malized with respect to TMS. Infrared spectra were determined with a Beckman IR-12 spectrophotometer; KBr pressings (solid state) were used because most of the materials were not soluble in good solvents for infrared studies.

Generalized Procedure for Anthraquinone Reductions. 1. 9,10-Dihydroxy-9,10-dihydroanthracenes. An anthraquinone (0.08–0.10 mol) was placed in methanol (400–500 ml) and the resulting suspension was stirred while cooling to 0–5° with an ice bath. Solid sodium borohydride (13–15 g, 0.35–0.40 mol) was added in small portions to the suspension at such a rate as to prevent a temperature rise (30–60 min). During continuous stirring at 0–5° (2–4 hr), the reaction mixture assumed an orange color and became nearly homogeneous, and often a white material precipitated. The reaction mixture was poured into an ice-water mixture and stirred. The white precipitate which formed was collected, thoroughly washed with water, and air dried, yield of product 80–90%.

2. Conversion of 9,10-Dihydroxy-9,10-dihydroanthracenes to Anthrones. A suspension of 4 g of 9,10-dihydroxy-9,10-dihydroanthracene in hot 5 *N* HCl (125 ml) was stirred for 3–6 hr. The white, suspended material gradually assumed a yellow color. The anthrone was collected by filtration, thoroughly washed with water, and dried. Recrystallization or trituration afforded material of greater purity, yield of anthrone 80–95%.

3. Conversion of Anthrones to Anthracenes. An anthrone (0.08–0.10 mol) was suspended in 2-propanol (400–500 ml). After addition of sodium borohydride (0.40–0.90 mol), the reaction mixture was refluxed with stirring for 24–36 hr. The reddish-brown reaction mixture was poured with stirring into ice water which had been purged with nitrogen. In most instances, precipitation of the desired anthracene occurred. Addition of dilute acid was necessary in some instances in order to decompose unreacted sodium borohydride and to induce precipitation. The yellow solid was collected, washed thoroughly with water, and air dried. The dehydration of **4** is spontaneous under the reaction conditions, yield of crude anthracene 49–80%. Appropriate recrystallization was necessary for purification (ethanol or dichloromethane–methanol).

1,4-Dimethoxyanthraquinone (1j). Quinizarin (100 g, 0.42 mol), methyl *p*-toluenesulfonate (220 g, 1.18 mol), and sodium carbonate (70 g, 0.66 mol) were combined in *o*-dichlorobenzene (1.6 l.) and gently refluxed for 20 hr. The reaction mixture was allowed to cool to 95–100°, at which time water (100 ml) was added dropwise (5–10 min). The mixture was steam distilled to remove the solvent, and the precipitate which formed was collected by filtration and recrystallized from ethanol, yield 87.1 g (78%), mp 171–173° (lit.[17] mp 171°).

1,4-Dimethoxyanthracene. To a mixture of 50 g of 1,4-dimethoxyanthraquinone in 750 ml of diglyme at 5° was added sodium borohydride (30 g) in portions (15 min), and the mixture was stirred at 5–15° for 1.75 hr (total) before it was added to approximately 2.5 l. of ice water. An ether layer was added, and 200 ml of acetic acid was then added carefully. The reaction mixture (approximately 4 l.) was heated on a steam bath for 4 hr. Much bubbling occurred as the mixture was heated (at about 50°), and an orange precipitate began to form. The mixture was cooled overnight, and the orange precipitate was filtered off, washed, and dried to give 24.5 g (52%), mp 127–170°, of 1,4-dimethoxyanthrone.

To a mixture of 24.4 g of the anthrone in 375 ml of diglyme at 5–10° was added sodium borohydride (15 g). The mixture was stirred at 5–15° for 2 hr before it was added to approximately 2.0 l. of ice water. An ether layer was added, and 125 ml of acetic acid was then added carefully. Then 50 ml of concentrated hydrochloric acid was added, and the mixture was stirred at room temperature for 2 hr. The yellow precipitate was removed by filtration and washed with water to give 20.7 g, mp 127–132°.

Recrystallization and purification were effected by dissolving the crude product in 100 ml of methylene chloride and adding 400 ml of methanol dropwise. This mixture was cooled and a yellow product was obtained (14 g, 62%), mp 134–136°.

Acknowledgment. We wish to thank Dr. T. H. Regan and Mr. R. L. Young for their aid in interpretation of nmr spectra, Miss T. J. Davis for her discussion of infrared data, Mr. D. P. Maier for mass spectrometric data, Dr. C. V. Wilson for many helpful discussions, and Mr. B. J. Murray for technical assistance; all are from these laboratories.

Registry No.—**1a,** 84-65-1; **1b,** 84-54-8; **1c,** 1519-36-4; **1d,** 3286-01-9; **1e,** 82-44-0; **1f,** 131-09-9; **1g,** 82-46-2; **1h,** 82-43-9; **1i,** 6913-40-2; **1j,** 6119-74-0; **2a,** 35058-16-3; **2b,** 50259-81-9; **2c,** 50259-82-0; **2d,** 50259-83-1; **2f,** 50259-84-2; **2g,** 41187-73-9; **2h,** 50259-86-4; **2i,** 50259-87-5; **2j,** 50259-88-6; **3a,** 90-44-8; **3b,** 50259-89-7; **3d,** 50259-90-0; **3f,** 4887-99-4; **3g,** 50259-92-2; **3h,** 50259-93-3; **3j,** 50259-94-4.

References and Notes

(1) S. W. Chaikin and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 122 (1949).
(2) G. S. Panson and C. E. Weill, *J. Org. Chem.*, **22**, 120 (1957).
(3) D. S. Bapat, B. C. Subba Rao, M. K. Unni, and K. Venkataraman, *Tetrahedron Lett.*, (5), 15 (1960).
(4) C. J. Sanchorawala, B. C. Subba Rao, M. K. Unni, and K. Venkataraman, *Indian J. Chem.*, **1**, 19 (1963).
(5) M. Toji, Ph.D. Thesis, University of Colorado, 1963.
(6) J. S. Meek and L. L. Koh, *J. Org. Chem.*, **33**, 2942 (1968).
(7) R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 3738 (1948).
(8) E. Boyland and D. Manson, *J. Chem. Soc.*, 1837 (1951).
(9) A. Etienne and Y. Lepage, *C. R. Acad. Sci.*, **240**, 1233 (1955).
(10) B. H. Klanderman and T. R. Criswell, *J. Amer. Chem. Soc.*, **91**, 510 (1969).
(11) S. J. Cristol, W. Barasch, and C. H. Tieman, *J. Amer. Chem. Soc.*, **77**, 583 (1955).
(12) S. Coffey and V. Boyd, *J. Chem. Soc.*, 2468 (1954).
(13) R. von Perger, *J. Prakt. Chem.*, **23**, 146 (1881).
(14) S. J. Cristol and M. L. Caspar, *J. Org. Chem.* **33**, 2020 (1968).
(15) Molecular models demonstrate that the only reasonable conformation is the boat form. See also ref 16.
(16) S. J. Cristol, *Accounts Chem. Res.*, **4**, 393 (1971).
(17) K. Zahn and P. Ochwat, *Justus Liebigs Ann. Chem.*, **462**, 72 (1928).

Rearrangements of Azidoquinones. XII. Thermal Conversion of 2-Azido-3-vinyl-1,4-quinones to Indolequinones[1]

Paul Germeraad and Harold W. Moore*[2]

Department of Chemistry, University of California, Irvine, California 92664

Received August 2, 1973

2-Azido-3-vinyl-1,4-quinones (**1**) thermally undergo a facile ring closure to indolequinones (**2**). The synthetic utility of this reaction is illustrated in the synthesis of 1,2,5,10-tetrahydro-3*H*-pyrrolo[1,2-*a*]benzo[*f*]indole-5,10-dione (**12**), the naphthoquinone analog of the mitosene ring system. The mechanism of the thermal ring closure is also discussed and, based upon kinetic data, a concerted process is suggested.

