Rearrangements of Azidoquinones. XVI. Thermal and Photolytic Rearrangements of 2,5-Diazido-1,4-quinones. Synthesis and Chemistry of Cyanoketenes[1,2]

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Abstract: 2,5-Diazido- and 2,6-diazido-1,4-quinones undergo a unique thermal cleavage to cyanoketenes. This fragmentation proceeds in two distinct stages. The first is a ring contraction to 4-azido-2-cyano-4-cyclopentene-1,3-diones, and the second is the cleavage of these intermediates to two molecules of the corresponding cyanoketenes. This reaction is particularly useful for the synthesis of *tert*-butyl- and *tert*-pentylcyanoketene which reluctantly self-condense when generated in benzene but are very reactive toward nucleophilic and cycloaddition reactions. The scope and mechanism of this cleavage reaction as well as the chemistry of *tert*-butylcyanoketene are discussed.

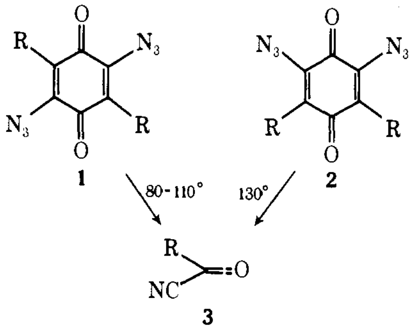
The previous paper[4] describes the thermal chemistry of 2,3-diazido-1,4-quinones. It was shown that these diazides undergo a ring contraction to 2-azido-2-cyano-4-cyclopentene-1,3-diones which subsequently ring expand to 2-aza-3-cyano-1,4-quinones. Reported here is an investigation of the thermal and photolytic chemistry of the isomeric 2,5-diazido- (**1**) and 2,6-diazido-1,4-benzoquinones (**2**). In analogy to the 2,3-diazido series, an initial ring contraction is also observed giving 4-azido-2-cyano-4-cyclopentene-1,3-diones. However, under the reaction conditions (80–110°), these compounds are labile and subsequently cleave to the corresponding cyanoketenes **3**. The main thrust of this paper is thus to describe the facile generation of cyanoketenes from the readily available and appropriately substituted diazidoquinones and to discuss certain aspects of the chemistry of these cummulenes.

The synthesis and chemistry of cyanoketenes has received only limited attention in the past. In fact, to our knowledge, the only previous reports in the literature regarding the synthesis of such cummulenes are those of DeSelm[5] and Schmidt and Ried[6] who have independently reported the unique synthesis of phenylcyanoketene upon treatment of 2-halo-1-phenylcyclobut-1-en-3,4-dione with sodium azide. More recently, the cycloaddition reactions of *tert*-butylcyanoketene, generated as described here, to allenes[7-9] and alkynes[10] have also appeared.

Synthetic Scope. It must be pointed out initially that the cyanoketenes generated as reported in this manuscript have not been isolated. Indeed, those bearing an alkyl substituent smaller than a *tert*-butyl group have not even been detected spectroscopically. However, evidence will be presented which clearly establishes their existence in solution. It will become apparent during the course of this discussion that this method of generating cyanoketenes is of particular synthetic utility for those substituted with bulky substituents, i.e., *tert*-butyl or *tert*-pentyl groups. Unlike their lower homologs these compounds are remarkably reluctant to undergo self condensation when generated in aromatic solvents and, thus, such solutions can be conveniently employed directly for studying the reactions of these ketenes with other substrates.

The synthetic scope of the thermal cleavage of 2,5- and 2,6-diazido-1,4-benzoquinones to cyanoketenes has not been extensively explored. However, this reaction does appear to be of some generality for those quinones substituted with alkyl or aryl groups. The availability of variously substituted quinones[11] and their ease of conversion to azidoquinones[12] provide a source of richly substituted starting materials for potentially a large variety of substituted cyanoketenes by the route outlined here. Those which have been studied are outlined in Scheme I.

