6bII hydrolyzed with 5% ethanolic potassium hydroxide yielding acid (+)-**6c**: $[\alpha]^{20}_{589}$ +40.0° (*c* 0.80, $CHCl_3$). Lithium aluminum hydride reduction of **6bII** gave (−)-**8**.

Acknowledgment. This work was supported by grants from the Polish Academy of Sciences (MRI-12.1.1.1 and 03.10.7.01.01).

Registry No. (*R*)-(−)-**1c**, 26315-61-7; **2**, 513-81-5; **3**, 592-57-4; (−)-**4c**, 70766-03-9; (*R*)-(+)-**5**, 70766-04-0; (±)-**5**, 70811-71-1; (±)-**6b**, 70811-72-2; **6bI**, 58437-92-6; **6bII**, 58393-27-4; (+)-**6c**, 70811-73-3; (−)-**8**, 70811-74-4; (+)-**8**, 70811-75-5; **9**, 70775-20-1; (*R*)-(+)-**10**, 70766-05-1; (*R*)-(−)-**11**, 70766-06-2; (±)-**15**, 70766-07-3; (+)-**15**, 70811-76-6; **17**, 70766-08-4; (*R*)-(−)-**18**, 53585-93-6; (±)-**19**, 70766-09-5; (−)-**19**, 70811-77-7; buta-1,3-diene, 106-99-0; (−)-ω-camphanyl chloride, 67375-29-5.

Photochemical Reaction of Duroquinone with Allenes and Ketenimines. Photoinduced Cycloaddition and Molecular Rearrangement

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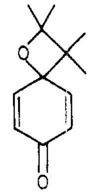
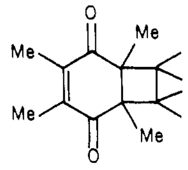
Received February 23, 1979

Photoinduced cycloadditions of duroquinone to allenes and some ketenimines and photoinduced molecular rearrangements of their adducts have been investigated. When irradiated in the presence of 1,1-dimethylallene, duroquinone afforded 7-methylenebicyclo[4.2.0]oct-3-ene-2,5-dione exclusively, whereas photocycloadditions of ketenimines occurred at the carbonyl function of duroquinone in spite of its π,π^* triplet excited state. Diphenyl-*N*-phenylketenimine afforded spiro 2-imino- and 3-iminooxetanes. Dimethyl-*N*-substituted ketenimines reacted to give hexamethyl-2-imino-1-oxaspiro[3.5]nona-5,8-dien-7-one derivatives which were isomerized by further photolysis to two consecutive products: spiro bicyclo[3.1.0]hexenones and 2-imino-3,3a-dihydrobenzofuran-6-ones. The last compounds underwent facile hydrolysis to afford hexamethyl-3,3a-dihydrobenzofuran-2,6-dione in good yields. Structural and mechanistic investigations have been done.

In recent years, much attention has been paid to the photoinduced cycloadditions of saturated and conjugated carbonyl compounds to alkenes and alkynes.[1] In photochemical reactions, *p*-quinones afford cycloadducts: oxetanes and/or cyclobutanes.[2] The first involves cycloaddition of the carbonyl function to the unsaturated C–C bond to give the oxetanes or their rearranged products,[3] and the second involves cycloaddition of the ring double bond of *p*-quinones to a C–C double or triple bond.[4] From theoretical and experimental investigations,[5] *p*-benzoquinone is thought to react from a lowest triplet state of the n,π^* excited state to yield exclusively oxetane adducts (**1**), while its tetramethyl derivative, duroquinone, whose lowest triplet should be π,π^*,[6] affords only cyclobutanes (**2**).



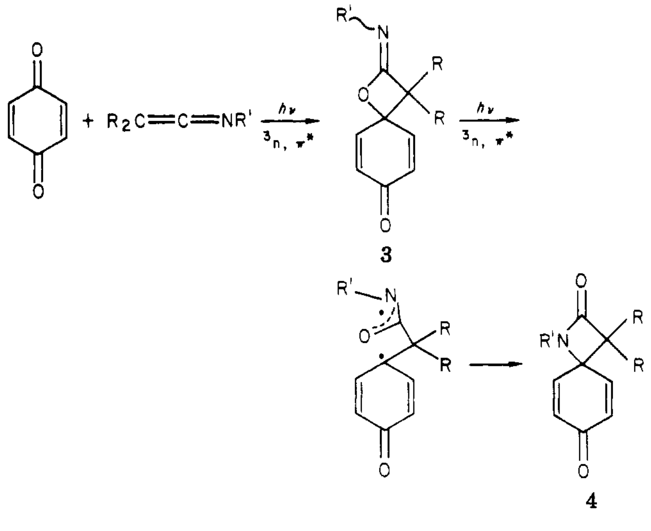
1



2

In addition, the photochemical transformations of cross-conjugated cyclohexadienones, i.e., santonin and related compounds, represent some of the most interesting and remarkable photochemical rearrangements.[7] The photoreactions of the simpler 4,4-diphenyl- and 4-methyl-4-(trichloromethyl)cyclohexa-2,5-dienones have been studied in great mechanistic detail.[8,9] In these studies, the presence of substituents on cyclohexadienones affects the types of rearrangements, solvent effects have been found to be very important, and reaction products are different, depending upon whether the solvent is neutral or acidic.[10]

