Rearrangements of Azidoquinones. XIII. Synthesis of 2-Alkenyl-2,3-dihydroindole-4,7-diones

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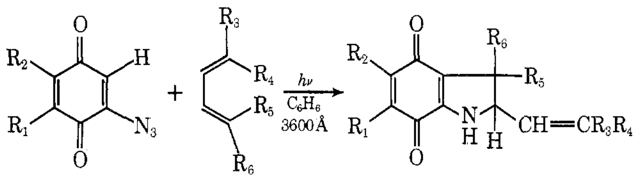
2-Azido-1,4-quinones which are unsubstituted at position 3 react with acyclic and cyclic dienes upon photolysis with 3600-Å light to give 2-alkenyl-2,3-dihydroindole-4,7-diones. The synthetic scope of this new reaction as well as its mechanism are discussed.

The preceding manuscript describes the facile thermal ring closure of 2-azido-3-vinyl-1,4-quinones to 2-alkyl- (or aryl-) indole-4,7-diones (indolequinones).[3] Described here is a related synthetic transformation which results in the formation of 2-alkenyl-2,3-dihydroindole-4,7-diones. Specifically, photolysis of azidoquinones (**1**) in the presence of various 1,3-dienes (**2**) results directly in the formation of the heterocyclic quinones (**3**), a transformation without precedent in quinone chemistry as well as in the photochemistry of organic azides. The general synthetic scope of this transformation is outlined by the equations shown in Scheme I which describe the reactions of 2-azido-5-*tert*-butyl-1,4-benzoquinone, 2-azido-5-methyl-1,4-benzoquinone and 2-azido-1,4-naphthoquinone with acyclic and cyclic dienes.

Scheme I

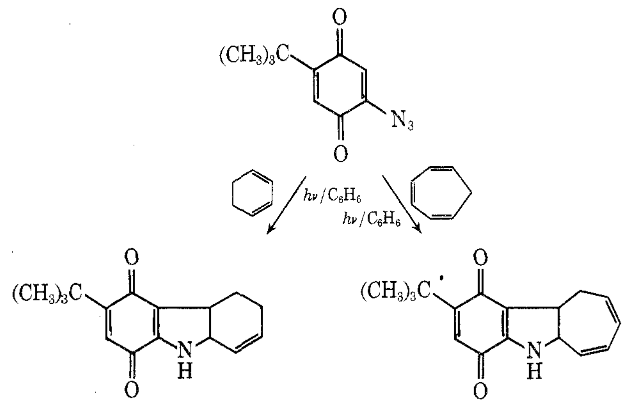


1 **2** **3**

	R_1	R_2	R_3	R_4	R_5	R_6	% yields[4]
3a	H	$C(CH_3)_3$	CH_3	H	H	H	96
3b	H	$C(CH_3)_3$	H	CH_3	H	H	73
3c	H	$C(CH_3)_3$	CH_3	H	H	CH_3	66
3d	H	$C(CH_3)_3$	H	CH_3	CH_3	H	53
3e	H	CH_3	CH_3	H	H	H	40
3f	H	CH_3	H	CH_3	CH_3	H	84
3g			CH_3	H	H	H	72
3h			H	CH_3	CH_3	H	82

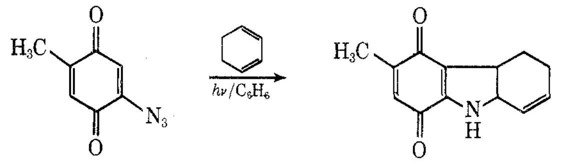
The transformation which are shown are conveniently run by irradiating an oxygen-free benzene solution of the azidoquinone and diene (1:10) with 3600-Å light for several hours. The heterocyclic quinone products function as internal filters for the incident irradiation, and, as a result, the reactions were not generally run to completion. The resulting intensely colored dihydroindolequinones were isolated by column chromatography on silica gel using benzene-petroleum ether (5:1) as the eluent. The structures of these products are all based upon their spectral and analytical properties (Experimental Section) which are in good agreement with their formulations.

All of the reactions are *regiospecific*, giving only those isomers having the alkenyl group at the 2 position. This assignment is easily made on the basis of the chemical shifts, spin-spin coupling, and proton count of the absorption due to the proton at position 2 (Experimental Section).

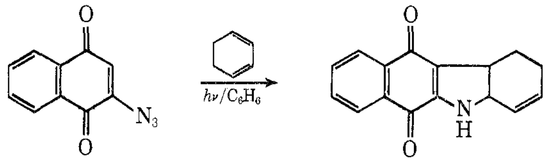


4, 53%

5, 29%

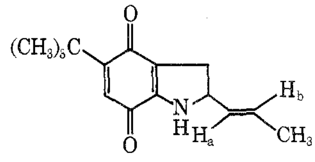


6, 37%

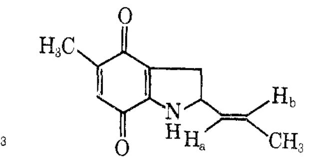


7, 74%

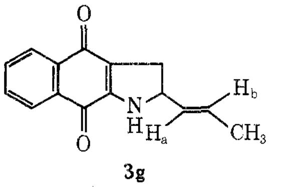
The reaction is stereospecific, with reference to the alkene double bond, only when the acyclic diene employed was *trans*-1,3-pentadiene. In this case, the azidoquinones (**1**) all gave only one detectable isomer, *i.e.*, **3a**, **3e**, and **3g**, respectively, in which the 2-propenyl group maintains its trans geometry. This assignment of trans stereochemistry for the alkene group in **3a**, **3e**, and **3g** is based upon a computer similation of their nmr spectra.[5] The best fit for