Scheme I

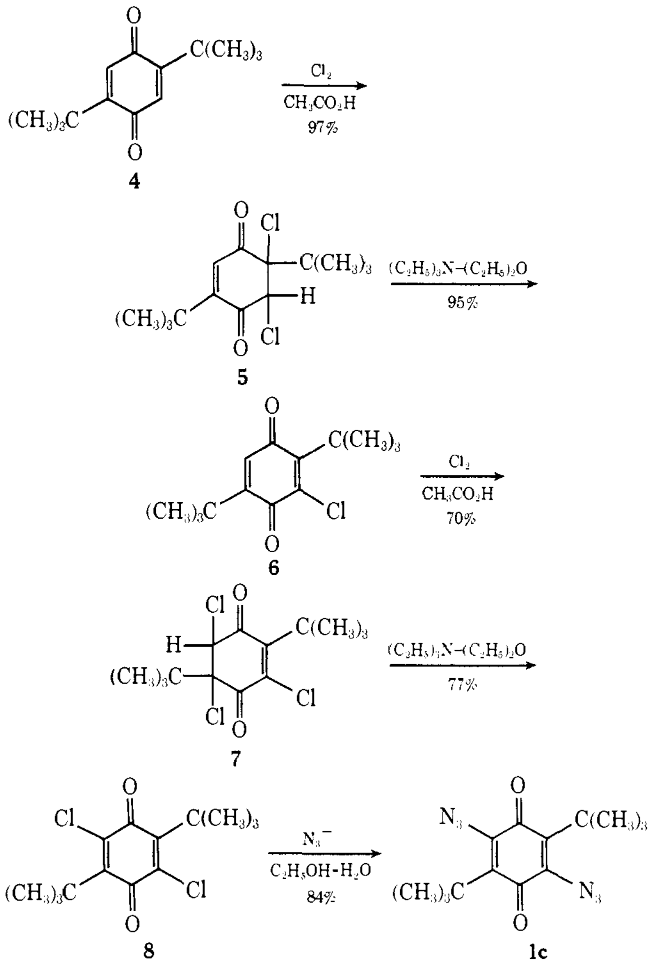


a, R = $-CH_3$
b, R = $-CH(CH_3)_2$
c, R = $-C(CH_3)_3$
d, R = $-C_6H_5$

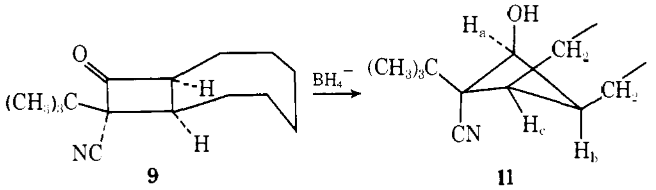
The 2,5-diazidoquinones **1a–e** undergo the above cleavage in refluxing benzene on toluene. The 2,6-diazido isomers **2a,b** require higher boiling solvents, chlorobenzene being particularly effective. Methyl-, isopropyl-, and phenylcyanoketene were not stable enough under the reaction conditions to be detected spectroscopically. However, when they were generated in the presence of methanol, the corresponding methyl esters were obtained in good yields which did not significantly vary as a function of the starting diazidoquinone isomer. For example, 2,6-diazido-3,5-dimethyl-1,4-benzoquinone (**1a**) in a methanol:chlorobenzene solvent at 130° (sealed tube) gave methyl 2-cyanopropanoate in 68% yield as determined by gas–liquid chromatography. Under the same conditions, 2,5-diazido-3,6-dimethyl-1,4-benzoquinone (**2a**) gave the same ester in 65% yield. In an analogous fashion, the isopropyl homologs of **1b** and **2b** gave methyl 2-cyano-3-methylbutanoate in 84 and 77% yields, respectively. Finally, 2,5-diazido-3,6-diphenyl-1,4-benzoquinone (**1e**) smoothly cleaves in 1:1 tetrahydrofuran–ethanol to give a 72% isolated yield of ethyl 2-cyano-2-phenylethanoate. These results are clearly in agreement with, but certainly not proof of, the intermediacy of the respective cyanoketene. However, unambiguous evidence for their generation from 2,5-diazidoquinones comes from an investigation of the thermal decomposition of 2,5-diazido-3,6-di-*tert*-butyl- (**1c**) and 2,5-diazido-3,6-di-*tert*-pentyl-1,4-benzoquinone (**1d**). These quinones smoothly cleave in refluxing benzene to give the corresponding ketenes as stable entities in solution. Such solutions show characteristic absorptions in the ir for the cummulene moiety at 2130 cm^{-1} and the expected pattern for the alkyl substituents in their ^1H NMR spectra. The yields of these bulky substituted ketenes are nearly quantitative as evidenced by the fact that some of their adducts are formed in >90% yield (vide infra). However, all attempts to isolate these cummulenes have failed. For example, concentration of the solutions in vacuo caused the ketenes to undergo self-condensation, giving white powdery polymers which show intense absorptions for ketenimine (2050 cm^{-1}) and carbonyl (1730 cm^{-1}) functionalities in their ir spectra. It is also noteworthy that the solvent employed in the generation of *tert*-butyl- and *tert*-pentylcyanoketene is critical. These ketenes are surprisingly stable in benzene; even after 3 days at the reflux temperature, only minor decomposition takes place as evidenced by their ir spectra. However, in cyclohexane after only a few hours at ambient temperature, they have undergone extensive self-condensation. For comparison, it is interesting to note that *tert*-butylcarbethoxyketene has been prepared by dehydrohalogenation of *tert*-butyl-α carbethoxyacetyl chloride, isolated by distillation, and shows no dimerization after 2 months when stored in the pure state.[14]

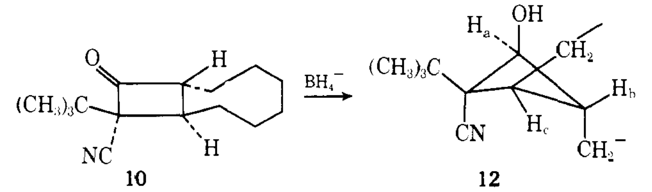
Chemistry of *tert*-Butylcyanoketene. 2,5-Diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**1c**), the most convenient precursor of *tert*-butylcyanoketene, can be prepared in bulk quantities as outlined in Scheme II.[15] Each step of this transformation proceeds in high yield, and the starting materials are relatively inexpensive and readily available. The experimental details of this procedure appear in ref 16 and thus will not be elaborated here. We have not experienced any hazards in handling large quantities of the diazide (20–30 g) which is stable for indefinite periods of time when stored in the dark at 0°. However, since this is a high energy compound, it is advisable to convert the dichloride **8** to the diazide **1c** immediately before its use. In approximately a 2-day period, the dichloride **8** can be prepared in 100-g quantities and has shown no decomposition even after 2 years while being kept in the dark at ambient temperature.