Scheme I



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(1) J. M. Bruce, *Q. Rev. Chem. Soc.*, **21**, 405 (1967); P. E. Eaton, *Acc. Chem. Res.*, 1, 50 (1968); P. G. Sammes, *Q. Rev., Chem. Soc.*, **24**, 37 (1970); *Synthesis*, 636 (1970); P. G. Bauslaugh, *ibid.*, 287 (1970); P. de Mayo, *Acc. Chem. Res.*, 4, 41 (1971).

(2) J. M. Bruce in "The Chemistry of the Quinonoid Compounds", S. Patai, Ed., Wiley-Interscience, New York, N.Y., 1974, Part 2, p 478.

(3) D. Bryce-Smith, G. I. Fray, and A. Gilbert, *Tetrahedron Lett.*, 3471 (1964); H. E. Zimmermann and L. Craft, *ibid.*, 2137 (1964); M. E. Kuehe and H. Linde, *J. Org. Chem.*, 37, 4031 (1972); A. Hassner and D. J. Blythin, *ibid.*, 37, 4209 (1972).

(4) G. O. Schenck, I. Hartman, and W. Metzner, *Tetrahedron Lett.*, 347 (1965); G. Koltzenburg, K. Kraft, and G. O. Schenck, *ibid.*, 353 (1965); C. H. Krauch and S. Faid, *Chem. Ber.*, **100**, 1685 (1967).

(5) N. J. Bunce, J. E. Ridley, and M. C. Zerner, *Theor. Chim. Acta*, **45**, 283 (1977).

(6) W. Herre and P. Weis, *Spectrochim. Acta, Part A*, **29a**, 203 (1973); D. R. Kemp and G. Porter, Proc. *R. Soc. London, Ser. A*, 326, 117 (1971); M. Sebti, F. Dupuy, G. Nouchi, and Y. Rousset, *C. R. Hebd. Seances Acad. Sci., Ser. B*, **270**, 1477 (1970).

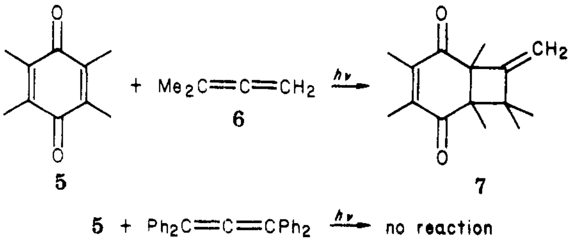
(7) H. E. Zimmermann, *Pure Appl. Chem.*, **49**, 389 (1977); W. M. Horspool, *Photochemistry*, 8, 262 (1977); O. L. Chopman and D. S. Weiss, *Org. Photochem.*, 3, 197 (1973); H. Hart, *Pure Appl. Chem.*, **33**, 247 (1973); G. Quinkert, *ibid.*, **33**, 285 (1973).

(8) H. E. Zimmermann, *Angew. Chem., Int. Ed. Engl.*, 8, 1 (1969), and references cited therein; H. E. Zimmermann and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); **84**, 4527 (1962).

(9) D. I. Schuster, *Acc. Chem. Res.*, 11, 65 (1978), and references cited therein.

(10) P. J. Kropp and W. F. Erman, *Tetrahedron Lett.*, 21 (1963); *J. Am. Chem. Soc.*, **85**, 2456 (1963); P. J. Kropp, *ibid.*, **85**, 3779 (1963); **86**, 4053 (1964).

Scheme II



We recently reported the interesting results of the photocycloadditions of *p*-quinones to ketenimines.[11] The initial adducts, 2-imino-1-oxaspiro[3.5]nona-5,8-dien-7-one derivatives, could be explained in terms of additions of the carbonyl function of *p*-quinones, from the n,π^* triplet states, to the C–C double bonds of ketenimines. By further photolysis of the adducts (**3**), the molecular rearrangements were observed to give 1-azaspiro[3.5]nona-5,8-diene-2,7-diones probably through n,π^* excited states.

We report here the photoinduced cycloadditions of duroquinone, whose lowest triplet state should be π,π^*,[6] to 1,1-dimethylallene and ketenimines. During their photoreactions, we found photoinduced molecular rearrangements of the initial adducts.

Results and Discussion

Photoreactions were carried out in a Pyrex vessel by external irradiation with a high-pressure mercury lamp under atmospheric conditions. The reactions were monitored by TLC after moderate time intervals. After a few hours of irradiation, the photoproducts were isolated by preparative TLC or column chromatography from the reaction mixtures. The isolated yields are lower limits of the extent of the photoproducts because of their photoisomerizations and decompositions on silica gel.

