL of MeOH was added 0.50 g (77 mmol) of NaN$_3$. The solution was protected from light and stirred for 2 h with slight cooling. The initial addition of NaN$_3$ turned the solution red brown in color. This color changed to yellow green as the reaction proceeded. The solvent was removed and the residue extracted with CHCl$_3$. The solution was dried over MgSO$_4$, filtered, and evaporated to yield 0.99 g (95.8%) of a yellow-green oil which was not further purified: IR (neat) 2115 (N$_3$), 1745 and 1697 (C=O), 1585 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.65 (q, 1 H, J = 7 Hz), 1.32 (s, 9 H), 1.21 (d, 3 H, J = 7 Hz); mass spectrum, *m/e* 151 (19.2%), 124 (9.4%), 123 (7.1%), 108 (34.8%), 57 (57.1%), 56 (100%).

4-Azido-5-*tert*-butyl-2,2-dimethylcyclopent-4-ene-1,3-dione (9). To a solution of 1.0 g (4.7 mmol) of 4-*tert*-butyl-5-chloro-2,2-dimethylcyclopent-4-ene-1,3-dione in 30 mL of MeOH was added 0.60 g (9.2 mmol) of NaN$_3$. The product was isolated as described above after 4 h of reaction time to give 1.30 g (100%) of a yellow-green oil: IR (neat) 2100 (N$_3$), 1744 and 1695 (C=O), 1584 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.30 (s, 9 H), 1.14 (s, 6 H); mass spectrum, *m/e* no parent, 168 (7.5%), 149 (33.8%), 141 (13.8%), 111 (17.5%), 95 (20.0%), 85 (30.0%), 57 (100%).

4-Azido-5-*tert*-butyl-2-ethyl-2-methylcyclopent-4-ene-1,3-dione (10). To a solution of 1.0 g (4.4 mmol) of 4-*tert*-butyl-5-chloro-2-ethyl-2-methylcyclopent-4-ene-1,3-dione in 25 mL of MeOH was added 0.55 g (8.46 mmol) of NaN$_3$. After 3 h the solvent was removed to yield 1.02 g (99%) of a light yellow oil which needed no further purification: IR (neat) 2115 (N$_3$), 1743, 1695 (C=O), 1587 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.67 (q, 2 H, J = 7 Hz), 1.21 (s, 9 H), 1.13 (s, 3 H), 0.72 (t, 3 H, J = 7 Hz); mass spectrum *m/e*, no parent, 151 (1.0%), 143 (20.7%), 116 (31.4%), 115 (48.5%), 85 (37.8%), 84 (100%), 69 (85%), 59 (50.8%), 57 (64.7%).

4-Azido-2-benzyl-5-*tert*-butyl-2-methylcyclopent-4-ene-1,3-dione (18). To a solution of 1.0 g (3.4 mmol) of 2-benzyl-4-*tert*-butyl-5-chloro-2-methylcyclopent-4-ene-1,3-dione in 30 mL of MeOH was added 0.40 g (6.2 mmol) of NaN$_3$. The reaction solution was covered and stirred with slight cooling for 6 h. The solvent was then removed and the product was isolated as described above to yield 0.96 g (94.1%) of a light yellow-green solid. The ^{1}H NMR spectrum indicated the presence of a slight impurity. The solid was eluted on a small column (5 × 15 cm) of silica with 1:1 chloroform/pentanes to yield 0.85 g (83.3%) of a light yellow-green solid: mp 57–59 °C dec; IR (Nujol) 2110 (N$_3$), 1692 (C=O), 1582 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.2 (br m, 5 H), 2.96 (s, 2 H), 1.23 (s, 3 H), 1.07 (s, 9 H).

4-Azido-2-cyano-2,5-dimethylcyclopent-4-ene-1,3-dione (25). To 1.0 g (5.4 mmol) of 4-chloro-2-cyano-2,5-dimethylcyclopent-4-ene-1,3-dione in 30 mL of THF and a couple of drops of water was added 0.50 g (7.7 mmol) of NaN$_3$. After 5 h the solvent was then removed and the residue was extracted with CHCl$_3$. The extract was dried with MgSO$_4$, filtered, and evaporated to yield 1.03 g (100%) of an orange oil. This oil was eluted on a silica column (5 × 15 cm) with chloroform to yield 0.88 g (85%) of a light yellow-green oil: IR (neat) 2128 (N$_3$), 1758 and 1706 (C=O), 1613 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.88 (s, 3 H), 1.54 (s, 3 H); mass spectrum, *m/e* 190 (1.6%), 134 (5.5%), 82 (38.6%), 81 (100%), 53 (51.6%), 52 (24.1%).