Scheme II

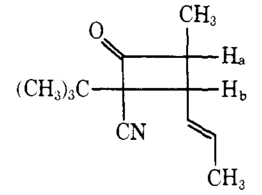


Tert-Butylcyanoketene (**3c**) reacts stereospecifically in a $[\pi\,^2s + \pi\,^2a]$ concerted cycloaddition with *cis*- and *trans*-cyclooctene giving respectively the cyclobutanones **9** and **10**.[7] In both cyclobutanones, the geometrical configuration of the parent alkene is maintained and the bulky *tert*-butyl group is cis to the adjacent CH_2. Such results are in complete accord with predictions of the Woodward–Hoffmann orbital symmetry conservation rule[17] as well as with the observed cycloaddition of ethoxyketene to alkenes[18] and dichloroketene to *cis*- and *trans*-cyclooctene.[19] The stereochemistry at the bridgehead positions in **9** and **10** is readily assigned from ^1H NMR decoupling experiments which show the coupling constants for the vicinal methine protons in **9** and **10** to be 10 and 6 Hz, respectively.[18] The cis relationship between the *tert*-butyl groups and the adjacent CH_2 substituents was established from the ^1H NMR spectra of the alcohols **11** and **12** which were obtained by sodium borohydride reduction of the respective ketones. The ^1H NMR spectra of these alcohols showed H_a and H_b to be in an axial-equatorial relationship (J = 9.7 Hz) in **11** and an equatorial-equatorial relationship (J = 5.0 Hz) in **12**.[20,21] Since the relative configurations at the bridgehead positions (H_b, H_c) were established from the decoupling experiments on the cyclobutanones, the stereochemical relationships between H_a and H_b in the alcohols allowed the assignment of the relative configurations at all four chiral centers. It is, of course, necessary to assume that the reduction of the carbonyls took place from the least hindered side of the molecules, i.e., the side opposite the bulky *tert*-butyl group. As a result, the *tert*-butyl substituent is trans to H_a and cis to the adjacent methylene in both alcohols **11** and **12**.





As expected, no 1,4 addition was observed when *tert*-butylcyanoketene was treated with *trans,trans*-2,4-hexadiene. The only product isolated (53%) was the cyclobutanone **13** which was formed in >80% yield as shown by GLC and ^1H NMR analysis. The stereochemistry of this adduct was not unambiguously established. However, a cis rather than the expected trans relationship between the two methine protons was suggested by its ^1H NMR spectrum which showed an absorption for H_a at δ 3.35 as a doublet of quartets with $J_{H_aH_b} = 9.5$ Hz.[18,19] Such a stereochemical outcome is most interesting from a mechanistic point of view, and additional work on the cycloadditions of cyanoketenes to dienes is warranted.



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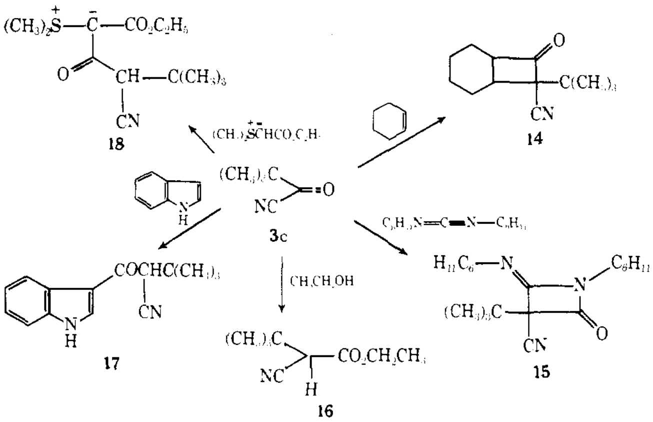
Other reactions of *tert*-butylcyanoketene which are in complete accord with its structural assignment are outlined in Scheme III. All of these reactions find precedence in the ketene literature.[22,23]

Scheme III



The method of generating *tert*-butylcyanoketene as outlined here has distinct advantages over other potential routes which would require dehydrohalogenation of the corresponding acid chloride. In fact, it was recently shown[24] that 2-cyano-3,3-dimethylbutanoyl chloride reacts with triethylamine to give 1,3-di-*tert*-butyl-1,3-dicyanoallene. *Tert*-butylcyanoketene was proposed as an intermediate in this reaction but could not be detected spectroscopically.

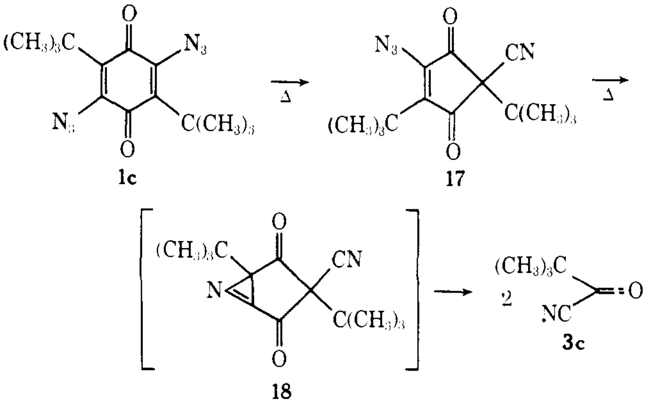
Mechanism. The propensity of 2-azido- and 2,3-diazido-1,4-quinones to thermally ring contract to respectively 2-cyano- and 2-azido-2-cyano-4-cyclopentene-1,3-diones[4,13] suggested an analogous initial rearrangement for 2,5- and 2,6-diazido-1,4-quinones. Specifically, such a rearrangement of these diazides would give 4-azido-2-cyano-4-cyclopentene-1,3-diones which could function as the penultimate precursors to the cyanoketenes. Indeed, this was shown to be the case. When 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone was partially decomposed in refluxing benzene, a 10% yield[25] of 4-azido-2,4-di-*tert*-butyl-2-cyano-4-cyclopentene-1,3-dione (**17**) was realized and, in refluxing benzene, this compound smoothly cleaved to *tert*-butylcyanoketene. In addition, the fact that 2,6-diazido-1,4-quinones also cleave to cyanoketenes strongly suggests that a common intermediate is formed from both the 2,6- and the 2,5-diazido-1,4-quinones. These data leave no doubt that an initial ring contraction to 4-azido-2-cyano-4-cyclopentene-1,3-diones constitutes the first stage in the thermal cleavage of diazidoquinones to cyanoketenes.

It is noteworthy that photolytic decomposition of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone in benzene with 3600-Å light gives a 75% yield of the ring contracted cyclopentenedione **17**, and no ketene products were observed.