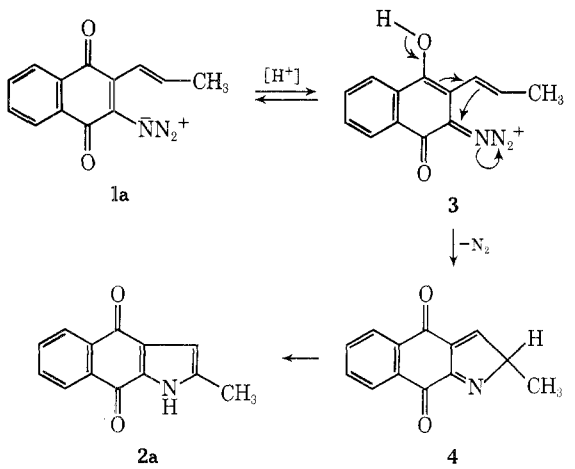
Azidoquinones are uniquely versatile synthetic reagents which are easily prepared and relatively stable under normal laboratory conditions. They are penultamate precursors to a large variety of other compounds, *e.g.*, α-cyanoalkylidene-$\Delta^{\alpha,\beta}$-butenolides,[3] 2-cyano-4-cyclopentene-1,3-diones,[4] azepine-2,5-diones,[5] diacyl cyanides,[6] 3-cyano-2-aza-1,4-quinones,[7] aminoquinones,[8] cyanoketenes,[9] 4-acetoxy-1,2-quinone-2-(*N*-acetyl)imines,[10] *trans,trans*-1,4-

diacetoxy-*cis*,*cis*-1,4-dicyano-1,3-butadienes[10] and 2-alkenyl-2,3-dihydroindole-4,7-diones.[11] Reported here are the results of an investigation of the thermal decomposition of 2-azido-3-vinyl-1,4-quinones (1), a reaction giving high yields of indolequinones (2). This transformation constitutes a new nonoxidative route to indolequinones, a ring system whose synthesis has been dominated by the Fremy salt (potassium nitrosodisulfonate)[12] oxidations of variously substituted hydroxy and aminoindoles.[13] Unfortunately, such substituted indoles cannot be obtained in good yields by any published methods and, of course, no substituents can reside on the indole nucleus which are labile to the oxidative conditions employed. These disadvantages are circumvented by the nonoxidative thermal ring closure of the 2-azido-3-vinyl-1,4-quinones (**1a–f**) reported here.

Synthetic Scope. Thermolysis of the azidoquinones (**1a–f**) in refluxing benzene results in their smooth transformation to the respective indolequinones (**2a–f**) (Scheme I). In most cases these products precipitate from the cooled reaction solution in good to excellent yield and in a high state of purity.

The structures of the indolequinones (**2a–f**) are based primarily upon their analytical and spectral properties which are in good agreement with their formulations (Experimental Section). Their ir spectra show particularly characteristic absorptions at 3400 cm^{-1} (NH) and 1675 and 1645 cm^{-1} (C=O), and their nmr spectra show the proper absorptions and proton counts.

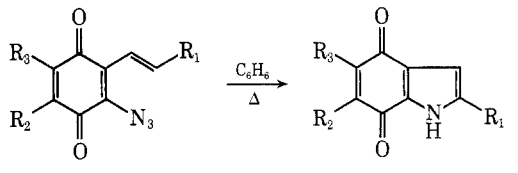
Interestingly, these ring closures can also be accomplished under photolytic or acidic conditions. Photolysis of benzene solutions of the azidoquinones (**1a, 1b,** and **1d**) with 3600-Å light gave the respective indolequinones (**2a, 2b,** and **2d**). None of these reactions was allowed to go to completion since the precipitated product nearly filled the reaction tube after a few hours. However, if the recovered starting material is taken into account, the yields are nearly quantitative. When the quinones (**1a, 1b,** and **1d**) were decomposed in concentrated sulfuric acid at 0° the corresponding indolequinones (**2a,** 67%; **2b,** 93%; and **2d,** 24%) were again isolated. This was a most unanticipated result since *all* other azidoquinones thus far studied rearrange under such acidic reaction conditions to γ-cyanoalkylidene-$\Delta^{\alpha,\beta}$-butenolides.[3] The mechanism of the formation of indolequinones under these acidic conditions is not clear. However, based upon analogy with the mechanism of butenolide formation[3] the following sequence involving the intermediate iminodiazonium ion (**3**) is envisaged.



1a **3** **2a** **4**

The synthesis of indolequinones as described herein is of particular utility since the starting materials are readily available. Several routes are reported for the construction of vinyl substituted quinones and hydroquinones;[14]

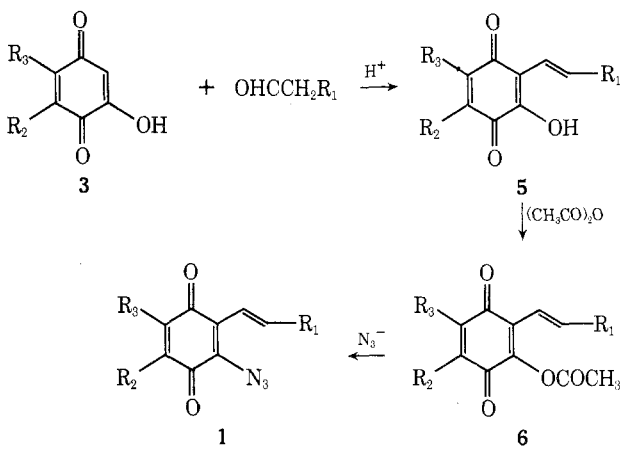
Scheme I



1 **2**

	R_1	R_2	R_3	% yield
2a	$-CH_3$	$-CH{=}CHCH{=}CH-$		90
2b	$-CH_2CH_2CH_3$	$-CH{=}CHCH{=}CH-$		81
2c	$-CH_2(CH_2)_8CH_3$	$-CH{=}CHCH{=}CH-$		87
2d	$-C_6H_5$	$-CH{=}CHCH{=}CH-$		92
2e	$-CH_2-(CH_2)_2-OCOCH_3$	$-CH{=}CHCH{=}CH-$		88
2f	$-C_6H_5$	$-CH_3$	$-CH_3$	66

Scheme II



3 **5** **1** **6**

	R_1	R_2	R_3
a	$-CH_3$	$-CH{=}CHCH{=}CH-$	
b	$-CH_2CH_2CH_3$	$-CH{=}CHCH{=}CH-$	
c	$-CH_2(CH_2)_8CH_3$	$-CH{=}CHCH{=}CH-$	
d	$-C_6H_5$	$-CH{=}CHCH{=}CH-$	
e	$-CH_2-(CH_2)_2-OCOCH_3$	$-CH{=}CHCH{=}CH-$	
f	$-C_6H_5$	$-CH_3$	$-CH_3$

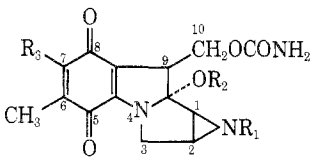
these include (1) the decarboxylation of 2,5-dihydroxycinnamic acids,[15] (2) the reduction of 2,5-dihydroxyacetophenone and subsequent dehydration,[15] (3) the reactions of Grignard reagents of hydroquinone diethers and ethylene oxide or acetaldehyde with subsequent dehydration,[15] (4) the reactions of 3-chloromethyl-4-methoxy-2-methyl-1-naphthol pivalate which is converted into the triphenyl phosphonium salt and then to vinyl derivatives by the Wittig reaction,[14] (5) the reactions of 1-hydroxy-4-methoxy-2-methyl-3-naphthaldehyde and an alkylidenetriphenylphosphorane,[14] (6) the condensation of aliphatic aldehydes with 2-hydroxy-1,4-naphthoquinone in the presence of a strong acid.[16] For the study now reported, this last method was employed since the 2-hydroxyl moiety could be converted to the desired azide *via* the corresponding acetate and its subsequent displacement with azide ion (Scheme II). This synthesis provides a general approach to a large variety of 2-azido-3-vinyl-1,4-quinones, from 2-halo-[3,4] or 2-acetoxy-3-vinyl-1,4-benzo- or -1,4-naphthoquinones, and, as a result, to the corresponding indolequinones.

Synthetic Utility. The mitomycins (**7**) constitute a synthetically challenging and biologically potent class of naturally occurring antineoplastic antibiotics.[17] Several attempts directed toward their laboratory construction

Table I
Rate of Decomposition of 2-Azido-3-(1-propenyl)-1,4-naphthoquinone as a Function of Temperature and Solvent

Temp, °C	Solvent	Time, sec^{-1}
64.30	Benzene	2.35×10^{-4}
64.30	Chlorobenzene	2.20×10^{-4}
64.30	Chlorobenzene	2.14×10^{-4}
64.30	Chlorobenzene	2.23×10^{-4}
53.65	Chlorobenzene	6.02×10^{-5}
53.65	Chlorobenzene	6.06×10^{-5}
53.65	Chlorobenzene	5.93×10^{-5}
81.38	Chlorobenzene	1.39×10^{-3}
81.38	Chlorobenzene	1.55×10^{-3}
81.38	Chlorobenzene	1.36×10^{-3}
64.30	*o*-Dichlorobenzene	2.04×10^{-4}
64.30	Dimethylformamide	2.13×10^{-4}

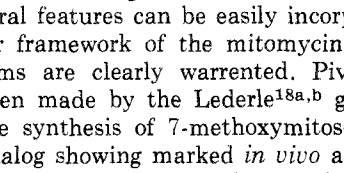
have appeared,[18] but, to date, such an objective has not been achieved.



