1346 *J. Org. Chem.* **1992,** *57,* 1346–1351

Direct Observation of the Cyclopropene–Vinylcarbene Rearrangement. Matrix Isolation of Bicyclo[3.1.0]hexa-3,5-dien-2-ones

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4-Oxocyclohexa-2,5-dienylidenes **4b–g** have been generated in argon matrices at 10 K by visible-light irradiation of the corresponding quinone diazides **5**. Carbenes **4** have been characterized by IR and UV–vis spectroscopy and by their characteristic thermal reaction with molecular oxygen. On irradiation into the longest-wavelength absorption (420–700 nm), carbenes **4c–g** rearrange to give the highly strained bicyclo[3.1.0]hexa-3,5-dien-2-ones **3c–g**, while **4b** is photostable under the same conditions. The photochemical **4** → **3** rearrangement is completely reversible: infrared irradiation or visible light irradiation ($\lambda > 470$ nm) of the cyclopropenes **3** lead back to triplet carbenes **4** quantitatively. In addition, several of the 1,3-bridged cyclopropenes **3** undergo a thermal rearrangement to give carbenes **4**. This indicates that the highly strained cyclopropenes **3** are thermodynamically less stable than the corresponding carbenes **4** and kinetically only stabilized by a shallow energy barrier. Even under the conditions of matrix isolation at cryogenic temperatures, cyclopropenes **3** are metastable compounds.

Introduction

Thermolysis or photolysis of cyclopropenes is an efficient route to products derived from vinylcarbenes (cyclopropene–vinylcarbene rearrangement).[1] The preparative usefulness of this reaction[1] and the notion that strained cyclopropenes could be intermediates in carbene rearrangements[2] have prompted a large number of mechanistic studies.[1a,3,4] The activation energy E_a for the cyclopropene–vinylcarbene rearrangement is of the order of 30–40 kcal/mol,[3b,c,4] depending on the pattern of substitution, and the equilibrium greatly favors the cyclopropenes. Electron-donating groups in the 3-position reduce E_a,[5] and 3,3-dialkoxycyclopropenes are used as masked vinylcarbenes for the synthesis of five-membered ring systems.[1a]

1 2

Scheme I

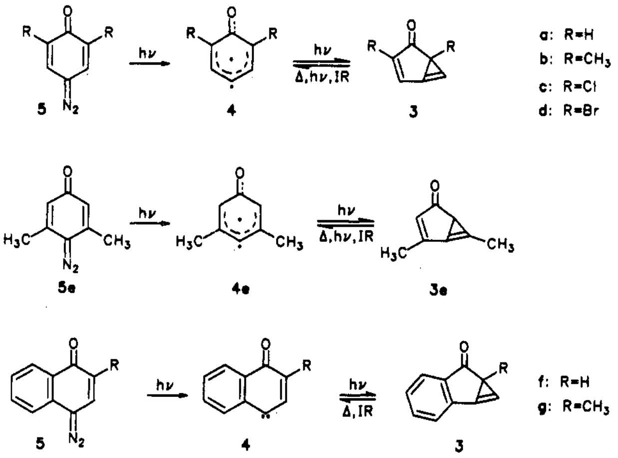

Table I. UV–Vis Spectroscopic Data of Carbenes 4a–g, Matrix Isolated in Argon at 10 K

carbene	λ_{max} (nm)
4a[a]	566, 550, 535, 521, 508, 496, 379, 367, 351, 338, 297, 290
4b	620, 606, 588, 572, 560, 544, 374, 364, 358, 346, 294, 248
4c	656, 628, 606, 578, 556, 372, 364, 356, 344, 310, 254, 248
4d	692, 666, 640, 614, 582, 374, 360, 356, 348, 342, 316, 252
4e	580, 398, 390, 382, 374, 368, 354, 286, 240
4f	550, 536, 522, 514, 506, 468, 440, 378, 362, 336, 320, 280, 232
4g	560, 528, 498, 464, 434, 384, 366, 336, 324, 250

[a] Reference 9.

Table II. UV–Vis Spectroscopic Data of Cyclopropenes 3a,c–f, Matrix Isolated in Argon at 10 K

carbene	λ_{max} (nm)
3a[a]	418, 356, 342, 272, 232
3c	408 (sh), 370, 364, 354, 338, 298, 268, 254, 248, 206, 198
3d	410 (sh), 376, 366, 356, 318 (sh), 192
3e	412, 328, 272, 196
3f	425, 402, 384, 362, 346, 282 (sh)

[a] Reference 9.

Bridging across the 1,3-position introduces additional strain to cyclopropenes. When the bridges are small enough—such as in bicyclo[3.1.0]hex-5-enes **1**—the equilibrium is shifted in favor of the vinylcarbene.[6] Thus **1** and its derivatives thermally open up to give cyclohexenylidenes **2**, which have been trapped in solution in several cases.[6-8] We have recently reported on the direct observation of the thermal rearrangement of 1*H*-bicyclo[3.1.0]hexa-3,5-dien-2-one **3a** to triplet 4-oxocyclohexa-2,5-dienylidene **4a**.[9,10] This rearrangement obeys first-order kinetics, and the Arrhenius parameters have been determined to $E_a = 2.6 \pm 0.2$ kcal/mol and log $A = 7 \pm 1$ s^{-1}.[9] We now wish to report further examples for the direct observation of the rearrangement of cyclopropenes to free carbenes. A series of 3,5-substituted (**4b–d**), 2,6-