The details of the mechanism for the conversion of 4-azido-2,4-di-*tert*-butyl-2-cyano-4-cyclopentene-1,3-dione (**17**) to *tert*-butylcyanoketene (**3c**) have not been elaborated. However, in analogy to the mechanism previously described for the ring contraction of 2-azido-1,4-quinones to 2-cyano-4-cyclopentene-1,3-diones,[13] the azirine intermediate **18** is proposed. Consistent with this is the fact that the rate of decomposition of **17** is accurately first order and shows no solvent effect (Table I). The activation parameters for this cleavage are $\Delta H^{\ddagger} = 25.2 \pm 0.02$ kcal/mol and $\Delta S^{\ddagger} = 0.5 \pm 0.1$ eu which compare favorably with those values obtained for the thermal rearrangements of 2-azido-1,4-quinones ($\Delta H^{\ddagger} = 26$–27.6 kcal/mol and $\Delta S^{\ddagger} = -4.6$ to 0.3 eu).[13] The azirine **18** is viewed as arising directly in the rate-determining step since the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are significantly lower than those observed for reactions where nitrenes have been established as intermediates resembling the transition state.[26] Whether the azirine spontaneously cleaves to *tert*-butylcyanoketene or ring contracts to 2,4-di-*tert*-butyl-2,4-dicyano-1,3-cyclobutanedione (a ketene dimer) which then fragments to the cummulene has not been determined.

Table I. Rate of Nitrogen Evolution for 4-Azido-2,5-di-*tert*-butyl-1,3-cyclopentenedione

Solvent	T, °C	$k \times 10^3$, sec^{-1}
Benzene	75.30	1.54
Benzene	75.30	1.44
Chlorobenzene	75.30	1.74
Chlorobenzene	75.30	1.55
o-Dichlorobenzene	75.30	1.62
Chlorobenzene	81.40	2.55
Chlorobenzene	81.40	2.45
Chlorobenzene	53.60	1.17
Chlorobenzene	53.60	1.19



Experimental Section

2,3-Dichloro-2,5-di-*tert*-pentyl-5-cyclohexene-1,4-dione. A mixture of 47.6 g (0.190 mol) of 2,5-di-*tert*-pentyl-1,4-benzoquinone in 200 ml of glacial acetic acid was vigorously stirred under a positive pressure of chlorine gas. After approximately 1.5 hr, the solutions become homogeneous, and shortly thereafter a precipitate formed. Nitrogen was then passed through the reaction mixture to remove excess chlorine. The reaction mixture was then stored at 0° for 12 hr and filtered, giving 59.4 g (98%) of 2,3-dichloro-2,5-di-*tert*-pentyl-5-cyclohexene-1,4-dione as a white crystalline solid. Recrystallization from diethyl ether gave the analytical sample, mp 96.5–97°.

Anal. Calcd for $C_{16}H_{24}Cl_2O_2$: C, 60.18; H, 7.52; Cl, 22.26. Found: C, 60.32; H, 7.39; Cl, 22.20.

Characteristic spectral properties of the dione follow: ir (Nujol) 1690 (C=O) 1600 cm^{-1} (C=C); ^{1}H NMR (CDCl$_3$) δ 0.7–1.1 (m, 6), 1.2 (s, 6), 1.3 (s, 6), 1.6–2.0 (m, 4), 4.78 (s, 1), 6.40 (s, 1).

2-Chloro-3,6-di-*tert*-pentyl-1,4-benzoquinone. A solution of 55.8 g (0.174 mol) of 2,3-dichloro-2,5-di-*tert*-pentyl-5-cyclohexene-1,4-dione in 400 ml of diethyl ether was treated with 12.79 g (0.174 mol) of diethylamine in 25 ml of water. Upon addition of the amine, the solution immediately became yellow, and diethylamine hydrochloride precipitated. The reaction mixture was then extracted three times with water and once with a saturated sodium chloride solution. The organic layer was then dried ($MgSO_4$) and the solvent removed in vacuo, giving 44.5 g (96%) of the chloroquinone as a yellow oil. This compound was used directly without further purification. However, its spectral properties were consistent with those of a pure compound: ^1H NMR ($CDCl_3$) δ 0.75 (m, 6), 1.22 (s, 6), 1.44 (s, 6), 1.86 (m, 4), 6.53 (s, 1).

2,5,6-Trichloro-3,6-di-*tert*-pentyl-2-cyclohexene-1,4-dione. Chlorine gas was bubbled through a solution of 44.5 g (0.157 mol) of 2-chloro-3,6-di-*tert*-pentyl-1,4-benzoquinone in 200 ml of glacial acetic acid for 5 hr. Nitrogen was then bubbled through the solution in order to expel excess chlorine. The reaction solution was then poured into 500 ml of water and then extracted with 200 ml of dichloromethane. The organic layer was dried ($MgSO_4$) and the solvent removed in vacuo to yield 52.1 g (94%) of the dione as a lemon-yellow oil. No further purification of this product mixture was attempted. It was used directly for the synthesis of 2,5-dichloro-3,6-di-*tert*-pentyl-1,4-benzoquinone.

2,5-Dichloro-3,6-di-*tert*-pentyl-1,4-benzoquinone. A solution of 51.9 g (0.146 mol) of the above dione in 350 ml of diethyl ether was treated with 11 g (0.15 mol) of diethylamine in 25 ml of ether. An instantaneous reaction occurred, resulting in the precipitation of the amine hydrochloride. The reaction mixture was extracted three times with water and once with saturated sodium chloride solution. The ether solution was then dried and the solvent removed in vacuo, giving 36.7 g (99%) of the quinone as a yellow-orange oil. Purification by preparative GLC gave the analytical sample. However, its spectral properties were not appreciably different from those of the crude product: ir (film) 1680 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.78 (t, 6, J = 7 Hz), 1.39 (s, 12), 1.88 (q, 4, J = 7 Hz).

Anal. Calcd for $C_{16}H_{22}Cl_2O_2$: C, 60.57; H, 6.94. Found: C, 60.72; 6.98.

