A Comparative Study of the Decomposition of o-Alkynyl-Substituted Aryl Diazo Ketones. Synthesis of Polysubstituted β-Naphthols via Arylketene Intermediates

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Received August 31, 1993®

The photochemical, thermal, and rhodium-catalyzed decomposition reactions of several closely related o-alkynyl or o-alkenyl α-diazoaceto- and propiophenone derivatives have been studied. The reaction outcome is markedly dependent upon the reaction conditions employed for nitrogen extrusion. Thermolysis or photolysis of o-alkynyl α-diazopropiophenone derivatives yields polysubstituted β-naphthols. These products are derived from Wolff rearrangement of the initially formed carbene to give an aryl ketene which undergoes intramolecular cyclization onto the o-alkynyl substituent. In direct contrast to the thermal and photochemical results, Rh(II)-catalyzed decomposition yields products derived from direct attack of a rhodium carbenoid onto the tethered π-system producing a vinyl carbenoid intermediate. Further reaction of the cyclized carbenoid with the starting diazo compound furnishes a vinyl indenone which undergoes a rapid intramolecular Diels–Alder reaction to produce a novel dimer whose structure was elucidated by an X-ray crystal analysis. Replacement of the methyl group on the diazo center with a sterically less demanding hydrogen atom was also found to play an important role in controlling the outcome of the Rh(II)-catalyzed reaction.

α-Diazo carbonyl compounds are widely used in organic synthesis for preparing heterocyclic and carbocyclic rings.[1-28] The Arndt–Eistert sequence employs the Wolff rearrangement of an α-diazo ketone to a ketene in the one-carbon homologation of carboxylic acids.[29] Ring contraction of cyclic diazo ketones represents a general method for the preparation of highly strained small-ring compounds.[30] α-Diazo carbonyl compounds are also precursors to metallocarbenoid intermediates when exposed to many metal complexes or salts.[31] Rhodium(II) carboxylates are particularly effective catatlysts for the decomposition of diazo compounds, and an increasing number of chemical syntheses are based on this catalytic methodology.[31-34] A good deal of the early work has centered on the cyclopropanation reaction of the resulting metallocarbenoid.[15] Elegant and practical examples of this reaction include the synthesis of gibberellin/gibberellic acid[35] and the triquinane sesquiterpenes.[36] Another synthetically useful process is the intramolecular rhodium carbenoid-mediated carbon–hydrogen (C–H) insertion reaction, and its use in carbocyclic and heterocyclic ring synthesis is well documented.[37] Over the past few years our research efforts have been concerned with the transition metal-catalyzed reaction of α-diazo ketones and the application of the resulting carbenoid moiety to the

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® Abstract published in *Advance ACS Abstracts,* October 15, 1993.

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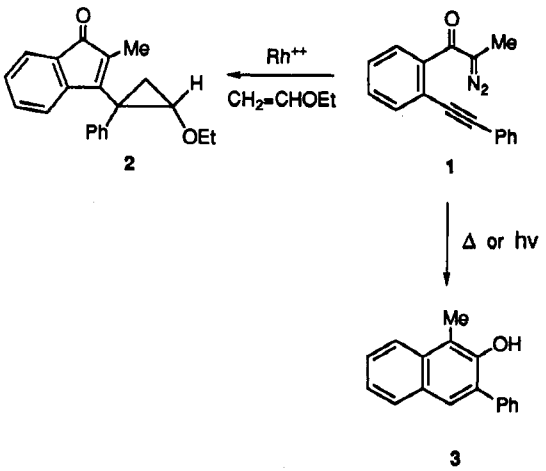
selective formation of polycyclic systems. Two distinct methodologies have been formulated based upon the strategy; the *tandem cyclization–cycloaddition* and *alkyne–carbenoid metathesis*.[38,39] During the course of these latter studies it became apparent to us that although much work has been reported upon the metal-catalyzed extrusion of nitrogen from α-diazo carbonyl compounds, very little attention has been paid to differentiating the chemical behavior of the resulting intermediate with respect to the conditions used for nitrogen extrusion. Since the metal-catalyzed cycloisomerization of acetylenic α-diazo ketone derivatives is well established, we decided that a comparative study dealing with nonmetalloid processes was in order.[40] We report here the results of a study which contrast the thermal, photochemical, and transition metal-catalyzed behavior of several closely related α-diazo ketones.

Results and Discussion

Our previous finding that *o*-alkynyl-substituted α-diazoacetophenone derivatives produced vinyl carbenoids suggested to us that these species might be trapped by electron-rich π-bonds to give indenyl cyclopropanes. This led us to study the rhodium(II) acetate-catalyzed reaction of α-diazo ketone **1**. Treatment of **1** with a catalytic quantity of $Rh_2(OAc)_4$ at 25 °C in the presence of 2 equiv of ethyl vinyl ether afforded cyclopropane **2** (91%) derived from a transient vinyl carbenoid. The thermal reaction of **1** differs significantly from the transition metal-catalyzed process. Thus, heating a methylene chloride solution of **1** in a sealed tube at 130 °C in the absence of $Rh_2(OAc)_4$ gave naphthol **3** in 69% yield. The same naphthol was also produced from the photolysis of **1** in methylene chloride.



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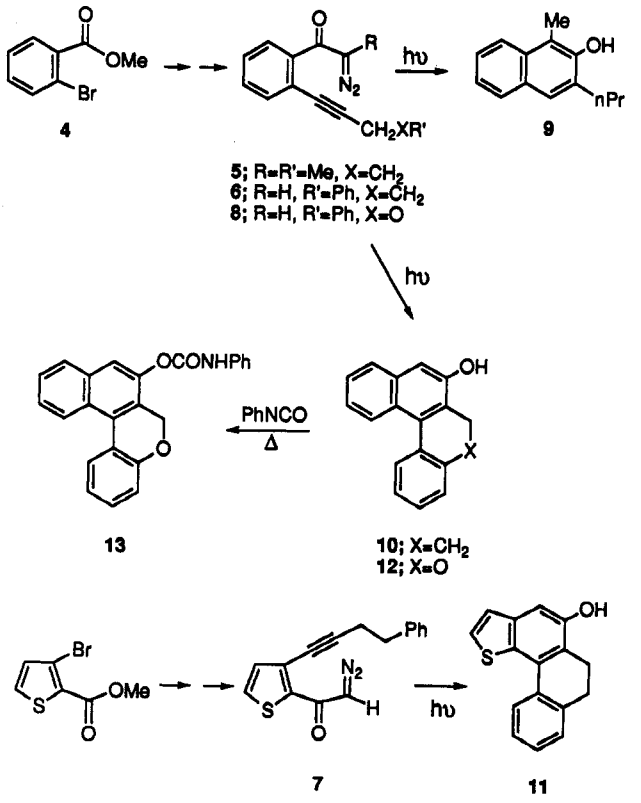
The isolation of a rearranged naphthol from the photolysis turned out to be quite general. Several *o*-alkynyl-substituted α-diazoacetophenone derivatives were prepared by treating methyl *o*-bromobenzoate with an acetylene under typical Castro–Stephens arylation conditions.[41] The resulting ester was hydrolyzed to the carboxylic acid which, in turn, was converted to the desired α-diazo ketone by treatment with methyl chloroformate followed by reaction with diazomethane. Irradiation or thermolysis of diazo ketones **5–8** afforded naphthols **9–12** in good yield. In the case of **8**, the initially isolated naphthol **12** (70%) was treated with phenyl isocyanate and the resulting carbamate derivative **13** was unequivocally established by an X-ray crystal structure analysis.