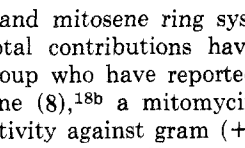
7

	R_1	R_2	R_3
Mitomycin A	H	CH_3	CH_3O
N-Methylmitomycin	CH_3	CH_3	CH_3O
Mitomycin B	CH_3	H	CH_3O
Mitomycin C	H	CH_3	NH_2
Porfiromycin	CH_3	CH_3	NH_2
7-Hydroxyporfiromycin	CH_3	CH_3	OH

One beauty of the mitomycins lies in the fact that a reasonably well-documented mechanism for their biological action has been put forward.[17] Extensive degradative studies have shown that for maximum biological potency the quinone nucleus and alkylating sites at C-1 (aziridine) and C-10 (carbamoyl) are necessary.[19] Therefore, detailed studies leading to versatile new ways in which such structural features can be easily incorporated into the molecular framework of the mitomycin and mitosene ring systems are clearly warrented. Pivotal contributions have been made by the Lederle[18a,b] group who have reported the synthesis of 7-methoxymitosene (**8**),[18b] a mitomycin analog showing marked *in vivo* activity against gram (+) bacteria. More recently, 1-substituted 7-methoxymitosenes, prepared analogously to the Lederle synthesis, were described.[18c] Also, Carelli, Cardellini, and Morlaichi[18g] have described the synthesis of 1-substituted 1,2,5,10-tetrahydro-3*H*-pyrrolo[1,2-*a*]benzo[*f*]indole-5,10-diones (**9**) by



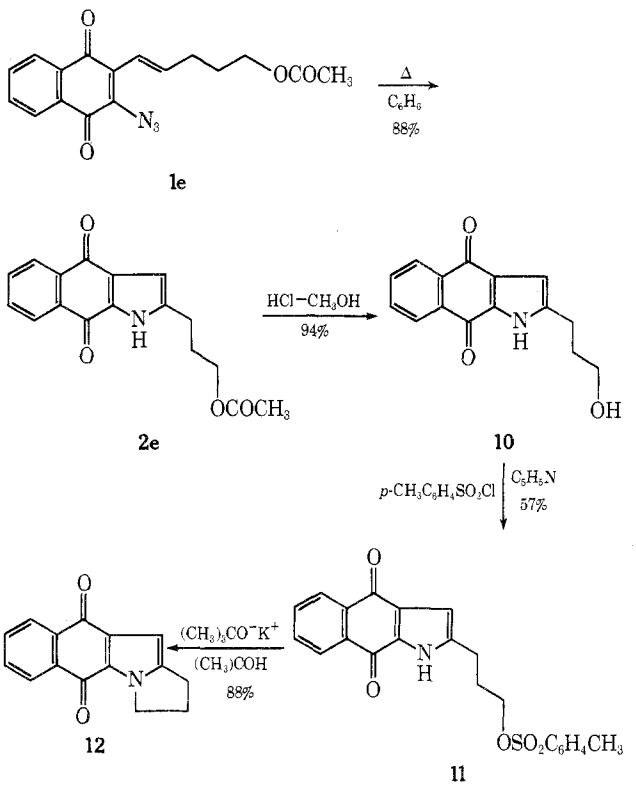
8



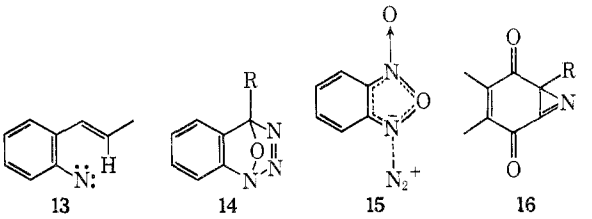
9, R = $NHCOCH_3$
R = NH_2
R = OH

the Friedel–Crafts acylation of 1-acetamido-1,2-dihydropyrrolizine with phthalic anhydride. One fundamental synthetic disadvantage of most of these reported synthetic approaches[18] to the mitomycins and related mitosenes lies in the fact that the quinone nucleus is constructed during the sequence. This often requires oxidative conditions which can cause the transformation to suffer in yields and selectivity.

The thermal ring closure of 2-azido-3-vinyl-1,4-quinones to indolequinones commences with the quinone nucleus intact. The utilization of this procedure for the elaboration of **12**, the naphthoquinone analog of the mitosene ring system, in seven steps from commercially available starting materials is now presented. Hydrolysis of 2-(3-acetoxypropyl)benzo[*f*]indole-4,9-dione (**2e**) in refluxing aqueous methanolic hydrogen chloride gave the alcohol **10** in 94% yield. Reaction of this alcohol with *p*-toluenesulfonyl chloride in pyridine gave the tosylate **11** in 57% yield which upon reaction with potassium *tert*-butoxide in *tert*-butyl alcohol gave **12** in 88% yield.

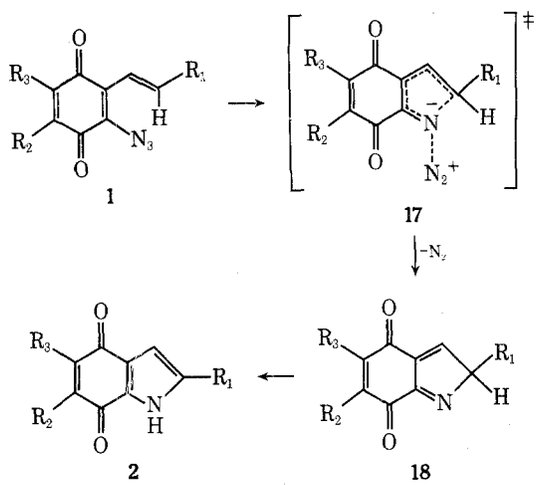


Mechanism. The closest analogies upon which to consider a mechanistic pathway for the pyrolytic conversion of 2-azido-3-vinyl-1,4-quinones to indolequinones are the observed transformations of various ortho-substituted phenyl azides to heterocyclic systems. For those compounds in which the ortho substituent has some type of α,β unsaturation, a variety of mechanistic routes have been suggested. *o*-Styryl azides efficiently ring close to indoles[20] under thermal conditions and nitrenes have been suggested as intermediates (**13**).[21] On the other hand, 2-azidobenzophenones cyclize to 3-phenylanthranils by a mechanism which apparently involves an initial cycloaddition of the azide group to the carbonyl moiety to give a triazole intermediate (**14**).[22] Finally, a concerted pathway, involving anchimeric assistance, *i.e.*, **15**, is strongly suggested for the thermal conversion of *o*-nitrophenyl azides to furoxans.[23] Consideration was given to these as well as to the feasibility of an azirine intermediate (**16**) which has



13 14 15 16

Scheme III

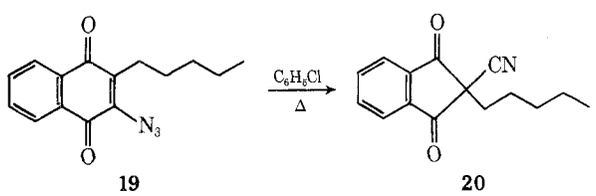


recently been shown to be generated in the thermal rearrangement of 2-azido-3-alkyl-1,4-quinones to 2-cyano-2-alkyl-4-cyclopentene-1,3-diones.[4]

The mechanism for the thermal conversion of 2-azido-3-vinyl-1,4-quinones (1) to the corresponding heterocyclic quinones (2) which best fits the available data is outlined in Scheme III. This involves anchimeric assistance by the 3-vinyl group in nitrogen loss giving the intermediate (18) which then tautomerizes to the observed products (2).

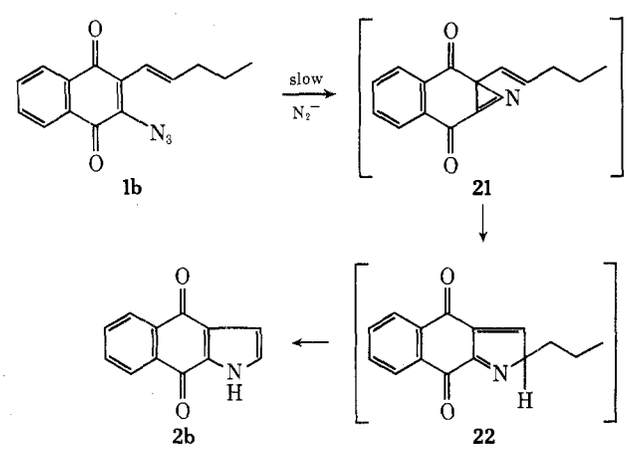
The above mechanism is based primarily upon a kinetic investigation of the thermal conversion of 2-azido-3-(1-pentenyl)-1,4-naphthoquinone (**1b**) to 2-propylbenzo[*f*]indole-4,9-dione (**2b**). The azidoquinone **1b** was thermally decomposed and the rate of nitrogen evolution was measured at three different temperatures and in several different solvents. Virtually no solvent effect was observed on the rate of decomposition of **1b** even though the range in solvent dipole moments varied from 2.30 (benzene) to 37.60 D (dimethylformamide) (Table I). The activation parameters for this clean first-order process follow: $\Delta H^* = 25.64$ kcal mol^{-1}, $\Delta S^* = +0.43$ eu.

