latter pathway we propose a diradical intermediate, **11**, which explains the lack of complete stereospecificity in the olefin product due to bond rotation in this intermediate.[14]

Acknowledgment. We wish to thank the U. S. Public Health Service, the National Science Foundation, the Petroleum Research Fund, administered by the American Chemical Society, Eli Lilly and Company, and Hoffmann La Roche for support of this research.

[14] Such intermediates are readily formed in high-temperature reactions of dipolar or ylide species; *cf.* J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970).

[15] A. P. Sloan Fellow, 1969–1971.

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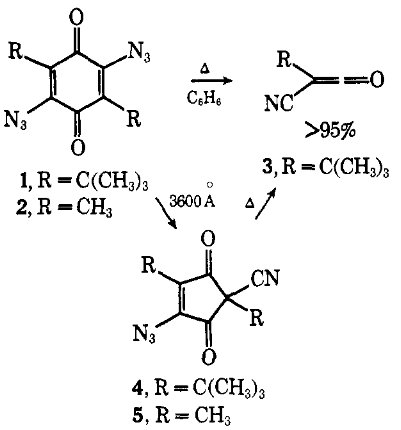
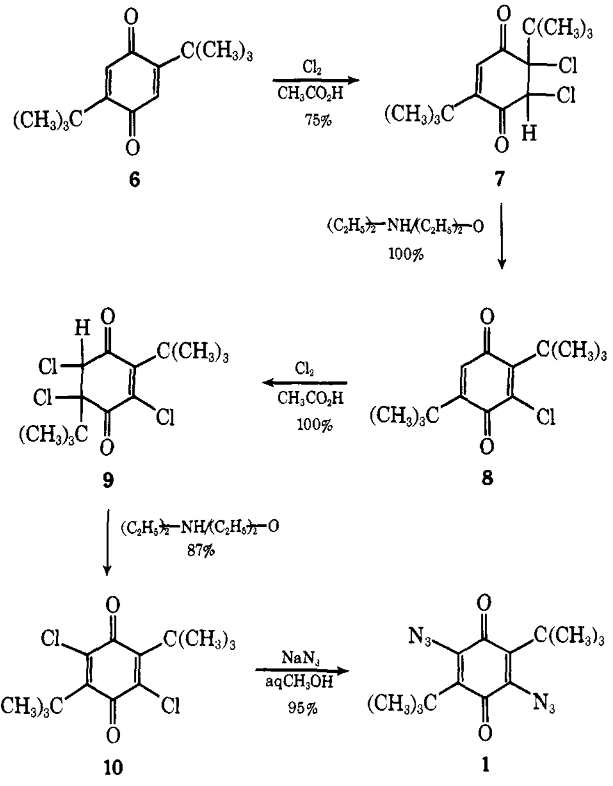
Rearrangements of Azidoquinones. VIII. Photolytic Rearrangement of 2,5-Diazido-1,4-benzoquinones to 2-Cyano-4-azido-1,3-cyclopentenediones, Precursors to Cyanoketenes

Sir:

In an earlier communication,[1] the pyrolytic cleavage of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**1**) to 2 mol of *tert*-butylcyanoketene (**3**) was reported. Described here is the photolysis of the diazidoquinones **1** and **2**[2] in anhydrous benzene with 3600-Å light. This reaction results in ring contraction to the 2-cyano-4-azido-1,3-cyclopentenediones, **4** and **5**, respectively. No ketene products are observed. However, subsequent thermal decomposition of 2-cyano-4-azido-2,5-di-*tert*-butyl-1,3-cyclopentenedione (**4**) in refluxing benzene results in a nearly quantitative yield of *tert*-butylcyanoketene (**3**).



2,5-Diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**1**) is conveniently prepared from 2,5-di-*tert*-butyl-1,4-benzoquinone (**6**) as outlined below. This method represents a pedestrian high-yield route to the diazide **1** from readily available starting materials.[3] The quinone **6** (44 g) was suspended in 400 ml of glacial acetic acid and chlorine gas was rapidly passed through the stirred reaction mixture for 30 min. The dichloride **7** was isolated (75%) by pouring the reaction solution into ice–water and recrystallizing the resulting white solid from diethyl ether. Dehydrohalogenation of **7** by slowly adding a stoichiometric amount of diethylamine, 10.8 g in 50 ml of ether, to a solution of **7**, 43.2 g in 500 ml of diethyl ether, gave 3-chloro-2,5-di-*tert*-butyl-1,4- benzoquinone (**8**) in quantitative yield. Chlorination of 38 g of chloroquinone **8** in 200 ml of glacial acetic acid at room temperature for 6 hr gave **9** as a light yellow oil.[4] Diethylamine (10.2 g) dehydrohalogenation of **9**, 45 g in 250 ml of diethyl ether, gave 2,5-di-*tert*-butyl-3,6-dichloro-1,4-benzoquinone (**10**) as a beautiful yellow crystalline solid in 87% yield. Reaction of a methanolic solution of **10**, 10 g in 750 ml of CH_3OH, with aqueous sodium azide,[2] 5 g in 15 ml of H_2O, gave 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**1**) in 95% isolated yield.[5] Spectral data for compounds **1** and **7–10** are presented in Table I.