4 9

5; R=R'=Me, X=CH_2
6; R=H, R'=Ph, X=CH_2
8; R=H, R'=Ph, X=O

13 10; X=CH_2
12; X=O

7 11

By analogy with other work on the thermolysis of cyclobutenones,[42] the formation of the naphthol ring can be explained in terms of a photochemical Wolff rearrangement[43] which proceeds to give an *o*-alkynyl-substituted arylketene intermediate **14**. Subsequent cyclization of the ketene leads to diradical **15** which either abstracts hydrogen from solvent (*e.g.*, **3** or **9**) or attacks the neighboring aromatic ring (R_2 = CH_2XPh) to give the cyclized product. Danheiser,[44] Liebeskind,[45] and Moore[46] have employed a somewhat related reaction for the

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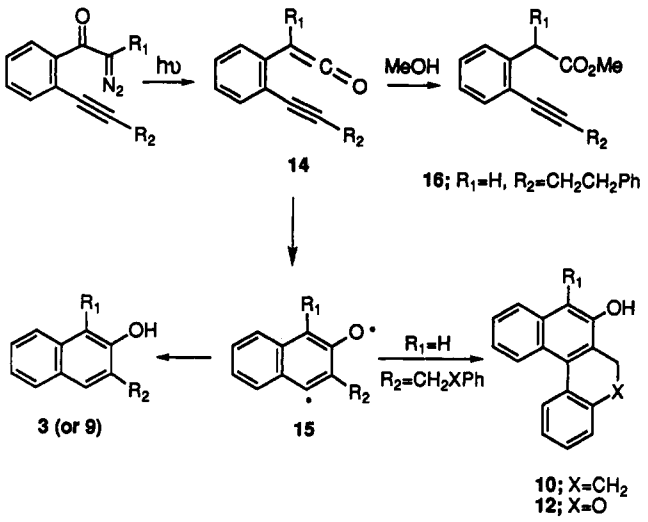
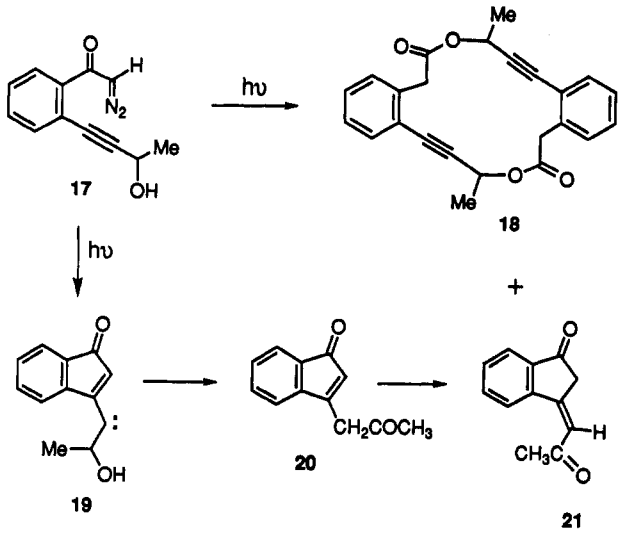
Scheme I



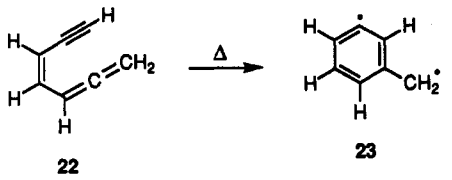
synthesis of highly substituted quinones. 4-Alkynyl or 4-vinyl-4-hydroxycyclobutenones were generated by the addition of an alkynyl or vinyllithium reagent to a cyclobutenone derivative. Thermolysis and oxidation leads to the 1,4-benzoquinone *via* a pathway related to that described in Scheme I.[47]

Supporting evidence for the proposed mechanism was obtained by carrying out the irradiation of the diazo ketone in the presence of 2 equiv of methanol. The isolation of methyl ester **16** in high yield provides excellent support for the arylketene intermediate. When the alcohol moiety was attached to the alkynyl group as in **17**, the photolysis (benzene) afforded the novel dimer **18** in 81% yield as a 1:1 mixture of *cis/trans* diastereomers. A small amount of indanone **21** (10%) was also produced from the photolysis of **17**. The formation of dimer **18** arises by intermolecular capture of the intermediate ketene of one molecule by the hydroxy group of another. Indanone **21** is derived from attack of the initially formed carbene onto the acetylenic π-system resuting in the formation of a rearranged carbene (*i.e*, **19**). A 1,2-hydrogen shift, tautomerization, and double bond migration then affords the observed product.

Much evidence has been accumulated that supports the involvement of 1,4-biradicals in the rearrangement of 1,5-diyne-3-enes to arene-1,4-diyls.[48-52] More recently, the



biradical-forming cycloaromatization reaction of *Z*-cumulene-ene-yne **22** to form α,3-dehydrotoluene **23** has been



described by Myers and co-workers.[53] Since the photochemical rearrangement reactions of *o*-alkynyl-substituted α-diazoacetophenones generate reactive ketenes (*i.e.*, **14**) which are closely related to the Myers *Z*-allenyl-ene-yne system **22**, we decided to test whether the resulting diradical **15** could also serve as a radical precursor for further cyclization onto an sp^2 carbon either five or six centers away.[54] To this end, the photochemical behavior of α-diazo-*o*-hex-5-en-1-ynylacetophenone (**24**) was examined.

When compound **24** was irradiated in methylene chloride, dihydrophenanthrol (**27**) was isolated in 75% yield. The formation of this compound was somewhat surprising since in general 5-*exo* cyclizations are faster than 6-*endo* cyclizations.[55] Attempts to shift the product distribution toward products derived from diradical **28** by employing higher concentrations of a hydrogen atom donor were unsuccessful. In all cases only dihydrophenanthrol **27** was obtained. Apparently, the planar nature of the σ,π-biradical **25** induces preferential 6-*endo* trig-cyclization. The σ,π-biradical **25** possesses substantial polar character (* = +,−) and this may also influence the stereoelectronics of the cyclization reaction.[56] Analogy for the 6-*endo* trig cyclization is found in the mechanistic pathway associated with the thermal rearrangement of 4-(3-phenylpropynyl)-

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(54) For an example where the Bergman diyl[52] has been used as a precursor for radical cyclization, see Grissom, J. W.; Calkins, T. L. *Tetrahedron Lett.* **1992**, *33*, 2315.

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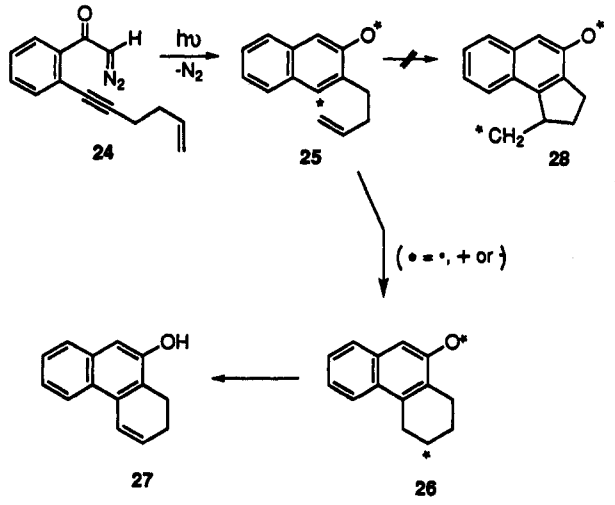
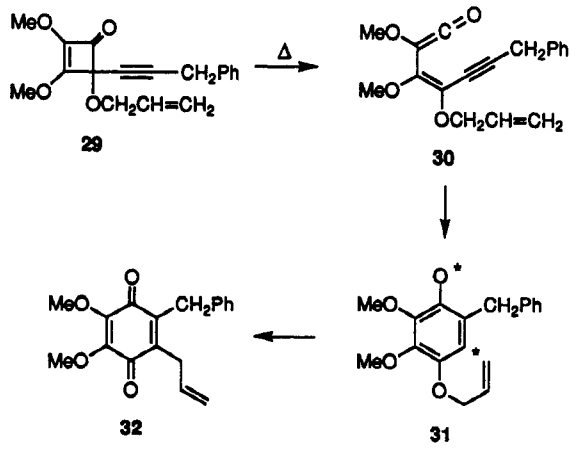
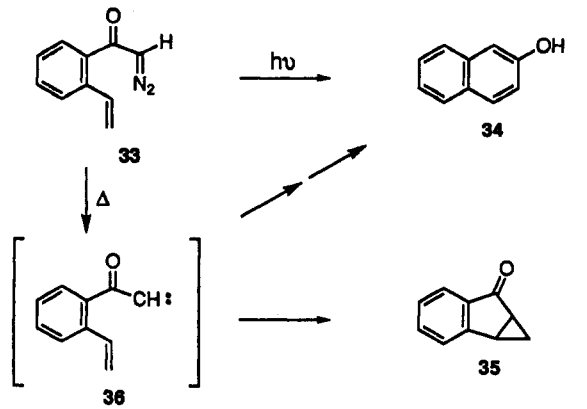
(56) Mechanistic studies suggest that the closely related α,3-dehydrotoluene is best described as a singlet σ,π-biradical with substantial polar character that can partition between polar and free radical reaction pathways in a manner influenced by biradical substitution and by the medium in which the intermediate is generated.[53]



4-(allyloxy)-2,3-dimethoxycyclobutenone (29).[57] This compound was shown to give the corresponding (alkynylethenyl)ketene 30 which cyclized to diradical 31 upon refluxing in *p*-xylene. Intramolecular addition of the ring-based radical center of 31 occurred in a 6-*endo* trig fashion inducing allyl group migration with the eventual formation of benzoquinone 32.