3a



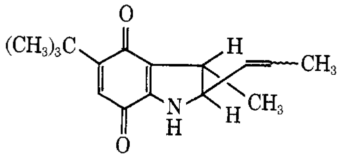
3e



3g

the vinyl proton region was obtained when the coupling constant between the alkenyl protons (J_{HaHb}) was 15.47 Hz, which is completely in agreement with the trans geometry.[6]

The reactions of the azidoquinones (1) with all other acyclic dienes employed gave the corresponding 2,3-dihydroindole-4,7-diones in a stereoselective manner. That is, 2-azido-5-*tert*-butyl-1,4-benzoquinone photolytically reacts with *cis*-1,3-pentadiene to give **3a** and its cis 2-alkene isomer in a ratio of 1.0:1.3, respectively. Further, the reactions of the above azidoquinones (1) with *trans,trans*- and/or *cis,cis*-2,4-hexadiene provide a most interesting dual stereochemical problem which now concerns the geometry of the 2-propenyl group as well as the stereochemical relationship of this moiety to the 3-methyl substituent. Isomerization of the carbon–carbon double bond is again observed. The predominant geometry of this alkene moiety in the product is the same as that of the corresponding alkene bond in the starting diene. More exciting is the fact that *the major isomer(s) always has a cis relationship between the substituents at the 2 and 3 positions, regardless of the stereochemistry of the starting diene.* Concerning this point, 2-azido-5-*tert*-butyl-1,4-benzoquinone reacts with *trans,trans*-2,4-hexadiene to give the isomeric pairs, *trans*-2,3-dihydro-*cis*- and -*trans*-2-propenyl-5-*tert*-butylindole-4,7-dione (**8**) and *cis*-2,3-dihydro-*cis*- and -*trans*-2-propenyl-5-*tert*-butylindole-4,7-dione (**9**) in a relative ratio of 1.0:3.5, respectively. Interestingly, the same azidoquinone gives **8** and **9** in a relative ratio of 1.0:6.7, respectively, when treated with *cis,cis*-2,4-hexadiene under the same conditions. In a like manner, 2-azido-5-methyl-1,4-benzoquinone reacts photolytically with *cis,cis*-2,4-hexadiene giving **10** and **11** in a ratio of 1.0:4.5 and 2-azido-1,4-naphthoquinone reacts with the same diene giving **12** and **13** in a relative ratio of 1.0:1.4, respectively. The ratios of the cis to trans 2-propenyl stereochemistry as determined from their nmr spectra, in each of these respective isomeric pairs, are as follows: **8–9**, 1.0:1.6 from *trans,trans*-2,4-hexadiene; **8–9**, 1.0:0.16 from *cis,cis*-2,4-hexadiene; **10–11**, 1.0:0.48 from *cis,cis*-2,4-hexadiene; **12–13**, 1.0:0.81 from *cis,cis*-2,4-hexadiene.



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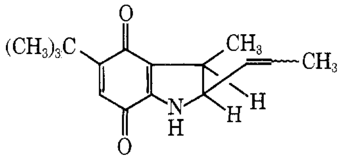
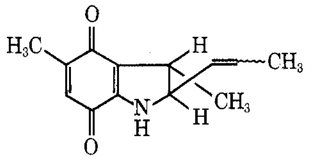


9

$1.0^{7a} : 3.5^{7a}$

$1.0^{7b} : 6.7^{7b}$



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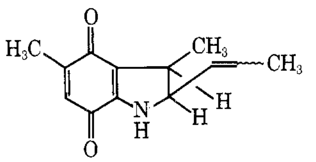
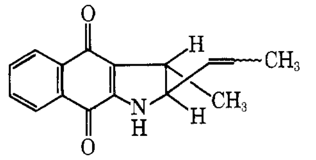


11

1.0 : 4.5



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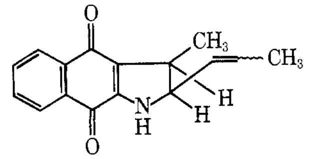