Thermolysis of 4-Azido-5-*tert*-butyl-2-cyano-2-methylcyclopent-4-ene-1,3-dione (27). A solution of 1.0 g (4.3 mmol) of **27** in 25 mL of freshly distilled benzene was heated to reflux. Evolution of gas was noticed at Ca. 55 °C. The progress of the reaction was followed by ^{1}H NMR. **27** [(benzene) δ 1.09 (s, 9 H), 1.00 (s, 3 H)] decomposed to yield *tert*-butylcyano- and methylcyanoketene [(benzene) δ 0.70 (s, 9 H) and 0.85 (s, 3 H)], respectively. The reaction was complete after 1 h at reflux to yield a yellow-green solution. After 5 h the light yellow-green solution

Table I. Ketene Generation

ketene	precursor	description	trap A, temp, °C	trap B, temp, °C
ketene	diketene	colorless solid	−78	−196
methylketene	propionic anhydride	colorless solid	−78	−196
dimethylketene	tetramethylcyclobutane-1,3-dione	yellow oil	−5	−78
ethylmethylketene	2-methylbutyric anhydride	yellow oil	0	−78

had turned to an orange-brown color. IR and ^{1}H NMR analyses indicated two ketenes still present; however, a significant amount of other products was being formed. No indication of cycloaddition products could be detected. Further, ^{1}H NMR analysis indicated that the methylcyanoketene was polymerizing at a faster rate than TBCK.

Thermolysis of 4-Azido-5-*tert*-butyl-2-methyl-cyclopent-4-ene-1,3-dione (8). Synthesis of 3-Methyl-4-(1-cyano-2,2-dimethylpropylidine)-2-oxetane-1-one (5). A solution of 1.03 g (4.97 mmol) of 8 was dissolved in 20 mL of freshly distilled anhydrous benzene and then heated to reflux for 1.5 h. The progress of the reaction was followed by ^{1}H NMR. The benzene was removed to yield 0.89 g of a faint yellow oil. Purification of this oil by Kugelrohr distillation yielded 0.80 g (90%) of a colorless oil: IR (neat) 2215 (CN), 1912 (C=O), 1680 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.34 (q, 1 H, J = 7 Hz), 1.56 (d, 3 H, J = 7 Hz), 1.22 (s, 9 H); mass spectrum m/e 179 (1.6%), 149 (26.3%), 112 (21.0%), 97 (22.3%), 83 (36%), 57 (100%).

Thermolysis of 4-Azido-5-*tert*-butyl-2,2-dimethylcyclopent-4-ene-1,3-dione (9). Synthesis of 2-*tert*-Butyl-2-cyano-4,4-dimethylcyclobutane-1,3-dione (6). A solution of 1.03 g (4.65 mmol) of 9 in 25 mL of freshly distilled anhy benzene was heated to reflux for 2 h. During the thermolysis the yellow-green solution became nearly colorless. Evaporation of the benzene yielded 0.83 g (92%) of a light yellow oil which solidified when scratched. This product was sublimed at 35 °C (0.5 torr) to yield 0.72 g (80%) of colorless cubes, mp 61–63 °C.

An analytical sample was prepared by a second sublimation to yield a white solid: mp 61–63 °C; IR (Nujol) 2212 (CN), 1763 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.55 (s, 3 H), 1.27 (s, 3 H), 1.19 (s, 9 H); mass spectrum, m/e 193 (3.8%), 165 (3.3%), 122 (19.1%), 108 (27.2%), 70 (100%).

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82. Found: 68.37; H, 7.76.

Thermolysis of 4-Azido-5-*tert*-butyl-2-ethyl-2-methylcyclopent-4-ene-1,3-dione (10). Synthesis of *E*- and *Z*-2-*tert*-Butyl-2-cyano-4-ethyl-4-methylcyclobutane-1,3-dione (7). A solution of 0.90 g (3.8 mmol) of 10 in 15 mL of freshly distilled anhy benzene was heated to 60 °C for 3h. Initial gas evolution was noticed at 50 °C. During the course of the reaction the bright yellow-green color of the reaction solution faded to nearly colorless. Evaporation of the benzene yielded 0.78 g (98%) of a light yellow-green oil. Purification of 0.59 g of oil by Kugelrohr distillation at 40 °C (0.05 torr) yielded 0.53 g (90%) of a colorless oil: IR (neat) 2220 (CN), 1755 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 220 MHz) two isomers formed in a 43%/57% ratio; minor isomer, δ 1.98 (q, 2 H, J = 7.5 Hz), 1.28 (s, 3 H), 1.22 (s, 9 H), 1.09 (t, 3 H, J = 7.5 Hz); mass spectrum, m/e no parent, 149 (53%), 110 (31%), 85 (35%), 84 (24%), 83 (21%), 77 (15%), 69 (31%), 57 (100%).

Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27. Found: C, 69.83; H, 8.27.

Thermolysis of 4-Azido-2-benzyl-5-*tert*-butyl-2-methylcyclopent-4-ene-1,3-dione (18). Synthesis of *E*- and *Z*-2-Benzyl-4-*tert*-butyl-4-cyano-2-methylcyclobutane-1,3-dione (22). A solution of 0.72 g (2.4 mmol) of 18 in 20 mL of freshly distilled anhydrous benzene was heated to 60 °C for 4 h. The solvent was removed to yield 0.62 g (95%) of a yellow-orange solid, mp 62–72 °C. The sample was purified by Kugelrohr sublimation at 65 °C (0.05 torr) to yield 0.56 g (86%) of a white solid, mp 79–103 °C. Two isomers were formed in a ratio of 54%/46%. Complete NMR assignments were made possible by the fact that the major isomer was more volatile than the minor. This enabled the sample to be enriched to a 3:1 ratio by a few consecutive sublimations. IR (Nujol) 2222 (CN), 1760 and 1710 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) major isomer, δ 7.35 (br m, 5 H), 2.97 (s, 2 H), 1.52 (s, 3 H), 1.10 (s, 9 H); minor isomer, δ 7.35 (br m, 5 H), 3.14 (s, 2 H), 1.28 (s, 3 H), 1.15 (s, 9 H).

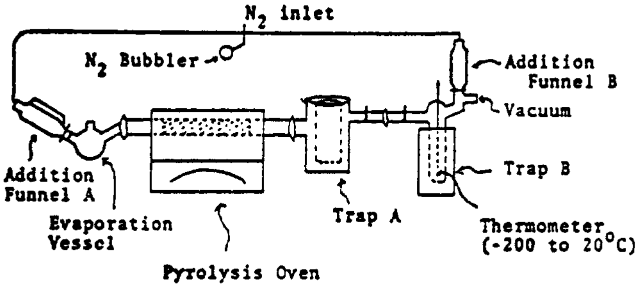

Figure 1. Pyrolysis apparatus.

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11. Found: C, 75.91; H, 7.27.

Generation of Ketenes for Cycloaddition Reactions. The preparation of the very reactive alkylketenes was carried out by vacuum pyrolysis of suitable precursors and the ketenes were trapped at low temperatures (see Table I). The pyrolysis apparatus utilized is shown in Figure 1. A general operational procedure for the pyrolyses was as follows. After the pyrolysis oven had stabilized at the desired temperature, the appropriate ketene precursor was placed in addition funnel A (liquid precursors) or the evaporation vessel (solid precursors). Trap B was evacuated to 0.5–1 torr and cooled to a temperature low enough to trap all ketene vapors. Trap A was then cooled so that it would condense any unpyrolyzed precursor or any side products, and the entire system was evacuated to 1–2 torr. If a liquid ketene precursor was used, the evaporation vessel was heated to 150 °C via a silicon oil bath and the precursor was added slowly from the addition funnel. However, if the precursor was a solid, it was placed directly into the evaporation vessel and was volatilized by the use of a heat gun. The precursor vapors were pulled through a quartz column (2.5 × 35 cm) packed with pieces of cut quartz tubing (heated to 580–600 °C) and the ketene was collected in trap B.

Once the ketene was generated and trapped, the vacuum was closed and the entire setup was brought to atmospheric presure with nitrogen. This avoids any potential hazard of explosion. The apparatus was then ready for the addition of the thermally stable *tert*-butylcyanoketene via addition funnel B.

General Procedure for Ketene Cycloadditions. By use of the pyrolysis apparatus described above, the desired ketene was generated and trapped. The system was brought to atmospheric pressure under nitrogen and a solution of *tert*-butylcyanoketene was added to the addition funnel (B). If liquid nitrogen was used as the cooling medium to trap the ketene, it was removed and the solution of *tert*-butylcyanoketene was added under nitrogen. If dry ice/acetone was used as the cooling medium for the ketene trap, the *tert*-butylcyanoketene (in toluene) was added before removing the cooling bath. Once the *tert*-butylcyanoketene solution was added, the reaction solution was allowed to come to room temperature slowly. The reaction progress was followed by IR and ^{1}H NMR analysis. The solvent was evaporated and the residue was vacuum distilled.

