Alkynylcyanoketenes. Unusual Rearrangements Arising from the Reactions of Alkynylcyanoketenes with Alkynes

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The reactions of selected alkynylcyanoketenes and enynylketenes with alkynes are reported to result in unusual rearrangements to variously substituted polycyclic aromatic compounds and/or bicyclo[4.2.0]octatrienones. The mechanisms and synthetic scope of these reactions are discussed.

The synthesis of alkynylcyanoketenes and the observation that they undergo facile [2 + 2] cycloadditions to alkenes giving cyclobutanones was previously reported.[1,2] We now describe a study of the reactions of these ketenes with alkynes. Unlike the alkene cycloadditions these reactions result in a series of unusual transformations ultimately giving polycyclic aromatic compounds and/or bicyclo[4.2.0]octa-1,4,7-trien-3-ones. The rearrangements are envisaged as arising from a series of reactions stemming from the initially formed [2 + 2] cycloaddition products, i.e., 4-alkynyl-4-cyanocyclobutenones.

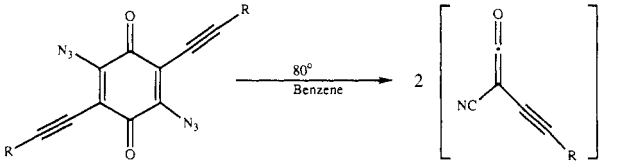
Synthesis of the alkynylcyanoketenes **2a–e** was accomplished using the previously reported method employing the thermolysis of appropriately substituted 2,5-diazido-3,6-dialkynyl-1,4-benzoquinones **1a–e** (Scheme I).[1,2] In turn, the azidoquinones were prepared from the corresponding 2,5-dialkynyl-3,6-dichloro-1,4-benzoquinones which stem from commercially available chloranilic acid.[1,3,4]

The unusual character of the rearrangements outlined here is illustrated by the reaction of (2-methylphenyl)-cyanoketene, **2a**, with diphenylacetylene to yield the dibenzopyran **3** (Scheme II). The isolated yield of the pyran could be increased as a function of the alkyne concentration. For example when the molar ratio of alkyne to ketene was, respectively, 2.1, 5.0, and 10.0 the respective isolated yield of the pyran was 40%, 67%, and 68%.

The rearrangement appears to have some generality as observed by the fact that dibenzopyrans **4a–c** were obtained when the same ketene, **2a**, was generated in the presence of other alkynes. Retrosynthetically, this reaction translates to the relationship of **4** to the alkynes **5** and the ketene precursor **1a** (Scheme II).

A proposed mechanism for these transformations is outlined in Scheme III. Here, the ketene **2a** is viewed as undergoing [2 + 2] cycloadditions to the alkynes leading to the corresponding cyclobutenones, **6**. Under the reaction conditions these then lead to the enynylketenes **7** upon electrocyclic ring opening. Subsequent ring closure gives the diradicals (or zwitterions) **8** which proceed to **9** upon hydrogen atom abstraction. These intermediates then collapse to the product **4** upon intramolecular radical/radical combination. Such a mechanistic proposal finds direct precedence in the recently reported ring expansions of 4-alkynyl-4-hydroxycyclobutenes to 1,4-benzoquinones which is also a transformation involving enynylketenes and

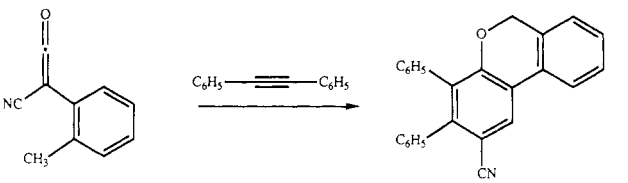
Scheme I



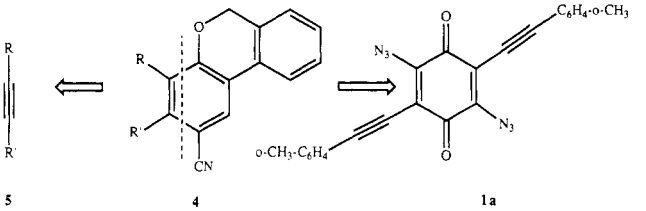
1

	R
a)	C_6H_4-o-CH_3,
b)	C_6H_4-o-OCH_3
c)	$CH_2CH_2C_6H_5$
d)	$CH_2OC_6H_5$
e)	C_6H_5

Scheme II



2a 3



5 4 1a

	R	R'	% YIELD
a)	CH_3	OC_2H_5	58
b)	C_2H_5	C_2H_5	29
c)	H	C_6H_5	19

diradical intermediates similar in structure to **7** and **8**.[5] In addition, a previously reported transformation in which an example of **7** was independently generated and shown to provide **4** is given in Scheme IV.[6] Specifically, the azidoquinone **10** was subjected to thermolysis **12**, a reaction which is also envisaged to proceed through the enynylketene intermediate, **11**.

Although the yields of product are poor, it is noted that these rearrangements have some synthetic generality in that the aromatic compounds **13** (40%), **14** (8%), and **15** (5%) were obtained from the reactions of the respective ketenes **2c**, **2d**, and **2b** with diphenylacetylene. The for-

(1) For the synthesis of alkynylketenes of any structural type, see: Nguyen, N. V.; Chow, K.; Moore, H. W. *J. Org. Chem.* **1987**, *52*, 1315.