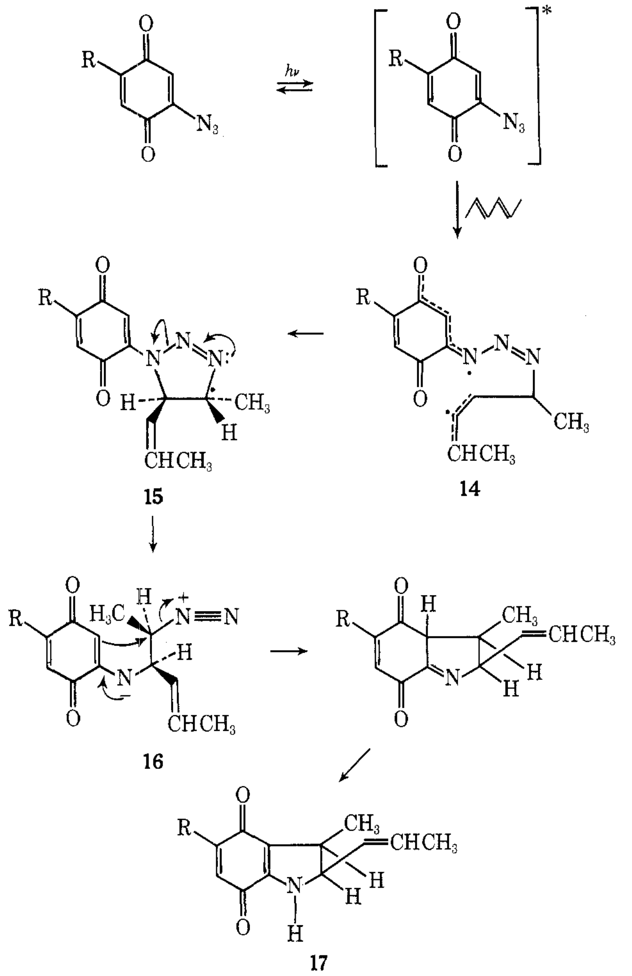
13

1.0 : 1.4

There are conceivably four geometric isomers in each of the above pairs, *i.e.*, cis–cis, cis–trans, trans–cis, and trans–trans. It is assumed that all four isomers are present. However, all attempted separations failed (glc, tlc, recrystallization, sublimation). The nmr spectrum of each purified isomeric mixture did show absorptions for cis and trans 2-propenyl and cis and trans 3-methyl, and the above stereochemical assignments are based upon interpretations of these spectra. For example, a computer simulation of the vinyl region of the nmr spectrum obtained on the mixture of **8** and **9**, shown by nmr to be 86% enriched in the isomer or isomers having one stereochemical form of the 2-propenyl group, gave the best fit when the coupling constant was 10.51 Hz. Such a value is in good accord with cis geometry.[12] Also, decoupling experiments were carried out on this same mixture which was shown by the ratio of the two 3-methyl absorptions to be 87% enriched in the isomer or isomers having either a cis or a trans 2,3 relationship. These decoupling experiments indicate a cis 2,3 configuration in the major isomer(s). That is, irradiation of the 3-methyl absorption revealed that the coupling constant between the protons at the 2 and 3 positions in the major isomer(s) was equal to 7 Hz. A coupling constant of this magnitude is consistent for adjacent protons having a dihedral angle of 20 or 150°[8] which is in accord for only the cis relationship. Analogous decoupling of the mixture of **8** and **9**, obtained from the reaction of 2-azido-5-*tert*-butyl-1,4-benzoquinone with *trans,trans*-2,4-hexadiene again showed the major isomer(s) to also have the cis configuration between the 2,3 substituents. The trans 2-propenyl methyl group in the **8** and **9** isomeric mixture absorbs at 0.25 ppm upfield from that of the cis. Also, the 3-methyl in the major cis 2,3 isomer(s) absorbs 0.1 ppm downfield from that of the trans. Analogous differences were observed in the spectra of the **10** and **11** and **12** and **13** mixtures, and it is upon these data that their indicated stereochemical assignments have been made.

Not all attempts to extend the synthetic scope of this reaction have met with success. Electron rich alkenes such as dihydropyran, furan, and cyclopentene failed to react. The electron deficient alkene, diethyl maleate, also was unreactive. The same was true for the electron poor dienes such as *trans,trans*-1,4-dicarbomethoxy-1,3-butadiene and *trans,trans*-1,4-diacetoxy-1,4-dicyano-1,3-butadiene.[9] Concerning the quinone component, the reaction appears to be limited to those azidoquinones which are unsubstituted at the position adjacent to the azide group. For example, photolysis of 2-azido-3-methyl-1,4-naphthoquinone in the presence of excess 1,3-pentadiene gave only 2-cyano-2-methyl-1,3-indandione.[10] This intramolecular

Scheme II



rearrangement can be induced either thermally or photolytically and has previously been discussed.[10]

Mechanism. A mechanism for the formation of the 2-alkenyl-2,3-dihydroindole-4,7-diones, which is generally consistent with the available data, is outlined in Scheme II. Such a mechanism describes an unsensitized, photolytic, nonconcerted cycloaddition of the azidoquinone to the diene to give the intermediate Δ^2-triazoline (**15**), which collapses to product *via* the betaine intermediate **16**. This mechanism nicely accounts for the observed stereoselectivity of the reaction. That is, the diradical (or zwitterion) intermediate **14** could allow for the partial isomerization of the allyl double bond. This diradical could then ring close to give, as the major isomer, the Δ^2-triazoline intermediate **15** having the ring substituents in the more stable trans orientation. Such a trans stereochemical consequence would, of course, be expected to be independent of the stereochemistry of the starting diene. Thermal cleavage of the triazoline to the diazonium betaine **16** has precedence[11] and such a species could then undergo back-side displacement of nitrogen as indicated to give the *cis*-2,3-dihydroindoles (**17**) as the major products.[12] Not only does the diradical **14** account for 2-propenyl isomerization but it also rationalizes the regiospecificity of the reaction. That is, one would certainly predict that **14**, which ultimately leads to the 2-propenyl substitution pattern, is also the most stable possible diradical (or zwitterion) intermediate. In addition, the photolytic cycloaddition of an azide (π_4) to an alkene double bond (π_2) would be expected to be a nonconcerted process on the basis of orbital symmetry and thus involve a two-step sequence.