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Table III. IR Spectroscopic Data of Carbenes 4b–g, Matrix Isolated in Argon at 10 K

compd	ν, cm^{-1} (rel intensity)
4b	3035.4 (5), 2990.1 (19), 1518.2 (100), 1511.9 (24), 1506.1 (25), 1500.8 (47), 1482.0 (8), 1462.7 (8), 1437.7 (23), 1434.3 (62), 1427.1 (25), 1404.4 (11), 1371.6 (13), 1267.0 (17), 1263.1 (47), 1201.4 (11), 1198.1 (6), 1029.8 (12), 1025.5 (10), 977.3 (7), 840.3 (48), 795.0 (6), 755.5 (11), 545.3 (17)
4c	3064.3 (5), 1546.4 (46), 1545.2 (49), 1537.5 (43), 1512.4 (7), 1495.0 (10), 1463.7 (42), 1459.4 (100), 1368.2 (14), 1347.5 (45), 1337.4 (74), 1301.2 (24), 1238.1 (19), 1233.7 (62), 1143.1 (13), 1068.4 (28), 1065.5 (84), 838.4 (24), 836.0 (31), 787.3 (51), 783.4 (83), 782.0 (81), 555.9 (12)
4d	3053.7 (5), 2987.2 (4), 1538.9 (90), 1484.4 (4), 1461.8 (8), 1453.1 (78), 1435.7 (10), 1341.2 (16), 1330.2 (100), 1323.4 (33), 1296.4 (17), 1228.4 (61), 1136.8 (27), 1033.7 (19), 1015.8 (14), 1000.4 (33), 837.9 (17), 742.9 (10), 703.4 (35), 700.5 (47), 694.2 (24), 543.3 (21)
4e	3007.0 (vw), 2977.6 (vw), 2936.6 (vw), 1514.8 (51), 1504.7 (100), 1478.2 (18), 1447.3 (42), 1379.8 (17), 1322.9 (21), 1275.7 (40), 1268.0 (23), 1195.2 (10), 1021.6 (27), 927.1 (5), 877.5 (18), 868.3 (53), 709.2 (7), 702.0 (10), 515.9 (36)
4f	3100.0 (vw), 3088.9 (vw), 3009.9 (vw), 1567.4 (21), 1556.8 (100), 1545.2 (32), 1541.3 (23), 1455.0 (6), 1381.7 (10), 1374.5 (5), 1319.6 (9), 1298.3 (9), 1285.8 (65), 1232.3 (8), 1217.8 (5), 1136.3 (6), 1123.3 (11), 1020.6 (8), 858.7 (6), 809.5 (11), 770.4 (17), 758.9 (52), 740.0 (31), 568.9 (8), 530.3 (7)
4g	3068.7 (5), 2993.5 (6), 1568.3 (42), 1558.2 (100), 1545.7 (60), 1477.2 (20), 1465.2 (19), 1426.1 (11), 1413.6 (12), 1401.5 (17), 1397.2 (17), 1287.7 (89), 1273.3 (16), 1183.6 (25), 921.8 (19), 844.2 (19), 757.4 (78), 683.6 (30), 591.1 (11)

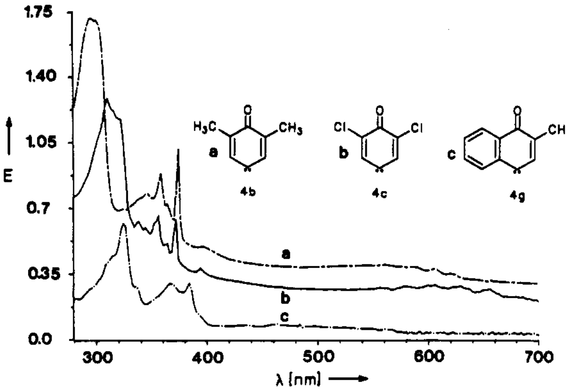


Figure 1. UV–vis spectra of carbenes **4b** (a), **4c** (b), and **4g** (c), matrix isolated in argon at 10 K.

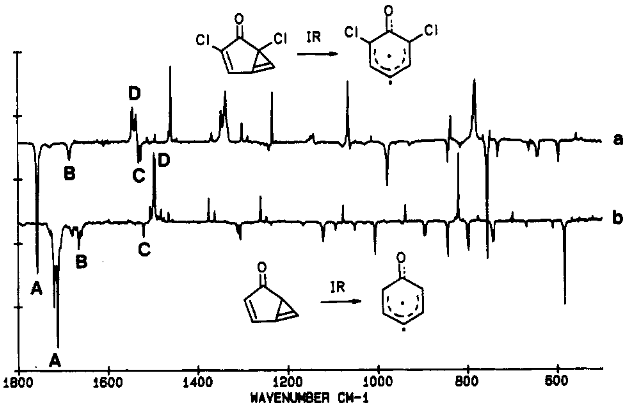


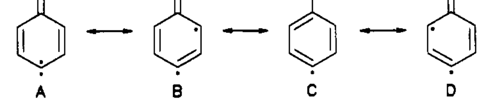
Figure 2. Difference IR spectra of the **3a** → **4a** rearrangement (a) and the **3c** → **4c** rearrangement (b). Bottom part of the difference spectra: peaks disappearing. Top part: peaks appearing on IR irradiation of the matrix. A: C = O str. modes of **3**. B: cyclopropene C = C str. modes of **3**. C: cyclopentene C = C str. modes of **3**. D: C = O str. modes of **3**.

substituted (**4e**), and benzoannellated (**4f–g**) 4-oxocyclohexa-2,5-dienylidenes has been generated and characterized in argon matrices at 10 K. The photochemistry and thermochemistry of these compounds is reported in this work.

Results and Discussion

Matrix Isolation of Carbenes 4. Carbenes **4b–g** have been generated by visible-light irradiation (Table VII) of the corresponding diazo compounds **5**, isolated in argon matrices at 10 K. After 1–2 h irradiation, carbenes **4** are formed in high yields. Due to weak-intensity absorptions in the visible part of the spectra (Figure 1, Table I), matrices containing the carbenes are colored violet to blue (**4b–e**) or orange (**4f** and **4g**). The long-wavelength absorptions in the range 420–700 nm exhibit pronounced vibrational fine structure, and the position of the maxima is sensitive to substitution. Compared to **4a** the maxima in **4b–d** are red-shifted by approximately 60–80 nm, while benzoannellation in **4f,g** causes a blue-shift of approximately 50 nm (Figure 1, Table I) and a decrease of the intensity of the absorption. Irradiation into this long-wavelength region leads to the rearrangement to cyclopropenes **3** (vide infra). Notable in the UV spectra of **4** is a sharp absorption at 370–380 nm (Table I), which is rather insensitive to substitution, and which is also characteristic of phenoxyl radicals.[11] This reveals the similarities between the π-systems of 4-oxocyclohexa-2,5-dienylidenes **4** and the phenoxyl radical.