Solutions (1%) of the azidoquinones **1** and **2** in anhydrous benzene were irradiated with 3600 Å light for 7 hr at ambient temperature. At the end of this time tlc and spectral (ir, nmr) analysis of the reaction solution showed only one major product, the cyclopentenediones. These compounds were isolated by column chromatography on 30 g of 40–60 mesh silica gel using 1:1 petroleum ether–chloroform as the eluent. Critical structural data for the cyclopentenediones follow:[6]

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[1] H. W. Moore and W. Weyler, Jr., *J. Amer. Chem. Soc.*, **92**, 4132 (1970).

[2] The azidoquinones are readily obtained in high yield *via* the reaction of sodium azide with 2,5-dichloro-3,6-dialkyl(or aryl)-1,4-benzoquinones in ethanol and/or tetrahydrofuran. For synthetic procedures to azidoquinones see H. W. Moore, H. R. Shelden, D. W. Deters, and R. J. Wikholm, *ibid.*, **92**, 1675 (1970).

[3] This is the only synthetic procedure we have been able to develop for the diazide **1**. All other methods failed primarily due to dealkylation reactions induced by hydrogen halides. For example, reaction of 2,5-di-*tert*-butyl-3-chloro(or bromo)-1,4-benzoquinone with HCl or HBr results in the loss of the 2-*tert*-butyl group giving the corresponding 2,3-dihalo-5-*tert*-butylquinol in high yields.

[4] The nmr spectrum of **9** showed it to be a mixture of isomers in the ratio of 1:3.4 as evidenced by the methine proton absorptions at δ 4.87 and 4.68.

[5] The diazide **1** can be recrystallized from C_2H_5OH–$CHCl_3$ (4:1) below 50°.

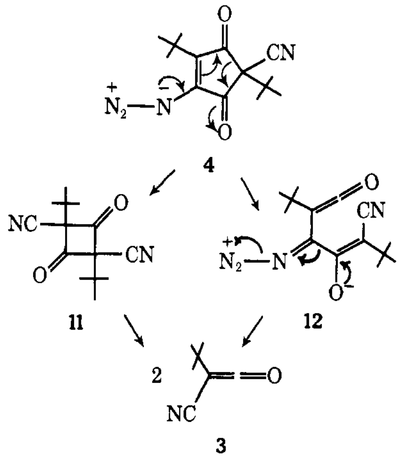
Table I. Spectral Properties of 2,5-Diazido-3,6-di-*tert*-butyl-1,4-benzoquinone and Synthetic Precursors

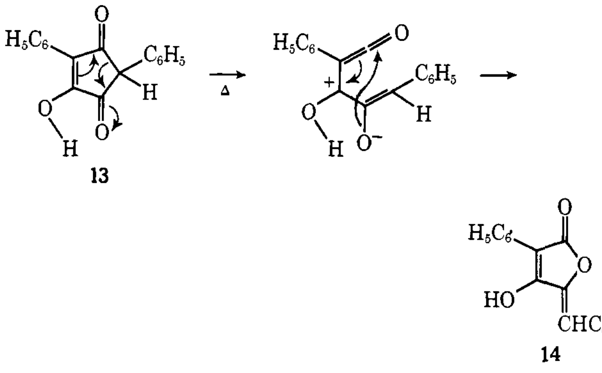
Compd[a]	Mp, °C	Ir (Nujol), cm^{-1}	Nmr[b] ($CDCl_3$), ppm
7	127–128	1700 (C=O) 1600 (C=C)	1.28 (9), s, $-C(CH_3)_3$ 1.37 (9), s, $-C(CH_3)_3$ 4.75 (1), s, -CH 6.47 (1), s, =CH
8	Oil	1680 (C=O) 1660 (C=C)	1.30 (9), s, $-C(CH_3)_3$ 1.46 (9), s, $-C(CH_3)_3$ 6.59 (1), s, =CH
9	Oil	1710 (C=O)	4.87,[c] s, -CH 4.68, s, -CH 1.1, 1.4 (18), $-C(CH_3)_3$
10	68–69	1660 (C=O)	1.45, s, $-C(CH_3)_3$
1	91–92	2110 ($-N_3$) 1640 (C=O)	1.31, s, $-C(CH_3)_3$

[a] Elemental analysis is consistent for assigned molecular formulations. [b] s = singlet, m = multiplet, number in parentheses corresponds to number of protons. [c] The ratio of the δ 4.87 to the 6.48 absorptions is 1:3.4. These absorptions result from the mixture of cis and trans isomers.

