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Rearrangement of Azidoquinones. VII. Thermal Cleavage of 2,5-Diazidoquinones to Cyanoketenes. Syntheses of *t*-Butylcyanoketene

Sir:

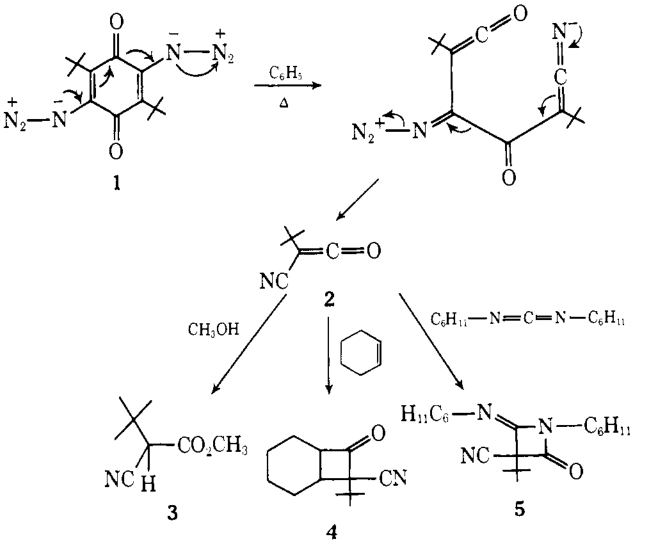
2,5-Diazido-3,6-di-*t*-butyl-1,4-benzoquinone (**1**)[1] undergoes a very facile thermal cleavage in refluxing benzene to give 2 mol of *t*-butylcyanoketene (**2**), a surprisingly stable yet very reactive ketene. This reaction constitutes a mild, noncatalytic entry into a previously unexplored class of ketenes.[2] To our knowledge, the only other reported members of this series are the parent, cyanoketene, and phenylcyanoketene, both of which have only been proposed as reactive intermediates.[3]

The ketene **2**, formed in nearly quantitative yield, is quite stable in solution. An anhydrous benzene solution of **2** which was kept at ambient temperature for 8 days showed (nmr) only minor decomposition. As yet, no attempts have been made to isolate the ketene since one can conveniently use benzene solutions of the compound for spectral and chemical investigations. The following procedure can be used for the preparation of benzene solutions of the ketene. A benzene solution consisting of 150 ml of anhydrous benzene and 5 g (0.0165 mol) of 2,5-diazido-3,6-di-*t*-butyl-1,4-benzoquinone (**1**), mp 89–90° dec, was refluxed for 45 min. During this time nitrogen evolved and the color of the reaction solution changed from bright orange to yellow. The ir and nmr spectra of such a solution indicated only the presence of the ketene. *t*-Butylcyanoketene (**2**) has a very simple ir spectrum showing characteristic absorptions at 2220 (w, CN), 2130 (s, C=C=O), and 1380, 1365 cm^{-1} (m, $C(CH_3)_3$). An nmr spectrum of a benzene solution of **2** shows only one sharp singlet at δ 0.75.

The ketene reacts instantaneously and nearly quantitatively with methanol to give methyl α-cyano-α-*t*-butylacetate (**3**). This colorless liquid shows the following characteristic spectral properties: ir 2270 (w, CN) and 1750 cm^{-1} (s, C=O); nmr ($CDCl_3$) δ 4.78 (3, s), 3.33 (1, s), 1.18 (9, s).