(2) The synthesis of cyanoketenes from diazidoquinones is a general method. See: Moore, H. W.; Weyler, W.; Duncan, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 6181. Moore, H. W.; Gheorghiu, M. D. *Chem. Soc. Rev.* **1981**, *10*, 289.

(3) Moore, H. W.; Sing, Y. L.; Sidhu, R. S. *J. Org. Chem.* **1980**, *45*, 5057.

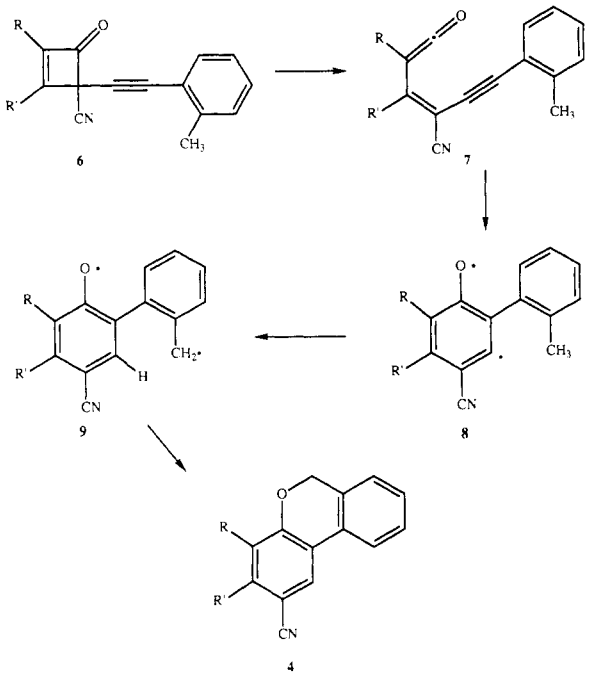
(4) Moore, H. W.; West, K. F.; Wriede, U.; Chow, K.; Fernandez, M.; Nguyen, N. V. *J. Org. Chem.* **1987**, *52*, 2537.

(5) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975.

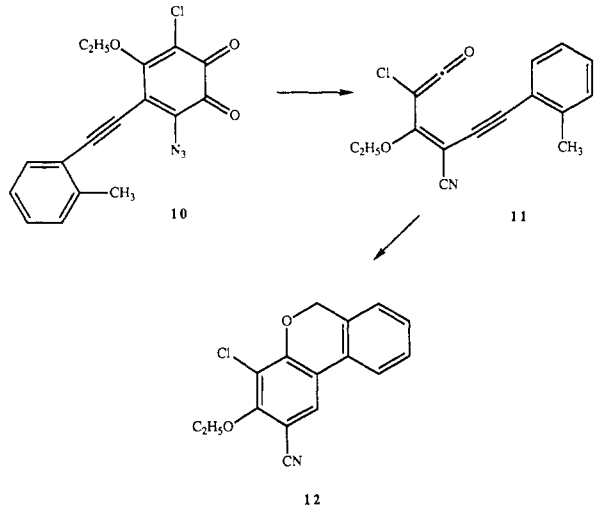
(6) Moore, H. W.; Chow, K.; Nguyen, N. V. *J. Org. Chem.* **1987**, *52*, 2530.