It is possible that the diradical **14** maintains the stereochemical integrity of the allyl radical and that the observed 2-propenyl isomerization results from secondary photochemical processes. That is, this isomerization may come from photochemical excitation of the alkene double bond in the product indoles **17**. The facts that allylic radicals, generated by other routes, have been shown to be stereochemically stable[13] and that intramolecular triplet energy transfer between a carbonyl and an alkene chromophore can result in alkene isomerization[14] are in agreement with this possibility.

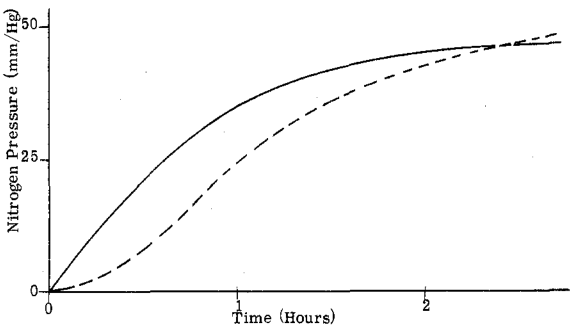


Figure 1. Rate of nitrogen evolution for the photolytic conversion of 2-azido-5-*tert*-butyl-1,4-benzoquinone and 1,3-pentadiene to 5-*tert*-butyl-2,3-dihydro-2-propenylindole-4,7-dione: (——) quinone in neat diene, (- - - -) 1% solution of quinone and diene in benzene.

The formation of the indoles **17** is indeed initiated by an unsensitized photochemical process. This was established by the observation that 2-azido-5-*tert*-butyl-1,4-benzoquinone did not react with 1,3-pentadiene under thermal conditions (ambient temperature) in the dark. However, photolysis of these components in either benzene or cyclohexane with 3600 Å light or with light greater than 4000 Å (sun lamp through a glass filter) readily resulted in 2,3-dihydroindole-4,7-dione formation. These latter experiments unambiguously rule out the possibility that light is initially being absorbed by either the diene or the benzene solvent since neither absorb light of such energy.

A nitrene intermediate in this reaction has been ruled out. Not only would such a species be inconsistent with the observed stereospecificity, it is also eliminated on the basis of kinetic studies. When 2-azido-5-*tert*-butyl-1,4-benzoquinone was photolyzed in neat 1,3-pentadiene the rate of nitrogen evolution was observed to initially follow first-order kinetics. However, when the rate of nitrogen evolution was determined for a 1% solution of the same azidoquinone in benzene, in the presence of an equimolar amount of 1,3-pentadiene, it deviated markedly from first order giving an "s" shaped curve when nitrogen pressure was plotted against time (Figure 1). *The important conclusion derived from this study is that the diene concentration affects the rate of nitrogen evolution.* The diene must therefore interact, before the step which involves the loss of nitrogen. The mechanism outlined in Scheme I illustrates such a possible interaction, *i.e.*, excited quinone reacting with ground state diene. Other possibilities exist. For example, excited quinone could conceivably sensitize the diene to its triplet state which could then react with ground-state quinone. In either event, the Δ^2-triazoline (**15**) would be generated as the penultimate precursor to the indolequinones (**17**).

All attempts to spectroscopically detect the intermediate triazoline **15** failed. However, this is not surprising in view of the fact that such Δ^2-triazolines carrying a strong electron-withdrawing substituent at the 1 position are quite unstable, even at room temperature and below, and readily cleave to the diazonium betaines analogous to **16** which then proceed to products. For example, the triazoline formed by reaction of benzoyl azide with norbornene decomposes at 40° and the analogous triazoline formed when benzenesulfoyl azide reacts with norbornene has yet to be detected.[15] The triazoline from 2,4-dinitrophenyl azide and norbornene could just be isolated while that from picryl azide could not be seen but its formation was established on kinetic grounds.[16-18]

These data are all in agreement with the mechanistic sequence outlined in Scheme II. One novel feature of this transformation is the photolytic cycloaddition of an organic azide to a carbon–carbon double bond. Such a reaction is certainly well known in the thermal chemistry of azides but appears to be without precedent under photolytic conditions.

Experimental Section

5-*tert*-Butyl-2,3-dihydro-2-*trans*-(1-propenyl)indole-4,7-dione (3a). A solution of 1.0 g (0.005 mol) of 2-azido-5-*tert*-butyl-1,4-benzoquinone and 5.0 ml (0.05 mol) of *trans*-1,3-pentadiene in 50 ml of benzene was deoxygenated by bubbling nitrogen through it for 15 min. Nitrogen was continuously passed through the reaction solution as it was irradiated for 3 hr with a 3600-Å light source.[19] Petroleum ether (10 ml, bp 30–60) was then added and the deep purple solution was chromatographed on 120 g of silica gel using benzene–petroleum ether (5:1) as the eluent. The first yellow band off the column was the starting azidoquinone (0.45 g, 45% recovery). The next was a light purple compound, 0.01 g, which was not identified. Finally 0.63 g (53% yield) of 5-*tert*-butyl-2,3-dihydro-2-*trans*-(1-propenyl)indole-4,7-dione (**3a**) was obtained as a dark purple crystalline solid, mp 72–73°. This was followed by 0.01 g of 2-amino-5-*tert*-butyl-1,4-benzoquinone.[20] Taking the recovered starting azidoquinone into account, the yield of 5-*tert*-butyl-2,3-dihydro-2-(*trans*-1-propenyl)indole-4,7-dione (**3a**) was 96%.