2,5-Diazido-3,6-di-*tert*-pentyl-1,4-benzoquinone. A solution of 1.58 g (5 mmol) of 2,5-dichloro-3,6-di-*tert*-pentyl-1,4-benzoquinone in 65 ml of methanol was cooled at 5°, and 1 g (15 mmol) of sodium azide in 5 ml of water was added over a 2-min period. The color of the reaction solution changed from yellow to orange. Cooling to −15° caused the azide **10b** to precipitate as a beautiful orange crystalline solid, 1.13 g (68%), mp 96–98° dec. Characteristic spectral properties of this diazidoquinone follow: ir (Nujol) 2110 (N_3), 1660 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 0.75 (t, 6, J = 7 Hz), 1.23 (s, 12), 1.82 (q, 4, J = 7 Hz).

Anal. Calcd for $C_{16}H_{22}N_6O_2$: C, 58.18; H, 6.66; N, 25.45. Found: C, 57.95; H, 6.68; N, 25.32.

***tert*-Pentylcyanoketene.** The ketene is conveniently prepared by refluxing a solution of 1 g of 2,5-diazido-3,6-di-*tert*-pentyl-1,4-benzoquinone in 25 ml of anhydrous benzene for 1 hr. During this time, nitrogen evolved, and the initial bright orange color of the reaction solution faded to a light lemon yellow. The reaction can be monitored by ir on aliquots of the reaction solution which clearly shows the disappearance of the azide peak (2110 cm^{-1}) and the appearance of the ketene absorption (2130 cm^{-1}). At the end of 1 hr, the ir spectrum shows characteristic absorption at 2220 (CN) and 2130 cm^{-1} (C=C=O), and the ^1H NMR spectrum shows only the characteristic *tert*-pentyl multiplet.

Methylcyanoketene. A solution of 51.7 mg (0.237 mmol) of 2,6-diazido-3,5-dimethyl-1,4-benzoquinone and 16 mg (0.5 mmol) of methanol in *ca.* 1.5 ml of chlorobenzene was heated at 130° for 1 hr in a sealed tube. Analysis of the reaction solution by GLC showed methyl 2-cyanopropanoate[27] to be present in 68% yield: NMR (chlorobenzene) δ 1.25 (d, 3, J = 7.5 Hz), 3.19 (q, 1, J = 7.5 Hz), 3.49 (s, 1).

The same methyl ester was generated in 65% yield (GLC) when 52.7 mg (0.242 mmol) of 2,5-diazido-3,6-dimethyl-1,4-benzoquinone[12] and 16 mg (0.5 mmol) of methanol in *ca.* 1.5 ml of chlorobenzene was heated at 130° for 1 hr in a sealed tube.

Isopropylcyanoketene. A solution of 77.8 mg (0.284 mmol) of 2,6-diazido-3,5-diisopropyl-1,4-benzoquinone and 20 mg (0.6 mmol) of methanol in *ca.* 1.5 ml of chlorobenzene was sealed in a glass ampule and heated at 130° for 45 min. Gas chromatographic analysis of the reaction solution (10% SAIB on Chrom W, NAW 20 ft × ⅛ in., 150°) showed the methanol adduct to isopropylcyanoketene, i.e., methyl 2-cyano-3-methylbutanoate. An analytical sample was collected by preparative GLC.

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.55; H, 7.86; N, 9.92. Found: C, 59.88; H, 7.71; N, 9.87.

Characteristic spectral properties for this methyl ester follow: ir (film) 2275 (CN), 1750 cm^{-1} (C=O); ^1H NMR (chlorobenzene) δ 0.89 (d, 6, J = 7 Hz), 0.93 (d, 6, J = 7 Hz), 2.1 (m, 1), 3.1 (d, 1, J = 5 Hz), 3.46 (s, 3).

The same ester was prepared in 84% yield when 62.6 mg (0.228 mmol) of 2,5-diazido-3,6-diisopropyl-1,4-benzoquinone and 16 mg (0.5 mmol) of methanol in 1 ml of chlorobenzene were heated at 130° for 1 hr in a sealed tube.

Phenylcyanoketene (3e). A solution of 2,5-diazido-3,6-diphenyl-1,4-benzoquinone (5.0 g, 0.014 mol) in ethanol–tetrahydrofuran (1:1, 400 ml) was refluxed for 4 hr. The solvent was then removed in vacuo, and the resulting dark liquid was vacuum distilled giving 3.8 g (72% yield) of ethyl 2-cyano-2-phenylacetate which was identical with an authentic sample prepared as described by DeSelm.[5]

2,6-Diazido-3,5-dimethyl-1,4-benzoquinone (2a). To an ice-cold solution of 2,6-dichloro-3,5-dimethyl-1,4-benzoquinone[29] (1.0 g, 4.88 mmol) in 250 ml of methanol was added 1.0 g (15.4 mmol) of sodium azide in 5 ml of water. After 2 days at ambient temperature in the dark, the solution was poured into water and the resulting red-orange precipitate collected to give 0.54 g (51%), mp 88–89° (from methanol–water).

Anal. Calcd for $C_8H_6N_6O_2$: C, 44.04; H, 2.77; N, 38.52. Found: C, 44.17; H, 2.86; N, 38.38.

Characteristic spectral properties for this diazidoquinone follow: ir (Nujol) 2130 (N_3), 1660 (C=O) 1625 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 1.97 (s).

2,6-Diisopropyl-1,4-benzoquinone. A solution of 17.8 g (0.1 mol) of 2,6-diisopropylphenol in 180 ml of 95% ethanol was mixed with a stirred solution of 67.0 g (0.25 mol) of Fremy's salt and 8.0 g (0.1 mol) of sodium acetate in 3 l. of water. The reaction was followed by gas–liquid chromatography and was found to be essentially complete after 17 hr. Extraction with dichloromethane gave 18.1 g (94% yield) of 2,6-diisopropyl-1,4-benzoquinone as a yellow oil: ir (film) 1650 (C=O), 1605 (C=C) cm^{-1}; ^1H NMR (CCl_4) δ 1.15 (d, 12, J = 6 Hz), 3.1 (h, 2, J = 6 Hz), 6.47 (s, 2). The spectral properties of this product as well as its thin layer and gas chromatographic analysis indicated a nearly pure compound. It was used without further purification.