Photocycloaddition of Duroquinone to 1,1-Dimethylallene. Photocycloaddition of duroquinone (**5**) to 1,1-dimethylallene (**6**) was carried out in benzene solution for 7 h. Only one product was isolated in significant quantity and was shown to be a 1:1 adduct of **5** and **6** on the basis of NMR analysis. In the NMR measurement of the initial reaction mixture, the observed signals were due to the starting materials and the product **7**, and no other signals (less than 5%) could be found. Consistent with the structure assignment, the adduct **7** showed cyclohexenedione and terminal methylene at 1665, 1630, and 1655 cm^{-1} in its IR spectrum; the ^{1}H NMR spectrum also supported the structure assignment: terminal methylene δ ($CDCl_3$) 4.82 (s, 1 H) and 4.92 (s, 1 H). From these spectral data, the adduct was considered to have a cyclobutane methide structure (**7**) which would be formed by regiospecific addition of the C–C double bond of **5** across the C_1–C_2 double bond of 1,1-dimethylallene (**6**), where the allene **6** acted as a simple olefin, instead of a cyclobutane dimethylmethide or spiro oxetane structure. The preference for photocycloaddition of the C_1–C_2 double bond over the C_2–C_3 bond of 1,1-dimethylallene should be due to the electron densities of the double bonds, and these types of regioselectivities of dimethylallene photoadditions to carbonyl functions were sometimes encountered.[12]

However, the photoreaction of duroquinone (**5**) with tetraphenylallene did not occur under a similar condition, and the starting materials were recovered even after a prolonged irradiation (24 h).

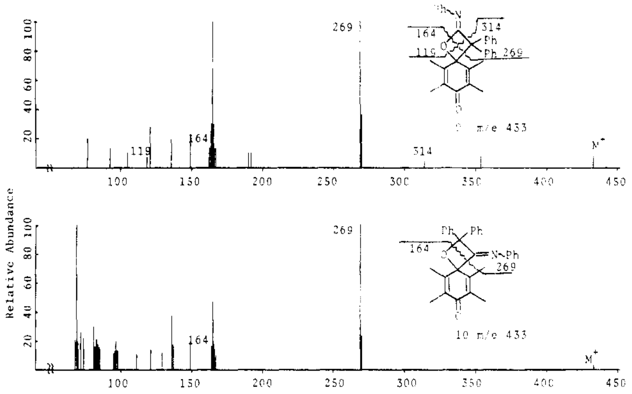
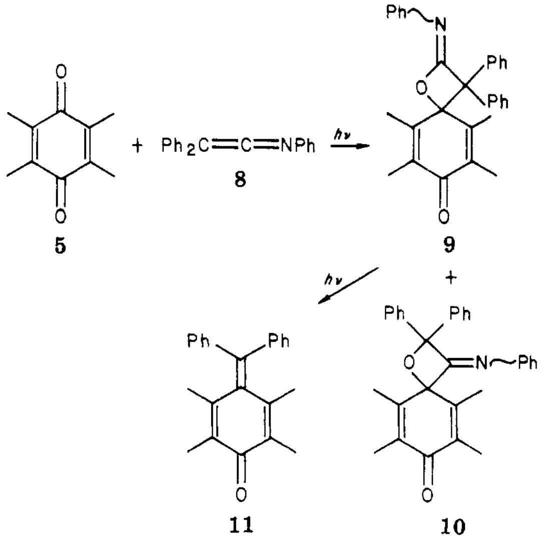


Figure 1. (Upper) Mass spectrum of the photoadduct **9**. (Lower) Mass spectrum of **10**.

Scheme III



Photocycloaddition of Duroquinone to Diphenyl-*N*-phenylketenimine. Photoinduced cycloaddition of duroquinone (**5**) to diphenyl-*N*-phenylketenimine (**8**) was examined in a similar manner. Two compounds which had quite similar NMR and UV spectral properties were isolated in 43% and 4% yields. The ratio of photoadducts initially present could not be determined because the adducts could not be distinguished in their NMR spectra and because the initial adduct photodecomposed. The IR spectra of the isolated adducts **9** and **10**, which were shown to be 1:1 adducts of duroquinone and ketenimine **8** on the basis of NMR and mass spectral analyses, exhibit strong bands due to iminooxetane at 1725 and 1750 cm^{-1} and cyclohexadienone at 1635 cm^{-1} in both compounds. The spectral data of the adduct **9** were quite similar to those of 2-imino-1-oxaspiro[3.5]nona-5,8-dien-7-one derivatives isolated by us in a previous study.[11] In addition, the assignment of the photoadducts to a spiro 2-imino- (**9**, major product) and a spiro 3-iminooxetane structure (**10**, minor product) was investigated on the basis of mass spectral cleavage patterns and photochemical properties of **9**. Namely, duroquinone diphenylmethide (**11**) was obtained by a prolonged irradiation of the isolated spiro 2-iminooxetane **9** with a partial recovery of the starting material, while spiro 3-iminooxetane **10** did not give **11**.