0022-3263/90/1955-3876$02.50/0

Scheme III



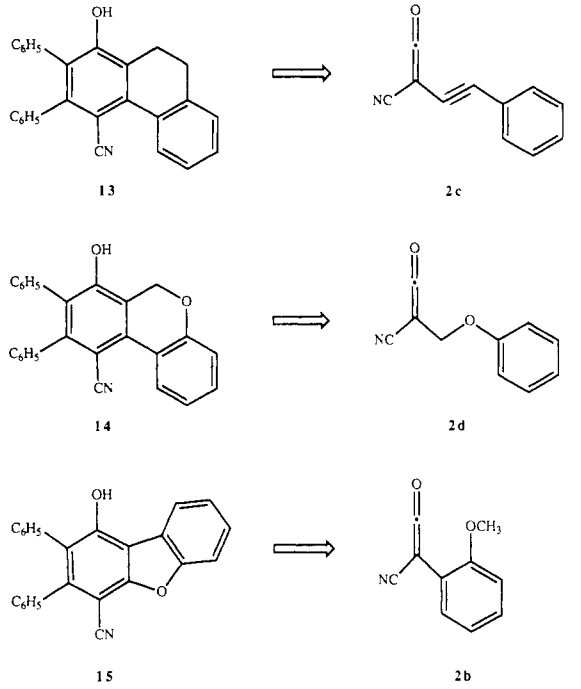
Scheme IV



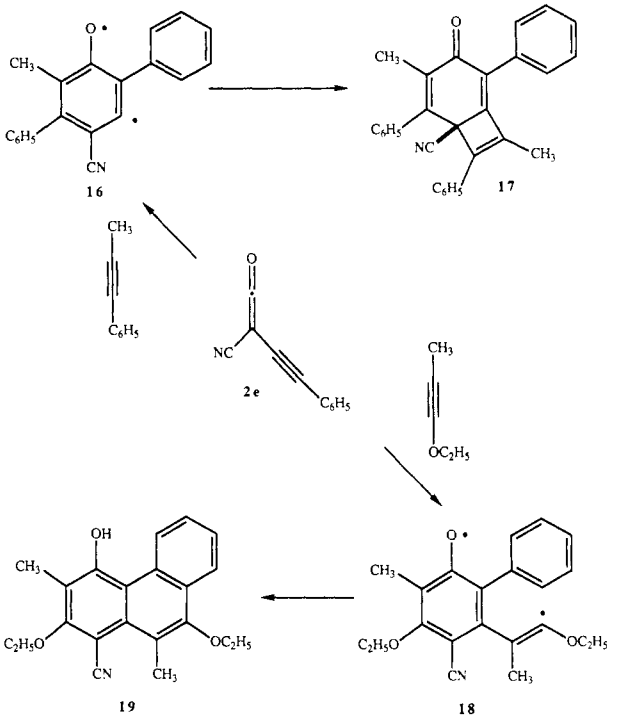
mation of **13** and **14** is considered to arise in analogy to the mechanism outlined above except that the diradical corresponding to **8** undergoes intramolecular arylation rather than hydrogen atom abstraction. The formation of **15** is somewhat more complicated, and the product yield is dependent upon the specific reaction conditions. For example, no products were isolated unless the reaction was accomplished in the presence of trimethylsilyl chloride, conditions previously observed to enhance product yields in related transformations of azidoquinones.[4] Under these conditions the reaction is considered to involve an oxonium ion intermediate. That is, the diradical (or zwitterionic) species is viewed as interacting with the methoxy group leading to a zwitterionic oxonium ion. Silylation of the phenoxide ion followed by demethylation by nucleophilic attack of the released chloride ion on the methyl group and subsequent desilylation upon workup then leads to **15**.

Still other unusual transformations were observed when phenylethynylcyanoketene **2e** was generated in the presence of selected alkynes (Scheme VI). For example, this ketene reacted with excess phenylpropyne to give the bicyclo[4.2.0]octatrienone **17** (40% yield), the structure of

Scheme V



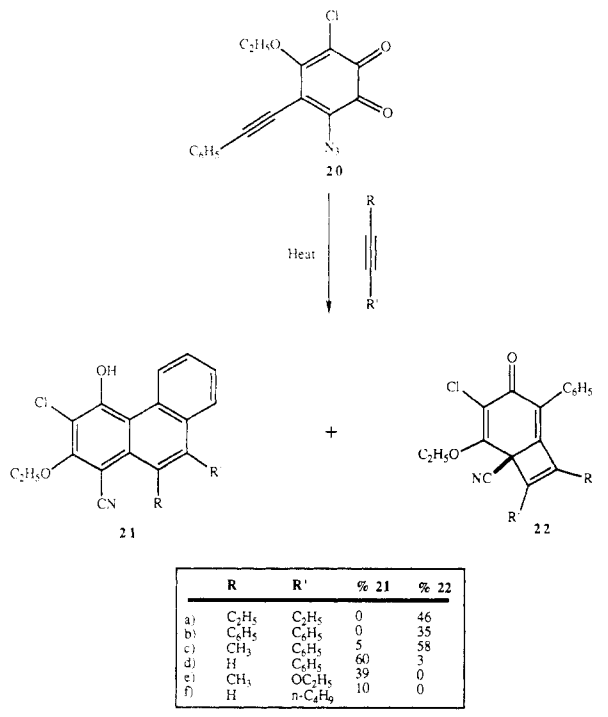
Scheme VI



which was determined by a single-crystal X-ray analysis.[7] The formation of **17** is again envisaged as involving a diradical intermediate, i.e., **16**. However, unlike the previous examples, **16** cannot readily undergo an intramolecular arylation or H atom abstraction. As a result, it reacts with an additional equivalent of 1-phenylpropyne at the 2-position, resulting in still a new diradical intermediate which now undergoes intramolecular radical/radical combination giving **17**. Interestingly, when the ketene **2e** is

(7) To our knowledge, examples of this ring system have not previously been reported. For the X-ray data for **17**, see: Nguyen, N. V. Ph.D. dissertation. Alkynylcyanoketenes and (2-alkynylethenyl)ketenes. Synthesis and Reactions. University of California, Irvine, 1985.

Scheme VII



	R	R'	% 21	% 22
a)	C_2H_5	C_2H_5	0	46
b)	C_6H_5	C_6H_5	0	35
c)	CH_3	C_6H_5	5	58
d)	H	C_6H_5	60	3
e)	CH_3	OC_2H_5	39	0
f)	H	n-C_4H_9	10	0

generated in the presence of ethoxypropyne the reaction takes a related, but different course. That is, in analogy to the above, the diradical **18** is formed. Now, however, rather than intramolecular ring closure to a bicyclooctatrienone, intramolecular radical/radical coupling involving the phenyl substituent takes place to give the phenanthrene **19**. The reason(s) for this selectivity are not clear but may be due to a difference in steric bulk of the alkyne substituents, i.e. ethoxy being smaller than phenyl allows formation of the presumably more stable phenanthrene **19**.

In order to gain further insight into the synthetic scope and mechanism of the above reaction the thermolyses of the azidoquinone **20** in the presence of a variety of alkynes varying in steric bulk were studied (Scheme VII) As noted earlier, thermolysis of 4-alkynyl-3-azido-1,2-benzoquinones leads to enynylketenes upon lose of nitrogen and carbon monoxide. Thus, thermolysis of **20** in the presence of alkynes was anticipated to give the corresponding ketene followed by diradical formation and subsequent alkyne trapping to give either phenanthrenes and/or bicyclooctatrienones. This was realized as evidence by the data given in Scheme VII. Specifically, thermolysis of **20** in the presence of the indicated alkynes gave the phenanthrenes **21c–f** and the bicyclooctatrienones **22a–d**. Here again, the trend that sterically bulky alkynes favor bicyclooctatrienone formation over phenanthrene was observed.