The only characteristic IR absorptions of **4** are C=O stretching vibrations at 1518.2 (**4b**), 1545.2 (**4c**), 1538.9 (**4d**), 1504.7 (**4e**), 1556.8 (**4f**), and 1558.2 cm^{-1} (**4g**) (Figure 2 and Table III). These rather low-frequency vibrations (1497.9 cm^{-1} in **4a**, Figure 2)[9] indicate the only partial double bond character of the C=O bond and substantial contribution of resonance structure C. π-Electron-donating substituents lead to higher contributions of resonance structures B and D, and consequently to blue shifts of the C=O stretching modes. Halogen substituents in **4c,d** and benzoannellation in **4f,g** are more effective than methyl groups in **4b** and **4e**.



Thermal Oxygenation. The rapid thermal reaction with molecular oxygen ($^3O_2$) in oxygen-doped argon matrices (0.5–2% O_2) is highly characteristic of triplet carbenes.[12] For triplet carbenes, this process is controlled by the diffusion rate of $^3O_2$, while singlet carbenes react slower than diffusionally controlled by several orders of magnitude.[12a,c,e] On annealing in O_2-doped argon matrices (0.5–1% O_2) at 35 K, carbenes **4b–g** are readily trapped by molecular oxygen, and carbonyl *O*-oxides **6b–d** are formed (Table V). Therefore, triplet ground states have been assigned to carbenes **4**. The triplet ground state of

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Table IV. IR Spectroscopic Data of Cyclopropenes 3c–g, Matrix Isolated in Argon at 10 K

compd	ν, cm^{-1} (rel intensity)
3c	3112.5 (1), 1758.8 (100), 1686.4 (16), 1532.2 (11), 1527.3 (19), 1027.4 (3), 978.2 (31), 928.6 (3), 842.7 (14), 840.3 (14), 814.8 (7), 755.0 (85), 731.4 (11), 662.4 (4), 644.6 (10), 640.7 (12), 598.8 (15), 595.9 (12)
3d	3140.0 (vw), 1745.3 (84), 1680.2 (17), 1521.1 (26), 1517.2 (15), 1240.0 (20), 1128.6 (9), 1118.5 (12), 1055.8 (12), 1052.5 (23), 955.6 (15), 936.3 (17), 931.9 (35), 842.3 (27), 804.7 (20), 732.3 (81), 713.5 (100), 661.0 (21), 656.6 (17), 631.6 (24), 625.3 (12), 574.2 (21)
3e	2997.3 (8), 2962.6 (7), 2924.5 (7), 1773.7 (20), 1724.5 (57), 1719.7 (100), 1700.9 (25), 1693.2 (21), 1680.2 (23), 1579.9 (16), 1442.5 (28), 1436.7 (14), 1419.4 (8), 1380.8 (18), 1291.1 (38), 1233.3 (6), 1143.6 (7), 1125.7 (14), 1106.0 (16), 1035.6 (7), 1001.4 (7), 948.8 (22), 944.0 (17), 860.6 (14), 852.9 (16), 849.5 (8), 837.0 (8), 829.2 (15), 743.4 (9), 722.7 (8), 533.2 (20)
3f	3454.8 (0.4), 3077.3 (3), 1730.3 (100), 1715.9 (20), 1696.1 (7), 1686.0 (37), 1682.1 (53), 1643.1 (4), 1602.6 (37), 1459.8 (27), 1444.9 (7), 1281.0 (17), 1272.8 (10), 1186.0 (24), 1175.4 (20), 1159.5 (14), 1158.0 (14), 1085.7 (7), 1052.9 (6), 1033.7 (11), 1011.0 (13), 982.6 (12), 958.9 (15), 883.2 (8), 820.1 (8), 801.3 (13), 764.6 (40), 762.7 (49), 743.9 (39), 727.5 (7), 691.4 (17), 636.9 (30), 619.5 (43), 618.1 (45)
3g[a]	1724.0 (s), 1665.7 (m), 1601.1 (m), 1458.9 (w), 1443.9 (vw), 1280.0 (w), 1182.1 (w), 1147.9 (vw), 1077.0 (w), 964.7 (w), 962.3 (w), 852.9 (w), 827.3 (vw), 763.7 (m), 743.9 (vw), 714.0 (vw), 694.2 (vw), 672.5 (s), 661.0 (s), 655.2 (s)

[a] Due to the low yield of **3g**, the intensities have been determined only qualitatively.

Table V. IR Spectroscopic Data of Carbonyl *O*-Oxides 6b–g, Matrix Isolated in Argon Doped with 1% O_2 at 10 K