For a comparison, the rate of the thermal decomposition of 2-azido-3-pentyl-1,4-naphthoquinone (**19**), the dihydro analog of **1b**, was also measured. This azidoquinone, now having a 3-alkyl substituent rather than a vinyl group, smoothly undergoes the known[4] ring contraction giving 2-cyano-2-pentyl-1,3-indandione (**20**). In chlorobenzene at 72.19° the rate of this reaction is 32 times slower than that for **1b** under the same conditions. The vinyl group in **1b** thus plays a direct role in nitrogen loss, and this participation is envisaged as represented by structure **17**.



The above experimental data are in good agreement with the mechanistic route outlined in Scheme III. A nitrene intermediate cannot account for the rate enhancement of **1b** over **19**. In addition, those reactions known to proceed *via* nitrenes show large positive enthalpies and entropies of activation. For example, the thermal decomposition of *p*-toluenesulfonyl azide, phenyl azide, and cyclohexyl azide show respectively the following activation parameters: $\Delta H^* = 36.5$ kcal mol^{-1}, $\Delta S^* = +7.0$ eu (*p*-toluenesulfonyl azide);[24] $\Delta H^* = 39.0$ kcal mol^{-1}, $\Delta S^* = +18.7$ eu (phenylazide);[25] $\Delta H^* = 47.5$ kcal mol^{-1}, $\Delta S^* = +32.0$ eu (cyclohexyl azide).[25] Comparison of these to $\Delta H^* = 25.64$ kcal mol^{-1} and $\Delta S^* = 0.43$ eu for **1b** argue against a nitrene mechanism for the thermal decomposition of **1b**. The entropy of activation for this reaction is also not in agreement to that which would be expected for a mechanism involving an intramolecular cycloaddition of the azide to the vinyl double bond giving a triazole analogous to **14**. Such a process would be expected to show a large negative entropy of activation. For example, in the addition of phenyl azide to alkenes, values of -30 to -35 eu have been reported.[26] For an intramolecular process ΔS^* would certainly be less negative but not actually positive as is observed here. Indeed, the thermal conversion of 2-azidobenzophenones to 3-phenylanthranils has been shown to involve such an intramolecular 1,3-dipolar cycloaddition giving **14** and the observed entropies of activation range from -6 to -21 eu.[22]

A conceivable mechanism for the cyclization reaction reported here would involve the concerted formation of the azirine **21** followed by ring expansion and subsequent tautomerization to **2b**. There are, in fact, literature precedents for these steps; *i.e.*, 2-azido-3-alkyl-1,4-quinones rearrange to 2-cyano-2-alkyl-4-cyclopentene-1,3-diones *via* an initial rate-determining azirine formation step[4] and 1-azido-1,3-butadienes thermally or photolytically decompose and rearrange to pyrroles *via* an intermediate vinyl substituted azirine.[27] This mechanism would predict that



the activation parameters for the conversion of **1b** to **2b** would be in the same range as those observed for the ring contraction of 2-azido-3-alkyl-1,4-quinones to 2-cyano-2-alkyl-4-cyclopentene-1,3-diones. This is in fact true; the enthalpies of activation for this latter reaction range from 26 to 27.6 kcal mol^{-1} and the entropies of activation from -4.6 to $+1.6$ eu.[4] However, the above mechanism does not account for the fact that 2-azido-3-pentyl-1,4-naphthoquinone (**19**) decomposes 32 times slower than 2-azido-3-(1-pentenyl)-1,4-naphthoquinone (**1b**), and for this reason the azirine mechanism is disregarded. This leaves as the most reasonable possibility, the mechanism outlined in Scheme III. Such a process would be expected to show a moderate ΔH^* and a very small if not negative ΔS^*. It should show little if any solvent effect and the absolute rate should be enhanced over that observed for the 2-alkyl series **19**. As indicated above, all such criteria were experimentally verified.

Experimental Section

2-Methylbenzo[*f*]indole-4,9-dione (2a). A solution of 103.3 mg (0.432 mmol) of 2-azido-3-(1-propenyl)-1,4-naphthoquinone (**1a**) in 15 ml of anhydrous benzene was refluxed for 1 hr. Upon cooling to 5° the yellow crystalline indole (**2a**) precipitated giving 32.2 mg (90% yield), mp 304–305° dec.

Anal. Calcd for $C_{13}H_9NO_2$: C, 73.92; H, 4.29; N, 6.63. Found: C, 73.81; H, 4.33; N, 6.76.

Characteristic spectral properties for **2a** follow: ir (Nujol, cm^{-1}) 3300, 1675, 1645; nmr (DMSO-d_6, δ) 2.31 s (3), 6.45 s (1), 7.5–8.2 m (4); uv ($CHCl_3$, nm) 261.5 (34.4×10^3).

2-Propylbenzo[*f*]indole-4,9-dione (2b). A solution of 69.2 mg (0.259 mmol) of 2-azido-3-(1-pentenyl)-1,4-naphthoquinone (**1b**) in 10 ml of anhydrous benzene was refluxed for 55 min. The solution was then concentrated to 1 ml *in vacuo* and cooled which resulted in the precipitation of 50 mg (81% yield) of 2-propylbenzo-[*f*]indole-4,9-dione (**2b**), mp, 211–212°.

Anal. Calcd for $C_{15}H_{13}NO_2$: C, 75.31; H, 5.44; N, 5.86. Found: C, 75.05; H, 5.62; N, 5.90.

Characteristic spectral properties for **2b** follow: ir (Nujol, cm^{-1}) 3240, 1655, 1640; nmr (DMSO-d_6, δ) 0.91 t (3) J = 6.5 Hz, 1.3–1.9 m (2), 2.3–2.8 m (2), 6.43 bs (1), 7.5–8.2 m (4); uv ($CHCl_3$, nm) 263.0 (32.4×10^3).

2-Decylbenzo[*f*]indole-4,9-dione (2c). A solution of 103.3 mg (0.283 mmol) of 2-azido-3-(1-dodecenyl)-1,4-napthoquinone (**1c**) in 10 ml of anhydrous benzene was refluxed for 5 hr. The solution was cooled and 10 ml of petroleum ether (bp 60–110°) was added. Upon cooling at 5° for 12 hr, 72.7 mg (76% yield) of the indolequinone **2c** precipitated and was collected. The mother liquor was concentrated *in vacuo* and the residue was recrystallized from petroleum ether giving 10.3 mg of **2c**. This brought the total yield of 2-decylbenzo[*f*]indole-4,9-dione (**2c**) to 83 mg (87% yield), mp 154–155°.

Anal. Calcd for $C_{22}H_{27}NO_2$: C, 78.34; H, 8.01; N, 4.15. Found: C, 78.46; H, 8.01; N, 4.18.

Characteristic spectral properties for **2c** follow: ir (Nujol, cm^{-1}) 3200, 1670; nmr ($CDCl_3$, δ) 0.85 t (3), 1.10–1.47 m (16), 2.41–2.96 m (2), 6.59 bs (1), 7.57–8.34 m (4); uv ($CHCl_3$, nm) 262.0 (31.7×10^3).

2-Phenylbenzo[*f*]indole-4,9-dione (2d). A solution of 536.7 mg (1.78 mmol) of 2-azido-3-(2-phenylvinyl)-1,4-naphthoquinone (**1d**) in 50 ml of anhydrous benzene was refluxed for 2 hr. The solution was then cooled to 5° and 446.8 mg (92% yield) of 2-phenylbenzo-[*f*]indole-4,9-dione (**2d**) was collected, mp 304–305° dec.

Anal. Calcd for $C_{18}H_{11}NO_2$: C, 79.12; H, 4.03; N, 5.13. Found: C, 78.86; H, 4.13; N, 5.03.

Characteristic spectral properties for **2d** follow: ir (Nujol, cm^{-1}) 3220, 1670, 1635; nmr (DMSO-d_6, δ) 7.3–8.2 m; uv ($CHCl_3$, nm) 289.0 (32.8×10^3).