Experimental Section

The purity of all title compounds was judged to be ≥95% by melting point and carbon and proton NMR spectral determinations.

3-Cyano-1,2-diphenyl-9*H*-dibenzo[*b*,*d*]pyran (3). A solution of 0.14 g (0.33 mmol) of **1a** in 75 mL of dry CCl_4 was added dropwise to a refluxing solution of 0.12 g (0.69 mmol) of diphenylacetylene in 500 mL of dry CCl_4 while under an argon atmosphere. The solution was heated at reflux for 3 h. The reaction mixture was concentrated, and the residue was absorbed onto silica gel and subjected to flash chromatography (4:1 hexanes/ethyl acetate) to afford 94.0 mg (40%) of a yellow solid, **3**: mp 218–220 °C; ^{1}H NMR ($CDCl_3$) δ 8.14 (s, 1 H), 7.77 (d, J = 8 Hz, 1 H), 7.04–7.50 (m, 13 H), 5.15 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 155.48, 146.01, 136.89, 134.67, 131.89, 130.66, 130.61, 129.92, 128.93, 128.27, 127.86, 127.84, 127.60, 127.44, 127.12, 124.78, 122.95, 122.33, 118.87, 106.52, 68.78; IR 3070 (w), 2210 (s), 1590 (s), 1465 (m), 1430 (s), 1410 (s), 1385 (s), 1000 (s); MS m/z 359 (EI), 360 (CI); MS exact mass calcd for $C_{26}H_{17}NO$ 359.1310, found 359.1296.

When the amount of diphenylacetylene was increased the yield of **3** also incresed as follows: 2.1 equiv (40%), 5.0 equiv (67%), 10.0 equiv (68%).

3-Cyano-2-ethoxy-1-methyl-9*H*-dibenzo[*b*,*d*]pyran (4a). A solution of 0.15 g (0.36 mmol) of **1a** in 75 mL of dry CCl_4 was added dropwise to a refluxing solution of 76 mL (0.76 mmol) of ethyl propynyl ether in 500 mL of dry CCl_4 while under an argon atmosphere. The solution was heated at reflux for 3 h. The reaction mixture was concentrated, and the residue was absorbed onto silica gel and subjected to flash chromatography (4:1 hexanes/ethyl acetate) to afford 0.11 g (58%) of an orange solid: mp 89.5–90.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.80 (s, 1 H), 7.60 (d, J = 7 Hz, 1 H), 7.18–7.59 (m, 2 H), 7.16 (d, J = 7 Hz, 1 H), 5.20 (s, 2 H), 4.19 (q, J = 7 Hz, 2 H), 2.18 (s, 3 H), 1.48 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 160.95, 157.86, 130.32, 129.10, 128.84, 128.48, 125.81, 124.89, 122.24, 121.57, 119.23, 117.72, 99.94, 70.90, 69.08, 15.89, 9.38; IR 3000 (w), 2940 (w), 2240 (m), 1610 (s), 1485 (m), 1450 (s), 1425 (m), 1395 (m), 1280 (m), 1255 (m), 1180 (m), 1120 (s), 1090 (s); MS m/z 265 (EI), 266 (CI); MS exact mass calcd for $C_{17}H_{15}NO_2$ 265.1102, found 265.1098.

3-Cyano-1,2-diethyl-9*H*-dibenzo[*b*,*d*]pyran (4b). A solution of 0.15 g (0.36 mmol) of **1a** in 75 mL of dry CCl_4 was added dropwise to a refluxing solution of 0.13 mL (1.14 mmol) of 3-hexyne in 500 mL of dry CCl_4 while under an argon atmosphere. The solution was heated at reflux for 2 h. The reaction mixture was concentrated, and the residue was absorbed onto silica gel and subjected to flash chromatography (4:1) hexanes/ethyl acetate) to afford 55.5 mg (29%) of yellow crystals: mp 71.5–72.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.85 (s, 1 H), 7.62 (d, J = 7 Hz, 1 H), 7.26–7.61 (m, 2 H), 7.16 (d, J = 7 Hz, 1 H), 5.16 (s, 2 H), 2.88 (q, J = 7 Hz, 2 H), 2.71 (q, J = 7 Hz, 2 H), 1.27 (t, J = 7 Hz, 3 H), 1.15 (t, J = Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 156.44, 147.35, 132.71, 130.83, 129.05, 129.02, 128.54, 126.17, 124.86, 122.32, 121.48, 119.22, 106.05, 68.89, 25.19, 19.70, 15.56, 14.67; IR 2980 (m), 2950 (w), 2890 (w), 2210 (s), 1600 (m), 1450 (s), 1420 (s), 1285 (s), 1260 (s), 1230 (m), 1210 (m), 1120 (m), 1030 (s); MS m/z 263 (EI); MS exact mass calcd for $C_{18}H_{17}NO$ 263.131, found 263.1302.