Ketene Mixed Dimerizations. *tert*-Butylcyanoketene and Ketene. Synthesis of 4-(1-Cyano-2,2-dimethylpropylidine)-2-oxetane-1-one (4). Ketene generated from the pyrolysis of 1.0 mL of ketene dimer at 580 °C (1 torr) (23.7 mmol of ketene at 100% conversion) was condensed in a liquid nitrogen trap. The reaction vessel was brought to atmospheric pressure with nitrogen while keeping the liquid nitrogen trap in place. The coolant bath was then removed and immediately replaced by a dry ice/acetone bath. A solution of cooled (−78 °C) *tert*-butylcyanoketene (12.4 mmol) in toluene was added slowly to the condensed ketene. The reaction solution was kept at −78 °C for 15 min and then allowed to slowly come to room temperature. A deep amber color ensued at about 5 °C. This color slowly returned to a yellow-orange color over a 2-h period. The reaction solution was then concentrated to yield 2.06 g (87.8%) of a yellow-orange oil which was stored at −30 °C overnight. The oil was purified by Kugelrohr sublimation to yield 0.85 g (36.2%) of a white solid: mp 52.5–55.5 °C; IR (Nujol) 2200 (CN), 1923 and 1864 (C=O), 1683 (C=C) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 4.18 (s, 2 H), 1.23 (s, 9 H); mass spectrum, *m/e* 165 (3.5%), 137 (6.1%), 123 (9.2%), 108 (100%), 80 (9.4%), 57 (21.4%), 53 (15.6%).

The sample was too unstable to obtain an elemental analysis.

Ketene Mixed Dimerizations. *tert*-Butylcyanoketene and Methylketene. Synthesis of 3-Methyl-4-(1-cyano-2,2-dimethylpropylidine)-2-oxetane-1-one (5). Methylketene, generated from the pyrolysis of 1.9 g of propionic anhydride at 580 °C (1 torr) (14.6 mmol of methylketene, 13.1 mmol for the observed 90% conversion), was condensed at liquid nitrogen temperature. This was then treated with TBCK as described above. After a 30-min reaction time the solvent was removed to yield a yellow-orange oil which was purified by vacuum distillation [bp 54–56 °C (0.3 torr)] to yield 1.15 g (48.9%) of a colorles oil. This oil was identical with the product obtained from the thermolysis of azidocyclopentenedione **8**.

Ketene Mixed Dimerizations. *tert*-Butylcyanoketene and Dimethyleketene. Synthesis of 2-*tert*-Butyl-2-cyano-4,4-dimethylcyclobutane-1,3-dione (6). Dimethylketene, generated from the pyrolysis of tetramethylcyclobutane-1,3-dione at 580–600 °C (1 torr) (13.5 mmol of dimethylketene at 100% conversion of 0.95 g of precursor), was condensed at −78 °C. This was then treated with TBCK as decribed above. After 1.5 h the solvent was removed and the crude reaction product was left in vacuo (ca. 15 torr) overnight to yield 2.13 g (83.54%) of a yellow-orange semisolid. The semisolid was purified by sublimation at 40 °C (1 torr) to yield 0.96 g (37.5%) of a colorless solid, mp 59–63 °C. Purification by a second sublimation yielded a white solid, mp 61–64 °C. This compound was identical with the product obtained from the thermolysis of azidocyclopentenedione **9**.

Ketene Mixed Dimerizations. *tert*-Butylcyanoketene and Ethylmethylketene. Synthesis of *E*- and *Z*-2-*tert*-Butyl-2-cyano-4-methylcyclobutane-1,3-dione (7). Ethylmethylketene, generated from the pyrolysis of 2-methylbutyric anhydride at 580 °C (1 torr) (2.5 mL of anhydride generated 13.4 mmol at 100% conversion), was condensed at −78 °C. This was then treated with TBCK as described above. The reaction was allowed to proceed for 4 h at room temperature and the solvent was removed to yield 2.28 g (83.2%) of a viscous yellow-orange oil. Purification of this oil by Kugelrohr distillation at 45 °C (0.1 torr) yielded 1.21 g (44.2%) of a colorless oil. This compound was identical spectroscopically with the product obtained from the thermolysis of azidocyclopentenedione **10**. In fact, the 220-MHz ^{1}H NMR spectrum indicated that the ratio of *E* and *Z* isomers was also exactly the same, i.e., a 43:47 ratio.