While the adduct **9** shows duroquinone diphenylmethide (*m/e* 314) and ketenimine (*m/e* 269) fragments, the adduct **10** shows only the ketenimine fragment at *m/e* 269 in mass spectra. This contrast in cleavages can be found in the cycloadducts of benzophenone or fluorenone to keten-

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[11] K. Ogino, S. Yamashina, T. Matsumoto, and S. Kozuka, *J. Chem. Soc., Perkin Trans. 1*, 1552 (1979).

[12] N. Ishibe, K. Hashimoto, and Y. Yamaguchi, *J. Chem. Soc., Perkin Trans. 1*, 318 (1975); H. J. T. Bos, C. Slagt, and J. S. M. Boleij, *Recl. Trav. Chim. Pays-Bas*, **89**, 1170 (1970).

imines reported by Singer and Davis.[13,14]

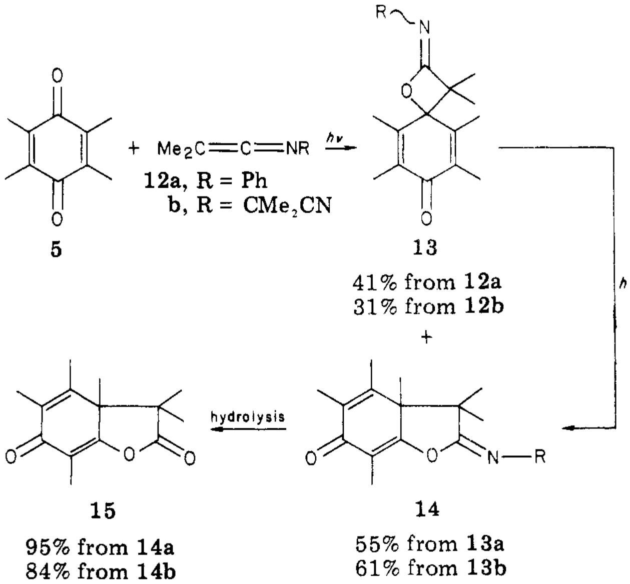
The photocycloaddition of duroquinone to ketenimine showed an entirely different mode compared with duroquinone–allene cycloaddition. One of the duroquinone–olefin systems, the photolysis with 4,5-dimethyl-1,3-diacetyl-Δ^4-imidazolin-2-one, has been known to give the initial adduct at the carbonyl group of duroquinone.[15] At this time we have no reasonable explanation for the difference in regioselectivity observed in cycloadditions between allene and ketenimine; however, the excited carbonyl function of duroquinone should add to the ground-state ketenimine to form the photoadducts **9** and **10** across the C–C double bond and not across the C=N bond of ketenimine. Iminooxetane formation may be explained by the extent of dipole–dipole interactions between the π,π^* excited state of the carbonyl group of duroquinone and ketenimine to cause the lack of the reactivity of the ring double bond of duroquinone.

The preference for the formation of the adduct **9** over the adduct **10** should be explainable in terms of steric and dipolar interactions in the transition state. The different types of cycloadducts, 2-imino- and 3-iminooxetanes, were observed in the photocycloadditions of aromatic aldehydes and ketones to ketenimines.[13] Singer and Davis suggested that the overall stereochemical results may be caused by a balancing of dipolar and steric orienting influences in their cycloadducts.[14] On the basis of our previous studies of *p*-quinones with ketenimines,[11] all products could be explained in terms of initial formation of the adduct spiro 2-iminooxetanes **3**, from the n,π^* triplet states of *p*-quinones; spiro 3-iminooxetane derivatives could not be found. The dipole moment of π,π^* duroquinone should be different from that of n,π^* *p*-quinones, and this effect could be contributed to afford the minor extent of spiro 3-iminooxetane formation.

Photocycloadditions of Duroquinone to Dimethyl-*N*-substituted-ketenimines and Photoinduced Molecular Rearrangements of the Adducts. We also carried out the photoinduced cycloadditions of duroquinone to dimethyl-*N*-substituted-ketenimines (**12a,b**) and found photoinduced molecular isomerizations of their adducts. From the reaction mixtures of duroquinone with ketenimines **12**, the photoadducts **13** were obtained with the further isomerized products **14** of the adducts **13**.