3-Cyano-2-phenyl-9*H*-dibenzo[*b*,*d*]pyran (4c). A solution of 0.15 g (0.36 mmol) of **1b** in 75 mL of dry CCl_4 was added dropwise to a refluxing solution of 83.6 mL (0.76 mmol) of phenylacetylene in 500 mL of dry CCl_4 while under an argon atmosphere. The solution was heated at reflux for 2 h. The reaction mixture was concentrated, and the residue was absorbed onto silica gel and subjected to flash chromatography (4:1 hexanes/ethyl acetate) to afford 39.2 mg (19%) of light orange crystals: mp 174.5–175.0 °C; ^{1}H NMR ($CDCl_3$) δ 8.10 (s, 1 H), 7.71 (d, J = 6 Hz, 1 H), 7.34–7.60 (m, 7 H), 7.18 (d, J = 6 Hz, 1 H), 7.10 (s, 1 H), 5.24 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 158.14, 146.88, 137.89, 130.79, 129.38, 129.21, 129.14, 129.11, 128.97, 128.76, 128.00, 125.15, 122.61, 122.36, 119.30, 119.20, 104.74, 68.95; IR 2220 (m), 1620 (m), 1595 (w), 1550 (m), 1490 (s), 1460 (s), 1415 (m), 1320 (w), 1290 (m), 1285 (m), 1235 (m), 1190 (s), 1015 (s); MS m/z 283 (EI), 284 (CI); MS exact mass calcd for $C_{20}H_{13}NO$ 283.0997, found 283.0995.

4-Cyano-2,3-diphenyl-1-hydroxy-9,10-dihydrophenanthrene (13). A solution of 0.20 g (0.45 mmol) of **1c** in 75 mL of dry CCl_4 was added dropwise to a refluxing solution of 0.17 g (0.95 mmol) of diphenylacetylene in 500 mL of dry CCl_4 while under an argon atmosphere. The solution was heated at reflux for 1.5 h. The reaction mixture was concentrated, and the residue absorbed onto silica gel and subjected to flash chromatography (7:3 hexanes/ethyl acetate) to afford 0.13 g (40%) of light orange crystals of **13**: mp 238.5–239.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.37 (d, J = 9 Hz, 1 H), 7.10–7.35 (m, 13 H), 5.54 (s, 1 H), 2.88 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 152.75, 146.24, 139.46, 139.15, 137.66, 133.33, 131.82, 130.62, 129.98, 129.29, 129.01, 128.46, 127.81, 127.76, 127.75, 127.26, 127.16, 126.85, 125.57, 119.59, 101.17, 28.69, 21.79; IR 3350 (br), 2230 (s), 1540 (s), 1450 (m), 1420 (s), 1205 (m); MS m/z 373 (EI); MS exact mass calcd for $C_{27}H_{19}NO$ 373.1466, found 373.1436.

5-Cyano-6,7-diphenyl-8-hydroxy-9*H*-dibenzo[*b*,*d*]pyran (14). A solution of 0.15 g (0.33 mmol) of **1d** in 75 mL of dry CCl_4

was added dropwise to a refluxing solution of 0.13 g (0.73 mmol) of diphenylacetylene in 400 mL of dry CCl_4 while under an argon atmosphere. The solution was heated at reflux for 2 h. The reaction mixture was concentrated, and the residue was absorbed onto silica gel and subjected to flash chromatography (7:3 hexanes/ethyl acetate) to afford 18.2 mg (8%) of yellow crystals: mp 222 °C dec; ^{1}H NMR ($CDCl_3$) δ 8.53 (d, J = 7 Hz, 1 H), 7.07–7.41 (m, 13 H), 5.61 (s, 1 H), 5.18 (s, 2 H); ^{13}C NMR ($CDCl_3$) 156.11, 151.13, 147.91, 137.20, 134.37, 132.51, 131.21, 130.52, 129.83, 129.43, 128.70, 128.00, 127.93, 127.56, 126.44, 122.46, 121.16, 120.24, 118.90, 117.59, 100.11, 62.97; IR 3330 (br), 2220 (m), 1585 (m), 1550 (s), 1430 (s), 1240 (s); MS m/z 375 (EI); MS exact mass calcd for $C_{26}H_{17}NO_2$ 375.1259, found 375.1268.

4-Cyano-1-hydroxy-2,3-diphenyldibenzofuran (15). A solution of 0.17 g (0.37 mmol) of **1d** in 75 mL of dry CCl_4 was added dropwise to a refluxing solution of 0.17 g (0.95 mmol) of diphenylacetylene and 0.23 mL (3.68 mmol) of trimethylsilyl chloride in 400 mL of dry CCl_4 while under an argon atmosphere. The solution was heated at reflux for 2 h. The reaction mixture was concentrated, and the residue was absorbed onto silica gel and subjected to flash chromatography (4:1 hexanes/ethyl acetate) to afford 12.3 mg (5%) of a yellow solid: mp 203–205 °C; ^{1}H NMR ($CDCl_3$) δ 8.12 (d, J = 9 Hz, 1 H), 7.68 (d, J = 9 Hz, 1 H), 7.13–7.53 (m, 12 H), 6.11 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 157.98, 156.01, 152.11, 144.87, 136.84, 132.61, 131.21, 130.01, 129.49, 128.60, 128.05, 127.93, 127.54, 123.93, 123.05, 122.98, 122.40, 115.04, 112.19, 111.73, 89.89; IR 3300 (br), 2920 (m), 2850 (w), 2220 (s), 1590 (s), 1410 (s), 1320 (m), 1295 (m), 1200 (s); MS m/z 361 (EI); MS exact mass calcd for $C_{25}H_{15}NO_2$ 361.110265, found 361.1105.