2-(3-Acetoxypropyl)benzo[*f*]indole-4,9-dione (2e). A solution of 100.9 mg (0.31 mmol) of 2-azido-3-(5-acetoxy-1-pentenyl)-1,4-naphthoquinone (**1e**) in 10 ml of anhydrous benzene was refluxed for 75 min and then cooled to 5°. The yellow crystalline precipitate which formed was collected and washed with petroleum ether. The crystals were then dried to give 81.0 mg (88% yield) of 2-(3-acetoxypropyl)benzo[*f*]indole-4,9-dione (**2e**), mp 180–181°.

Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.69; H, 5.05; N, 4.71. Found: C, 68.46; H, 4.85; N, 4.91.

Characteristic spectral properties of **2e** follow: ir (Nujol, cm^{-1}) 3140, 1730, 1670, 1640; nmr (DMSO-d_6) 1.71–2.24 m (2), 1.99 s (3), 2.71 t (2) J = 7 Hz, 4.00 t (2) J = 6.5, 7.31 s (1), 7.62–8.13 m (4); uv ($CHCl_3$, nm) 261.0 (33.2×10^3).

5,6-Dimethyl-2-phenylindole-4,7-dione (2f). A solution of 66.7 mg (0.24 mmol) of 2-azido-3-(2-phenylvinyl)-5,6-dimethyl-1,4-benzoquinone (**1f**) in 7 ml of anhydrous benzene was refluxed for 2.2 hr. Upon cooling at 5° for several hours 29.8 mg (66% yield) of 5,6-dimethyl-2-phenylindole-4,7-dione (**2e**) was collected, mp 291–292°.

Anal. Calcd for $C_{16}H_{13}NO_2$: C, 76.49; H, 5.18; N, 5.58. Found: C, 76.00; H, 5.23; N, 5.47.

Characteristic spectral properties of **2e** follow: ir (Nujol, cm^{-1}) 3260, 1670, 1640; nmr (DMSO-d_6) 1.98 s (6), 7.00 s (1), 7.32–8.07 m (5); uv ($CHCl_3$, nm) 280.5 (36.0×10^3).

Acid-Catalyzed Decomposition of 2-Azido-3-(1-propenyl)-1,4-napthoquinone (1a). Formation of 2-Methylbenzo[*f*]indole-4,9-dione (2a). 2-Azido-3-(1-propenyl)-1,4-naphthoquinone (**1a**) (102.9 mg, 0.4 mmol) was slowly added in very small portions to rapidly stirred cold (0–5°) concentrated sulfuric acid (10 ml). The solution turned dark and gas was evolved upon addition of the azide. After complete addition, the solution was stirred for an additional 5 min and then poured into water. The resulting precipitate (60.4 mg, 67% yield) was collected and shown to be 2-methylbenzo[*f*]indole-4,9-dione (**2a**) by comparison of its spectral properties to those of an authentic sample which was prepared as described above.

Acid-Catalyzed Decomposition of 2-Azido-3-(1-pentenyl)-1,4-napthoquinone (1b). Formation of 2-Propylbenzo[*f*]indole-4,9-dione (2b). 2-Azido-3-(1-pentenyl)-1,4-naphthoquinone (**1b**) (101.2 mg, 0.38 mmol) was slowly added to cold (0–5°) concentrated sulfuric acid (10 ml). Vigorous stirring was maintained throughout the addition. After complete addition, the reaction solution was stirred an additional 5 min and then poured into water. The resulting precipitate (83.9 mg, 93% yield) was collected and shown to be 2-propylbenzo[*f*]indole-4,9-dione (**2b**) by comparison of its spectral properties to those of an authentic sample.

Acid-Catalyzed Decomposition of 2-Azido-3-(2-phenylvinyl)-1,4-naphthoquinone (1d). Formation of 2-Phenylbenzo[*f*]indole-4,9-dione (2d). 2-Azido-3-(2-phenylvinyl)-1,4-naphthoquinone (**1d**) (110.9 mg, 0.37 mmol) was ground in a mortar with 0.4 g of calcium chloride. This mixture was then added in very small portions to 12 ml of rapidly stirred and cold (0–5°) concentrated sulfuric acid. The addition took 40 min and then the solution was allowed to return to room temperature with continued stirring. The solution was then poured into ice and the resulting precipitate recrystallized from benzene to give 24.2 mg (24% yield) of 2-phenylbenzo[*f*]indole-4,9-dione (**2d**), as determined by comparison of its spectral properties to those of an authentic sample.

Photolysis of 2-Azido-3-(1-propenyl)-1,4-naphthoquinone (1a). Formation of 2-Methylbenzo[*f*]indole-4,9-dione (2a). A solution of 130.6 mg (0.5 mmol) of 2-azido-3-(1-propenyl)-1,4-naphthoquinone (**1a**) in 15 ml of anhydrous benzene was irradiated with 3600-Å light for 1 hr while nitrogen was continuously passed through the solution. The solvent was then removed *in vacuo* and the residue analyzed by nmr which showed it to be a mixture of staring azide (30%) and 2-methylbenzo[*f*]indole-4,9-dione (**2a**) (70%). Trituration of the crude residue with benzene gave 51.7 mg (45% yield) of the indolequinone (**2a**).

Photolysis of 2-Azido-3-pentenyl-1,4-naphthoquinone (1b). Formation of 2-Propylbenzo[*f*]indole-4,9-dione (2b). A solution of 102.7 mg (0.39 mmol) of 2-azido-3-pentenyl-1,4-naphthoquinone (**1b**) in 10 ml of anhydrous benzene was irradiated with 3600-Å light for 2.5 hr while nitrogen was continuously passed throeugh the solution. Petroleum ether (4 ml) was then added and the solution cooled for several hours. The resulting precipitate (72.3 mg, 79% yield) was shown to be 2-propylbenzo[*f*]indole-4,9-dione (**2b**) by comparing its physical and spectral properties to those of an authentic sample.

Photolysis of 2-Azido-3-(2-phenylvinyl)-1,4-naphthoquinone (1d). Formation of 2-phenylbenzo[*f*]indole-4,9-dione (2d). A solution of 106.7 mg (0.35 mmol) of 2-azido-3-(2-phenylvinyl)-1,4-naphthoquinone (**1d**) in 11 ml of benzene was irradiated for 45 min with 3600-Å light while nitrogen was continuously passed through the solution. The precipitate which formed during this period was collected to give 29.1 mg (30% yield) of 2-phenylbenzo-[*f*]indole-4,9-dione (**2d**). The mother liquor was concentrated *in vacuo* and analyzed by nmr spectroscopy which showed it to be composed of approximately 50% starting azide and 50% **2d**.

2-Azido-3-(1-propenyl)-1,4-naphthoquinone (1a). To a solution of 380 mg (1.5 mmol) of 2-acetoxy-3-(1-propenyl)-1,4-naphthoquinone (**6a**)[16] in 25 ml of 95% ethanol was added 98 mg (1.5 mmol) of sodium azide dissolved in 2 ml of water. The reaction solution was stirred overnight and then 50 ml of water was added giving an orange precipitate. Recrystallization of this crystalline solid gave 50 mg (14% yield) of 2-azido-3-(1-propenyl)-1,4-naphthoquinone (**1a**), mp 112° dec.

Characteristic spectral properties of **1a** follow: ir (Nujol, cm^{-1}) 2100, 1645; nmr ($CDCl_3$, δ) 1.98 doublet of doublets (3) J = 6.2, 1.4 Hz, 6.57 d (1) J = 17 Hz, 7.10 m (1), 7.6–8.3 m (4).

2-Azido-3-(1-pentenyl)-1,4-naphthoquinone (1b). A solution of 2.1 g (7.4 mmol) of 2-acetoxy-3-(1-propenyl)-1,4-naphthoquinone (**6b**) in 200 ml of 95% ethanol was cooled to 5° and 0.53 g of sodium azide in 5 ml of water was added. The mixture was stirred for 12 hr and then 200 ml of water was added and the mixture cooled at −5° for an additional 12 hr. The resulting precipitate was collected and recrystallized from a chloroform–methanol–water mixture to give 0.51 g (26% yield) of yellow crystalline 2-azido-3-(1-propenyl)-1,4-naphthoquinone (**1b**), mp 70–71° dec.

Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.42; H, 4.87; N, 15.73. Found: C, 67.27; H, 4.77; N, 15.55.

Characteristic spectral properties for **1b** follow: ir (Nujol, cm^{-1}) 2105, 1660, 1625; nmr ($CDCl_3$, δ) 0.94 t (3) J = 6.5 Hz, 1.2–1.9 m (2), 2.0–2.5 m (2), 6.48 bd (1) J = 18 Hz, 6.8–7.4 m (1), 7.5–8.2 m (4); uv ($CHCl_3$, nm) 273.0 (24.8×10^3).