t-Butylcyanoketene (**2**) is *surprisingly* reactive in $2 + 2$ cycloaddition reactions. For example, decomposition of the diazide (**1**) in cyclohexene (3 hr at reflux temperature) gives the cyclobutanone (**4**) in 63% isolated yield. Cyclohexene is normally quite unreactive in cycloaddition reactions with ketenes. For example, Staudinger and Suter[4] found that diphenylketene reacted with cyclohexene to give a 60% yield of the cyclobutanone after 10 days at 100°. Butylethylketene was shown by Martin and coworkers[5] to react with cyclohexene after 12 hr at 180° to give a 47% yield of the adduct. The white crystilline cyclobutanone (**4**) shows the following characteristic properties: mp, 68–69°; ir (Nujol) 2220 (w, CN) and 1775 cm^{-1} (s, C=O); nmr ($CDCl_3$) δ 3.89 (1, m, CH), 2.92 (1, m, CH), 1.55 (8, m, CH_2), 1.20 (9, s, $C(CH_3)$). *Anal.* Found: C, 76.17; H, 9.32; N, 6.85.

A benzene solution of the ketene (**2**) readily undergoes cycloaddition to dicyclohexylcarbodiimide giving the imino-β-lactam (**5**) in 84% isolated yield. The structure of this compound is based upon the following characteristic[6-8] properties: mp 111–112°; ir (Nujol) 2220 (w, CN), 1815 (s, C=O), and 1680 cm^{-1} (s, C=N); nmr ($CDCl_3$) δ 3.5 (2, m, CH), 1.1–2.1 (20, m, CH_2), 1.22 (9, s, $C(CH_3)$). *Anal.* Found: C, 72.88; N, 12.67; H, 9.43.



The above cycloaddition reactions of **2** are particularly interesting in view of De Selms'[3] recent report that phenylcyanoketene *does not* react with cyclopentadiene, cyclopentene, cyclohexene, diphenylacetylene, or benzalaniline.

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(1) This azidoquinone is readily available *via* the reaction of sodium azide with 2,5-di-*t*-butyl-3,6-dichloro-1,4-benzoquinone. For synthetic procedures to azidoquinones see H. W. Moore, H. R. Shelden, D. W. Deters, and R. J. Wikholm, *J. Amer. Chem. Soc.*, **92**, 1675 (1970).

(2) This reaction has been applied to other 2,5-diazido-1,4-benzoquinones, *e.g.*, 2,5-diazido-3,6-dimethyl- and 2,5-diazido-3,6-diphenyl-1,4-benzoquinones. The ketenes resulting from the thermal decomposition of these diazides were trapped by ethanol to give the corresponding ethyl esters. These results will be detailed in a forthcoming paper.

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Continued investigations of the decompositions of diazidoquinones and related compounds as well as a study of the chemistry of cyanoketenes are in progress.

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Spectra and Structure of a Tetrahedrally Distorted Low-Spin Nickel(II) Complex with P_2I_2 as the Donor Set

Sir:

Several complexes with NiP_2X_2 chromophore (X = halogen) are known, and some of their structures have been determined by X-ray analysis. Among the complexes with monodentate phosphines, those with triphenylphosphine and X = Cl[1] or Br[2] have been found to have a distorted tetrahedral geometry, whereas the triethylphosphine derivative with X = Br[3] and the chloro complex with tricyclohexylphosphine[4] have been found to be rigorously planar.

Among the complexes of NiX_2 with the ditertiary diphenyldiphosphines $Ph_2P(CH_2)_nPPh_2$, those with n = 1, 2, and 3 are low-spin with a square-planar geometry and those with n = 4 or 5 are high-spin with a distorted tetrahedral geometry, both indicated by spectroscopic data.[5,6] The introduction of an oxygen atom in the place of the central methylene group in the diphenyldiphosphine complex with NiX_2 and n = 5 gives rise again to high-spin tetrahedral complexes. In this case the oxygen atom is not bonded to the metal, as showed by the X-ray analysis of the complex $[Ph_2P(CH_2)_2O(CH_2)_2PPh_2]NiCl_2$ (chromophore NiP_2Cl_2).[7]

Also the complexes of NiX_2 with the diphosphine $Ph_2P(CH_2)_8PPh_2$ are high-spin distorted tetrahedral.[8] Now if two methylene groups (positions 3 and 6) are substituted by two oxygen atoms, the ligand 1,8-bis(diphenylphosphino)-3,6-dioxaoctane (POOP), $Ph_2P(CH_2)_2O(CH_2)_2O(CH_2)_2PPh_2$, is obtained, which reacts with NiI_2 to form a monomeric diamagnetic complex. The allowable stereochemistries for this complex are therefore the four- or five-coordinate, depending on whether the ligand is bi- or tridentate.