6-Cyano-4,8-dimethyl-5,7-diphenylbicyclo[4.2.0]octa-1,4,7-trien-3-one (17). A solution of 1.00 g (2.56 mmol) of 2,5-diazido-3,6-bis(phenylethynyl)-2,5-cyclohexadiene-1,4-dione, **1e**, in 40 mL of dry benzene was added dropwise to a refluxing solution of 5.93 g (51.20 mmol) of phenylpropyne in 300 mL of dry benzene over a period of 1 h while under an atmosphere of argon. The solution was then refluxed for an additional 3 h during which time it turned from dark red to brown. The solution was concentrated, and the dark oily residue was absorbed onto silica gel and subjected to flash column chromatography (hexanes/ethyl acetate) to give a yellow solid. Recrystallization (dichloromethane/hexanes) yielded 0.41 g (40%) of **17** as a yellow crystalline solid: mp 202–203 °C; ^{1}H NMR ($CDCl_3$) δ 7.00–7.47 (m, 15 H), 2.01 (s, 3 H), 1.83 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 185.88, 151.87, 145.59, 144.53, 142.60, 141.21, 136.12, 132.06, 130.30, 129.83, 129.53, 128.81, 128.63, 128.33, 128.25, 128.10, 127.77, 127.65, 125.86, 119.27, 47.84, 14.50, 13.56; IR (KBr) 3070, 3018, 2915, 2218, 1650, 1601, 1561, 1498; MS m/z 399 (EI), 400 (CI); MS exact mass calcd for $C_{29}H_{21}NO$ 399.1623, found 399.1625.

1-Cyano-2,9-diethoxy-3,10-dimethyl-4-hydroxyphenanthrene (19). A solution of 0.95 g (2.43 mmol) of 2,5-diazido-3,6-bis(phenylethynyl)-2,5-cyclohexadiene-1,4-dione, **1e**, and 2.04 g (24.35 mmol) of 1-ethoxypropyne in 300 mL of dry benzene was refluxed for 3 h. The solution was then concentrated, and the residue was subjected to flash chromatography (silica gel, hexanes/ethyl acetate) to give a yellow semisolid. Recrystallization from dichloromethane/hexanes yielded 0.21 g (13%) of a white crystalline solid: mp 211–212 °C; ^{1}H NMR ($CDCl_3$) δ 9.43–9.47 (m, 1 H), 8.20–8.24 (m, 1 H), 7.60–7.64 (m, 2 H), 6.21 (s, 1 H), 4.19 (q, J = 7 Hz, 2 H), 4.09 (q, J = 7 Hz, 2 H), 2.99 (s, 3 H), 2.43 (s, 3 H), 1.34 (t, J = 7 Hz, 3 H), 1.11 (t, J = 7 Hz, 3 H); IR (KBr) 3355, 3096, 2990, 2940, 2898, 2228, 1608, 1571; MS m/z 335 (EI); MS exact mass calcd for $C_{21}H_{21}NO_3$ 335.1521, found 335.1517.

4-Chloro-6-cyano-7,8-diethyl-5-ethoxy-2-phenylbicyclo[4.2.0]octa-1,4,7-trien-3-one (22a). A solution of 0.40 g (1.22 mmol) of 3-azido-6-chloro-5-ethoxy-4-(phenylethynyl)-3,5-cyclohexadiene-1,2-dione, **20**, in 40 mL of dry carbon tetrachloride was added dropwise (1 h) to a refluxing solution of 0.50 g (6.11 mmol) of 3-hexyne in 150 mL of dry carbon tetrachloride under an atmosphere of argon. The solution was relaxed for an additional 3 h, during which time the color changed from purple to yellow. The solution was then concentrated, and the dark oily residue was absorbed onto silica gel and subjected to flash column chromatography (hexane/ethyl acetate) to give a crude yellow solid. Recrystallization from dichloromethane/hexane yielded 0.20 g (46%) of **22a**, a yellow crystalline solid: mp 94–95 °C; ^{1}H NMR ($CDCl_3$) δ 7.23–7.37 (m, 5 H), 4.55 (dq, J = 7 Hz, J' = 2.85 Hz, 1 H), 4.28 (dq, J = 7 Hz, J' = 2.85 Hz, 1 H), 2.53 (hept, J = 7 Hz, 4 H), 1.36 (t, J = 7 Hz, 3 H), 1.30 (t, J = 7 Hz, 3 H), 1.10 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 180.73, 158.02, 153.97, 149.06, 147.19, 132.42, 130.09, 129.01, 123.36, 124.16, 118.45, 117.96, 70.05, 47.96, 21.77, 20.36, 15.79, 11.35, 11.44; IR (KBr) 3059, 2978, 2917, 2221, 1660, 1602, 1573; MS m/e 353 (EI), 354 (CI); MS exact mass calcd for $C_{21}H_{20}ClNO_2$ 353.1189, found 353.1176.

4-Chloro-6-cyano-5-ethoxy-2,7,8-triphenylbicyclo[4.2.0]-octa-1,4,7-trien-3-one (22b). In a manner similar to that described for the preparation of **22a**, 0.40 g (1.22 mmol) of **20** was subjected to thermolysis in the presence of 0.51 g (6.11 mmol) of diphenylacetylene to give 0.25 g (35%) of **22b** as a bright yellow crystalline solid: mp 152–153 °C; ^{1}H NMR ($CDCl_3$) δ 6.86–7.75 (m, 15 H), 4.80 (dq, J = 7 Hz, J' = 2.7 Hz, 1 H), 4.51 (dq, J = 7 Hz, J' = 2.7 Hz, 1 H), 1.32 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 180.53, 157.94, 147.39, 145.62, 143.28, 131.45, 131.30, 130.95, 130.04, 129.65, 129.21, 129.07, 128.92, 128.71, 128.44, 128.15, 128.07, 125.54, 119.03, 118.04, 70.81, 47.71, 15.70; IR (KBr) 3050, 2951, 2910, 2872, 2220, 2102, 1641, 1565, 1439; MS m/z 449 (EI), 450 (CI); MS exact mass calcd for $C_{29}H_{20}ClNO_2$ 449.1182, found 449.1172.