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.47; H, 7.76; N, 5.71. Found: C, 73.23; H, 7.81, N, 5.62.

Characteristic spectral properties of **3a** follow: ir (Nujol, cm^{-1}) 3300, 1670; nmr (CDCl$_3$, δ) 1.23 s (9), 1.65 broad d (3) J = 5 Hz, 4.18–4.62 m (1), 4.70–4.98 b (1), 5.54–5.78 m (2), 6.30 s (1); uv (CHCl$_3$, nm) 281.5 (11.5 × 10^3).

5-*tert*-Butyl-2,3-dihydro-2-(*cis*- and -*trans*-1-propenyl)indole-4,7-diones. Reaction of 2-Azido-5-*tert*-butyl-1,4-benzoquinone with *cis*-1,3-Pentadiene. A deoxygenated solution of 0.2014 g (0.001 mol) of the azidoquinone and 1.0 ml (0.01 mol) of *cis*-1,3-pentadiene in 20 ml of benzene was irradiated with 3600 Å light for 105 min. To this solution was added 2 ml of petroleum ether and then it was chromatographed on 130 g of silica gel using benzene–petroleum ether as the eluent. This gave 0.1006 g (50%) recovery of the azidoquinone and 0.0881 g (37%) of the mixture of 5-*tert*-butyl-2,3-dihydro-2-(*cis*- and -*trans*-1-propenyl)indole-4,7-dione, mp 78–79°. The stereochemistry of the 2-propenyl group was shown by nmr to be 44% trans and 56% cis. Attempted separation of these geometric isomers by thin-layer and gas chromatography, recrystallization, or sublimation were unsuccessful. Taking into account the amount of recovered starting azidoquinone, the yield of this isomeric mixture of indole-4,7-diones was 73%.

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.47; H, 7.76; N, 5.71. Found: C, 73.23; H, 8.03; N, 5.61.

Characteristic spectral properties follow: ir (Nujol) 3200, 1670; nmr (CDCl$_3$, δ) 1.30 s (9), 1.80 and 1.83 two sets of doublets (3) J = 5 Hz, 2.36–3.43 m (2), 4.65–4.80 m (1), 4.81–4.92 b (1), 5.43–5.65 m (2); 6.32 s (1); uv (CHCl$_3$, nm) 281.0 (10.3 × 10^3).

2,3-Dihydro-5-methyl-2-(*trans*-1-propenyl)indole-4,7-dione (3e). A deoxygenated solution of 0.3157 g (0.002 mol) of 2-azido-5-methyl-1,4-benzoquinone and 2.0 ml (0.02 mol) of *trans*-1,3-pentadiene in 30 ml of anhydrous benzene was irradiated for 4.25 hr with 3600-Å light. Chromatography of the reaction solution on 130 g of silica gel as described above gave 0.0344 g (11%) starting azidoquinone and 0.1387 g (35%) of the blue 2,3-dihydro-5-methyl-2-(*trans*-1-propenyl)indole-4,7-dione (**3e**), mp 86–87°. Taking into account the amount of recovered starting azidoquinone the yield of **3e** was 40%.

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.94; H, 6.40; N, 6.90. Found: C, 71.33; H, 6.70; N, 6.94.

Characteristic spectral properties for **3e** follow: ir (Nujol, cm^{-1}) 3300, 1655, 1635; nmr (CDCl$_3$, δ) 1.69 d (3) J = 5 Hz, 2.03 d (3) J = 1.5 Hz, 2.44–3.38 m (2), 4.23–4.62 m (1), 4.65–5.69 b (1), 5.46–5.67 m (2), 6.25 q (1) J = 1.5 Hz; uv (CHCl$_3$, nm) 273.5 (7.6 × 10^3).

2,3-Dihydro-2-(*trans*-1-propenyl)benzo[*f*]indole-4,9-dione (3g). A deoxygenated solution of 0.2090 g (0.001 mol) of 2-azido-1,4-naphthoquinone and 1.0 ml (0.01 mol) of *trans*-1,3-pentadiene in 20 ml of anhydrous benzene was irradiated with 3600 Å light for 2 hr. The deep purple reaction solution was worked up chromatographically as described above to give 0.1015 g (49%) of recovered starting azidoquinone and 0.0936 g (37%) of deep purple crystalline 2,3-dihydro-2-(*trans*-1-propenyl)benzo[*f*]indole-4,9-dione (**3g**), mp 143–144°. Taking into account the recovered starting azidoquinone, the yield of **3g** was 72%.

Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.31; H, 5.44; N, 5.86. Found: C, 75.42; H, 5.42; N, 5.73.