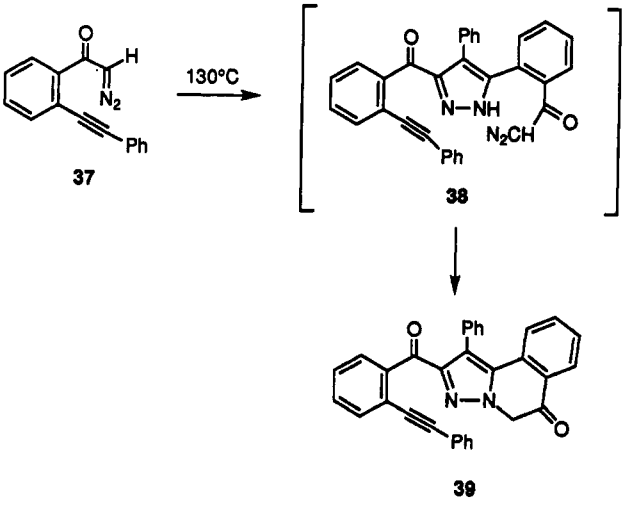


The 6-*endo* trig cyclization pathway is not limited to *o*-alkynyl-substituted α-diazoacetophenones as the *o*-alkenyl-substituted system displays similar behavior. Thus, photolysis of α-diazo-2-vinylacetophenone (33) resulted in the formation of naphthol 34 in 81% yield. The



thermolysis of 33 also produced naphthol 34 (50%) but in this case a significant amount (25%) of benzobicyclo[3.1.0]-hexane (35) was also obtained. Intramolecular cyclopropanation[15] of the initially generated keto carbene to form 35 competes with the Wolff rearrangement.

Although the thermolysis of *o*-alkynyl-substituted α-diazoacetophenone derivatives generally affords β-naphthols as the major products, sometimes alternative reaction pathways were observed. For example, in contrast to diazomethane 1, the closely related diazomethane derivative 37 was found to undergo an entirely different reaction upon thermolysis. The only product formed was dimer 39. Under the thermal conditions, the reaction proceeds



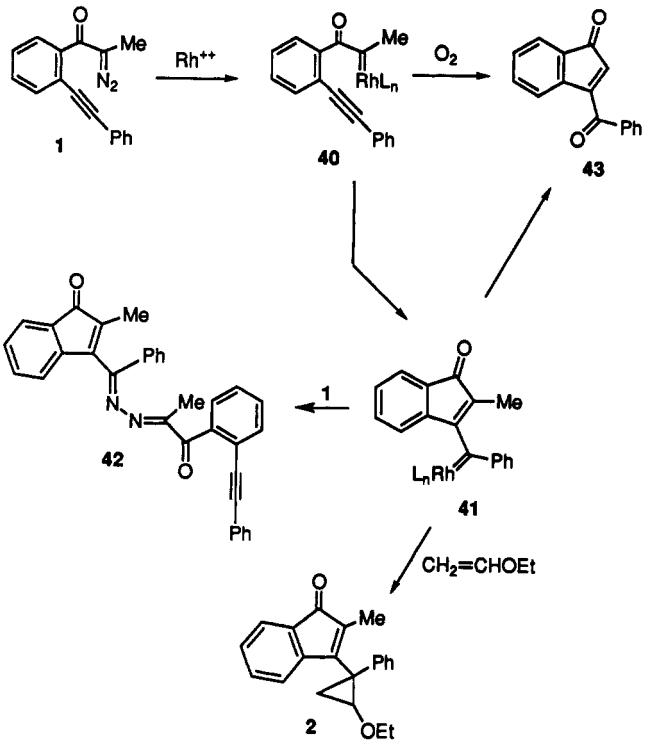
by 1,3-dipolar cycloaddition of the diazo group of one molecule across the acetylenic π-bond of another diazo compound. The initially formed cycloadduct undergoes a proton shift to produce a transient pyrazole (*i.e.*, 38) which subsequently inserts into the neighboring diazo center to give 39. Introduction of a methyl substituent on the diazo carbon as previously shown with diazoketone 1 significantly retards bimolecular dimerization and instead, formation of naphthol 3 occurs.

The rhodium(II)-catalyzed reaction of α-diazo ketones follows a pathway significantly different from that observed by photo or thermal activation. Exposure of a typical *o*-alkynyl-substituted α-diazo ketone (*i.e.*, 1) to a rhodium(II) catalyst results in cyclization of the α-keto carbenoid 40 to an intermediate (41) in which carbene-like reactivity has appeared on one of the original alkyne carbon atoms. In the presence of a reactive olefinic α-bond, cyclopropanation can occur both intramolecularly[38] and bimolecularly[39] (*i.e.*, formation of compound 2). In the absence of a trapping agent, the resulting vinyl carbenoid 41 reacts with another molecule of starting material to give azine 42 in 75% yield. A small amount (10%) of the oxygen-trapped indenone 43 was also obtained.

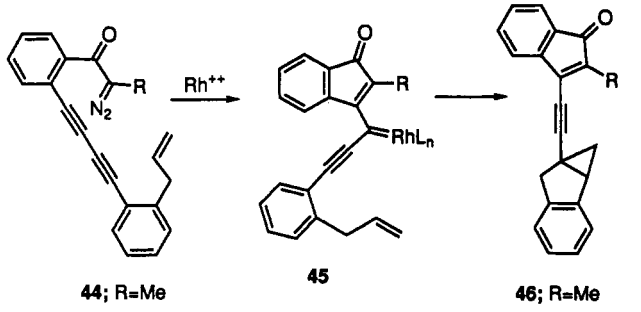
In an earlier report[58] we had demonstrated the high efficiency of the tandem cyclization–rearrangement–cycloaddition reaction of α-dialkynyl α-diazo ketone 44 (R = Me). Thus, treatment of 44 with a catalytic quantity of $Rh_2(OAc)_4$ at 25 °C in methylene chloride proceeded smoothly (95%) to give benzobicyclohexene 46. All of our

(57) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, R.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975. Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 989.

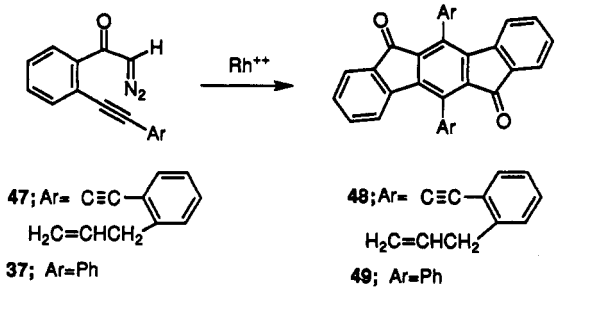
(58) Padwa, A.; Austin, D. J.; Gareau, Y.; Kassir, J. M.; Xu, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2637.



attempts to induce a related alkynyl rearrangement using α-diazo ketone **47** (R = H) failed; only dimer **48** was formed.

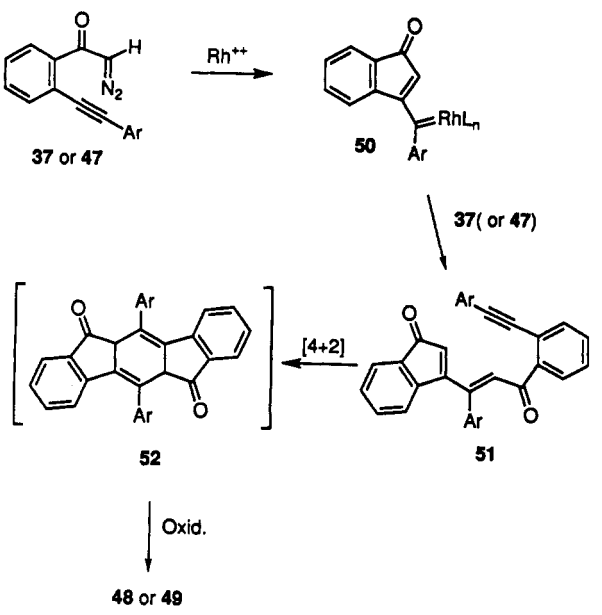


An analogous reaction occurred using α-diazo ketone **37** which produced dimer **49**. The structure of **49** was established by an X-ray crystal analysis.