Methanolysis of Cyclobutanedione (6). Synthesis of Methyl 4-Cyano-3-oxo-2,2,5,5-tetramethylhexanoate (19). A solution of 226 mg (1.17 mmol) of 2-*tert*-butyl-2-cyano-4,4-dimethylcyclobutane-1,3-dione (**6**) dissolved in 2.0 mL of anhydrous MeOH was heated to reflux for 7 h. The progress of the reaction was followed by ^{1}H NMR. After 4 h at reflux the reaction was greater than 90% complete. Evaporation of the MeOH yielded 253 g (96.1%) of a faint yellow oil which was purified by Kugelrohr distillation at 40–45 °C (0.3 torr), yielding 230 mg (87.5%) of a colorless solid: mp 28–30 °C; IR (neat) 2225 (CN), 1751 and 1726 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.71 (s, 3 H), 3.62 (s, 1 H), 1.43 (s, 3 H), 1.36 (s, 3 H), 1.09 (s, 9 H).

Anal. Calcd for $C_{12}H_{19}NO_3$: C, 63.98; H, 8.50. Found: C, 63.94; H, 8.61.

Methanolysis of 4-Azido-5-*tert*-butyl-2,2-dimethylcyclopent-4-ene-1,3-dione (9) and 2-*tert*-Butyl-2-cyano-4,4-dimethylcyclobutane-1,3-dione (6). A solution of 180 mg (0.86 mmol) of 4-azido-5-*tert*-butyl-2,2-dimethylcyclopent-4-ene-1,3-dione (**9**) in 1.8 mL of anydrous MeOH was maintained at 62 °C for 1.5 h. The solvent was then removed in vacuo. The resulting residue was analyzed by ^{1}H NMR which showed only absorption due to methyl 2-cyano-3,3-dimethylbutanoate (**20**),[11] methyl 2-methylpropanoate (**21**),[11] and methyl 4-cyano-2,2,5,5-tetramethyl-3-oxohexanoate (**19**) in a ratio of approximately 3:3:4, respectively. In an analogous experiment 100 mg (0.47 mmol) of 2-*tert*-butyl-2-cyano-4,4-dimethylcyclobutane-1,3-dione (**6**) in 1 mL of MeOH was thermolyzed for 1.5 h at 62 °C. ^{1}H NMR analysis of the crude reaction mixture showed 38% **19** and 62% starting cyclobutanone **6**.

Acknowledgment. We thank the National Science Foundation (CHE-02103) for financial support of this work.

Registry No. **3**, 29342-22-1; **4**, 74987-47-6; **5**, 68364-34-1; **6**, 68364-33-0; *cis*-**7**, 74987-48-7; *trans*-**7**, 74987-49-8; **8**, 68364-36-3; **9**, 68364-37-4; **10**, 74987-50-1; **14**, 74987-51-2; **15**, 74987-52-3; **16**, 74987-53-4; **17**, 74987-54-5; **18**, 74987-55-6; **19**, 68364-35-2; **20**, 55712-10-2; **21**, 547-63-7; *cis*-**22**, 74987-56-7; *trans*-**22**, 74987-57-8; **25**, 74987-58-9; **27**, 74987-59-0; **28**, 57681-10-4; 2-*tert*-butyl-6-chloro-5-methyl-1,4-benzoquinone, 29666-43-1; 4-*tert*-butyl-5-chloro-2-cyano-2-methylcyclopent-4-ene-1,3-dione, 74987-52-3; 4-*tert*-butyl-5-chloro-2,2-dimethylcyclopent-4-ene-1,3-dione, 74987-60-3; methyl iodide, 74-88-4; 4-*tert*-butyl-5-chloro-2-ethyl-2-methylcyclopent-4-ene-1,3-dione, 74987-61-4; ethyl iodide, 75-03-6; 2-benzyl-4-*tert*-butyl-5-chloro-2-methylcyclopent-4-ene-1,3-dione, 74987-62-5; benzyl bromide, 100-39-0; 4-chloro-2-cyano-2,5-dimethylcyclopent-4-ene-1,3-dione, 74987-63-6; 2-azido-6-chloro-3,5-dimethyl-1,4-benzoquinone, 74987-64-7; ketene, 463-51-4; methylketene, 6004-44-0; dimethylketene, 598-26-5; ethylmethylketene, 36854-53-2; diketene, 674-82-8; propionic anhydride, 123-62-6; tetramethylcyclobutane-1,3-dione, 933-52-8; 2-methylbutyric anhydride, 1519-23-9.