Characteristic spectral properties of **3g** follow: ir (Nujol, cm^{-1}) 3280, 1670; nmr (CDCl$_3$, δ) 1.69 d (3) J = 4.0 Hz, 2.57–3.52 m (2), 4.24–4.80 m (1), 5.03–5.32 b (1), 5.47–5.77 m (2), 7.42–8.10 m (4); uv (CHCl$_3$, nm) 278.5 (23.7 × 10^3).

5-*tert*-Butyl-2,3-dihydro-2,3-(1,3-pentadieno)indole-4,7-dione (5). A deoxygenated solution of 0.2091 g (0.001 mol) of 2-azido-5-*tert*-butyl-1,4-benzoquinone and 2.0 ml of cycloheptatriene in 20 ml of anhydrous benzene was irradiated with 3600-Å light for 6 hr. Chromatography of the resulting purple reaction solution on 120 g of silica gel using benzene–petroleum ether (5:1) as the eluent gave 0.0523 g (25%) of recovered azidoquinone and 0.0594 g (22%) of the indole-4,7-dione derivative **5**, mp 60–62°. Taking into account the amount of recovered starting azidoquinone, the yield of **5** was 29%.

Characteristic spectral properties of **5** follow: ir (Nujol, cm^{-1}) 3400, 1670; nmr (CDCl$_3$, δ) 1.27 s (9), 2.04–2.07 m (2), 3.06–3.37 m (1), 3.43–3.83 m (1), 4.08–4.50 b (1), 5.62–5.95 m (4), 6.30 s (1); uv (CHCl$_3$, nm) 284.0 (9.99 × 10^3).

6-Methyl-3,4,4a,9a-tetrahydrocarbazole-5,8-dione (6). A solution of 0.2984 g (0.0018 mol) of 2-azido-5-*tert*-butyl-1,4-benzoquinone and 3.0 ml of 1,3-cyclohexadiene in 30 ml of anhydrous benzene was irradiated for 4 hr with 3600-Å light. Chromatography of the reaction solution on 130 g of silica gel using benzene–petroleum ether (5:1) gave 0.0366 g (12%) of recovered starting azidoquinone and 0.1263 (24%) of the carbazole derivative **6**, mp 116–117°. Taking into account the amount of recovered starting azidoquinone, the yield of 6-methyl-3,4,4a,9a-tetrahydrocarbazole-5,8-dione (**6**) was 37%.

Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.56; H, 6.05, N, 6.51. Found: C, 72.62; H, 6.23; N, 6.38.

Characteristic spectral properties of **6** follow: ir (Nujol, cm^{-1}) 3250, 1670, 1630; nmr (CDCl$_3$, δ) 1.81–2.14 m (4), 2.03 d (3) J = 1.5 Hz, 3.19–3.63 m (1), 4.10–4.40 m (1), 4.73–5.17 b (1), 5.49–6.08 m (2) 6.28 q (1) J = 1.5 Hz; uv (CHCl$_3$, nm) 2805 (11.5 × 10^3).

3,4,4a,11a-Tetrahydrobenzo[*g*]carbazole-5,10-dione (7). A deoxygenated solution of 0.2017 g (0.001 mol) of 2-azido-1,4-naphthoquinone and 1.0 ml of 1.3-cyclohexadiene in 20 ml of anhydrous benzene was irradiated with 3600-Å light for 3 hr. Chromatography of the resulting deep purple solution on 120 g of silica gel using benzene–petroleum ether (5:1) gave 0.0995 g (49%) of recovered starting azidoquinone and 0.0955 g (88%) of the carbazole derivative **7**, mp 164–165°. Taking into account the amount of recovered starting material, the yield of 3,4,4a,11a-tetrahydrobenzo[*g*]carbazole-5,10-dione (**7**) was 74%.

Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.49; H, 5.18; N, 5.58. Found: C, 76.39; H, 5.39; N, 5.47.

Characteristic spectral properties for **7** follow: ir (Nujol, cm^{-1}) 3250, 1675; nmr (CDCl$_3$, δ) 1.83–2.27 m (4), 3.34–3.75 m (1), 4.17–4.52 m (1), 5.00–5.52 b (1), 5.53–6.33 m (2), 7.48–8.25 m (4); uv (CHCl$_3$, nm) 279.5 (18.8 × 10^3).

5-*tert*-Butyl-2,3-dihydro-3-methyl-2-(1-propenyl)indole-4,7-dione. Isomeric Mixture of 8 and 9 from *trans,trans*-2,4-Hexadiene. A deoxygenated solution of 0.2049 g (0.001 mol) of 2-azido-5-*tert*-butyl-1,4-benzoquinone and 1.0 ml (0.009 mol) of *trans,trans*-2,4-hexadiene in 20 ml of anhydrous benzene was irradiated for 125 min with 3600-Å light. Chromatography of the resulting deep purple solution on 120 g of silica gel using benzene–petroleum ether (5:1) gave 0.0400 g (20%) of recovered azidoquinone and 0.1339 g (52%) of the 5-*tert*-butyl-2,3-dihydro-3-methyl-2-(1-propenyl)indole-4,7-dione as a mixture of isomers. The nmr spectra of this purple oil showed it to be composed of two types of isomers, those differing in stereochemistry of the 2-propenyl group (39% cis and 61% trans 1.0:1.6) and those differing in stereochemistry of the 2,3-dihydroindole ring (22% trans and 78% cis). Separation of these four isomers could not be accomplished. Taking into account the amount of recovered starting azidoquinone, the yield of the isomeric mixture of indole-4,7-dione derivatives was 81%.