Clearly, replacement of the methyl group with the sterically less demanding hydrogen atom on the α-diazo carbon plays an important role in controlling the outcome of these Rh(II)-catalyzed reactions. An additional point worth noting is that the Rh(II)-catalyzed dimerization process differs significantly from the thermal dimerization reaction. Our view of how the metal-catalyzed dimerization proceeds is shown in Scheme II. Exposure of the starting α-diazo ketone to the Rh(II) catalyst results in cyclization to the expected vinyl carbenoid **50**. A further

Scheme II



reaction with the starting diazo compound furnishes indenone **51** as a transient compound which undergoes a rapid intramolecular Diels–Alder reaction to produce **52**. This material is rapidly oxidized to the observed dimer.

In summary, the reaction outcome for the decomposition of o-alkynyl-substituted α-diazoacetophenone and propiophenone derivatives is highly dependent upon the experimental conditions employed for nitrogen extrusion. Thermolysis or photolysis leads to β-naphthols which are formed via cyclization of an arylketene intermediate. The Rh(II)-catalyzed reaction follows a pathway significantly different from that observed by photo or thermal activation. This process proceeds by addition of the rhodium-stabilized carbenoid onto the acetylenic π-bond to give a vinyl carbenoid. We are continuing to explore the scope and mechanistic details of these cyclization reactions and will report additional findings at a later date.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in oven-dried glassware under an atmosphere of extra-dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column using an ethyl acetate–hexane mixture as the eluent unless specified otherwise.

General Procedure for the Castro–Stephens Arylation Reaction. To a degassed solution containing 5.0 mmol of the appropriate aryl halide and 5.0 mmol of the terminal alkyne in 100 mL of anhydrous triethylamine was added 25 mg of *trans*-bis(triphenylphosphine)palladium(II) chloride and 50 mg of cuprous iodide. The reaction mixture was stirred at 25 °C for 12 h. The resulting slurry was filtered through a pad of Celite. Removal of the solvent under reduced pressure followed by silica gel chromatography using a hexane–ethyl acetate mixture as the eluent afforded the coupled product in good yield.

General Procedure for the Preparation of α-Diazo Ketones from the Corresponding Methyl Esters. To a stirred solution containing 5.0 mmol of potassium trimethylsilanolate in 100 mL of anhydrous ether was added, in one portion, 5.0 mmol of the appropriate methyl benzoate derivative. The reaction mixture was heated at reflux for 2 h under a nitrogen atmosphere. After being cooled to 0 °C, 5.0 mmol of methyl chloroformate was added and the resulting mixture was stirred for 2 h at 25 °C. The mixture was filtered through a pad of Celite. The filtrate was concentrated to *ca.* 20 mL and to this

solution was added a 30 mmol excess of an ethereal diazomethane (or diazoethane) solution at 0 °C. The resulting mixture was allowed to stir at 25 °C for 16 h and the excess diazoalkane and ether were removed by bubbling N_2 into the solution within a fume hood. The residue was chromatographed on silica gel using a hexane–ethyl acetete mixture as the eluent to give the appropriate α-diazoketone, which was used in the next step without further purification.

Reaction of [o-(2-Phenylethynyl)benzoyl]diazoethane (1) with Rhodium(II) Acetate and Ethyl Vinyl Ether. The Castro–Stephens reaction of 2.0 g (7.6 mmol) of methyl o-iodobenzoate and 0.9 g (9 mmol) of phenylacetylene gave 1.6 g (85%) of methyl o-(2-phenylethynyl)benzoate: IR (neat) 2211, 1433, 1288 cm^{-1}; NMR ($CDCl_3$, 75 MHz), δ 3.90 (s, 3H), 7.20 (m, 4H), 7.62 (m, 5H). A 1.5-g (5.7 mmol) sample of the above compound was converted in the normal fashion into 0.6 g (40%) of [o-(2-phenylethynyl)benzoyl]diazoethane (1): IR (neat) 2079, 1602, 1355 cm^{-1}, NMR ($CDCl_3$, 90 MHz) δ 2.15 (s, 3H), 7.30 (m, 5H), 7.52 (m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 61.2, 65.3, 86.2, 92.8, 120.3, 122.5, 127.3, 128.3, 129.8, 131.9, 140.4, 189.8.

A 0.2-g (0.7 mmol) sample of 1 was treated with 0.50 g (7 mmol) of ethyl vinyl ether and 3 mg of rhodium(II) acetate in 15 mL of dichloromethane. The major fraction (93%) obtained after standard workup was identified as 3-(2-ethoxy-1-phenylcyclopropyl)-2-methylinden-1-one (2): IR (neat) 1715, 1425, 1340, 970 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.03 (t, 3H, J = 7.0 Hz), 1.29 (t, 1H, J = 7.0 Hz), 1.88 (dd, 1H, J = 7.0, 4.0 Hz), 1.99 (s, 3H), 3.42 (m, 2H), 3.72 (dd, 1H, J = 7.0, 4.0 Hz), 7.05–7.45 (m, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 8.5, 14.7, 20.3, 28.6, 63.0, 65.9, 120.2, 121.8, 126.4, 127.6, 128.0, 128.2, 130.8, 132.8, 133.3, 136.0, 145.0, 198.7. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.85; H, 6.63. Found: C, 82.73; H, 6.52.

Irradiation of [o-(2-Phenylethynyl)benzoyl]diazoethane (1). A solution containing 50 mg of α-diazo ketone 1 in 20 mL of dichloromethane was photolyzed using a 450-W mercury lamp equipped with a Vycor filter sleeve. The photolysis was complete in 1 h, the solution was concentrated under reduced pressure, and the residue was chromatographed on silica gel. The major fraction contained 25 mg (54%) of 1-methyl-3-phenylnaphthalen-2-ol (3) as a colorless oil: IR (neat) 3552, 3054, 2927, 1630, 1602 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.63 (s, 3H), 5.35 (s, 1H), 7.33–7.40 (m, 1H), 7.43–7.58 (m, 6H), 7.71 (s, 1H), 7.79 (d, 1H, J = 8.1 Hz), 7.96 (d, 1 H, J = 8.6 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 10.9, 116.2, 123.1, 123.4, 126.2, 127.1, 127.2, 128.3, 128.4, 129.3, 129.4, 130.1, 133.6, 137.2, 147.9; HRMS calcd for $C_{17}H_{14}O$ 234.1044, found 234.1045.

A solution containing 50 mg (0.19 mmol) of α-diazoketone 1 in 12 mL of dichloromethane was heated at 125 °C in a sealed tube for 10 h. Concentration of the solution under reduced pressure followed by silica gel chromatography gave 29 mg (69%) of naphthol 3.

Preparation and Thermolysis of [o-(1-Pentynyl)benzoyl]diazoethane (5). Treatment of 3.0 g (11.5 mmol) of methyl 2-iodobenzoate and 1.35 mL (13.7 mmol) of 1-pentyne in 100 mL of anhydrous triethylamine gave 1.95 g (84%) of methyl 2-(1-pentynyl)benzoate as a clear oil: IR (neat) 2988, 2093, 2632, 1400 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.07 (t, 3H, J = 7.5 Hz), 1.66 (sext, 2H, J = 7.5 Hz), 2.46 (t, 2H, J = 7.5 Hz), 3.91 (s, 3H), 7.30–7.33 (m, 1H), 7.40–7.43 (m, 1H), 7.50–7.52 (m, 1H), 7.86–7.89 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 13.3, 21.5, 21.9, 51.7, 79.2, 95.6, 124.2, 126.9, 129.8, 131.2, 131.7, 133.9, 166.6. A 2.0-g (9.9 mmol) sample of this compound was converted in the normal fashion to 2.24 g (42%) of [o-(1-pentynyl)benzoyl]diazoethane (5): IR (neat) 2966, 2078, 1617, 1347, 756 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 1.03 (t, 3H, J = 7.5 Hz), 1.62 (sext, 2H, J = 7.5 Hz), 2.11 (s, 3H), 2.39 (t, 2H, J = 7.5 Hz), 7.32–7.41 (m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 8.4, 13.2, 21.2, 21.8, 65.0, 94.0, 120.9, 126.6, 127.6, 129.5, 132.2, 139.8.