2-(1-Dodecenyl)-3-hydroxy-1,4-naphthoquinone (5c). A solution of 5.0 g (37.0 mmol) of 2-hydroxy-1,4-naphthoquinone in 85 ml of acetic acid was warmed to 75°, and 25 ml of concentrated hydrochloric acid and 41 ml of dodecanal were added. The resulting solution was rapidly stirred at 75–80° for 30 min and then poured into 300 ml of water and allowed to stand at ambient

temperature for 6 hr. The oily mixture was then extracted with 300 ml of benzene. The benzene solution was extracted with 1% sodium hydroxide (500 ml). This basic solution was then washed twice with benzene, acidified, and finally extracted with dichloromethane. The dried ($MgSO_4$) dichloromethane solution was concentrated *in vacuo* to give a brown oil which was absorbed onto 70 g of silica gel. This was then placed in a Soxhlet extraction thimble and extracted with petroleum ether (30–60°) for 14 hr. Evaporation of the solvent gave 34 mg of the crude orange solid 2-(1-dodecenyl)-3-hydroxy-1,4-naphthoquinone, mp 65–77°. This was then recrystallized from benzene–petroleum ether to give the pure product, mp 91–92°.

Characteristic spectral properties of **5c** follow: ir (Nujol, cm^{-1}) 3500, 1670; nmr ($CDCl_3$, δ) 0.87 t (3) J = 7 Hz, 1.12–2.56 m (16), 2.01–2.48 m (2), 6.49 d (1) J = 17 Hz, 6.80–7.27 m (1), 7.46–8.15 m (4).

2-Acetoxy-3-(1-dodecenyl)-1,4-naphthoquinone (6c). A solution of 34 mg (1.0 mmol) of 2-(1-dodecenyl)-3-hydroxy-1,4-naphthoquinone in 12 ml each of acetic anhydride and pyridine was allowed to stand at ambient temperature for 24 hr and then poured into ice. The resulting precipitate was filtered and washed with 5% sulfuric acid and then water to give 20 mg (52% yield) of the acetate (**6c**). Recrystallization from ethanol gave pure 2-acetoxy-3-(1-dodecenyl)-1,4-naphthoquinone (**6c**), mp 74–76°.

Characteristic spectral properties of **6c** follow: ir (Nujol, cm^{-1}) 1770, 1670; nmr ($CDCl_3$, δ) 0.84 t (3) J = 7 Hz, 1.12–2.56 m (16), 2.03–2.49 m (2), 2.36 s (3), 6.79–7.32 m (2), 7.53–8.18 m (4).

2-Azido-3-(1-dodecenyl)-1,4-naphthoquinone (1c). a solution of 1.75 g (4.9 mmol) of 2-acetoxy-3-(1-dodecenyl)-1,4-naphthoquinone in 75 ml of 95% ethanol was treated with 0.5 g (7.7 mmol) of sodium azide in 1 ml of water. The resulting dark solution was stirred at room temperature for 24 hr at −5°. The resulting precipitate was collected and recrystallized from chloroform–methanol (1:3) to give 30 mg (18% yield) of 2-azido-3-(1-dodecenyl)-1,4-naphthoquinone, mp 59–60°.

Characteristic spectral properties of (**1c**) follows: ir (Nujol, cm^{-1}) 2110, 1670; nmr ($CHCl_3$, δ) 0.88 t (3), 1.11–1.50 m (16), 2.05–2.49 m (2), 6.57 d (1) J = 17 Hz, 6.98–7.37 m (1), 7.64–8.22 m (4); uv ($CHCl_3$, nm) 273.0 (19.0 × 10^3).

2-Azido-3-(2-phenylvinyl)-1,4-naphthoquinone (1d). To a solution of 2.0 g (6.3 mmol) of 2-acetoxy-3-(2-phenylvinyl)-1,4-naphthoquinone (**6d**) in 400 ml of 95% ethanol was added 455 mg (7 mmol) of sodium azide in 10 ml of water. The resulting precipitate (1.76 g) was recrystallized from chloroform–methanol to give 1.1 g (58% yield) of red crystalline 2-azido-3-(2-phenylvinyl)-1,4-naphthoquinone (**1d**), mp 119° dec.

Anal. Calcd for $C_{18}H_{11}N_3O_2$: C, 71.76, H, 3.65; N, 13.95. Found: C, 71.56; H, 3.77; N, 13.93.

Characteristic spectral properties of **1d** follow: ir (Nujol, cm^{-1}) 2105, 1655; nmr ($CDCl_3$, δ) 7.1–8.3 m; uv ($CDCl_3$, nm) 290.0 (30 × 10^3).

2-Hydroxy-3-(5-hydroxy-1-pentenyl)-1,4-naphthoquinone (5e). A solution of 10.0 g (75 mmol) of 2-hydroxy-1,4-naphthoquinone in 175 ml of glacial acetic acid was heated to 80° and rapidly stirred while 30 ml of concentrated hydrochloric acid and 40 ml (3.75 mmol) of 5-hydroxypentanal were added. After an initial temperature rise to 85° the solution was maintained at 75–80° for 20 min and then poured into 1 l. of water. The resulting black oil was washed twice with 500-ml portions of 1% sodium hydroxide. This aqueous basic solution was acidified and then extracted twice with ether. Evaporation of the ether extract gave 3.09 g (16% yield) of the yellow-brown 2-hydroxy-3-(5-hydroxy-1-pentenyl)-1,4-naphthoquinone (**5e**). This solid could be used without further purification. However, it could be puried further by Soxhlet extraction using 30–60° petroleum ether to give 2-hydroxy-3-(5-hydroxy-1-pentenyl)-1,4-naphthoquinone as an orange solid, mp 100–110°.

Characteristic spectral properties of **5e** follow: ir (Nujol, cm^{-1}) 3470, 1675; nmr ($CDCl_3$, δ) 1.79 m (2), 2.30 t (2) J = 7 Hz, 3.65 t (2) J = 6.5 Hz, 6.33–7.04 m (2), 7.48–8.07 m (4).

2-Aceetoxy-3-(5-acetoxy-1-pentenyl)-1,4-naphthoquinone (6e). A solution of crude 2-hydroxy-3-(5-hydroxy-1-pentenyl)-1,4-naphthoquinone (3.09 g, 11.9 mmol) in 40 ml of a 1:1 mixture of acetic anhydride–pyridine was allowed to stand at ambient temperature for 24 hr. It was then poured into ice water and the resulting precipitate was chromatographed on 250 g of silica gel using dichloromethane as the eluent giving 2.37 g (58% yield) of 2-acetoxy-3-(5-acetoxy-1-pentenyl)-1,4-naphthoquinone (**6e**), mp 75–76°.

Anal. Calcd for $C_{19}H_{18}O_6$: C, 66.67; H, 5.26. Found: C, 66.93; H, 5.38.

Characteristic spectral properties for **6e** follow: ir (Nujol, cm^{-1}) 1760, 1730, 1670; nmr ($CDCl_3$, δ) 1.80 m (2), 2.02 s (3), 2.29 t (2) J = 6.5 Hz, 2.38 s (3), 4.07 t (2) J = 6.5 Hz, 6.18–7.22 m (2), 7.51–8.13 m (4).

2-Azido-3-(5-acetoxy-1-pentenyl)-1,4-naphthoquinone (1e). A solution of 1.53 g (4.48 mmol) of 2-acetoxy-3-(5-acetoxy-1-pentenyl)-1,4-naphthoquinone (**6e**) in 23 ml of 95% ethanol was treated with 1.45 g (22.4 mmol) of sodium azide in 5 ml of water. The solution was cooled to −5° and allowed to stand for 12 hr. The resulting yellow crystalline solid was collected giving 400 mg (27% yield) of 2-azido-3-(5-acetoxy-1-pentenyl)-1,4-naphthoquinone (**1e**), mp 41–42°.

Characteristic spectral properties of **1e** follow: ir (Nujol, cm^{-1}) 2100, 1725, 1670; nmr ($CDCl_3$, δ) 1.58–2.01 m (2), 2.03 s (3), 2.29 t (2) J = 6.5 Hz, 4.09 t (2) J = 6.5 Hz, 6.30–7.31 m (2), 7.52–8.13 m (4).