The reflectance spectrum of this complex shows bands at 12.5 (sh), 13.7, 21.2, and 27.5 kK (Figure 1). The d–d band in the absorption spectrum in benzene (Figure 1) falls at 14.8 kK and shows a remarkable red shift with respect to the corresponding band found for some square-planar NiP_2X_2 complexes (Table I).[9] Because of the bathochromic contribution of the iodine atoms, the greatest shift is found for the $(Et_3P)_2NiBr_2$ complex, for which the structure has been established by X-ray analysis.[3] On the other hand, the spectra of $Ni(POOP)I_2$ differ from those of low-spin nickel(II) complexes with trigonal-bipyramidal[10] or square-pyramidal[11] geometries. Therefore, it is not possible to assign unequivocally either a square-planar, or a five-coordinate structure.

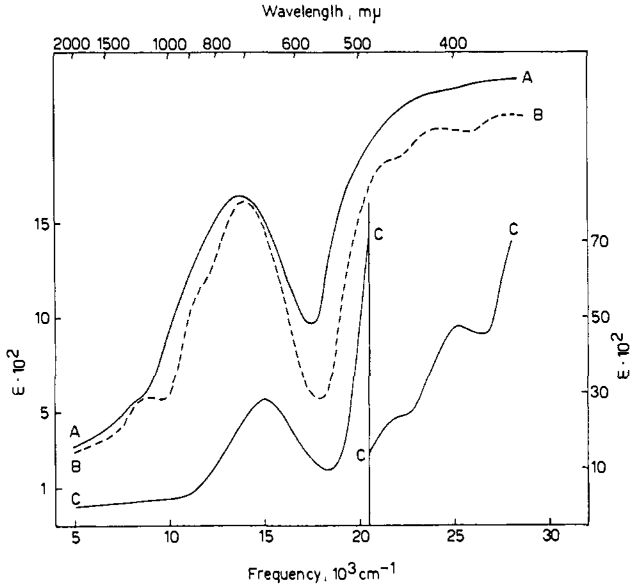

Figure 1. Solid-state spectra (arbitrary scale) of $Ni(POOP)I_2$ at 19° (A) and at −160° (B). Absorption spectrum in benzene of $Ni(POOP)I_2$ (C).

Table I

Compound	Absorption maxima in benzene, kK (log ε)		
$(Et_3P)_2NiBr_2$	25.0 (3.79)		18.5 (2.55)
$(Et_3P)_2NiI_2$	26.8 (3.67)	21.8 (3.46)	16.4 (2.69)
$(Bu_2PhP)_2NiI_2$	27.0 (3.61)	21.6 (3.44)	16.6 (2.69)
$Ni(POOP)I_2$	25.1 (3.68)	21.7 (3.39)	14.8 (2.76)

To give a definitive answer on this problem, an X-ray analysis on the $Ni(POOP)I_2$ complex was undertaken. The crystal data are: space group $P2_1/c$, a = 11.564 ± 0.011, b = 18.316 ± 0.027, c = 14.878 ± 0.035 Å, β = 118° 28′ ± 12′, Z = 4, D_c = 1.80, D_m = 1.79 g cm^{-3}.

The 1564 independent reflections observed were measured on integrated Weissenberg films, using Cu Kα radiation. The structural determination was carried out with one Patterson and two three-dimensional Fourier syntheses. These were refined by a full-matrix least-squares treatment with anisotropic temperature factors for iodine, nickel, and phosphorus atoms and isotropic factors for the other atoms, to an R factor of 0.091.

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