compd	ν, cm^{-1} (rel intensity)
6b	1628.6 (12), 1614.1 (57), 1610.8 (84), 1602.6 (25), 1562.5 (12), 1544.7 (3), 1440.6 (14), 1429.0 (21), 1380.8 (14), 1362.5 (15), 1355.7 (12), 1345.1 (4), 1248.7 (21), 1243.4 (36), 1126.2 (22), 1120.9 (21), 1048.1 (8), 1042.3 (36), 1040.9 (36), 1036.6 (26), 1003.8 (17), 998.9 (100), 970.0 (10), 922.8 (35), 897.2 (23), 839.4 (50), 760.3 (10), 662.4 (13)
6c	3079.8 (2), 1641.6 (78), 1511.4 (27), 1428.0 (38), 1178.3 (100), 1066.4 (66), 1024.0 (48), 917.9 (53), 892.4 (16), 812.4 (16), 803.2 (42), 801.8 (35), 657.1 (28), 566.5 (10)
6d	3252.4 (2), 3101.9 (2), 3082.7 (1), 1636.8 (100), 1629.1 (13), 1506.6 (27), 1420.8 (21), 1416.5 (24), 1338.8 (5), 1187.9 (8), 1170.6 (88), 1067.9 (7), 1060.7 (69), 1052.5 (32), 1046.2 (8), 1000.4 (8), 892.9 (30), 890.0 (19), 883.2 (10), 776.7 (9), 763.7 (9), 725.1 (79), 643.6 (44), 556.4 (20)
6e	3207.0 (2), 2990.1 (2), 2941.9 (4), 2936.1 (5), 1617.5 (100), 1598.7 (29), 1566.9 (8), 1452.6 (7), 1441.0 (15), 1389.5 (13), 1381.7 (11), 1318.6 (19), 1313.3 (11), 1246.3 (34), 1241.0 (27), 1224.6 (8), 1220.7 (10), 1063.1 (38), 1027.4 (67), 1014.4 (45), 914.1 (30), 829.2 (4), 624.3 (19)
6f	3085.5 (5), 3081.7 (4), 1653.2 (66), 1647.9 (64), 1606.4 (11), 1599.2 (28), 1588.1 (23), 1556.8 (40), 1404.9 (9), 1395.7 (6), 1383.2 (13), 1361.0 (6), 1308.9 (7), 1300.3 (25), 1295.0 (31), 1274.7 (55), 1216.9 (31), 1194.7 (12), 1145.5 (14), 1135.9 (5), 1086.2 (11), 1073.7 (38), 1027.9 (8), 1025.9 (7), 1012.0 (47), 970.5 (5), 949.8 (100), 844.7 (6), 838.9 (5), 781.0 (5), 765.1 (41), 752.6 (5), 634.9 (16), 608.4 (9), 561.7 (5), 549.6 (8)
6g	3074.0 (3), 2931.8 (3), 1677.3 (22), 1647.4 (72), 1645.5 (72), 1613.6 (15), 1602.6 (32), 1595.3 (26), 1584.7 (22), 1466.1 (10), 1442.0 (13), 1392.4 (22), 1382.2 (21), 1375.0 (16), 1368.2 (15), 1352.8 (12), 1329.7 (19), 1296.4 (48), 1288.7 (57), 1268.4 (41), 1194.7 (25), 1182.6 (31), 1157.1 (15), 1095.4 (14), 1026.4 (22), 1016.3 (22), 1000.4 (15), 994.1 (91), 984.0 (21), 969.5 (25), 964.7 (58), 933.9 (100), 773.8 (21), 767.5 (20), 693.3 (18), 625.3 (13)

4a has already been confirmed by ESR spectroscopy in an earlier study.[10,13] The IR (Table V) and UV–vis spectra of **6b–g** are similar to that of **6a** and clearly establish the presence of the C–O–O functional group.[12a,14] Long-wavelength irradiation (λ > 515 nm) transforms **6** to spirodioxiranes **7** in high yields. Shorter-wavelength irradiation (λ > 400 nm) causes all bands assigned to **7** to disappear and new absorptions assigned to 2,5-oxepinediones **8** to grow in. The characterization of **7** and **8** was achieved by comparison of the IR and UV–vis spectra with that of **7a** and **8a**.[14,15] The sequence **4** → **6** → **7** → **8** has been observed in many carbene–oxygen reactions[12a] and can be considered being diagnostic for **4** and the oxygen-containing intermediates **6–8**.

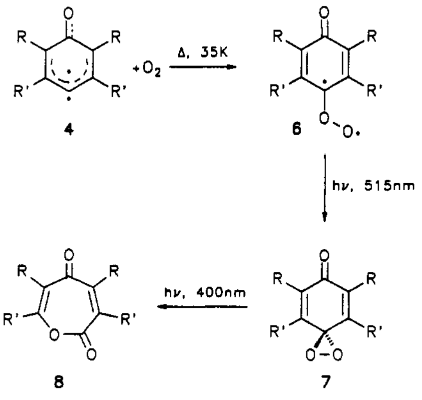

Table VI. Characteristic IR Modes of Cyclopropenes 3, Matrix Isolated in Argon at 10 K

	ν, cm^{-1}		
cyclopropene	C═O str	C═C str 3-ring	C═C str 5-ring
3a[a]	1713.2	1665.2	1520.6
3a-d_4[a]	1706.5	1623.6	1475.0
3c	1757.3	1685.5	1531.7
3d	1745.3	1684.5	1522.0
3e	1714.9	1773.7	1573.6
3f	1730.3	1682.1	1602.6[b]
3g	1724.0	1665.7	1601.1[b]

[a] Reference 9. [b] C═C str mode of the benzene ring.

Table VII. Irradiation Conditions To Produce Carbenes 4 and Cyclopropenes 3 in Argon Matrices at 10 K

5 → 4	λ,[a] nm	4 → 3	λ,[b] nm	% yield of 3
5a[c]	>515	**4a**[c]	543	84
5b	>495	**4b**	543, >515	0
5c	>515	**4c**	>550	65
5d	>515	**4d**	>550	73
5e	>515	**4e**	>515	>95
5f	>515	**4f**	>475	91
5g	>515	**4g**	>495	<10

[a] Wavelength used to produce carbene 4 in almost quantitative yield after 1–2 h. [b] Wavelength which gave highest yield of 3. [c] Reference 9.

Photochemistry of Carbenes 4. On irradiation into the long-wavelength triplet–triplet absorption (430–650 nm, Table I), carbenes **4** exhibit quite different reactivity (Table VII). **4b** is completely unreactive even at prolonged irradiation, while carbenes **4c–g** slowly yield cyclopropenes **3c–g**. After 10–20-h irradiation, photostationary equilibria **3** ⇄ **4** are achieved (Table VII).