The IR spectra of the isolated adducts **13a** and **13b** at R_f 0.55 and 0.50 by TLC analyses, respectively, which were shown to be 1:1 adducts of duroquinone and ketenimines on the basis of the NMR and mass spectra, exhibit strong bands due to 2-iminooxetane and a conjugated carbonyl absorption at 1745–1735 and 1640–1635 cm^{-1}, respectively. From their spectral data, the photoadducts were assigned as 3,3,5,6,8,9-hexamethyl-2-imino-1-oxaspiro[3.5]nona-5,8-dien-7-ones (**13a,b**) formed by cycloadditions of the carbonyl function of duroquinone, which are similar to the adduct **9** and not to the adduct **10**. The relatively low isolated yields of the adducts **13** were partially due to the subsequent photoisomerization of the adducts **13**. Therefore, at the maximum presence of the adducts the photoreactions should be stopped for separation of the adducts **13**, which can be checked by TLC analysis.

Scheme IV



A spiro 3-iminooxetane type compound could not be obtained, even by a careful experiment. Electron-donating dimethyl substituents should cause a change of the electronic nature of the C–C double bond and the dipole moment of ketenimines **12**, compared with those for diphenyl-substituted ketenimine **8**, and then give the more regiospecific adduct formation to afford spiro 2-iminooxetane **13**, exclusively.

The second products, **14**, were also obtained from the reaction mixtures of duroquinone with ketenimines **12**. The same products, **14a** and **14b**, were obtained directly from benzene solutions of duroquinone and ketenimines by prolonged irradiations (**14a** gave a 61% yield and **14b** a 55% yield from the photoreaction of duroquinone with the corresponding ketenimines). Therefore, these products should be derived from the initial adducts **13**. Namely, the benzene solutions of the photoadducts **13** were irradiated to afford the rearranged products **14** in good yields.

We recently reported the photoisomerizations of spiro 2-iminooxetanes **3** to spiro β-lactams **4**.[11] But these isolated rearrangement products **14** exhibit different spectral behaviors in comparison with those of spiro β-lactam type compounds **4**.

The products **14a** and **14b** were assigned by their physical properties and chemical behaviors. In IR spectra of both rearranged products **14**, strong bands due to imino, carbonyl, and C=C functions were observed at 1750–1740, 1690–1685, and 1630 cm^{-1}, respectively. The chemical shifts of all six methyl groups of **14a** in the ^{1}H and ^{13}C NMR spectra were not equivalent. The IR and ^{13}C NMR signals of **14a** show the presence of cyclohexadienone and vinyl–γ-lactone–anil systems. All these spectral data were consistent with 3,3,3a,4,5,7-hexamethyl-2-anil-3,3a-dihydrobenzofuran-6-one structure **14a**.

Both γ-lactoneimines **14a** and **14b** underwent facile hydrolysis by concentrated hydrochloric acid to afford the same γ-lactone **15** and the corresponding amines in good yields. This γ-lactone **15** has a similar skeleton to that of **14** and is assigned as 3,3,3a,4,5,7-hexamethyl-3,3a-dihydrobenzofuran-2,6-dione by its physical properties.

However, it is difficult to believe that 2-iminodihydrobenzofuran-6-one structures **14** are formed directly from the initial photoadducts **13**. A careful reexamination of the photorearrangement of the adduct **13a** to **14a** revealed the presence of the transient intermediate from the studies by ^{1}H NMR analysis and TLC measurement after irradiation for a moderate time. Namely, in addition to the methyl signals of the starting material **13a** and the rearranged product **14a**, six methyl signals appeared in the spectrum of the reaction mixture, and after prolonged

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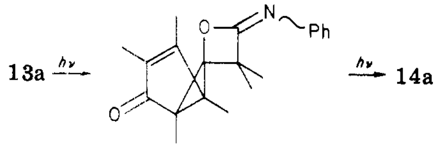
[13] L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 3961 (1967); L. A. Singer, G. A. Davis, and V. P. Muralidharan, *ibid.*, **91**, 897 (1969).

[14] L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 941 (1967).

[15] S. Guido and G. O. Schenck, *Chem. Ber.*, **100**, 3961 (1967).

Scheme V



16a

irradiation all signals were identical with the same signals of the rearranged product **14a**. Failure to isolate the pure intermediate **16a** from the reaction mixture of duroquinone with **12a** was due to partial decomposition of **16a** on silica gel. In the IR spectrum of this intermediate, strong bands due to 2-iminooxetane and cyclopentenone functions were observed in the 1750, 1700, and 1640 cm^{-1} regions. The ^{13}C NMR spectrum of **16a** strongly suggests bicyclo[3.1.0]hexenone skeleton. Other physical data for this intermediate supported oxaspiro bicyclo[3.1.0]hexenone structure **16a**. The stereochemistry about the spiro carbon atom of **16a** was difficult to determine from its spectral data. However, this intermediate should be assigned as *endo*-spiro-bicyclo[3.1.0]hexenone, because the chemical shifts of methyl groups of the oxetane ring were observed to indicate no shielding or deshielding effect by cyclopentenone moiety.