2,3-Dichloro-2,6-diisopropyl-5-cyclohexene-1,4-dione. Chlorine gas was added to a stirred solution of 18.1 g (94 mmol) of 2,6-diisopropyl-1,4-benzoquinone in 180 ml of acetic acid, for 1 hr. The flask was stoppered and stirred an additional 2 hr. Nitrogen was passed through the solution to remove the excess chlorine, and the solution was poured into water. Extraction with dichloromethane gave 23.7 g (96% yield) of a yellow oil. This product appears to be a 1:1 mixture of cis and trans isomers as evidenced by the methine and vinyl proton absorptions in its ^1H NMR spectrum.

Characteristic spectral properties of this mixture follow: ir (film) 1700 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.16 (m, 24), 2.0–3.6 (m, 4), 4.57 (d, 1, J = 1.5 Hz), 4.79 (d, 1, J = 1.5 Hz), 6.37 (t, 1, J = 1.5 Hz), 6.57 (m, 1).

2-Chloro-3,5-diisopropyl-1,4-benzoquinone. To a stirred solution of 18.7 g (71.0 mmol) of 2,3-dichloro-2,6-diisopropyl-5-cyclohexene-1,4-dione in 200 ml of ether was added dropwise 5.5 g (75.3 mmol) of diethylamine. A white precipitate of diethylamine hydrochloride began to form immediately. The reaction mixture was poured into water and extracted with ether. Evaporation gave 16.1 g (96% yield) of a red-brown oil. Gas–liquid chromatography showed a mixture composed of 80% of the desired product and 20% of 2,6-dichloro-3,5-diisopropyl-1,4-benzoquinone.

Characteristic spectral properties of 2-chloro-3,5-diisopropyl-1,4-benzoquinone follow: ir (film) 1670 cm^{-1}; (C=O); ^1H NMR (CCl_4) δ 1.17 (d, 6, J = 7 Hz), 1.33 (d, 6, J = 7 Hz), 2.7–3.7 (m, 2), 6.62 (d, 1, J = 1 Hz).

2,3,5-Trichloro-2,6-diisopropyl-5-cyclohexene-1,4-dione. Chlorine gas was passed through a solution of 16.1 g (71 mmol) of 2-chloro-3,5-diisopropyl-1,4-benzoquinone in 160 ml of acetic acid for 30 min. The flask was stoppered and stirred an additional 2 hr. Nitrogen was passed through the solution to remove excess chlorine, and the solution was poured into water. Extraction with dichloromethane gave 21.0 g (99% yield) of the dione as an oil which showed the following spectral properties: ir (film) 1715 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 0.9–1.5 (m, 12), 2.8 (m, 1), 3.35 (m, 1), 4.82 (d, 1).

2,6-Dichloro-3,5-diisopropyl-1,4-benzoquinone. To a stirred 5% ethereal solution of 2,3,5-trichloro-2,6-diisopropylcyclohex-5-ene-1,4-dione (16.1 g, 71.0 mmol) was added dropwise 5.7 g (78 mmol) of diethylamine. After 5 min, the reaction mixture was poured into water and extracted with ether. Evaporation gave 18.1 g of a dark liquid which was purified by chromatography over 400 g of silica gel to give 15.6 g (84% yield) of 2,6-dichloro-3,5-diisopropyl-1,4-benzoquinone. The sample was a low melting solid which melted just above room temperature. Characteristic spectral properties for this quinone follow: ir (film) 1680 (C=O), 1650 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 1.33 (d, 12, J = 8 Hz), 3.45 (h, 2, J = 8 Hz).

Anal. Calcd for $C_{12}H_{14}Cl_2O_2$: C, 55.19; H, 5.40; Cl, 27.15. Found: C, 55.11; H, 5.26; Cl, 27.17.

2,6-Diazido-3,5-diisopropyl-1,4-benzoquinone (2b). To a stirred solution of 5.53 g (0.02 mol) of 2,6-dichloro-3,5-diisopropyl-1,4-benzoquinone in 250 ml of methanol (0°) was added a solution of 11.0 g (0.17 mol) of sodium azide in 50 ml of water. The solution was allowed to stand at ambient temperature for 54 hr and then diluted with water and extracted with dichloromethane. The resulting red-brown oil was purified by column chromatography over 500 g of silica gel. Elution with 5% ether in pentane gave 1.42 g (25% yield) of the quinone **2b** as a red oil which was a single component by thin layer chromatography: ir (film) 2125 (N_3), 1700, 1660 (C=O), 1620 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 1.19 (d, 12, J = 7 Hz), 3.22 (h, 2, J = 7 Hz).

Anal. Calcd for $C_{12}H_{14}N_6O_2$: C, 52.55; H, 5.11. Found: C, 52.73; H, 4.92.

***cis*-9-Cyano-9-*tert*-butylbicyclo[7.2.0]undecan-10-one (9).** A solution of *tert*-butylcyanoketene was prepared by refluxing a solution of 4.3 g (14 mmol) of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone[16] in 125 ml of anhydrous benzene for 2 hr. This solution was cooled to ambient temperature and 3.13 g (28 mmol) of *cis*-cyclooctene was added. After 36 hr, the solvent was removed in vacuo and the semisolid residue was sublimed to give 4.7 g (72%) of the cycloadduct **9**. Two recrystallizations from methanol gave an analytical sample, mp 72–73°, which showed the following spectral properties: ir (nujol) 2225, 1780 cm^{-1}; ^1H NMR (CCl_4) δ 1.18 (s, 9), 1.2–2.5 (b, 12), 3 (m, 1), 3.62 (m, 1, J = 10–11 Hz) (determined by spin decoupling).

Anal. Calcd for $C_{15}H_{23}NO$: C, 77.25; H, 9.87; N, 6.00. Found: C, 77.27; H, 9.86; N, 5.93.