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(15) Details of the spectroscopic characterization and photochemistry of 6 and 7 will be published elsewhere.

Cyclopropenes **3** have been identified by comparison of their IR spectra (Table IV) and UV–vis spectra (Table II) to that of **3a**.[9] Characteristic vibrational modes are the C=O stretching mode, the C=C stretching mode of the cyclopentene ring, and the C=C stretching mode of the cyclopropene ring (Table VI). The C=O stretching modes of **3** are observed between 1713.2 (**3a**) and 1757.3 cm^{-1} (**3c**). Methyl substitution in the 4,6-positions (**3e**) or benzoannelation (**3f,g**) give rise to small blue-shifts; more pronounced high-frequency shifts are found for the halogenated cyclopropenes **3c** and **3d**.

1,3-Disubstitution hardly effects the C=C stretching modes of the cyclopentene moiety, while in 4,6-dimethyl-substituted **3e** a high-frequency shift of 53 cm^{-1} is observed. In **3f,g** this vibration corresponds to C=C stretching modes of the aromatic systems at 1602.6 and 1601.1 cm^{-1}, respectively.

The position of the C=C stretching mode in cyclopropenes is highly sensitive to the pattern of substitution in a characteristic way.[2c] In cyclopropene itself the C=C stretching mode is observed at 1653 cm^{-1} and on deuteriation of one olefinic position shifted by −45 cm^{-1}. Substituents in the 3-position hardly effect the position of this vibration while substituents (alkyl or aryl) in 1- or 2-position give rise to blue-shifts of more than 100 cm^{-1}.[2c] In **3**, deuteriation causes a red-shift of 41.6 cm^{-1} (**3a**-d_4)[9] and a methyl group in the olefinic 6-position (**3e**) gives rise to a blue-shift of 108.5 cm^{-1}, while substituents in other positions have only small effects (Table VI). These IR data provide further evidence for the assignment of the bicyclo[3.1.0]hex-5-ene skeleton to compounds **3**.

The UV–vis spectra of cyclopropenes **3** exhibit broad absorptions of medium intensity at 408–425 nm (Table II). These absorptions are not associated with the cyclopentenone chromophor but rather with the cyclopropene moiety[9] and are relatively insensitive toward substitution.

The yield of cyclopropenes **3** in the photostationary equilibrium depends greatly on the nature of the substituents (Table VII). Methyl substitution in the 3- (and 5-) positions drastically reduces the yield of cyclopropenes **3** (0% and <10% in **4b** and **4g**, respectively), while methyl substitution in the 2- and 6-positions increases the yield (>95% in **4e**). Halogen substitution in the 3,5-positions also slightly reduces the yield, while benzoannellation has almost no effect. From our experiments it is not clear whether **3b** is not formed photochemically or is simply too short-lived (very fast thermal back-reaction) to be observed under the experimental conditions. Because of the very slow thermal back-reaction of **3g** (vide infra), it is more likely that 3,5-methyl substitution influences the photostationary **3b** ⇄ **4b** equilibrium rather than increasing the rate of the thermal **4b** → **3b** rearrangement. The relative amounts of **3** and **4** in the photostationary equilibria depend on the absorbance of **3** and **4** at the wavelength of irradiation and on the ratio of the quantum yields of the **3** → **4** and **4** → **3** photochemistry. **4g** shows an intense fluorescence, which decreases the quantum yield of the photochemical **4g** → **3g** rearrangement and thus the yield of **3g**.

The formation of (singlet) S-3 from triplet carbenes T-4 requires an intersystem crossing (ISC) step along the reaction coordinate. Possible pathways are

$$\text{T-4} \rightarrow \text{T*-4} \rightarrow \text{S-4} \rightarrow \text{S-3} \qquad (1)$$

with ISC on the side of the carbenes **4** and S-4 as an intermediate and

$$\text{T-4} \rightarrow \text{T*-4} \rightarrow \text{T-3} \rightarrow \text{S-3} \qquad (2)$$

with ISC on the side of the cyclopropenes and T-3 as an intermediate. According to ab initio calculations, T-**3a** lies ca. 104 kcal/mol above S-**3a** and is unlikely to be thermally populated from T*-**4a**, as it is required in pathway eq 2.

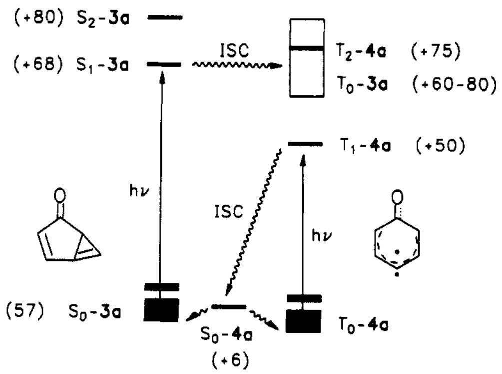
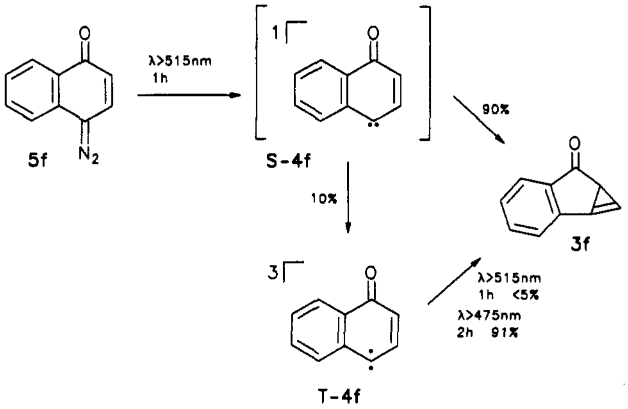


Figure 3. Jablonski diagram showing experimentally or theoretically determined energy levels of low-lying electronic states of **3a** and **4a**. S_0-**3a** and T_0-**3a** are the MP2/6-31G(d) values (ref 9), S_1-**3a**, S_2-**3a**, T_1-**4a**, and T_2-**4a** have been obtained from the UV–vis spectra (ref 9). S_0-**4a** has been estimated by methanol quenching experiments in a laser-flash photolysis study (ref 22). Energy values in kilocalories/mole, S_0-**3a** and T_0-**4a**, respectively, as reference.