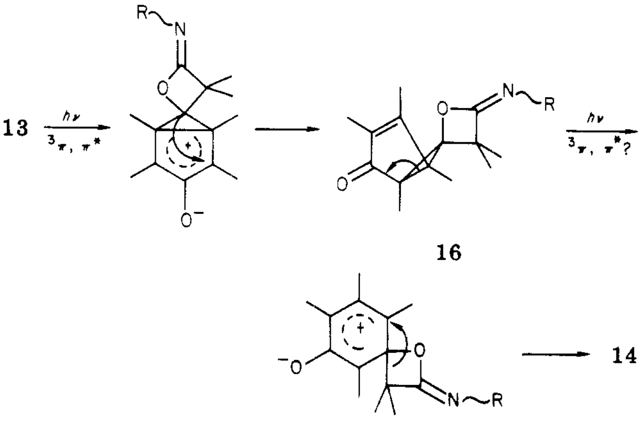
Obviously the isolated intermediate **16a** afforded the final rearranged product **14a** by photolysis in a quantitative yield.

The photoisomerizations of spiro 2-iminooxetanes **3** to spiro β-lactams **4** in Scheme I should proceed through an n,π* triplet excited state of cyclohexadienone functions.[11] Similar photoinduced isomerization was found in the 2-iminothietane systems.[16] The introduction of tetramethyl substituents on the cyclohexadienone moiety of these spiro 2-iminooxetanes should cause the different excited states,[7] namely, the lowest triplet state of a π,π* excitation, to yield the different modes of molecular rearrangements. Hexamethyl substituents on cyclohexadienone lead to the overlap of the n,π* and π,π* bands and preclude selective excitation of the n,π* band.[17] α-Santonin, a naturally occurring cross-conjugated cyclohexadienone[7,10] that has a methyl substituent at C-4, undergoes the formation of bicyclo[3.1.0]hexenone skeleton, referred as a lumi-ketone product in nonacidic solvent. Thermal and photochemical molecular rearrangements of bicyclo[3.1.0]hexenones were also known to give several types of products depending upon solvents, substituents, and their reaction conditions.[18] Although the electronic states in excitations of **13a** and **16a** are not obvious at the present time, the most reasonable explanation for these molecular rearrangements should be as follows: whole through the carbonium ion-like intermediates, zwitterionic species, stabilized with the solvent molecules in photoexcitation. From these considerations, Scheme VI may be formulated for these photoinduced molecular rearrangements of **13** to **14**.

Experimental Section

Materials. Commercial duroquinone and 3-methylbutane-1,2-diene were used without further purification. Ketenimines **8**, **12a**, and **12b** were prepared by the procedures according to the reports.[19,20] Solvents used were distilled in usual methods.

Scheme VI



Photoreaction of Duroquinone with 3-Methylbutane-1,2-diene (6). A nondegassed solution of 1,1-dimethylallene (204 mg, 3 mmol) and duroquinone (328 mg, 2 mmol) in 40 mL of benzene was irradiated with a 150-W high-pressure Hg lamp through a Pyrex filter for 7 h. Removal of solvent in vacuo gave a slightly yellow solid which was recrystallized from petroleum ether to give **7** in 87% yield (based on duroquinone): mp 70.5–71.5 °C; IR (KBr disk) 1665, 1655, 1630, 1380, 1270, 905 cm^{-1}; NMR (CDCl$_3$) δ 0.92 (s, Me), 1.16 (s, Me), 1.30 (s, Me), 1.35 (s, Me), 1.96 (s, Me), 1.98 (s, Me), 4.82 (s, 1 H), 4.92 (s, 1 H). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.30; H, 8.71.

Photoreaction of Duroquinone with Diphenyl-*N*-phenylketenimine (8). A 50 mL benzene solution containing duroquinone (328 mg, 2 mmol) and diphenyl-*N*-phenylketenimine (538 mg, 2 mmol) was irradiated for 2.5 h. After removal of solvent, chromatography of the residue was carried out on 50 g of silica gel to give the solid (448 mg). Recrystallization from methylene chloride–petroleum ether gave colorless needles (353 mg) of **9**: mp 158–159 °C; IR 1725, 1635, 1600, 1495, 1455, 1380, 1220, 880 cm^{-1}; NMR (CDCl$_3$) δ 1.40 (q, J = 0.1 Hz, 2 Me), 1.80 (q, J = 0.1, 2 Me), 7.0–7.7 (m, 3 Ph); UV (CHCl$_3$) λ_{max} 256 nm. Anal. Calcd for $C_{30}H_{27}NO_2$: C, 83.11; H, 6.28; N, 3.23. Found: C, 83.28; H, 6.08; N, 3.08. The residue from the filtrate was rechromatographed on silica gel eluted with benzene; two solid materials were obtained. The first eluted compound was recrystallized from ether to give colorless prism clusters (35 mg) of **10**: mp 159–162 °C; IR 1750, 1635, 1600, 1495, 1455, 870 cm^{-1}; NMR (CDCl$_3$) δ 1.40 (q, J = 0.1 Hz, 2 Me), 1.83 (q, J = 0.1, 2 Me), 7.0–7.7 (m, 3 Ph); UV (CHCl$_3$) λ_{max} 255 nm. Found: C, 83.26; H, 6.33; N, 3.21. The last fraction was identical with **9** (20 mg). R_f values of **9** and **10** are, in benzene, 0.50 and 0.58, respectively. Mass spectral data of **9** and **10** are shown in Figure 1.

