REARRANGEMENT OF o-ALKYNYL SUBSTITUTED α-DIAZOACETOPHENONES. CONVERSION TO β-NAPHTHOLS VIA ARYLKETENE INTERMEDIATES

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Abstract: *In contrast to the rhodium (II) mediated cycloisomerization of o-alkynyl substituted α-diazoaceto-phenones, irradiation leads to β-naphthols which are formed via cyclization of an arylketene intermediate*

The role of α-diazo carbonyl compounds in organic synthesis is well established [1-4] The Arndt-Eistert sequence employs the Wolff rearrangement of an α-diazoketone to a ketene in the one-carbon homologation of carboxylic acids [5] Ring contraction of cyclic diazo ketones represents a general method for the preparation of highly strained small ring compounds [6] α-Diazo carbonyl compounds are also precursors to metallo-carbenoid intermediates when exposed to many metal complexes or salts [7] Rhodium (II) carboxylates are particularly effective catalysts for the decomposition of diazo compounds and an increasing number of chemical syntheses are based on this catalytic methodology [7-10] Even though much work has been done in this area, very little attention has been paid to sorting out the difference in chemical behavior as a function of the experimental conditions used to extrude nitrogen from a particular diazo compound Recently, we outlined a method for the construction of diverse polycyclic skeletons which makes use of the rhodium (II) acetate catalyzed reaction of α-diazo alkynyl substituted ketones [11] At about the same time, Hoye's group also described the cycloisomerization of α-diazo ketones bearing tethered alkyne units using similar chemistry [12] We report here the results of a study which contrasts the thermal, photochemical and transition metal catalyzed behavior of several closely related α-diazo ketones

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 Our initial efforts focused on the rhodium (II) acetate catalyzed reaction of α-diazo ketone 1 Treatment of 1 with a catalytic quantity of Rh_2OAc_4 at 25°C in the presence of 2 equiv of ethyl vinyl ether afforded cyclopropane 2 (91%) derived from a transient vinyl carbenoid [13] 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_2OAc_4 gave naphthol 3 in 60% yield The same naphthol was also produced from the photolysis of 1 in methylene chloride Interestingly, the closely related diazomethane derivative 4 was found to undergo an entirely
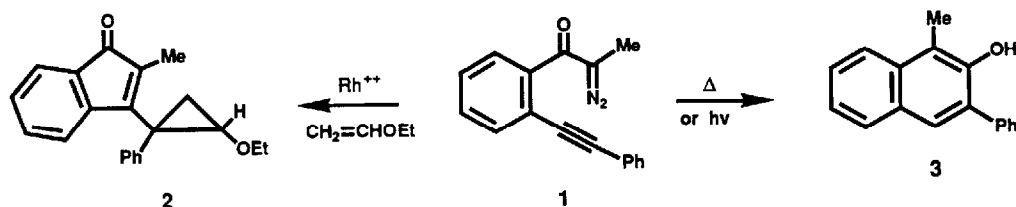
different reaction upon thermolysis The major product formed corresponded to dimer **6** which was isolated in near quantitative yield Under the thermal conditions, the reaction proceeds by 1,3-dipolar cycloaddition of the diazo group of one molecule across the acetylenic π-bond of another diazo compound The initially formed cycloadduct undergoes a proton shift to produce a transient pyrazole (i e **5**) which subsequently inserts into the neighboring diazo center to give **6** Introduction of a methyl substituent on the diazo carbon significantly retards bimolecular dimerization and instead, naphthol formation occurs
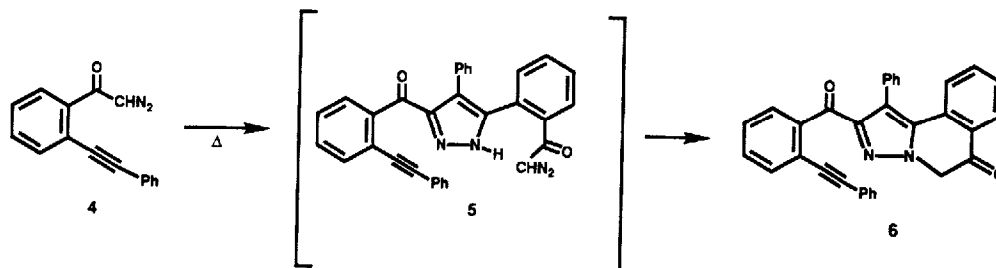