Scheme II



Experimental evidence to discriminate pathways eqs 1 and 2 is given by the photochemistry of **5f**. Photolysis of diazo compounds **5** provides a clean source of S-4 without passing through T-4. S-4 is short-lived in the matrix and rapidly thermally relaxes to T-4 (ISC) or rearranges to S-3 (eq. 1, Figure 3). If S-3 is produced directly in a one-photon process from quinonediazide **5**, S-4 must be an intermediate, and the ratio T-4:S-3 is a measure for the efficiency of the ISC compared to the rearrangement. Unfortunately, in most cases **5** and T-4 absorb in the same range (500–600 nm), and thus under the conditions necessary for the photochemical cleavage of **5**, T-4 is also excited (Table VII). Only in T-**4f** the longest-wavelength absorption is blue-shifted enough to separate the photochemistry of **4f** and **5f**: upon irradiation with >515 nm **5f** is rapidly photolyzed and a 9:1 ratio of **3f**:**4f** is formed, while under the same conditions T-**4f** isomerizes to **3f** only extremely slowly (Scheme II). The 9:1 ratio represents the branching ratio of S-**4f**, which means that the ISC to T-**4f** is slower than the rearrangement to **3f** and strongly suggests that eq 1 describes the photochemistry of **4**.

According to the mechanism outlined in eq 1, the photochemical generation of **3** depends critically on the relative ordering of the states: S-4 must lie energetically above S-3 (Figure 3). Substituents which stabilize S-4 more than S-3 can reverse the order of states and thus prevent the photochemical formation of **3**. The failure to photochemically produce **3b** from T-**4b** (ground state) might therefore be rationalized by the large stabilization of S-**4b** by the 3,5-dimethyl substituents.

Thermal Rearrangement of Cyclopropenes 3. Cyclopropenes **3** are highly labile, even under the conditions of matrix isolation in argon at cryogenic temperatures. Infrared irradiation (Globar and appropriate filters to remove visible light)[9] or visible-light irradiation ($\lambda > 470$ nm) reverse the long-wavelength photochemistry and produce the corresponding triplet carbenes **4** quantitatively. The IR-induced **3** → **4** rearrangement of **3f,g** is slower than the **3a** → **4a** rearrangement,[9] while in the case of the other cyclopropenes **3** the IR-induced rearrangement is faster than that of **3a**.

The thermal **3** → **4** rearrangement was monitored by IR spectroscopy.[9] In argon at 10 K, first-order kinetics were followed and the rates have been determined to $k = 1.7 \times 10^{-5}$ s^{-1} (**3c**), 2.4×10^{-5} s^{-1} (**3d**), and $<10^{-7}$ s^{-1} (**3f,g**). Compared to the rate for the **3a** → **4a** rearrangement (Ar, 10 K, $k = (1.4 \pm 0.1) \times 10^{-6}$ s^{-1}), the rearrangement of the halogenated cyclopropenes **3c,d** is faster by 1 order of magnitude and the rearrangement of the benzoannellated systems slower by at least 1 order of magnitude. Due to the very low rates it was not possible to obtain accurate data for the thermal rearrangement of **3f,g**.

The rate of the formally "spin foridden" rearrangement of S-**3** to T-**4** is determined by the intersystem crossing rate, which depends on heavy atom effects (internal and external), density of vibrational states of **4** (in the case of an "off-resonance" coupling of **3** and **4**),[16] the mass of atoms involved in the rearrangement (if tunnelling is important), and matrix site effects.[9] Thus there is no straightforward prediction of substituent effects on the rates.

In the case of the **3a** → **4a** rearrangement the low preexponential Arrhenius factor and the substantial external heavy atom effect (in xenon and krypton compared to argon matrices) suggest that ISC is the rate-determining step in the reaction, and **4a** is directly formed from **3a** without further intermediates involved. The internal heavy atom effect of chlorine and bromine atoms increases the rate of ISC, and therefore of the thermal rearrangement. On the other hand, the difference in the rates of **3c,d** is smaller than what is expected for bromine compared to chlorine substitution, which suggests that the internal heavy atom effect is not the only explanation for the increased rates. Due to the close proximity of the halogen substituents to the centers which undergo the largest movements during rearrangement, this is not unexpected. The higher mass and larger steric requirement in the matrix cage of halogen atoms compared to hydrogen should reduce the rates in opposition to the heavy atom effect.

As with the **4** → **3** photochemistry, the order of states and the energy gaps are critical for the **3** → **4** rearrangement (Figure 3): T-**4** must be below S-**3**, and T-**4** is formed directly without S-**4** as an intermediate.

Conclusions

The characterization of a series of bicyclo[3.1.0]hexa-3,5-dien-4-ones **3** clearly demonstrates that the reversible formation of these cyclopropenes is not restricted to the parent carbene **4a**, although the yields of **3** depend much on substituents at the carbene. Evidence has been presented that excited singlet states S-**4** are key intermediates in the photochemical generation of **3**.

The highly strained cyclopropenes **3** are thermodynamically less stable than the corresponding carbenes **4** and kinetically stabilized by a shallow energy barrier only. Thus, these unusual species are among the least stable carbocyclic molecules known to organic chemistry. In the photochemistry and thermochemistry of the cyclopropene–vinylcarbene system investigated in this work, several close lying electronic states are involved: T-**4**, S-**4**, and S-**3**. Substituents as well as matrix effects influence the energy gaps and possibly even the relative order of these states and thus give rise to the drastic differences in yields of **3** and kinetics of the **3** → **4** rearrangement.