Photodecomposition of the Adduct 9. A solution of 250 mg of the adduct **9** in 50 mL of benzene was irradiated for 4 h. The resulting mixture was evaporated to dryness and the residue was chromatographed over 25 g of silica gel. Elution of methylene chloride gave 181 mg of the starting material **9** and 41 mg of duroquinone diphenylmethide (**11**): mp 155–159 °C (recrystallized from chloroform–*n*-hexane); IR 1610, 1590, 1580, 1460, 1445, 770, 705, 700 cm^{-1}; NMR (CDCl$_3$) δ 1.56 (s, 2 Me), 2.05 (s, 2 Me), 7.3–7.6 (m, 2 Ph). Anal. Calcd for $C_{23}H_{22}O$: C, 87.86; H, 7.05. Found: C, 87.79; H, 6.86.

Photoreaction of Duroquinone with Dimethyl-*N*-phenylketenimine (12a). Photoreaction of duroquinone (492 mg, 3 mmol) and dimethyl-*N*-phenylketenimine (653 mg, 4.5 mmol) in 50 mL of benzene was irradiated for 1.5 h in a similar manner to that of **5** with **8**. After evaporation of the solvent under reduced pressure, the partially oily residue was separated by TLC on silica gel (GF$_{254}$, type 60, Merck), using chloroform as eluant. Four bands were observed at the R_f values 0.9, 0.7, 0.55, and 0.35. Extractions with chloroform–acetone (9:1) gave the starting

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(16) R. G. Visser, J. P. B. Baaij, A. C. Brouwer, and H. J. T. Bos, *Tetrahedron Lett.*, 4343 (1977); A. Dondoni, A. Battaglia, and P. Giorgiami, *Chim. Ind.* (*Milan*), 59, 459 (1977).

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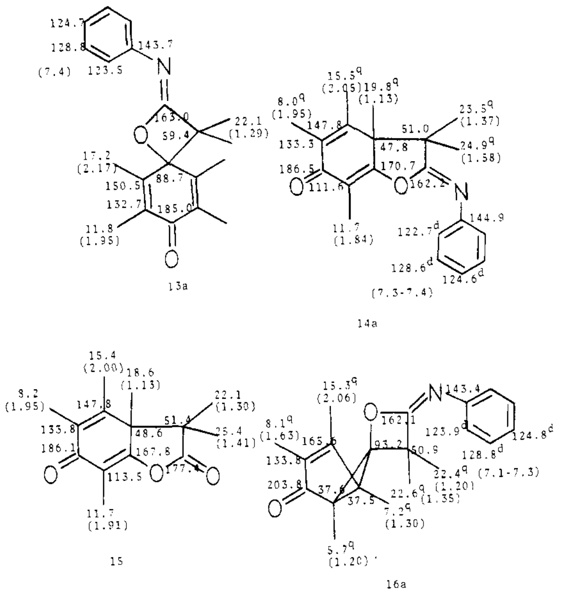

Figure 2. ^1H and ^{13}C NMR data of products ($CDCl_3$, δ).

duroquinone (R_f 0.9, 59 mg), **14a** (R_f 0.7, 224 mg), and the main band **13a** (R_f 0.55, 383 mg); from R_f 0.35 a mixture of **16a** and isobutyrylanilide, which came from hydrolysis of ketenimine **12a**, was obtained. Physical properties of **13a** and **14a** are as follows. Adduct **13a**: mp 132–134 °C (recrystallized from methylene chloride–petroleum ether); IR 1735, 1635, 1600, 1380, 865 cm^{-1}; mass spectrum (relative intensity) *m/e* 309 (82, m$^+$), 294 (50), 175 (30), 146 (30), 145 (100), 144 (39), and 77 (49). Anal. Calcd for $C_{20}H_{23}NO_2$: C, 77.64; H, 7.49; N, 4.53. Found: C, 77.70; H, 7.54; N, 4.43. Product **14a**: mp 113–115 °C (recrystallized from methylene chloride–petroleum ether); IR 1750, 1690, 1600, 1360, 1155, 1090, 1070, 1045, 890 cm^{-1}; UV ($CHCl_3$) λ_{max} 247 and 284 (sh) nm; mass spectrum *m/e* 309 (100, M$^+$), 294 (15), 206 (19), 148 (55), 145 (46), 105 (24). Found: C, 77.46; H, 7.62; N, 4.48. ^1H and ^{13}C NMR data of **13a** and **14a** are shown in Figure 2. The physical properties of **16a** are described in the next section.