***trans*-9-Cyano-9-*tert*-butylbicyclo[7.2.0]undecan-10-one (10).** A solution of *tert*-butylcyanoketene from 4.3 g (14 mmol) of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone[16] in 125 ml of benzene was prepared as described above. At ambient temperature, 3.13 g (28 mmol) of *trans*-cyclooctene was added, resulting in an instantaneous and slightly exothermic reaction. The solvent was removed in vacuo to yield 6.9 g of a yellow powder which, after sublimation at 65° (0.05 Torr), gave 6.18 g of a slightly cream-colored crystalline material melting at 81–92°. An additional sublimation at 55° gave 6.0 g (92%) of the cycloadduct **10**, mp 92–94°, which showed the following spectral properties: ir (Nujol) 2250, 1790 cm^{-1}; ^1H NMR (CCl_4) δ 1.06 (s, 9), 1.1–2.8 (b, 12), 3.27 (b, 2, J = 6–7 Hz) (determined by spin decoupling).

Anal. Calcd for $C_{15}H_{23}NO$: C, 77.25 H, 9.87; N, 6.00. Found: C, 77.22; H, 9.81; N, 5.95.

***cis*-9-Cyano-9-*tert*-butylbicyclo[7.2.0]undecan-10-ol (11).** To a suspension (0°) of 1.30 g (5.6 mmol) of **9** in 40 ml of methanol was added an excess of $NaBH_4$ in small portions. The reaction mixture was allowed to stir for 5 min after all of the material had gone into solution and was then diluted with water and extracted three times with 15-ml portions of dichloromethane. The solution was dried with anhydrous $MgSO_4$ and filtered, and the solvent was removed in vacuo to yield 1.28 g (5.5 mmol) of the crude alcohol **11** which appeared to be a single compound by ^1H NMR analysis. Recrystallization from nitromethane gave an analytical sample: mp 108–111°; ir (Nujol) 3480, 2230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (s, 9), 1.3–2.4 (b, 12), 2.5–3.2 (b, 3), 4.75 (q, 1, addition of D_2O caused this quartet to collapse to a doublet, J = 9.7 Hz).

Anal. Calcd for $C_{15}H_{25}NO$: C, 76.54; H, 10.71; N, 5.95. Found: C, 76.69; H, 10.56; N, 5.99.

***trans*-9-Cyano-9-*tert*-butylbicyclo[7.2.0]undecan-10-ol (12).** To a suspension of 2.08 g (8.9 mmol) of **10** in methanol was added an excess of $NaBH_4$. The reaction solution was stirred for 15 min at 5°, and then it was diluted with water and extracted with two 35-ml portions of dichloromethane. This organic solution was washed twice with distilled water and then dried with anhydrous $MgSO_4$. The solvent was removed after filtration to give 2.18 g of crude product as an oil. A ^1H NMR spectrum of this product showed two products in the ratio of 4 to 1 as was indicated by two *tert*-butyl absorptions. This mixture was taken up in 15 ml of hot nitromethane, filtered, and cooled to obtain 1 g of the major product **12.** A second crop of 0.5 g of **12** was obtained upon further cooling. One further recrystallization of the first crop gave an analytical sample: mp 94–96°; ir (Nujol) 3410, 2230 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17 (s, 9), 2.1–3.0 (b) and 2.74 (d, 3), 4.62 (t, 1, addition to D_2O caused this triplet to collapse to a doublet, J = 5.0 Hz).

Anal. Calcd for $C_{15}H_{25}NO$: C, 76.54; H, 10.71; N, 5.95. Found: C, 76.64; H, 10.68; N, 5.89.

The minor product from this reduction was not identified.

2-*tert*-Butyl-2-cyano-4-methyl-3-*trans*-propenylcyclobutanone (13). A 5% benzene solution of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone[16] (5.0 g, 16.6 mmol) was heated 2 hr at 80° and cooled to room temperature. *trans,trans*-2,4-Hexadiene (3.0 g, 36.5 mmol) was added, and the solution was allowed to stand for 72 hr at ambient temperature. The solvent was removed in vacuo to give 6.0 g of an oil. Gas-liquid chromatography (5 ft × 0.25 in. SS, 3% SE30 on Variport 30, 120°, 40 ml/min) of the reaction mixture showed one major peak (>80%) with a retention time of 11.5 min as well as minor peaks with retention times of 3.0, 3.9, 12.7, and 14 min. The crude reaction product was subjected to column chromatography on 300 g of silica gel. Elution of the column chromatograph with 10% ether in pentane gave 3.8 g (56% yield) of **13** which was a single component by thin layer and gas–liquid chromatography. An analytical sample of the cyclobutanone derivative was prepared by short-path distillation and then preparative gas–liquid chromatography and showed the following spectral properties: ir (film) 2220, 1775 cm^{-1}; ^1H NMR (CCl_4) δ 1.03 (s, 9), 1.32 (overlapping d, 3, J = 7.5 Hz), 1.74 (m, 3), 2.62 (m, 1), 3.35 (d of q, J_{HH} = 9.5 J_{HCH_3} = 7.5 Hz), 5.6 (m, 2).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 75.94; H, 9.22; N, 6.95.

Ethyl 2-Cyano-3,3-dimethylbutanoate (16). A benzene solution (90 ml) of 0.033 mol (based upon starting 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzenoquinone) of *tert*-butylcyanoketene in benzene was prepared as described previously. Ethanol (10 ml) was added and, after 15 min, the solvent was removed in vacuo. ^1H NMR analysis of the crude reaction product showed it to be essentially pure ester. Distillation of this liquid [bp 43–45° (0.3 mm)] gave 3.01 g (58%) of the pure ester **16** which showed the following spectral properties: ir (film) 2240, 1740 cm^{-1} ^1H NMR ($CDCl_3$) δ 1.16 (s, 9), 1.32 (t, 3, J = 8 Hz), 3.32 (s, 1), 4.25 (q, 2, J = 7 Hz).