Experimental Section

All reactions were carried out under argon or nitrogen. 2,6-Dimethyl-*p*-benzoquinone, 4-amino-2,6-dibromophenol, 4-amino-2,6-dichlorophenol, 4-amino-1-naphthol hydrochloride, and 2-methyl-1,4-naphthoquinone were obtained from Aldrich and were used as received. 2,6-Dimethyl-4*H*-pyran-4-one was purchased from Janssen.

4-Diazo-2,6-dimethyl-2,5-cyclohexadienone (5b). Quinone diazide **5b** was prepared from 2,6-dimethyl-*p*-benzoquinone according to the procedure described by Ried and Dietrich.[17] IR (Ar, 10 K): 2068.8 (vs), 2064.4 (vs), 2053.3 (m), 1618.0 (s), 1608.3 (s), 1592.9 (m), 1532.6 (vw), 1481.1 (vw), 1455.5 (w), 1428.5 (w), 1382.7 (w), 1365.8 (w), 1268.4 (w), 1254.9 (s), 1199.5 (vw), 1135.4 (w), 1037.5 (w), 1011.0 (m), 942.5 (w), 932.4 (w), 872.1 (m), 531.3 cm^{-1} (w).

4-Diazo-2,6-dichloro-2,5-cyclohexadienone (5c). Diazo ketone **5c** was prepared from 4-amino-2,6-dichlorophenol following the method of Ried and Appel.[18] IR (Ar, 10 K): 2101.1 (vs), 2095.3 (s), 2086.6 (s), 2082.3 (s), 2076.5 (vs), 1660.9 (m), 1648.8 (vs), 1645.0 (m), 1638.7 (m), 1632.9 (m), 1631.5 (m), 1623.8 (w), 1579.9 (vs), 1352.8 (w), 1203.8 (vs), 1189.9 (m), 1187.0 (m), 1048.1 (w), 920.8 (vw), 896.7 (m), 807.1 (m), 798.9 (m), 764.6 cm^{-1} (vw).

4-Diazo-2,6-dibromo-2,5-cyclohexadienone (5d). Compound **5d** was synthesized from 4-amino-2,6-dibromophenol analogously to compound **5c**.[18] IR (Ar, 10 K): 2090.0 (vs), 2088.0 (vs), 2085.6 (vs), 1643.5 (m), 1635.3 (w), 1607.9 (w), 1575.6 (s), 1195.2 (s), 1184.6 (w), 864.9 (w), 735.2 (m), 727.0 cm^{-1} (vw).

4-Diazo-3,5-dimethyl-2,5-cyclohexadienone (5e). Quinone diazide **5e** was prepared in a five-step synthesis starting with 2,6-dimethyl-4*H*-pyran-4-one. The pyrone was first converted to 2,6-dimethyl-4-ethoxypyrylium tetrafluoroborate by ethylation with neat diethyl sulfate, followed by addition of 50% HBF_4 according to a literature procedure.[19] 3,5-Dimethyl-4-nitrophenetol: A solution of 1.12 g (10 mmol) of potassium *tert*-butanolate in 15 mL of *tert*-butyl alcohol is added dropwise to a refluxing solution of 1.13 g (5 mmol) of 2,6-dimethyl-4-ethoxypyrylium tetrafluoroborate in 5 mL of nitromethane. After 1-h reflux the mixture is poured into dilute hydrochloric acid (1 mL 7 N HCl/100 mL H_2O). The solution is extracted with 20 mL of chloroform five times; the collected extracts are dried over K_2CO_3. Evaporation of the solvent in vacuo yields an oily residue which is purified by column chromatography (SiO_2/CH_2Cl_2/20% hexane). Yield: 0.67 g (72%) of yellow needles, mp 52 °C.

3,5-Dimethyl-4-nitrophenol. A solution of 1.75 g (9 mmol) of 3,5-dimethyl-4-nitrophenetol in 33 mL of 48% hydrobromic acid and 16.5 mL of glacial acetic acid is refluxed for 3 h. The mixture is then extracted with three 20-mL portions of chloroform; the collected extracts are dried over Na_2SO_4. Evaporation of the solvent in vacuo yields a residue which is purified twice over a silica column (CH_2Cl_2/2% CH_3OH). Yield: 0.93 g (62%) of yellow crystals (mp 104 °C).

4-Amino-3,5-dimethylphenol Hydrochloride. To a solution of 318 mg (8.4 mmol) of sodium borohydride and 4 mg of Pd/C (10% Pd) in 10 mL of degassed water a solution of 0.7 g (4.2 mmol) of 3,5-dimethyl-4-nitrophenol in 10 mL of degassed methanol is added dropwise. After stirring for 30 min at ambient temperature

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(TLC control), the reaction mixture is acidified with 3 N HCl. Then the catalyst is filtered off and the solvent is removed in vacuo. The residue was used without further purification, assuming that the reduction had occurred quantitatively.