Isolation of the Transient Intermediate 16a. The photoisomerization of **13a** was carried out by 30-min irradiation of 500 mg of the adduct **13a** in 30 mL of benzene. Three spots were observed by TLC analysis and the separation of the transient intermediate **16a** was at the maximum at this point. R_f values are as above. After removal of the solvent, the oily residue was chromatographed on a Lobar column (LiChroprep Si 60, Merck). Elution with *n*-hexane–chloroform (1:3) afforded **14a** from the first fraction and the starting material **13a** from the second, which were identified by comparing with the compounds isolated from the photoreaction of duroquinone with ketenimine **12a**. Further elution gave the pure transient intermediate **16a** (79 mg, 15 % yield) as an oil: IR 2980, 2930, 1750, 1700, 1640, 1600, 1365, 1235, 1125, 950 cm^{-1}; ^1H and ^{13}C NMR data are shown in Figure 2. Found: C, 77.55; H, 7.56; N, 4.46. The photoinduced isomerization of the isolated adduct **13a** to **14a** was monitored by ^1H NMR. During irradiation, the signals corresponding to the starting adduct **13a**, the intermediate **16a**, and the final product **14a** were observed, and after 3 h of irradiation all signals matched those of **14a**. Also the isolated intermediate **16a** was irradiated in an NMR tube for 3 h to show only the signals due to the final product **14a**.

Prolonged Irradiation of Duroquinone with Dimethyl-*N*-phenylketenimine (12a). Irradiation of the mixture of duroquinone and ketenimine **12a** was carried out under the same conditions given above. After 5 h of irradiation and removal of the solvent, the residue was subjected to TLC (silica gel/chloroform). The main band at R_f 0.7 gave a colorless solid (374 mg, 61% yield), which has the same physical properties with the final product **14a**.

Photoreaction of Duroquinone with Dimethyl-*N*-(2-cyano-2-propyl)ketenimine (12b). A solution of duroquinone (492 mg, 3 mmol) and dimethyl-*N*-(2-cyano-2-propyl)ketenimine (**12b**) (612 mg, 4.5 mmol) in 50 mL of benzene was irradiated for 1.5 h. The usual workup and TLC separation yielded products **13b** and **14b**. Adduct **13b**: mp 146–149 °C (recrystallized from methylene chloride–petroleum ether); IR 2230, 1745, 1640, 1385, 865 cm^{-1}; NMR ($CDCl_3$) δ 1.20 (s, 2 Me), 1.73 (s, 2 Me), 1.95 (br s, 2 Me), 2.18 (br s, 2 Me); mass spectrum *m/e* 300 (7, M$^+$), 285 (3), 218 (3), 191 (4), 165 (6), 137 (14), 136 (65), 69 (100). Anal. Calcd for $C_{18}H_{24}N_2O_2$: C, 71.97: H, 8.05; N, 9.33. Found: C, 72.21; H, 8.01; N, 9.23. Product **14b**: oil; IR 2230, 1740, 1690, 1640, 1380, 1080 cm^{-1}; NMR ($CDCl_3$) δ 1.02 (s, Me), 1.30 (s, Me), 1.41 (s, Me), 1.69 (s, 2 Me), 1.95 (s, 2 Me), 2.00 (s, Me). Found: C, 71.89; H, 8.11; N, 9.35. The product **16b** was also observed by TLC analysis, but pure **16b** could not be isolated because of partial decomposition of **16b** on silica gel.

Prolonged irradiation of duroquinone with **12b** was also carried out under a similar condition and the final product **14b** (493 mg, 55 % yield) could be isolated.

Acid-Catalyzed Hydrolysis of 2-Imino-3,3a-dihydrobenzofuran-6-ones 14a and 14b. A mixture of 2-anilinodihydrobenzofuran-6-one **14a** (246 mg, 0.8 mmol) in 10 mL of concentrated hydrochloric acid was heated at 60–70 °C for 30 min. The reaction mixture was quenched by pouring into ice–water. The mixture was extracted with chloroform, and the chloroform extract was worked up to afford colorless crystalline (168 mg, 95 % yield) **15**: mp 153–154 °C; IR 1820, 1705, 1635, 1375, 1070, 1035, 890 cm^{-1}; mass spectrum *m/e* 234 (59, M$^+$), 219 (38), 206 (7), 191 (36), 178 (12), 165 (100), 164 (30), 163 (20), 136 (22), 70 (17). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.65; H, 7.60. ^1H and ^{13}C NMR data of **15** are shown in Figure 2. The water layer was made alkaline with a 2 N sodium hydroxide solution and extracted with chloroform to give aniline, 72 mg.

Acid-catalyzed hydrolysis of **14b** was also examined to give the same dihydrobenzofuran-2,6-dione, **15** (84% yield).

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