A solution containing 50 mg (0.22 mmol) of α-diazo ketone 5 in 10 mL of dichloromethane was heated at 140 °C in a sealed tube for 5 h. Concentration under reduced pressure left an orange oil which was chromatographed on silica gel to give 12 mg (27%) of 1-methyl-3-propylnaphthalen-2-ol (9): IR (neat) 2948, 1601, 1204, and 755 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz), δ 1.03 (t, 3H, J = 7.2 Hz), 1.75 (quin, 2H, J = 7.2 Hz), 2.54 (s, 3H), 2.75 (t, 2H, J = 7.2 Hz), 4.91 (s, 1H), 7.31 (t, 1H, J = 7.5 Hz), 7.43 (t, 1H, J = 7.5 Hz), 7.48 (s, 1H), 7.71 (d, 1 H, J = 7.5 Hz), 7.86 (d, 1H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 10.7, 14.1, 22.8, 33.1, 114.5, 122.9, 123.1, 125.4, 126.4, 127.9, 129.1, 130.0, 132.4, 149.8; HRMS calcd for $C_{14}H_{16}O$ 200.1201, found 200.1200.

Preparation and Irradiation of o-(4-Phenyl-1-butynyl)-α-diazoacetophenone (6). A mixture containing 1.0 g of methyl o-bromobenzoate and 0.73 g of 4-phenyl-1-butyne in 40 mL of anhydrous triethylamine was coupled in the standard fashion to give 990 mg (80%) of methyl (2-(4-phenyl-1-butynyl)benzoate: IR (neat) 1730, 1590, 1250, 1080, 750 cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 2.87 (m, 4H), 3.81 (s, 1H), 7.26–8.05 (m, 9H). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.70; H, 6.32.

A stirred solution containing 900 mg of the above benzoate was converted into 560 mg (60%) of o-(4-phenyl-1-butynyl)-α-diazoacetophenone (6): IR (neat) 1620, 1350, 1020, 870, 770 cm^{-1}; δ 2.85 (m, 4H), 5.96 (s, 1H) 7.27–7.95 (m, 9H); UV (CH_2Cl_2) 324 sh (ε 15200, 296 (ε 35,200). A solution containing 100 mg of α-diazo ketone 6 in 300 mL of methylene chloride was irradiated under argon with a 450-W Hanovia lamp equipped with a Uranium filter sleeve for 20 min. Removal of the solvent under reduced pressure left a dark red oil which was subjected to silica gel chromatography to give 50 mg (56%) of a solid, mp 62–63 °C, whose structure was assigned as 7,8-dihydrobenzo[c]phenanthren-6-ol (10) on the basis of its spectral properties: IR (KBr) 1600, 1430, 1210, 1070, 910, 830, 740 cm^{-1}; NMR ($CDCl_3$, 250 MHz) δ 2.92 (m, 4H), 5.45 (bs, 1H), 7.33–8.45 (m, 9H); ^{13}C-NMR ($CDCl_3$, 63 MHz), δ 23.2, 29.3, 109.0, (bs, 1H), 7.33–8.45 (m, 9H); ^{13}C-NMR ($CDCl_3$, 63 MHz) δ 23.2, 29.3, 109.0, 123.4, 125.3, 125.5, 125.7, 125.8, 126.6, 127.6, 128.3, 128.8, 129.7, 133.5, 134.3, 139.8, 154.9; MS m/e 246 (M^+, base), 231, 215, 202, 176, 163, 151, 123, 113, 101, 94, 81, 63; UV (ethanol) 346 sh (ε 285), 318 (ε 510), 306 sh (ε 450), 240 sh (ε 1490), 228 (ε 1615). Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.70; H, 5.67.

A solution containing 100 mg of 6 in 300 mL of methanol was irradiated under argon with a 450-W Hanovia lamp equipped with a uranium filter sleeve for 20 min. Removal of the solvent under reduced pressure left a yellow oil which was subjected to silica gel chromatography to give 99 mg of a pale yellow oil (98%) which was identified as [2-(4-phenyl-but-1-ynyl)phenyl]acetic acid methyl ester (16) on the basis of its spectral properties: IR (neat) 1710, 1590, 1480, 1250, 1020, 750 cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 2.84 (m, 4H), 3.65 (s, 3H), 3.74 (s, 2H), 7.10–7.37 (m, 9H); ^{13}C-NMR ($CDCl_3$, 63 MHz) δ 21.5, 34.9, 39.6, 51.8, 79.2, 94.1, 124.0, 126.2, 126.9, 127.7, 128.3, 129.4, 132.0, 135.9, 140.5, 171.7. Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.51. Found: C, 81.93; H, 6.54. The same compound was isolated in 95% yield by carrying out the thermolysis of 100 mg of 6 in 3.5 mL of methanol at 135 °C in a sealed tube for 30 min.

Preparation and Irradiation of 2-(1-Oxo-2-diazoethyl)-3-(4-Phenyl-1-butyl)thiophene (7). A mixture containing 1.03 g of 3-bromo-2-(methoxycarbonyl)thiophene and 0.73 g of 4-phenyl-1-butyne in 40 mL of anhydrous triethylamine was coupled in the standard fashion to give 820 mg (65%) of 2-(methoxycarbonyl)-3-(4-phenyl-1-butynyl)thiophene: IR (neat) 1720, 1600, 1430, 1250, 1130, 880, 700 cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 2.87 (m, 4H), 3.83 (s, 1H), 7.01 (d, 1H, J = 5.1 Hz), 7.24–7.63 (m, 6H). Anal. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22; S, 11.86. Found: C, 71.00; H, 5.28, S, 11.83.

A stirred solution containing 800 mg of the above compound was converted into 567 mg (60%) of 2-(1-oxo-2-diazoethyl)-3-(4-phenyl-1-butynyl)thiophene (7): IR (neat) 1580, 1400, 870, 730, 690 cm^{-1}; NMR ($CDCl_3$, 250 MHz) δ 2.79 (m, 2H), 2.93 (m, 2H), 6.19 (s, 1H), 6.98 (d, 1H, J = 5.1 Hz), 7.15–7.28 (m, 5H), 7.30 (d, 1H, J = 5.1 Hz); MS m/e 290 (base) 252, 235, 223, 209, 191, 189, 135, 110, 91; UV (ethanol) 336 sh (ε 11600), 326 sh (ε 16900), 304 (ε 22360), 292 sh (ε 19700).

A solution containing 100 mg of α-diazo ketone 7 in 300 mL of methylene chloride was irradiated under similar conditions to those described for compound 5. The reaction mixture was subjected to silica gel chromatography to give 59 mg of a pale yellow solid (66%) which was identified as 6,7-dihydrophenanthro[4,3-b]thiophen-5-ol (11) on the basis of its spectral properties: mp 128–129 °C, IR (KBr) 1660, 1600, 1420, 1260, 1090, 920, 820, 700 cm^{-1}; NMR ($CDCl_3$, 250 MHz) δ 2.85 (m, 4H), 5.20 (bs, 1H), 7.01–7.28 (m, 6H), and 7.28 (d, 1H, J = 5.1 Hz); ^{13}C-NMR ($CDCl_3$, 63 MHz) δ 21.0, 27.5, 105.6, 108.4, 109.8, 114.5,

122.2, 122.7, 125.7, 126.4, 126.9, 127.1, 133.2, 137.4, 148.6; MS *m/e* 252 (M^+, base), 224, 169, 135, 115, 91; UV (ethanol) 350 sh (ε 283), 320 (ε 500), 310 sh (ε 470), 242 sh (ε 1480), and 232 (ε 1655). Anal. Calcd for $C_{16}H_{12}OS$: C, 76.16; H, 4.79; S, 12.70. Found: C, 76.09; H, 4.73; S, 12.62.

Preparation and Irradiation of o-(3-Phenoxy-1-propynyl)-α-diazoacetophenone (8). A mixture containing 1.0 g of 2-methyl o-bromobenzoate and 0.78 g of 3-phenoxy-1-propyne in 40 mL of anhydrous triethylamine was coupled in the standard fashion to give 870 mg (70%) of methyl 2-(3-phenoxy-1-propynyl)benzoate: IR (neat) 1720, 1590, 1430, 1250, 1070, 820, 750 cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 3.80 (s, 3H), 4.86 (s, 2H), 6.92–8.05 (m, 9H). Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.63; H, 5.33. A solution containing 800 mg of the above benzoate was converted into 623 mg (75%) of o-(3-phenoxy-1-propynyl)-α-diazoacetophenone (8): IR (neat) 1600, 1500, 1440, 1350, 1200, 1010, 750 cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 4.98 (s, 2H), 5.93 (s, 1H), 6.87–7.69 (m, 9H); UV (ethanol) 333 sh (ε 11900), 328 sh (ε 17000), 306 (ε 22500), 292 sh (ε 19800).