4-Diazo-3,5-dimethyl-2,5-cyclohexadienone (5e). A 174-mg (1-mmol) portion of 4-amino-3,5-dimethylphenol hydrochloride is dissolved in 4 mL of dilute sulfuric acid (0.05 mL H_2SO_4/4 mL H_2O). Now a solution of 0.11 g (1.6 mmol) of sodium nitrite in 4 mL of H_2O is added slowly; the temperature should not exceed 5 °C. After stirring the solution at 20 °C for 20 min; 10 mL of benzene and 2.8 g of barium carbonate are added. Separation of the organic layer and evaporation of the solvent at 20 °C yields a residue which is purified over a silica column: Eluation with CH_2Cl_2/20% pentane first yields 2,6-dimethyl-1,4-benzoquinone. Subsequent elution with CH_2Cl_2/20% CH_3OH then yields 90 mg (61%) of **5e** as orange crystals. Mp: 124 °C. Precision mass calcd 148.0636, found 148.0636 ± 2 ppm. ^{1}H-NMR ($CDCl_3$): δ 2.24 (s), 6.21 (s). ^{13}C-NMR (CD_3COCD_3): δ 18.0, 77.8, 125.6, 140.6, 181.8. MS: *m/e* 149 (9), 148 (molecular peak; 26), 120 (42), 107 (46), 93 (6), 92 (34), 91 (100), 79 (10), 77 (35), 74 (5), 66 (5), 65 (20), 63 (11), 61 (6), 53 (9), 52 (20), 51 (29), 50 (17), 45 (9), 44 (40). IR (Ar, 10 K): 2090.5 (w), 2070.7 (vs), 2067.3 (s), 2062.0 (m), 2059.1 (m), 2052.4 (m), 1634.4 (vs), 1618.5 (w), 1607.9 (vw), 1599.7 (vw), 1596.3 (vw), 1464.2 (vw), 1434.8 (vw), 1359.6 (vw), 1354.3 (w), 1350.4 (m), 1284.4 (vw), 1280.5 (vw), 1239.0 (m), 907.3 (vw), 904.0 (vw), 875.0 (vw), 708.2 cm^{-1} (vw).

4-Diazobenzo-2,5-cyclohexadienone (5f). Diazo ketone **5f** was prepared from 4-amino-1-naphthol hydrochloride according to a literature procedure.[20] IR (Ar, 10 K): 2071.7 (vs), 2051.4 (w), 1645.9 (s), 1643.5 (s), 1636.8 (m), 1624.3 (vw), 1610.3 (w), 1600.7 (w), 1585.7 (w), 1556.8 (vw), 1482.5 (w), 1471.4 (vw), 1293.5 (vw), 1272.3 (m), 1224.6 (w), 1152.7 (w), 1148.9 (vw), 1133.0 (vw), 1014.9 (vw), 826.3 (vw), 756.0 (w), 688.5 cm^{-1} (vw).

4-Diazo-2-methylbenzo-2,5-cyclohexadienone (5g). Compound **5g** was synthesized from 2-methyl-1,4-naphthoquinone following a literature procedure.[17] IR (Ar, 10 K): 2062.0 (vs), 2052.4 (m), 1635.8 (s), 1605.9 (s), 1600.6 (w), 1484.0 (m), 1472.4 (vw), 1380.3 (vw), 1304.1 (s), 1224.6 (vw), 1211.1 (m), 1201.1 (vw), 1111.3 (vw), 1073.7 (vw), 1037.0 (vw), 1033.7 (w), 1014.9 (vw), 941.6 (vw), 756.4 (w), 694.7 cm^{-1} (vw).

Matrix Spectroscopy. Matrix-isolation experiments were performed by standard techniques with an Air Products CSW-202 Displex closed cycle helium cryostat.[12e] Argon (Linde, 99.9999%) or a mixture of oxygen (Messer Griesheim, 99.998%) and argon (0.5% O_2) was deposited at 30 K on top of a CsI (IR) or sapphire (UV–vis) window with a rate of approximately 0.15 mmol/min. Quinone diazides **5b** and **5e** were warmed to 40 °C and codeposited. For the deposition of diazo compounds **5c,d,f,g**, which are less volatile, an electrically heated oven with a small distance between sample and window was utilized. Sample temperatures at deposition were 60, 65, 40, 40 °C for **5c,d,f,g**, respectively. Infrared spectra were recorded by using a Bruker IFS66 FTIR spectrometer. Standard spectra were taken with a resolution of 1 cm^{-1} in the range 4000–500 cm^{-1}. UV–vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer with a resolution of 2 nm. Irradiations were carried out with use of Osram HBO 500 W/2 mercury high-pressure arc lamps in an Oriel housing equipped with quartz optics. IR irradiation from the lamps was absorbed by a 10-cm path of water and by a Schott KG1 filter. For broad-band irradiation, Schott cut-off filters were used (50% transmission at the wavelength specified); for narrow-band irradiation, interference filters (Schott) in combination with cut-off filters to isolate mercury lines were used.

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[21] The set up for matrix isolation is described in ref 12e. IR spectra were recorded on a Bruker IFS66 FT-IR spectrometer in the range 4000–450 cm^{-1}, the standard resolution was set to 1 cm^{-1}. Irradiation was performed by using a 500-W high-pressure mercury arc lamp, dichroic mirrors to preselect the range of irradiation and appropriate cut-off filters.

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Regiochemistry on Photoamination of Stilbene Derivatives with Ammonia via Electron Transfer

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The regiochemistry of photoamination of 1,2-diarylethene (1) with ammonia in the presence of *p*-dicyanobenzene (DCNB) has been investigated. The photoamination of stilbene and *p,p'*-dimethoxystilbene gave 1-amino-1,2-diphenylethane and 1-amino-1,2-bis(*p*-methoxyphenyl)ethane, respectively. The photoamination of unsymmetric 1-aryl-2-phenylethene having an alkoxy group on the para position occurred selectively to give 1-amino-2-aryl-1-phenylethane. On the other hand, the photoamination of 1-aryl-2-phenylethene having a methyl and chloro group on the para position or methoxy group on the meta and ortho positions gave both 1-amino-2-aryl-1-phenylethane and 1-amino-1-aryl-2-phenylethane. The regiochemistry is related with the distribution of positive charge in the cation radicals of 1 generated from photochemical electron transfer to DCNB.

Nucleophilic addition induced by photochemical electron transfer has received much attention as a potentially useful procedure for organic synthesis.[1] Especially regio- and stereoselective photoinduced nucleophilic additions have high synthetic potential. The regiochemistry for anti-Markovnikov addition of nucleophiles to aryl-substituted alkenes[2,3] (e.g., 1,1-diphenylethylene) and aryl-

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