2,3-Dimethyl-5-hydroxy-6-(2-phenylvinyl)-1,4-benzoquinone (5f). A solution of 2,3-dimethyl-5-hydroxy-1,4-benzoquinone (4.20 g, 27.6 mmol) in 85 ml of glacial acetic acid was vigorously stirred at 75° while 14.2 ml of concentrated sulfuric acid and a solution of 16.2 ml of concentrated sulfuric acid, 16.2 ml of phenylacetaldehyde, and 16.2 ml of 95% ethanol was added. After 20 min at 75–80° the reaction solution was poured into water (800 ml). The resulting residue was washed several times with water, dissolved in benzene, and then extracted with 500 ml of 1% sodium hydroxide. Upon acidification 3.60 g (51% yield) of purple 2,3-dimethyl-5-hydroxy-6-(2-phenylvinyl)-1,4-benzoquinone (**5f**) was collected. Recrystallization from benzene–petroleum ether gave the pure product, mp 165–167°.

Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.59; H, 5.51. Found: C, 75.71; H, 5.64.

Characteristic spectral properties of **5f** follow: ir (Nujol, cm^{-1}) 3350, 1625; nmr ($CDCl_3$, δ) 2.03 s (6), 5.27 s (1), 7.01–7.98 m (7).

2-Acetoxy-5,6-dimethyl-3-(2-phenylvinyl)-1,4-benzoquinone (6f). A solution of 3.60 g (14.2 mmol) of 2,3-dimethyl-5-hydroxy-6-(2-phenylvinyl)-1,4-benzoquinone (**5f**) in 10 ml of acetic anhydride–pyridine (1:1) was allowed to stand at ambient temperature for 12 hr and then poured into water. The resulting residue was chromatographed on 300 g of silica gel using dichloromethane as the eluent to give 90 mg (12% yield) of 2-acetoxy-5,6-dimethyl-3-(2-phenylvinyl)-1,4-benzoquinone (**6f**), mp 145–146°.

Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.97; H, 5.41. Found: C, 72.64; H, 5.80.

Characteristic spectral properties of **6f** follow: ir (Nujol, cm^{-1}) 1670, 1650; nmr ($CDCl_3$, δ) 2.05 s (6), 2.38 s (3), 6.84–7.91 m (7); uv ($CHCl_3$, nm) 274.5 (19.6 × 10^3).

2-Azido-5,6-dimethyl-3-(2-phenylvinyl)-1,4-benzoquinone (1f). A solution of 942 mg (3.1 mmol) of 2-acetoxy-5,6-dimethyl-3-(2-phenylvinyl)-1,4-benzoquinone (**6f**) in 75 ml of 95% ethanol was treated with 228 mg (3.5 mmol) of sodium azide in 7 ml of water. It was then cooled to −5° and allowed to stand overnight. The precipitate which had formed was collected to give quantitatively the crude azide. Recrystallization from chloroform–methanol–water gave pure 2-azido-5,6-dimethyl-3-(2-phenylvinyl)-1,4-benzoquinone (**1f**), mp 87–88° dec.

Characteristic spectral properties for **1f** follow: ir (Nujol, cm^{-1}) 2100, 1645; nmr ($CDCl_3$, δ) 2.06 s (6), 7.02–8.15 m (7).

2-(3-Hydroxypropyl)benzo[*f*]indole-4,9-dione (10). A suspension of 2-(3-acetoxypropyl)benzo[*f*]indole-4,9-dione (197.3 g, 0.66 mol) in 20 ml of methanol, 4 ml of water, and 8 drops of concentrated hydrochloric acid was refluxed for 2 hr. It was then poured into water and cooled at −5° for 12 hr. The resulting yellow crystalline precipitate was collected to give 158.9 mg (94% yield) of 2-(3-hydroxypropyl)benzo[*f*]indole-4,9-dione (10), mp 214–216°.

Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.59; H, 5.10; N, 5.49. Found: C, 70.46; H, 5.03; N, 5.22.

Characteristic spectral properties of **10** follows: ir (Nujol, cm^{-1}) 3400, 3200, 1670, 1640; nmr (DMSO-d_6, δ) 1.94–2.37 m (2), 2.82 t (2) J = 7 Hz, 3.66 t (2) J = 6.5 Hz, 6.52 s (1), 7.67–8.28 m (4); uv ($CHCl_3$, nm) 262.5 (33.5 × 10^3).

2-(3-Tosylpropyl)benzo[*f*]indole-4,9-dione (11). A solution of 68.4 mg (0.27 mmol) of 2-(3-hydroxypropyl)benzo[*f*]indole-4,9-dione (**10**) and 108.3 mg (0.57 mmol) of *p*-toluenesulfonyl chloride in 1 ml of anhydrous pyridine was allowed to stand at ambient temperature for 24 hr. The reaction solution was then poured into water and the resulting yellow crystalline precipitate was collected to give 62.8 mg (57% yield) of 2-(3-tosylpropyl)benzo[*f*]indole-4,9-dione (**11**), mp 210–211°.

The infrared spectrum (Nujol) showed characteristic absorptions at 3250, 1645, and 1175 cm^{-1}.

1,2,5,10-Tetrahydro-3*H*-pyrrolo[1,2-*a*]benzo[*f*]indole-5,10-

dione (12). 2-(3-Tosylpropyl)benzo[*f*]indole-4,7-dione (0.0628 g, 0.000154 mol) was added under nitrogen to a solution consisting of potassium (0.0060 g, 0.000154 mol) dissolved in 1.5 ml of dry *tert*-butyl alcohol. The resulting purple suspension was magnetically stirred for 24 hr. At this time the yellow-green suspension was poured into 10 ml of water. The residue was collected by filtration and washed with water to give 0.0322 g (88% yield) og benzo[*f*]-pyrrolidinyl[1,2-α]indole-4,7-dione, mp 181–184°. An analytical sample, mp 188–189°, was obtained by recrystallization from chloroform–petroleum ether.

Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.95; H, 4.64, N, 5.91. Found: C, 75.76; H, 4.60; N, 6.02.

Characteristic spectral properties of **12** follow: ir (Nujol, cm^{-1}) 1660; nmr ($CDCl_3$, δ) 2.33–3.07 m (4), 4.33 t (2) J = 6.5 Hz, 6.41 s (1), 7.54–8.35 m (4); uv ($CHCl_3$, nm) 262.0 (33.5×10^3).

2-Acetoxy-3-pentyl-1,4-naphthoquinone. 2-Hydroxy-3-pentyl-1,4-naphthoquinone[16] (10.0 g, 0.039 mol) was suspended in 40 ml each of acetic anhydride and pyridine. This solution was allowed to stand overnight at room temperature. It was then poured into ice–water and extracted with ether. The ether layer was washed with 5% sulfuric acid solution and with water and then dried over anhydrous magnesium sulfate. Filtration and evaporation of the solvent gave a red semisolid. This was dissolved in an equal volume (approximately 50 ml) of hot 95% ethanol and cooled in the freezer. The yellow crystals were collected and dried to give 7.0 g. (63% yield) of 2-acetoxy-3-pentyl-1,4-naphthoquinone. This was recrystallized from ethanol to give the clean product, mp 56–57°.

Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.33; H, 6.29. Found: C, 71.27; H, 6.33.

Characteristic spectral properties of 2-acetoxy-3-pentyl-1,4-naphthoquinone follow: ir (Nujol, cm^{-1}) 1670; nmr ($CDCl_3$, δ) 0.89 t (3) J = 6 Hz, 1.08–1.68 m (6), 2.40 s (3), 2.49 q (2) J = 6 Hz, 7.63–8.30 m (4).

2-Azido-3-pentyl-1,4-naphthoquinone (19). 2-Acetoxy-3-pentyl-1,4-naphthoquinone (3.1 g, 0.011 mol) was dissolved in 30 ml of 95% ethanol by heating. When the solution had cooled to room temperature sodium azide (0.72 g, 0.011 mol) in 3 ml of water was added slowly with swirling. The solution turned dark and was allowed to stand at room temperature for 10 min. The solution was then put into the refrigerator for 18 hr. The precipitate which formed was collected, washed with a liitle methanol–water (5:1), and dried. This gave 1.5 g (51% yield) of yellow 2-azido-3-pentyl-1,4-naphthoquinone (**19**). This was recrystallized from ethanol and water to give the clean product, mp 64–66°.

Characteristic spectral properties of **19** follow: ir (Nujol, cm^{-1}) 1670 and 1640; nmr ($CDCl_3$, δ) 0.90 t (3) J = 6 Hz, 1.12–1.74 m (6), 2.58 t (2) J = 7 Hz, 7.64–8.30 m (4).

2-Cyano-2-pentyl-1,3-indandione (20). 2-Azido-3-pentyl-1,4-naphthoquinone (0.1210 g, 0.00045 mol) was refluxed in 15 ml of dry benzene for 18 hr. The solution was then rotary evaporated to a brown-gold oil. This residue was then chromatographed on a silica gel column with benzene as the solvent. A light yellow band came off first and was discarded. This was followed by another yellow band which upon evaporation of the solvent gave 0.0800 g (74% yield) of 2-cyano-2-pentyl-1,3-indandione as a light brown oil. This was recrystallized with great difficulty from petroleum ether to give the clean white product, mp 30.5–31°.