4-Chloro-6-cyano-2,7-diphenyl-5-ethoxy-8-methylbicyclo-[4.2.0]octa-1,4,7-trien-3-one (22c). In a manner similar to that described for the preparation of **22a**, 0.70 g (2.14 mmol) of **20** was subjected to thermolysis in the presence of 2.48 g (21.41 mmol) of 1-phenylpropyne to give 0.48 g (58%) of **22c** as a white crystalline solid: mp 178–179 °C; ^{1}H NMR ($CDCl_3$) δ 7.76–7.81 (m, 2 H), 7.34–7.52 (m, 8 H), 4.74 (dq, J = 7 Hz, J' = 2.8 Hz, 1 H), 4.50 (dq, J = 7 Hz, J' = 2.8 Hz, 1 H), 2.04 (s, 3 H), 1.34 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 180.05, 157.91, 147.79, 146.44, 143.12, 131.39, 130.48, 130.24, 129.59, 128.90, 128.68, 128.29, 128.06, 124.98, 118.92, 117.70, 70.55, 47.46, 15.44, 13.71; IR (KBr) 3071, 2993, 2941, 2241, 1668, 1597, 1578; MS m/z 387 (EI); MS exact mass calcd for $C_{24}H_{18}ClNO_2$ 387.1026, found 387.1042.

3-Chloro-1-cyano-2-ethoxy-4-hydroxy-10-methyl-9-phenylphenanthrene (21c). From the above experiment 0.04 g (5%) of **21c** was isolated as a white crystalline solid: mp 255–256 °C; ^{1}H NMR ($CDCl_3$) δ 9.59 (dq, J = 8.5 Hz, J' = 0.6 Hz, 1 H), 7.24–7.64 (m, 9 H), 4.41 (q, J = 7 Hz, 2 H), 2.74 (s, 3 H), 1.56 (t, J = 7 Hz, 3 H); IR (KBr) 3351, 3079, 3018, 2996, 2940, 2214, 15928 1570, 1480; MS m/z 387 (EI); MS exact mass calcd for $C_{24}H_{18}ClNO_2$ 387.1026, found 387.1048.

4-Chloro-6-cyano-5-ethoxy-2,7-diphenylbicyclo[4.2.0]-octa-1,4,7-trien-3-one (22d). In a manner similar to that described for the preparation of **22a**, 0.40 g (1.22 mmol) of **20** was subjected to thermolysis in the presence of 0.63 g (6.11 mmol) of phenylacetylene to give 0.02 g (3%) of **22d** as a yellow crystalline solid: mp 151–152 °C; ^{1}H NMR ($CDCl_3$) δ 7.79–7.84 (m, 2 H), 7.38–7.54 (m, 8 H), 7.25 (s, 1 H), 4.77–4.86 (m, 1 H), 4.50–4.62 (m, 1 H), 1.41 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 180.03, 157.35, 151.45, 145.63, 133.59, 131.89, 131.77, 129.24, 129.09, 129.04, 128.76, 128.61, 127.87, 124.60, 119.27, 117.28, 70.90, 49.08, 15.74; IR (KBr) 3093, 3050, 2978, 2911, 2215, 1650, 1580, 1482, 1442; MS exact calcd for $C_{23}H_{16}ClNO_2$ 373.0869, found 373.0878.

3-Chloro-1-cyano-2-ethoxy-4-hydroxy-9-phenylphenanthrene (21d). From the above experiment 0.27 g (60%) of **21d** was isolated as a white crystalline solid: mp 178–179 °C; ^{1}H NMR ($CDCl_3$) δ 9.66 (d, J = 8.23 Hz, 1 H), 7.99 (s, 1 H), 7.95 (dd, J = 1.36 Hz, J' = 8.16 Hz, 1 H), 7.46–7.55 (m, 7 H), 7.31 (s, 1 H), 4.47 (q, J = 7 Hz, 2 H), 1.57 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 157.64, 154.76, 143.86, 139.86, 133.39, 131.50, 130.03, 128.62, 128.17, 128.09, 127.79, 127.30, 127.06, 123.45, 116.07, 116.01, 112.13, 96.87, 71.94, 15.33; IR (KBr) 3281, 3022, 2971, 2914, 2216, 1610, 1561, 1440, 1402; MS exact mass calcd for $C_{23}H_{16}ClNO_2$ 373.0869, found 373.0853.

3-Chloro-1-cyano-2,9-diethoxy-4-hydroxy-10-methylphenanthrene (21e). In a manner similar to that described for the preparation of **22a**, 0.30 g (0.91 mmol) of **20** was subjected to thermolysis in the presence of 0.39 g (4.58 mmol) of 1-ethoxypropyne to give 0.13 g (39%) of **21e** as a white crystalline solid: mp 199–200 °C; ^{1}H NMR ($CDCl_3$) δ 9.49–9.53 (m, 1 H), 8.20–8.24 (m, 1 H), 7.62–7.66 (m, 2 H), 7.24 (s, 1 H), 4.37 (q, J = 7 Hz, 2 H), 4.06 (q, J = 7 Hz, 2 H), 2.98 (s, 3 H), 1.57 (t, J = 7 Hz, 3 H), 1.59 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 159.45, 155.29, 154.65, 135.59, 129.74, 128.13, 127.42, 127.27, 124.33, 122.63, 121.39, 117.74, 115.39, 111.96, 96.42, 71.85, 70.05, 15.86, 15.77; IR (KBr) 3255,

3079, 2970, 2878, 2219, 1595, 1551, 1480; MS m/z 355 (EI), 356 (CI); MS exact mass calcd for $C_{20}H_{18}ClNO_3$ 355.0975, found 355.0984.