A solution containing 100 mg of α-diazo ketone 8 in 300 mL of methylene chloride was irradiated under similar conditions to those described for compound **4a**. The reaction mixture was subjected to silica gel chromatography to give 63 mg of a solid (70%), mp 148–149 °C, which was identified as 6*H*-benzo[*b*]naphtho[1,2-*d*]pyran-7-ol (**12**) on the basis of its spectral properties: IR (KBr) 1620, 1600, 1430, 1340, 1240, 1100, 990, 820, 730 cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 5.22 (s, 2H), 5.70 (bs, 1H), 6.99–8.55 (m, 9H); ^{13}C-NMR ($CDCl_3$, 63 MHz) δ 64.4, 109.5, 117.6, 121.7, 124.0, 124.3, 124.8, 125.3, 127.1, 128.1, 128.9, 134.9, 148.5, 156.5; MS *m/e* 248 (M^+, base), 247, 236, 231, 219, 189, 167, 149, 137, 123, 111, 97, 95, 84, 69; UV (ethanol) 350 sh (ε 283), 320 (ε 500), 310 sh (ε 470), 242 sh (ε 1480), 232 (ε 1655). Anal. Calcd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.21; H, 4.84.

A solution containing 60 mg of **12** and 40 mg of phenyl isocyanate in 25 mL of anhydrous benzene was heated at reflux for 6 h. At the end of this time, the solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column to give 68 mg (70%) of the expected urethane **13** as a white solid: mp 155–156 °C; IR (KBr) 1710, 1590, 1420, 1230, 1120, 1080, 790 cm^{-1}, ^1H-NMR ($CDCl_3$, 80 MHz) δ 5.12 (s, 2H), 6.83–8.79 (m, 15H); MS *m/e* 249, 248, 247, 231, 219, 181, 119, 101, 91. Anal. Calcd for $C_{24}H_{17}NO_3$: C, 78.46; H, 4.66; N, 3.81. Found: C, 78.43; H, 4.67; N, 3.80. Crystals of **13** suitable for an X-ray crystallographic structure determination were grown from a methylene chloride–hexane solution.[59]

Preparation and Irradiation of o-(3-Hydroxy-1-butynyl)-α-diazoacetophenone (17). A mixture containing 3.0 g (11.5 mmol) of methyl o-iodobenzoate and 1.0 g (13 mmol) of 3-butyn-2-ol in 40 mL of anhydrous triethylamine was converted into 2.0 g (85%) of methyl o-(3-hydroxy-1-butynyl)benzoate: IR (neat) 3483, 2989, 1730, 1488 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.60 (d, 3H, *J* = 7.0 Hz), 3.45 (s, 1H), 3.98 (s, 3H), 470 (q, 1H, *J* = 7.0 Hz), 7.40 (m, 3H), 7.92 (m, 2H). A stirred solution containing 2.0 g of methyl o-(3-hydroxy-1-butynyl)benzoate was converted in the normal fashion into 1.4 g (60%) of o-(3-hydroxy-1-butynyl)-α-diazoacetophenone (**17**): IR (neat) 3413, 2976, 2101, 1606, 1112 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.52 (d, 2H, *J* = 6.0 Hz), 3.85 (bs, 1H), 4.80 (q, 1H, *J* = 6.0 Hz), 6.20 (s, 1H), 7.35–7.75 (m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 23.8, 57.4, 58.4, 81.8, 97.4, 120.2, 127.6, 127.7, 128.3, 130.9, 133.7, 138.8, 197.3.

A solution containing 200 mg of α-diazo ketone **17** in 50 mL of anhydrous methylene chloride was irradiated under argon with 450-W Hanovia lamp equipped with a uranium filter sleeve for 30 min. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel to give 250 mg (75%) of a solid whose structure was assigned as 5,17-dimethyl-4,16-dioxatricyclo[18.4.0.0.8.13]tetracosa-1(24),8(13),9,11,20,22-hexaene-6,18-diyne-3,15-dione (**18**): mp 249–250 °C; IR (KBr) 1730, 1403, 1332, 1175 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.53 (d, 3H, *J* = 6.6 Hz), 3.78 (1H, *J* = 16.2 Hz), 5.70 (q, 1H, *J* = 6.6 Hz), 3.89 (d, 1H, *J* = 16.2 Hz), 7.25 (m, 3H), 7.45 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 21.3, 39.9, 60.1, 82.3, 91.8, 122.8, 127.1, 130.0, 131.9, 136.1, 169.7; HRMS calcd for $C_{24}H_{20}O_4$ 372.1172, found 372.1169.

The second fraction isolated from the column contained 17 mg (10%) of a light yellow oil whose structure was assigned as 3-(2-oxopropylidene)indan-1-one (**21**) on the basis of its spectral properties: IR (KBr) 2961, 1716, 1680, 1253, 1120 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.36 (s, 3H), 3.70 (bs, 2H), 6.87 (s, 1H), 7.05–7.90 (m, 4H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 31.6, 42.2, 117.4, 121.7, 123.7, 131.6, 134.7, 138.2, 147.5, 197.6, 202.1. Anal. Calcd for $C_{12}H_{10}O_2$: C, 77.39; H, 5.42. Found: C, 77.26; H, 5.35.

Preparation and Irradiation of 2-(6-Hexen-1-ynyl)-α-diazoacetophenone (24). A solution containing 3.35 g of methyl 2-bromobenzoate and 1.5 g of 4-pent-yn-1-ol in 200 mL of anhydrous triethylamine was converted into 2.70 g (80%) of methyl 2-(5-hydroxy-1-pentynyl)benzoate: IR (neat) 1480, 1430, 1310, 1120, 1090, 920, 750 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.78 (m, 2H), 2.51 (t, 2H, *J* = 6.6 Hz), 3.34 (bs, 1H), 3.71 (t, 2H, *J* = 6.6 Hz), 3.80 (s, 3H), 7.15–7.50 (m, 3H), 7.72–7.91 (m, 1H).

To a stirred suspension containing 1.88 g (8.72 mmol) of pyridinium chlorochromate and 0.142 g (1.73 mmol) of sodium acetate in 10 mL of anhydrous dichloromethane was added 1.5 g (5 mmol) of the above benzoate and the mixture was allowed to stir for 2 h. Anhydrous ether was added to the solution, the mixture was extracted, the organic phase was decanted, and the residue was extracted with ether. The combined extracts were filtered through a pad of florosil. The solvent was removed under reduced pressure and the residue was chromatographed on a silica gel column to give 0.83 g (80%) of a light yellow oil which was identified as methyl 2-(5-oxo-1-pentynyl)benzoate on the basis of its spectral properties: IR (neat) 1750, 1710, 1590, 1470, 1440, 1300, 1080, 950, 750 cm^{-1}; ^1H-NMR ($CDCl_3$, 80 MHz) δ 2.79 (bs, 4H), 3.90 (s, 3H), 7.16–7.62 (m, 3H), 7.75–8.02 (m, 1H); MS *m/z* 216 (M^+), 188 (base), 173, 155, 129, 115, 103, 76, 72.

To a stirred solution containing 1.6 g of methyl triphenylphosphonium bromide in 120 mL of anhydrous tetrahydrofuran was added 2.25 mL of phenyllithium solution at −30 °C under a nitrogen atmosphere. The reaction was stirred for 30 min at −30 °C and then a solution containing 0.42 g of methyl 2-(5-oxo-1-pentynyl)benzoate in 10 mL of tetrahydrofuran was added dropwise over 5 min. The reaction mixture was stirred for 1 h at −30 °C and then for 14 h at room temperature. The mixture was diluted with 400 mL of ether, filtered, washed with a 10% hydrochloric acid solution and water, and then dried over magnesium sulfate. Removal of the solvent under reduced pressure was followed by silica gel chromatography to give 0.27 g of a yellow oil (65%) which was identified as methyl 2-(6-hexen-1-ynyl)benzoate on the basis of its spectral properties: IR (neat) 1720, 1640, 1580, 1460, 1240, 1120, 1080, 900, 750 cm^{-1}; ^1H-NMR ($CDCl_3$, 80 MHz) δ 2.48 (m, 4H), 3.91 (s, 3H), 5.12 (m, 2H), 5.95 (m, 1H), 7.22-7.61 (m, 3H), 7.73–8.01 (m, 1H).