4, yield 41%; mp 75–77° dec; ir cm^{-1} (Nujol) 2100 s ($-N_3$), 1750 w, 1690 s (>C=O), 1580 s (>C=C<); nmr δ (C_6H_6) 0.90 and 1.10 ($-C(CH_3)_3$); **5**, yield 55%; oil; ir cm^{-1} (Nujol) 2140 s ($-N_3$), 1760 w, 1720 s (>C=O), 1625 s (>C=C<); nmr δ ($CDCl_3$) 1.64 and 1.86 ($-CH_3$).

Thermal decomposition of 200 mg of the cyclopentenedione **4** in refluxing anhydrous benzene gave only *tert*-butylcyanoketene[1] as evidenced by the ir (($\nu_{C=O}$), 2210 cm^{-1} (>C=C=O)) and nmr (δ 0.75, $-C(CH_3)_3$) spectra of the reaction solution. Addition of methanol to the reaction solution gave a quantative yield of α-cyano-α-*tert*-butylmethyl acetate.[1]





These results strongly suggest the mechanism **1** → **4** → **3** for the pyrolytic conversion of 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**1**) to *tert*-butylcyanoketene.[1] The first step is an example of the known thermal ring contraction of monoazidoquinones.[7] In fact, 2-cyano-4-azido-2,5-di-*tert*-butyl-1,3-cyclopentenedione (**4**) can be detected (tlc) and isolated in low yield when 2,5-diazido-3,6-di-*tert*-butyl-1,4-benzoquinone (**1**) is partially decomposed in refluxing benzene. The previously unobserved cleavage of 4-azido-1,3-cyclopentenedione (**4**) to cyanoketenes is a new reaction and warrants further study. Two intriguing possible pathways for this facile fragmentation would be either a concerted ring contraction to the ketene dimer **11** which then dissociates to ketene **3** or an electrocyclic ring opening of **4** to a zwitterionic intermediate **12** followed by cleavage to the cummulene. An analogous electrocyclic ring opening may be involved in the pyrolytic rearrangements of certain 1,3-cyclopentenediones to γ-alkylidine(or arylidine)-$\Delta^{\alpha,\beta}$-butenalides, *e.g.*, 2,6-diphenyl-5-hydroxy-1,3-cyclopentenedione (**13**) → pulvinone (**14**).[8]

Acknowledgment. The authors are grateful to the National Science Foundation (GP 19268) for financial support of this project.

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(6) Combustion analyses for these compounds are in agreement with their molecular formula.

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Isolation of an Isomeric Form of the Compound of Empirical Composition $[(CH_3)_3Si]_2Fe(CO)_4$

Sir:

All compounds of the type $R_2Fe(CO)_4$ (R = C_2F_5,[1] C_3F_7,[1] SiH_3,[2] $SiCl_3$,[3,4] $Si(C_2H_5)_3$,[4] $Ge(C_2H_5)_3$,[4] $GeCl_3$,[5] $GeBr_3$,[5] GeI_3,[5] $Sn(CH_3)_3$,[6,7] $Sn(C_2H_5)_2Cl$,[7] $Sn(C_4H_9)_2Cl$,[7] $Sn(C_6H_5)_3$,[8] $SnCl_3$,[5] $SnBr_3$,[5] $Pb(C_2H_5)_3$,[6] $Pb(C_6H_{11})_3$,[9] or $Pb(C_6H_5)_3$[9]) described in the literature have either been reported as, or have been assumed to be, monomeric species having octahedral coordination about the iron. Analogously, compounds such as $R(H)Fe(CO)_4$ (R = H_3Si,[2] Cl_3Si,[10,11] or $(C_6H_5)_3Si$[11]) have been described as monomeric, octahedral species containing an Fe–H bond. We have recently synthesized new compounds of the empirical composition $[(CH_3)_3Si]_2Fe(CO)_4$ and $(CH_3)_3Si(H)Fe(CO)_4$, both of which we believe are dimers. Spectroscopic and chemical evidence are consistent with their having a basic tetrahedral frame-

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