The isolation of a rearranged naphthol from the photolysis turned out to be quite general We found that the irradiation of diazo ketones **7-10** afforded naphthols **11-14** in good yield In the case of **10**, the initially isolated naphthol **14** (70%) was treated with phenyl isocyanate and the resulting carbamate derivative **15** was unequivocally established by an X-ray crystal structure analysis
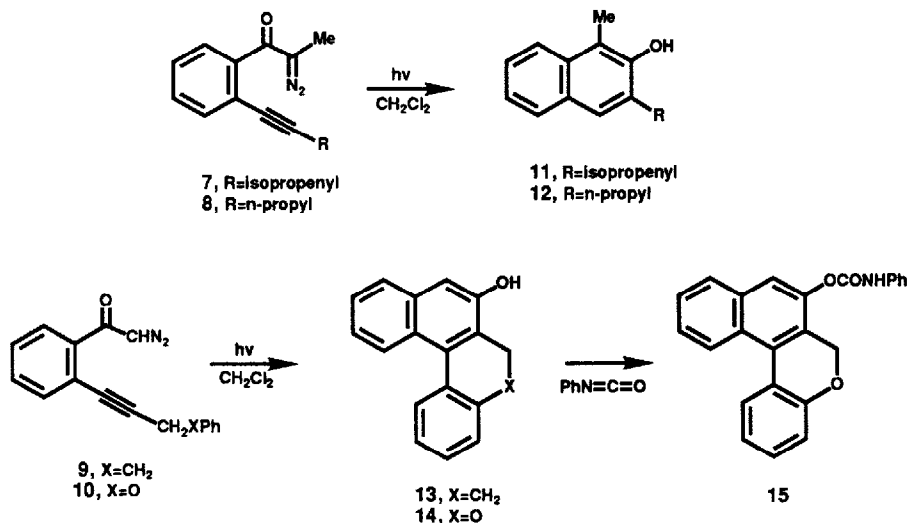

Formation of the naphthol ring can be explained in terms of a photochemical Wolff rearrangement which proceeds to give an o-alkynyl substituted arylketene (**16**) intermediate Subsequent cyclization of the ketene leads to diradical **17** which either abstracts hydrogen from solvent (e g **3**) or attacks the neighboring aromatic ring (R_2=CH$_2$XPh) to give the cyclized product Danheiser[14], Liebeskind[15], and Moore[16] have employed a somewhat related reaction for the 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 cyclobutenedione derivative Thermolysis and oxidation leads to the 1,4-benzoquinone via a pathway related to that described in Scheme I [17] Supporting evidence for the proposed mechanism was obtained by carrying out the irradiation of the diazoketone in the presence

Scheme I
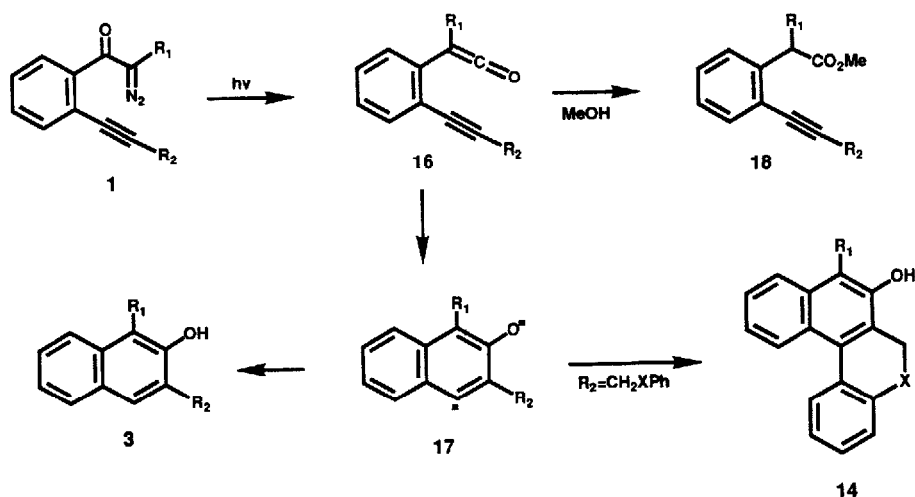
of 2 equiv of methanol The isolation of methyl ester **18** in high yield (>90%) provides excellent support for the arylketene intermediate When the alcohol moiety was attached to the alkynyl group, the photolysis (benzene) afforded the novel dimer **20** in 81% yield as a 1 1-mixture of cis/trans diastereomers The formation of **20** involves trapping of the initially generated ketene with the available hydroxyl group
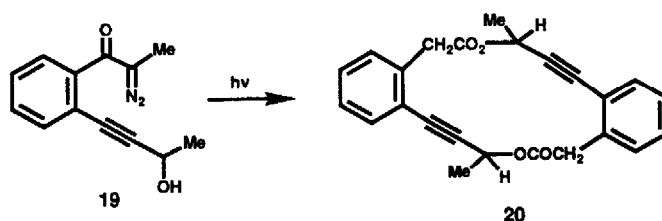
We are continuing to investigate the diverse chemical behavior of alkynyl substituted α-diazo ketones and the use of these compounds for the formation of more complex ring systems We will report our findings in due course

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13   The isolation of 2 represents the first reported example of a bimolecular cyclopropanation reaction of the cyclized rhodium carbenoid with a π-bond The previous examples all involved intramolecular cyclopropanations [11,12] NMR 2 (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 and 4 0 Hz), 1 99 (s, 3H), 3 42 (m, 2H), 3 72 (dd, 1H, J=7 0 and 4 0 Hz), and 7 08-7 40 (m, 4H), ^{13}C-NMR (CDCl$_3$, 75 MHz) δ 8 5, 14 7, 20 3, 28 6, 63 0, 65 9, and vinyl and aromatic carbons

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