A stirred solution containing 150 mg of the above benzoate was converted in the normal fashion to 100 mg (64%) of o-(6-hexen-1-ynyl)-α-diazoacetophenone (**24**): IR (neat) 1600, 1350, 1200, 1000, 900, 740 cm^{-1}; ^1H-NMR ($CDCl_3$, 80 MHz) δ 2.46 (m, 4H), 5.15 (m, 2H), 5.92 (m, 1H), 6.27 (s, 1H), 7.21–7.25 (m, 3H), 7.61–7.82 (m, 1H). A stirred solution containing 100 mg of α-diazo ketone **24** in 300 mL of anhydrous dichloromethane was irradiated under similar conditions to that described for compound **5**. The reaction mixture was subjected to silica gel chromatography to give 66 mg of a yellow solid (75%) which was identified as 7,8-dihydrophenanthren-9-ol (**27**) on the basis of its spectral properties: mp 115–116 °C; IR (neat) 1600, 1380, 1200, 1080, 905, 830, 740 cm^{-1}; ^1H-NMR ($CDCl_3$, 80 MHz) δ 2.58 (m, 4H), 5.42 (bs, 1H), 6.19 (m, 1H), 7.35–8.18 (m, 7H); ^{13}C-NMR ($CDCl_3$, 63 MHz) δ 23.3, 29.2, 119.0, 123.4, 125.6, 128.9, 130.1, 134.7, 148.3, 155.1; MS *m/e* 206 (M^+, base), 191, 175, 142, 100, 81, 63. Anal. Calcd for $C_{14}H_{12}O$: C, 85.71; H, 6.12. Found: C, 85.67; H, 6.07.

Preparation and Reaction of o-Ethenyl-α-diazoacetophenone (33). A 1.60-g (10 mmol) sample of methyl 2-ethynylbenzoate in 40 mL of petroleum ether containing 50 mg of Lindlar catalyst and 1.0 mL of quinoline was hydrogenated for 12 h. The mixture was filtered and concentrated under reduced pressure, and the crude residue was purified by silica gel chromatography, producing 1.55 g (96%) of methyl 2-ethenylbenzoate as a colorless oil: IR (neat) 1720, 1600, 1580, 990 cm^{-1}; ^1H-NMR ($CDCl_3$, 300

(59) The authors have deposited atomic coordinates for structures **13** and **49** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

MHz) δ 3.82 (s, 3H), 5.38 (dd, 1H, J = 10.5 and 1.5 Hz), 5.68 (dd, 1H, J = 17.0 and 1.5 Hz), 7.18 (dd, 1H, J = 17.0 and 10.5 Hz), and 7.31-7.69 (m, 4H). Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22. Found: C, 73.95; H, 6.13.

A 1.0-g (6.2 mmol) sample of the above benzoate was converted in the normal fashion into 180 mg of *o*-ethenyl-α-diazoacetophenone (**33**): IR (neat) 2101, 1617, 1355, 1144 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 5.34 (d, 1H, J = 14.4 Hz), 5.69 (d, 1H, J = 9.3 Hz), 7.09–7.20 (m, 1H), 7.30–7.34 (m, 1H), 7.40–7.45 (m, 2H), 7.55–7.60 (m, 1H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 57.0, 116.6, 126.6, 127.1, 127.5, 130.9, 134.5, 136.2, 136.6.

A degassed solution containing 25 mg (0.15 mmol) of α-diazo ketone **33** in 20 mL of dichloromethane was photolyzed using a 450-W mercury lamp equipped with a Vycor filter sleeve. The photolysis was complete in 1 h and the solution was concentrated under reduced pressure. The crude oil was chromatographed on silica gel to give 17 mg (81%) of naphthalen-2-ol (**34**). A solution containing 50 mg (0.30 mmol) of α-diazo ketone **33** in 20 mL of dichloromethane was heated at 140 °C in a sealed tube for 3 h. Concentration of the solution under reduced pressure followed by silica gel chromatography gave 32 mg (76%) of a 2:1 mixture of 2-naphthol (**34**) and 1a,6a-dihydro-1*H*-cyclopropa[*a*]inden-6-one (**35**):[60] IR (neat) 1720, 1610, 990 cm^{-1}; ^1H-NMR ($CDCl_3$, 300, MHz) δ 1.30–1.35 (m, 1H), 1.55–1.64 (m, 1H), 2.46–2.53 (m, 1H), 2.90–2.96 (m, 1H), 7.28–7.33 (m, 1H), 7.42–7.50 (m, 2H), 7.62–7.68 (m, 1H).

Thermolysis of *o*-(2-Phenylethynyl)-α-diazoacetophenone (37). Castro–Stephens reaction of 15.0 g (57.3 mmol) of methyl *o*-iodobenzoate and 7.6 g (74.5 mmol) of phenylacetylene gave 10.3 g (76%) of methyl *o*-(2-phenylethynyl)benzoate. A 5.0-g (21.1 mmol) sample of the above compound was converted in the normal fashion into 2.3 g (44%) of *o*-(2-phenylethynyl)-α-diazoacetophenone (**37**): IR (neat) 2097, 1611, 1349 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 6.25 (bs, 1H), 7.29–7.68 (m, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 56.9, 87.7, 95.4, 120.6, 122.6, 128.0, 128.4, 128.8, 131.0, 131.4, 133.4, 139.1.

A solution containing 100 mg of *o*-(2-phenylethynyl)-α-diazoacetophenone (**37**) in 50 mL of methylene chloride was heated at 135 °C in a sealed tube for 30 min. The solvent was removed under reduced pressure and the resulting yellow solid was crystallized from ether to give 180 mg (98%) of 1-phenyl-2-[2-(phenylethynyl)benzyl]pyrazolo[5,1-*a*]isoquinolin-6-one (**39**): mp 169–170 °C; IR (KBr) 1750, 1744, 1424, 1260 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.78 (s, 2H), 7.09 (m, 2H), 7.30 (m, 6H), 7.52 (m, 6H), 7.80 (m, 2H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 39.3, 87.5, 94.1, 120.8, 122.7, 123.6, 125.6, 127.3, 128.0, 128.1, 128.4, 128.5, 128.8, 129.6, 130.4, 130.9, 131.3, 131.9, 134.0, 135.2, 136.2, 136.6, 139.7, 144.7, 148.3, 167.8, 176.7, 198.7; HRMS calcd for $C_{32}H_{20}N_2O_2$ 464.2128, found 464.2125.

Dimerization Reaction of [*o*-(2-Phenylethynyl)benzoyl]-diazoethane (1) with Rh(II) Acetate. A solution containing 100 mg (0.4 mmol) of α-diazo ketone **1** in 20 mL of anhydrous CH_2Cl_2 was treated with a catalytic amount of rhodium(II) acetate dimer at 25 °C. The reaction mixture was stirred for 20 min at 25 °C, concentrated under reduced pressure, and subjected to silica gel chromatography. The major fraction contained 147 mg (75%) of 3[[[1-methyl-2-oxo-2-[(2-phenylethynyl)phenyl]ethylidene]hydrazono]phenylmethyl]-2-methylinden-1-one (**42**): mp 141–142 °C, IR (neat) 3064, 1713, 1684, 1182, 935 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.39 (s, 3H), 2.30 (s, 3H), 6.45 (d, 1H, J = 6.9 Hz), 6.95–7.60 (m, 16 H), 7.83 (d, 2H, J = 6.9 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 8.7, 12.3, 87.6, 94.1, 120.8, 121.2, 122.7, 127.5, 133.7, 134.0, 134.4, 141.3, 143.9, 149.8, 155.5, 159.2, 195.7, 197.6. Anal. Calcd for $C_{34}H_{24}N_2O_2$: C, 82.90; H, 4.91; N, 5.69. Found: C, 82.81; H, 4.88; N, 5.47.

The minor fraction contained 11 mg (10%) of 3-benzoylinden-1-one (**43**); IR (neat) 3064, 1717, 1655, 1499, 1225 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.77 (s, 3H), 6.95–7.80 (m, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 9.3, 121.3, 123.3, 128.4, 128.3, 128.9, 129.1, 129.5, 133.9, 134.2, 135.4, 136.3, 144.4, 149.7, 193.6, 197.5. Anal Calcd for $C_{17}H_{12}O_2$: C, 82.23; H, 4.87. Found: C, 82.05; H, 4.62.

Dimerization Reaction of 2-[4-[2-(2-Propenyl)phenyl]-buta-1,3-diynyl]-α-diazoacetophenone (47) with Rhodium-(II) Mandelate Dimer. A solution containing 18.0 g (63.2 mmol) of 2-bromoiodobenzene and 7.44 g (75.7 mmol) of (trimethylsilyl)-acetylene in 180 mL of anhydrous triethylamine was converted into 14.1 g (89%) of 1-bromo-2-[2-(trimethylsilyl)ethynyl]-benzene: IR (neat) 2180, 1470, 1255, 1030, 870, cm^{-1}; ^1H-NMR ($CDCl_3$ 90MHz) δ 0.40 (s, 9H), 7.25–7.80 (m, 4H).