Characteristic spectral properties of **20** follow: ir (neat, cm^{-1}) 2230, 1755, 1730; nmr ($CDCl_3$, δ) 0.85 t (3), 1.06–1.68 m (6), 2.10 q (2), 8.04 s (4). These data are analogous to those reported for 2-cyano-2-methyl-1,3-indandione which was prepared by the thermolysis of 2-azido-3-methyl-1,4-naphthoquinone.[4]

Procedure for the Kinetic Runs of 2-Azido-3-(1-pentenyl)-1,4-naphthoquinone and 2-Azido-3-pentyl-1,4-naphthoquinone. The apparatus used was that described by Martin and Timberlake.[28] The solvent (10 ml) was equilibrated in the constant temperature bath with the system open to the atmosphere and then 0.08 g (0.0003 mol) of 2-azido-3-(1-pentenyl)-1,4-naphthoquinone or 0.06 g (0.0002 mol) of 2-azido-3-pentyl-1,4-naphthoquinone dissolved in 0.5 ml of the solvent was injected. Nitrogen was bubbled through the solution for 90 sec before the system was closed and the rate of the increasing pressure recorded. The reaction was allowed to go to completion in order to obtain a P_∞. The rate constants were obtained by having a computer program plot first the natural logarithm of the quantity ($P_\infty - P$) *vs.* time and then determine the slope of this line. The program also ran a least-squares fit of the points and varied the P_∞ value in order to obtain the smallest deviation. The azidoquinones used were pure as determined by their melting point, and the solvents employed were purified immediately before use.

Registry No.—**1a,** 42244-91-7; **1b,** 42244-92-8; **1c,** 42244-93-9; **1d,** 42244-94-0; **1e,** 42244-95-1; **1f,** 42244-96-2; **2a,** 42244-97-3; **2b,** 42244-98-4; **2c,** 42244-99-5; **2d,** 42207-71-6; **2e,** 42245-00-1; **2f,** 42245-01-2; **5c,** 49827-67-0; **5e,** 49827-68-1; **5f,** 49827-69-2; **6a,** 49827-70-5; **6b,** 49827-71-6; **6c,** 49827-72-7; **6d,** 49827-73-8; **6e,** 49827-74-9; **6f,** 49827-75-0; **10,** 42245-03-4; **11,** 42245-02-3; **12,** 42245-04-5; **19,** 49827-78-3; **20,** 49827-79-4; 2-hydroxy-1,4-naphthoquinone, 83-72-7; dodecanal, 112-54-9; 5-hydroxypentanal, 4221-03-8; 2,3-dimethyl-5-hydroxy-1,4-benzoquinone, 1760-68.5; phenylacetaldehyde, 122-78-1; 2-acetoxy-3-pentyl-1,4-naphthoquinone, 49827-81-8; 2-hydroxy-3-pentyl-1,4-naphthoquinone, 41245-53-8.

References and Notes

(1) A preliminary account of this work has appeared, P. Germeraad and H. W. Moore, *J. Chem. Soc., Chem. Commun.*, 358 (1973).
(2) The authors are grateful to the National Cancer Institute of the Public Health Service for Grant No. CA 11890-03 which partially supported this investigation.
(3) H. W. Moore, H. R. Shelden, D. W. Deters, and R. J. Wikholm, *J. Amer. Chem. Soc.*, **92,** 1675 (1970).
(4) W. Weyler, Jr., D. S. Pearce, and H. W. Moore, *J. Amer. Chem. Soc.*, **95,** 2603 (1973).
(5) H. W. Moore, H. R. Shelden, and W. Weyler, Jr., *Tetrahedron Lett.*, 1243 (1969).
(6) J. A. Van Allen, W. J. Priest, A. S. Marshall, and G. A. Reynolds, *J. Org. Chem.*, **33,** 1100 (1968).
(7) D. S. Pearce and H. W. Moore, unpublished data.
(8) L. F. Fieser and J. L. Hartwell, *J. Amer. Chem. Soc.*, **57,** 1482 (1935); H. W. Moore and H. R. Shelden, *J. Org. Chem.*, **33,** 4019 (1968).
(9) W. Weyler, Jr., and H. W. Moore, *J. Amer. Chem. Soc.*, **93,** 2812 (1971).
(10) D. S. Pearce, M. S. Lee, and H. W. Moore, *J. Org. Chem.*, in press.
(11) P. Germeraad, Walter Weyler, Jr., and H. W. Moore, *J. Org. Chem.*, **9,** 781 (1974).
(12) H. Zimmer, D. C. Lankin, and S. W. Horgan, *Chem. Rev.*, **71,** 229 (1971).
(13) H. J. Teuber, and G. Thaler, *Chem. Ber.*, **91,** 2253 (1958); H. J. Teuber and G. Staiger, *ibid.*, **87,** 1251 (1954); **92,** 2385, (1959); B. Clifford, P. Nixon, C. Salt, and M. Tomlinson, *J. Chem. Soc.*, 3516 (1961); G. R. Allen, J. F. Poletto, and M. J. Weiss, *J. Amer. Chem. Soc.*, **86,** 3878 (1964); W. A. Remers, P. N. James, and M. J. Weiss, *J. Org. Chem.*, **28,** 1169 (1963); G. R. Allen, J. F. Poletto, and M. J. Weiss, *J. Amer. Chem. Soc.*, **86,** 3887 (1964).
(14) W. E. Bondinell, S. J. DiMari, B. Frydman, I. Matsumoto, and H. Rapoport, *J. Org. Chem.*, **33,** 4351 (1968).
(15) H. C. Cassidy and K. A. Kun, *Polym. Rev.* **11,** 0000 (1965).
(16) S. C. Hooker, *J. Amer. Chem. Soc.*, **58,** 1163, 1168 (1936).
(17) W. Szybalski and V. N. Iyer in "Antibiotics," D. Gottlieb and P. D. Shaw, Ed., Springer-Velag, West Berlin, 1967, pp 211–245.
(18) (a) W. A. Remers, R. H. Roth, and M. J. Weiss, *J. Org. Chem.*, **30,** 2910 (1965); (b) G. R. Allen, Jr., J. F. Poletto, and M. J. Weiss, *ibid.*, **30,** 2997 (1965); (c) D. L. Fost, N. N. Ekwuribe, and W. A. Remers, *Tetrahedron Lett.*, 131 (1973); (d) T. Hirata, Y. Yamada, M. Matsui, *ibid.*, 4107 (1969); (e) R. W. Franck and K. F. Bernady, *J. Org. Chem.*, **33,** 3050 (1968); (f) R. W. Franck and J. Auerbach, *ibid.*, **36,** 31 (1971); (g) V. Carelli, M. Cardellini, and F. Morlacchi, *Tetrahedron Lett.*, 765 (1967); (h) R. J. Friary, J. M. Gilligan, R. P. Szajewski, K. J. Falci, and R. W. Franck, *J. Org. Chem.*, **38,** 3487 (1973).
(19) (a) S. Oboski, M. Matsui, S. Ishii, N. Masago, S. Wakaki, and K. Uzu, *Gann*, **58,** 315 (1967); (b) S. Kinoshita, K. Uzu, K. Nakano, M. Shimizu, and T. Takahashi, *J. Med. Chem.*, **14,** 103 (1971).
(20) R. J. Sundberg, H. F. Russell, W. V. Ligon, Jr., and L. S. Lin, *J. Org. Chem.*, **37,** 719 (1972).
(21) D. V. Banthorpe, "The Chemistry of the Azido Group," S. Patai, Ed., Interscience, New York, N. Y., 1971.
(22) J. H. Hall, F. E. Behr, and R. L. Reed, *J. Amer. Chem. Soc.*, **94,** 4952 (1972).
(23) L. K. Dyall and J. E. Kemp, *J. Chem. Soc. B*, 976 (1968).
(24) D. S. Breslow, M. F. Sloan, M. F. Newburg, and N. B. Renfrow, *J. Amer. Chem. Soc.*, **91,** 2273 (1969).
(25) P. Walker and W. A. Waters, *J. Chem. Soc.*, 1632 (1962).
(26) P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Amer. Chem. Soc.*, **87,** 306 (1965).
(27) K. Isomura, M. Okada, and H. Taniguchi, *Chem. Lett.* **1** (7), 629 (1972); *Chem. Abstr.*, **77,** 87555 (1972).
(28) J. C. Martin and J. W. Timberlake, *J. Amer. Chem. Soc.*, **92,** 978 (1970).