9-Butyl-3-chloro-1-cyano-2-ethoxy-4-hydroxyphenanthrene (21f). In a manner similar to the above using 0.49 g (1.49 mmol) of **20** and 0.61 g (7.48 mmol) of 1-hexyne, 0.05 g (10%) of **21f** was isolated as a white crystalline solid: mp 145-146 °C; ^{1}H NMR ($CDCl_3$) δ 9.57-9.61 (m, 1 H), 8.12-8.16 (m, 1 H), 7.87 (s, 1 H), 7.66-7.72 (m, 2 H), 7.22 (s, 1 H), 4.44 (t, J = 7 Hz, 2 H), 3.13 (t, J = 7 Hz, 2 H), 1.72-1.85 (m, 2 H), 1.46-1.59 (m, 5 H), 1.00 (t, J = 7 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 157.30, 154.62, 142.56, 133.58, 131.27, 129.77, 128.34, 127.39, 126.97, 124.40, 122.08, 116.01, 115.48, 111.98, 96.13, 71.87, 33.65, 32.44, 23.12, 15.85, 14.12; IR (KBr) 3300, 2971, 2950, 2881, 2240, 1573, 1418; MS m/z 353 (EI), 354 (CI); MS exact mass calcd for $C_{21}H_{20}ClNO_2$ 353.1182, found 353.1176.

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Supplementary Material Available: ^{13}C NMR spectra for **4a-c** and an ORTEP drawing and single-crystal X-ray data for **17** (10 pages). Ordering information is given on any current masthead page.

Synthesis and Reactions of α-Chloro-β,γ-unsaturated Esters. 1†

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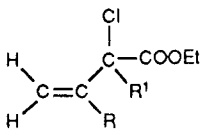
Four new α-chloro-β,γ-unsaturated esters were prepared in good yield by the reaction of hypochlorous acid with substituted ethyl 2-butenoates. Reaction of these substituted allylic chlorides with several nucleophiles has been investigated. Thiophenol in the presence of aqueous sodium hydroxide react with ethyl 2-chloro-3-methyl-3-butenoate (**2**) to give **6**, whereas ethyl 2-chloro-2,3-dimethyl-3-butenoate (**1**) is unreactive. Tertiary allylic chlorides **1**, **3**, and **4** react with secondary amines to give exclusive abnormal S_N2 reaction products. With benzylamine abnormal S_N2 substitution is followed by cyclization to give 1-benzyl-3-pyrrolin-2-ones. While ethyl lithioacetate reacts with **1** to give acylation product **18**, sodium diphenylmethide in liquid ammonia undergoes alkylation on the tertiary carbon possibly by an electron-transfer reaction pathway. Lithio-1,3-dithiane reacts with **1** to give 2,3-dimethyl-6,10-dithiaspiro[4.5]dec-2-en-1-one (**20**) via a two-step process, viz., acylation followed by a novel variation of the intramolecular abnormal S_N2 reaction. Raney nickel desulfurization of **20** gave 2,3-dimethyl-2-cyclopenten-1-one. Synthetic and mechanistic implications of these results are discussed.

In connection with one of our ongoing projects, we required the use of certain highly substituted allylic halides, in particular, α-chloro-β,γ-unsaturated esters of the general structure



1: R = CH_3, R^1 = CH_3
2: R = CH_3, R^1 = H
3: R = Ph, R^1 = H
4: R = Ph, R^1 = CH_3

A literature survey revealed that there was no general and efficient synthesis for this type of compound. The synthesis of 2-bromo-3-butenoic acid from acrolein cyanohydrin proceeds in too poor a yield to be of synthetic utility.[1] Furthermore, this procedure has not been extended to other substituted 2-halo-3-butenoic acids. The other known described example is the synthesis of ethyl 2-bromo-3-phenyl-3-butenoate by kinetic deconjugation[2] of ethyl 2-bromo-3-methylcinnamate with LDA/THF. The Darzens condensation of ethyl 2-bromopropionate with acetone followed by the lithium salt catalyzed rearrangement of the glycidic ester to give ethyl 2-hydroxy-2,3-dimethyl-3-butenoate has also been reported.[3,4] Although this route will eventually lead to a synthesis of our desired allylic halides, we sought a simpler synthetic route.

Wolinsky[5] and co-workers have shown that by a judicious choice of reaction conditions, hypochlorous acid can convert highly substituted α,β-unsaturated ketones into α-chloro-β,γ-unsaturated ketones. Recently Buynak[6] has extended this reaction to alkylidene β-lactams.

The ready availability of alkyl/aryl-substituted acrylic esters by the Horner[7] modification of the Wittig reaction prompted us to explore the Wolinksy[8] reaction on sub-

† This work was completed at Petrolite Corporation and is covered by two Pending U.S. patents assigned to Petrolite Corporation, St. Louis, MO.

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(8) The term Wolinsky reaction is used to imply the deconjugative chlorination of unsaturatd carbonyl compounds in its original scope.

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