To a solution containing 14.1 g (55.6 mmol) of the above acetylene in 400 mL of anhydrous ether at −78 °C was added, dropwise, 69.1 mL of a 1.7 M solution of *tert*-butyllithium. After stirring for 20 min at −78 °C, a solution of 20.2 g (167 mmol) of allyl bromide in 70 mL of ether was added dropwise over a period of 10 min. The reaction was warmed to 25 °C and stirred for 12 h. The solution was poured into a saturated aqueous NH_4Cl solution, extracted with ether, and dried over magnesium sulfate. Concentration of the ether solution afforded of 2-(2-propenyl)-[(trimethylsilyl)ethynyl]benzene which was identified on the basis of its spectral properties and was used without further purification: IR (neat) 3080, 2980, 2900, 2160, 1630, 1480, 1250, 870, 760 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 0.25 (s, 9H), 3.55 (d, 2H, J = 6.0 Hz), 4.95 (s, 1H), 5.15 (d, 1H, J = 5.5 Hz), 5.70–6.20 (m, 1H), 7.10–7.50 (m, 4H).

To a solution containing 12.0 g (56 mmol) of 2-(2-propenyl)-[(trimethylsilyl)ethynylbenzene in 200 mL of a THF–water mixture (10:1) at 0 °C was added dropwise 165 mL of a 1.0 M tetrabutylammonium fluoride solution. The reaction mixture was poured into saturated NH_4Cl solution and extracted with ether. The combined ether extracts were washed with water and brine, dried over magnesium sulfate, and concentrated under reduced pressure. Distillation of the residue under reduced pressure (49–50 °C) (2 mm)) afforded 6.16 g (78%) of 2-(2-propenyl)-1-ethynylbenzene: IR (neat) 3300, 3090, 2970, 2120, 1640, 1450, 925, 765 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 3.28 (s, 1H), 3.61 (d, 2H J = 6.5 Hz), 5.07 (d, 1H, J = 1.5 Hz), 5.11 (d, 1H, J = 7.5 Hz), 5.94–6.07 (m, 1H), 7.15–7.32 (m, 3H), 7.49 (d, 1H, J = 7.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 38.1, 80.7, 81.8, 115.7, 121.2, 125.6, 128.4, 128.5, 132.4, 135.9, 142.1.

To a solution of 2.9 g (20.3 mmol) of the above acetylene and 19.9 g (16.6 mmol) of carbon tetrabromide in 40 mL of anhydrous dichloromethane was added 31.5 g (120 mmol) of triphenylphosphine under an argon atmosphere. The reaction was stirred for 20 min at rt and then poured into 200 mL of ether. Filtration and evaporation of the solvent afforded 2.2 g (47%) of a pale yellow oil. The crude oil dissolved in 8.5 mL of ethanol was added dropwise to a mixture of 1.3 g (8.1 mmol) of methyl 2-ethynylbenzoate, 1.5 g (21.6 mmol) of hydroxylamine hydrochloride, and 0.04 g (0.2 mmol) of cuprous chloride in 17.5 mL of ethanol which contained 4.4 mL of *n*-butylamine. After stirring at rt for 1 h, the reaction was poured into 200 mL of water and extracted with ether. The combined ether extracts were dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Chromatography of the residue on silica using benzene as the eluent afforded 1.25 g of a yellow oil (42%) which was identified as methyl 2-[4-[2-(2-propenyl)phenyl]buta-1,3-diynyl]benzoate on the basis of its spectral properties: IR (neat) 3069, 2951, 2213, 1736, 1480, 1292, 1080, 751 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 3.61 (d, 2H, J = 8.5 Hz), 3.95 (s, 3H), 5.12 (d, 1H, J = 17.2 Hz), 6.00 (ddt, 1H, J = 17.4, 8.5, 6.6 Hz), 7.20–7.57 (m, 6H), 7.65 (d, 1H, J = 7.6 Hz), 7.98 (d, 1H, J = 7.6 Hz); ^{13}C-NMR ($CDCl_3$, 75MHz) δ 38.1, 51.7, 72.2, 76.7, 77.1, 77.2, 78.3, 80.0, 81.4, 115.8, 120.7, 121.9, 125.6, 128.1, 128.3, 128.9, 130.0, 131.3, 131.9, 132.7, 134.5, 135.5, 142.9, 165.3.

To a solution of 0.53 g (4.1 mmol) of potassium trimethylsilanolate in 75 mL of anhydrous ether was added 1.25 g (4.16 mmol) of methyl 2-[4-[2-(2-propenyl)phenyl]buta-1,3-diynyl]-benzoate. The reaction mixture was stirred for 5 h at rt under N_2. After cooling to 0 °C, 1.18 g (12.5 mmol) of methyl chloroformate was added and the mixture was stirred for an additional 4 h at 25 °C. The solution was filtered and an ethereal diazomethane solution (33 mmol) was added and the solution was stirred for 16 h. The excess diazomethane and ether was removed by bubbling N_2 into the solution within a fume hood and the resulting residue was chromatographed on silica gel to give 903 mg (70%) of 2-[4-[2-(2-propenyl)phenyl]buta-1,3-diynyl]-α-diazoacetophenone (**47**): IR (neat) 2247, 2211, 2103, 1612, 1354, 905, 740 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.58 (d, 2H, J = 6.5 Hz). 5.09 (d, 1H, J = 11.0 Hz), 5.11 (d, 1H, J = 4.0 Hz),

(60) House, H. O.; McDaniel, W. C.; Sieloff, R. F.; Vanderveer, D. *J. Org. Chem.* **1978**, *43*, 4316.

5.95 (ddt, 1H, J = 13.1, 6.5, 4.0 Hz), 6.16 (bs, 1H), 7.10–7.75 (m, 8H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 38.5, 56.9, 77.2, 79.5, 80.0, 82.4, 116.4, 119.4, 120.8, 126.2, 128.0, 128.9, 129.1, 129.6, 131.0, 133.2, 134.7, 135.9, 140.0, 143.4.

To a solution of 100 mg (3.2 mmol) of 47 in 25 mL of anhydrous CH_2Cl_2 was added a catalytic amount of rhodium(II) mandelate dimer under N_2. The reaction was stirred at rt until N_2 evolution ceased. The mixture was filtered through a Celite pad and concentrated under reduced pressure. After washing the red solid with ether, recrystallization of the residue from a CH_2Cl_2–ether mixture afforded 58 mg (29%) of 5,11-bis[(2-allylphenyl)-ethynyl]indeno[1,2-*b*]fluorene-6,12-dione (48): mp 126–127 °C; IR (CH_2Cl_2) 2247, 2211, 2103, 1612, 1354, 905, 740 cm^{-1}; NMR (CD_2Cl_2, 300 MHz) δ 3.90 (d, 1H, 6.0 Hz), 5.10 (m, 2H), 6.15 (m, 3H), 7.30–8.00 (m, 3H), 8.55 (d, 1H, J = 7.0 Hz). Anal. Calcd for $C_{42}H_{26}O_2$: C, 89.65; H, 4.66. Found: C, 89.54; H, 4.63.

Dimerization Reaction of o-(2-Phenylethynyl)-α-diazoacetophenone (37) with Rh(II) Acetate. A solution containing 100 mg (0.4 mmol) of α-diazo ketone **37** in 20 mL of anhydrous CH_2Cl_2 was treated with a catalytic amount of rhodium(II) acetate dimer at 25 °C. The reaction mixture was stirred for 20 min at 25 °C, concentrated under reduced pressure, and subjected to silica gel chromatography. The major fraction contained 75 mg (75%) of 5,11-diphenylindeno[1,2-*b*]fluorene-6,12-dione (**49**), whose structure was assigned on the basis of X-ray analysis:[59] mp 250–251 °C; IR (KBr) 3010, 1710, 1595, 1467, 1303 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 6.24 (m, 1H), 7.15–7.64 (m, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 29.5, 122.3, 123.8, 128.1, 128.4, 128.7, 128.8, 134.2, 134.5, 135.3, 135.4, 135.7, 142.6, 144.1, 192.1; HRMS calcd for $C_{32}H_{20}O_2$ 436.1540, found 436.1542.

Acknowledgment. A.P. gratefully acknowledges support of this work by the National Science Foundation and the National Institutes of Health (CA-26751). U.C. thanks the MURST for partial financial support. Use of the high-field NMR spectrometer used in these studies was made possible through equipment grants from the NIH and NSF.

Supplementary Material Available: Copies of ^{1}H-NMR and ^{13}C-NMR (75 MHz) spectra of new compounds lacking analyses (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.