Characteristic spectral properties of this **8** and **9** mixture follow: ir (Nujol, cm^{-1}) 3400, 1670; nmr (DMSO-d_6, δ) 1.24 broad s (9), 1.03 and 1.24 two sets of doublets in ratio of 1.6:1.0, respectively, (3) J = 6.5 Hz, 1.69 and 1.73 two sets of doublets in ratio of 1.0:3,5, respectively, (3) J = 5 Hz, 2.65–3.14 m (1), 3.67–4.01 m (1), 5.47–7.79 m (2), 6.18 s (1); uv (CHCl$_3$, nm) 281.5 (10.3 × 10^3).

5-*tert*-Butyl-2,3-dihydro-3-methyl-2-(1-propenyl)indole-4,7-dione. Isomeric Mixture of 8 and 9 from *cis,cis*-2-4-Hexadiene. A deoxygenated solution of 0.2221 g (0.001 mol) of 2-azido-5-*tert*-butyl-1,4-benzoquinone and 1.0 ml (0.009 mol) of *cis,cis*-2,4-hexadiene in 20 ml of anhydrous benzene was irradiated for 2 hr with 3600-Å light. Chromatography of the resulting deep purple solution in 120 g of silica gel using benzene–petroleum ether (5:1) as the eluent gave only a trace amount of starting azidoquinone and 0.1618 g (66%) of the 5-*tert*-butyl-2,3-dihydro-3-methyl-2-(1-propenyl)indole-4,7-dione as a mixture of isomers, mp 71–73°. The nmr spectrum of this mixture showed it to be composed of two types of isomers, those differing in stereochemistry of the 2-propenyl group (86% cis, 14% trans; 1.0:0.16) and those differing in stereochemistry of the 2,3-dihydroindole ring (13% trans, 87% cis; 0.16:1.0).

Anal. Calcd for $C_{16}H_{21}NO_2$: C, 74.13; H, 8.11; N, 5.41. Found: C, 74.06; H, 8.11; N, 5.14.

Characteristic spectral properties for this **8** and **9** mixture follow: ir (Nujol, cm^{-1}) 3300, 1670; nmr (DMSO-d_6, δ) 1.24 s (9), 1.03 and 1.24 two sets of doublets in a ratio of 1.0:0.16, respectively, (3) J = 6.5 Hz, 1.69 and 1.73 two sets of doublets in a ratio of 6.7:1.0, respectively, (3) J = 5 Hz, 2.68–3.14 m (1), 4.09–4.40 m (1), 5.20–5.88 m (2), 6.18 s (1); uv (CHCl$_3$, nm) 282.5 (11.8 × 10^3).

2,3-Dihydro-3,5-dimethyl-2-(1-propenyl)indole-4,7-dione. Isomeric Mixture of 10 and 11 from *cis,cis*-2,4-Hexadiene. A deoxygenated solution of 0.2058 g (0.0013 mol) of 2-azido-5-methyl-1,4-benzoquinone and 2.0 ml (0.018 mol) of *cis,cis*-2,4-hexadiene in 30 ml of anhydrous benzene was irradiated with 3600-Å light for 4 hr. Chromatography of the resulting purple solution on 130 g of silica gel using benzene–petroleum ether (5:1) as the eluent gave 0.0188 g (9%) of recovered azidoquinone and 0.2218 g (81%) of the 2,3-dihydro-3,5-dimethyl-2-(1-propenyl)indole-4,7-dione as a mixture of isomers **10** and **11**, mp 98–99°. The nmr spectrum of this product showed it to consist of two types of isomers, those differing in the stereochemistry of the 2-propenyl group (67% cis, 33% trans; 1.0:0.48) and those differing in stereochemistry of the 2,3-dihydroindole ring (18% trans, 82% cis; 1.0:4.5). These four isomers, *i.e.*, trans–trans, trans–cis, cis–cis, cis–trans, could not be separated. Taking into account the amount of recovered starting azidoquinone the yield of the **10** and **11** mixture was 84%.

Characteristic spectral properties of this **10** and **11** isomeric mixture follow: ir (Nujol, cm^{-1}) 3300, 1660; nmr (CDCl$_3$, δ) 1.11 and 1.32 two sets of doublets in a ratio 4.5:1.0, respectively, (3) J = 7 Hz, 1.67 and 1.71 two sets of doublets in a ratio of 3.4:1.0, respectively, (3) J = 5 Hz, 2.02 d (3) J = 1.5 Hz, 2.88–3.33 m (1), 4.12–4.45 m (1), 4.72–5.03 b (1), 5.39–5.87 m (2), 6.27 g (1) J = 1.5 Hz; uv (CHCl$_3$, nm) 280.0 (11.9 × 10^3).