Anal. Calcd for $C_9H_{15}NO_2$: C, 63.90; H, 8.88; N, 8.28. Found: C, 63.97; H, 8.79; N, 8.12.

7-Cyano-7-*tert*-butylbicyclo[4.2.0]octan-8-one (14). A solution of 1 g (3.3 mmol) of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone[16] in 15 ml of freshly distilled ($LiAlH_4$) cyclohexene was refluxed for 4 hr. The solvent was removed in vacuo, and the resulting semisolid was analyzed by gas chromatography which showed it to be 73% of the cyclobutanone **14.** Recrystallization of **14** from aqueous ethanol followed by sublimation [95° (0.025 Torr)] gave an analytical sample, mp 68–69°. Characteristic spectral properties of 7-cyano-7-*tert*-butylbicyclo[4.2.0]octan-8-one follow: ir (Nujol) 2235 (CN), 1780 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.23 (s, 9), 1.2–2.3 (b, 8), 2.90 (m, 1), 3.87 (m, 1).

Anal. Calcd for $C_{13}H_{19}NO$: C, 76.05; H, 9.27; N, 6.82. Found: C, 76.17; H, 9.32; N, 6.85.

Reaction of *tert*-Butylcyanoketene with Dicyclohexylcarbodiimide. A solution of *tert*-butylcyanoketene was prepared from 3.7 g (11.9 mmol) of the corresponding diazidoquinone **1c** in 67 ml of benzene. To this solution was added 6 g (29.1 mmol) of dicyclohexylcarbodiimide at room temperature. The reaction solution immediately became warm and was allowed to stand at ambient temperature for 2 hr. The solvent was removed in vacuo and the resulting crude product recrystallized from acetonitrile to give 6.6 g (82%) of the β-lactam (**15**). A small sample was recrystallized two additional times and finally sublimed to give an analytical sample, mp 111–112°. Characteristic spectral properties for **15** follow: ir (Nujol) 2220, 1815, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (s, 9), 1.1-2.1 (m, 20), 3.50 (m, 2).

Anal. Calcd for $C_{20}H_{31}N_3O$: C, 72.90; H, 9.49; N, 12.76. Found: C, 72.88; H, 9.44; N, 12.62.

3-(2-Cyano-3,3-dimethylbutyryl)indole (17). A solution of 1.0 g (3.3 mmol) of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone[16] in 10 ml of anhydrous benzene was refluxed for 1 hr. After cooling to room temperature, a solution of 0.773 g (6.6 mmol) of indole in 10 ml of anhydrous benzene was added. A precipitate began to form after approximately 15 min and was collected after 3 hr (0.653 g, 41%). Recrystallization from ethanol gave the analytical sample, mp 235-236°. Characteristic spectral properties for the indole derivative follow: ir (Nujol) 3140, 2230, 1600 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 1.20 (s, 9), 4.43 (s, 1), 7.35 (m, 3), 8.40 (m, 2).

Anal. Calcd for $C_{15}H_{16}N_2O$; C, 74.97; H, 6.71; N, 11.66. Found: C, 75.15; H, 6.68, N, 11.65.

Reactions of *tert*-Butylcyanoketene with Dimethylsulfuranylidenylacetate. A 10% benzene solution of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (1.0 g, 3.3 mmol) was refluxed for 1 hr. Upon cooling to room temperature, a solution of 0.98 g (6.6 mmol) of ethyl dimethylsulfuranylidenylacetate in 10 ml of benzene was added. After 30 min, the solvent was removed in vacuo. Column chromatography over silica gel gave 1.11 g (56%) of the ylide **18**, mp 119-121°. Recrystallization from ether gave the analytical sample. Characteristic spectral properties for the ylide follow: ir (Nujol) 2245, 1668 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.13 (s, 9), 1.29 (overlapping triplet, 3, J = 6 Hz), 2.92 (s, 3), 2.95 (s, 3), 4.12 (q, 2, J = 6 Hz), 5.28 (s, 1).

Anal. Calcd for $C_{13}H_{21}NO_3S$: C, 57.53; H, 7.80; N, 5.16. Found: C, 57.48; H, 7.70; N, 5.24.

4-Azido-2-cyano-2,5-di-*tert*-butyl-4-cyclopentene-1,3-dione (17). (a) Thermal Method. A solution of 1.5 g (4.9 mmol) of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone[16] in 25 ml of anhydrous benzene was refluxed for 10 min, resulting in partial decomposition of the diazide. The solvent was removed by freeze-drying to yield 1.45 g of an orange-yellow solid which was chromatographed on 150 g of silica gel (1:1 pentane-dichloromethane) to yield 189 mg (14%) of the cyclopentenedione **17**. A small sample of **17** was dissolved in benzene and heated in an NMR tube. It was observed that **17** cleaved to give *tert*-butylcyanoketene as evidenced by the *tert*-butyl absorption (δ 0.74)[2] in the NMR and the fact that the ir spectrum of this solution was identical with that of an authentic sample of the ketene in benzene.[2,16] An analytical sample of **17** was obtained by recrystallization from methanol, mp 78-79°. Characteristic spectral properties for **17** follow: ir (Nujol) 2140, 1760, 1700, 1580 cm^{-1}; ^{1}H NMR (benzene) δ 0.92 (s); uv (cyclohexane) λ_{max} 300 nm (1.74×10^4).

Anal. Calcd for $C_{14}H_{18}N_4O_2$: C, 61.31; H, 6.56; N, 20.43. Found: C, 61.29; H, 6.69; N, 20.20.

(b) Photolytic Method. A solution of 5 g of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone[16] in 300 ml of anhydrous benzene was irradiated for 2 hr (75% completion) using the output of a medium-pressure mercury light source filtered with a 400-nm cutoff. The sample of **17** was isolated by column chromatography as described above to give 1.2 g (76% based on consumed starting material) of the pure product.

References and Notes

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