2,3-Dihydro-3-methyl-2-(1-propenyl)benzo[*f*]indole-4,9-dione. Isomeric Mixture of 12 and 13 from *cis,cis*-2,4-Hexadiene. A deoxygenated solution of 0.2065 g (0.001 mol) of 2-azido-1,4-naphthoquinone and 1.0 ml (0.009) of *cis,cis*-2,4-hexadiene in 20 ml of anhydrous benzene was irradiated with 3600-Å light for 3 hr. Chromatography of the resulting red solution on 120 g of silica gel using benzene–petroleum ether (5:1) as the eluent gave 0.0972 g (47%) of recovered azidoquinone and 0.114 g (44%) of the red 2,3-dihydro-3-methyl-2-(1-propenyl)benzo[*f*]indole-4,9-dione as an isomeric mixture, mp 106–108°. The nmr spectrum of this product showed it to be composed of two types of isomers, those differing in stereochemistry at the 2-propenyl group (55% cis, 45% trans; 1.0:0.81) and those differing in stereochemistry at the 2,3-indole ring positions (41% trans, 59% cis; 1.0:1.4). Attempts to separate these four isomers failed. Taking into account the amount of recovered starting azidoquinone the yield of 2,3-dihydro-3-methyl-2-(1-propenyl)benzo[*f*]indole-4,9-dione was 82%.

Characteristic spectral properties of this **12** and **13** mixture follow: ir (Nujol, cm^{-1}) 3400, 1675, 1630; nmr (CDCl$_3$, δ) 1.17 and 1.42 two sets of doublets in ratio of 1.0:1.4, respectively, (3) J = 7 Hz, 1.71 and 1.75 two sets of doublets in ratio of 1.2:1.0, respectively, (3) J = 5 Hz, 2.97–3.64 m (1), 4.19–5.50 m (1), 4.92–5.13 b (1), 5.45–5.76 m (2), 7.47–8.13 m (4); uv (CHCl$_3$, nm) 279.0 (21.9 × 10^3).

Photolysis of 2-Azido-5-*tert*-butyl-1,4-benzoquinone in the Presence of 1,3-Pentadiene Using Cyclohexane as Solvent. A deoxygenated solution of 2-azido-5-*tert*-butyl-1,4-benzoquinone (0.1 g, 0.0005 mol) in 10 ml of anhydrous cyclohexane was irradiated with 3600-Å light. The product 2,3-dihydro-5-*tert*-butyl-2-(1-propenyl)indole-4,7-dione was detected by thin-layer chromatography. After a few hours, the thin-layer chromatograms were identical in appearance with those obtained from the same reaction when benzene was employed as the solvent.

Photolysis of 2-Azido-5-*tert*-butyl-1,4-benzoquinone in the Presence of 1,3-Pentadiene Using Benzene as the Solvent and Light of >4000 Å. A deoxygenated solution of 0.1 g (0.0005 mol) of 2-azido-5-*tert*-butyl-1,4-benzoquinone and 0.5 ml of 1,3-pentadiene in 10 ml of anhydrous benzene was irradiated with a sunlamp (Sylvania, 250 W) through a Corning 3-73 glass filter which cuts off light below 4000 Å. After a few hours the thin-layer chromatograms showed appreciable buildup of the 2,3-dihydro-5-*tert*-butyl-2-(1-propenyl)indole-4,7-dione.

Kinetics. The apparatus used was a modified version of that reported by Weyler.[21] Rather than a reaction vessel which was suspended in a constant temperature bath, a water jacketed sample tube was used in which 31.50° water was circulated during the kinetic run. The 2-azido-5-*tert*-butyl-1,4-benzoquinone (0.05 g, 0.25 mmol) was dissolved in 7 ml of dry benzene and injected into the sample tube. An equal molar amount of 1,3-pentadiene was then added. The sample was deoxygenated by bubbling nitrogen through it for 15 min and then the system was closed. The cover over the ultraviolet lamps was removed and the rate of increasing pressure was recorded. In order to obtain a P infinity value the reaction was allowed to go to completion. All the samples used were pure as determined by their melting points. In addition to the above, two runs were done in which the 2-azido-5-*tert*-butyl-1,4-benzoquinone was dissolved in 7 ml of the neat 1,3-pentadiene rather than the benzene.

Registry No.—**1a**, 27977-24-8; **1e**, 27977-26-0; **1g**, 15707-29-6; *cis*-**2a**, 1574-41-0; *trans*-**2a**, 2004-70-8; *cis,cis*-**2c**, 6108-61-8; *trans,trans*-**2c**, 5194-51-4; *cis*-**3a**, 49827-80-7; *trans*-**3a**, 49827-83-0; **3e**, 49827-84-1; **3g**, 49827-85-2; **5**, 49827-86-3; **6**, 49827-87-4; **7**, 49827-88-5; **8–9**, 49827-89-6; **10–11**, 49827-90-9; **12–13**, 49827-91-0; cycloheptatriene, 544-25-2; 1,3-cyclohexadiene, 592-57-4.

References and Notes

(1) This work is taken primarily from the Ph.D. thesis of P. G.

(2) The authors are grateful to the National Cancer Institute of the National Institute of Health for Grant CA 11890 which provided financial support of this project.

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(4) Yields are based on consumed starting azidoquinone and correspond to isolated products.

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(7) (a) Product ratio from the reaction of 2-azido-5-*tert*-butyl-1,4-benzoquinone with *trans,trans*-2,4-hexadiene. (b) Product ratio from the reaction of 2-azido-5-*tert*-butyl-1,4-benzoquinone with *cis,cis*-2,4-hexadiene.

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