# ON THE APPLICABILITY OF THE WOLFF REARRANGEMENT TO
## STRAINED HYDROCARBONS

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Correlation of reactivity and bonding has provided the impetus for the synthesis of many strained ring systems.  One of the most useful approaches is ring contraction of diazoketones $\underline{via}$ their corresponding ketocarbenes.[1] In this Communication, we wish to consider one aspect of the constraints on this approach.

In the synthesis of 4,8-dihydrodibenzo[cd,gh]pentalene, a Wolff rearrangement was employed to create the carbon skeleton of this system (see Scheme 1).[2]  Carrying out the reaction by photolysis of diazoketone 1 at room temperature in benzene in the presence of $\underline{t}$-butylamine led only to a 2% yield of the desired ring contracted product 3.  The major product, isolated in 20% yield, was identified as 1a,5a-dihydro-(4,5-methylene-9,10-phenanthra)-[d]benzo[b]furan (4, X = H) on the basis of spectral data and its facile dehydrogenation with DDQ to 4,5-methylene-9,10-phenanthra[d]-benzo[b]furan (5), mp 146.0-147.5°.

Compound 4 (X = H):  Ir (CCl$_4$) cm$^{-1}$ 3063, 2906, 1626, 1590, 1500; nmr (CDCl$_3$) δ7.78-6.95 (9H, m), 6.95-6.04 (2H, m), 5.42-4.93 (1H, m), and 3.50 (2H, bs); uv (95% C$_2$H$_5$OH) $\lambda_{max}^{nm}$ (log ε) 241 sh (4.49), 251 sh (4.61), 256 (4.71), 258 (4.71), 280 sh (4.15), 300 (4.11), 311 (4.14), 327 (3.92), and 351

Scheme 1.  Photolysis of 9-Diazo-10-keto-4,5-methylenephenanthrene
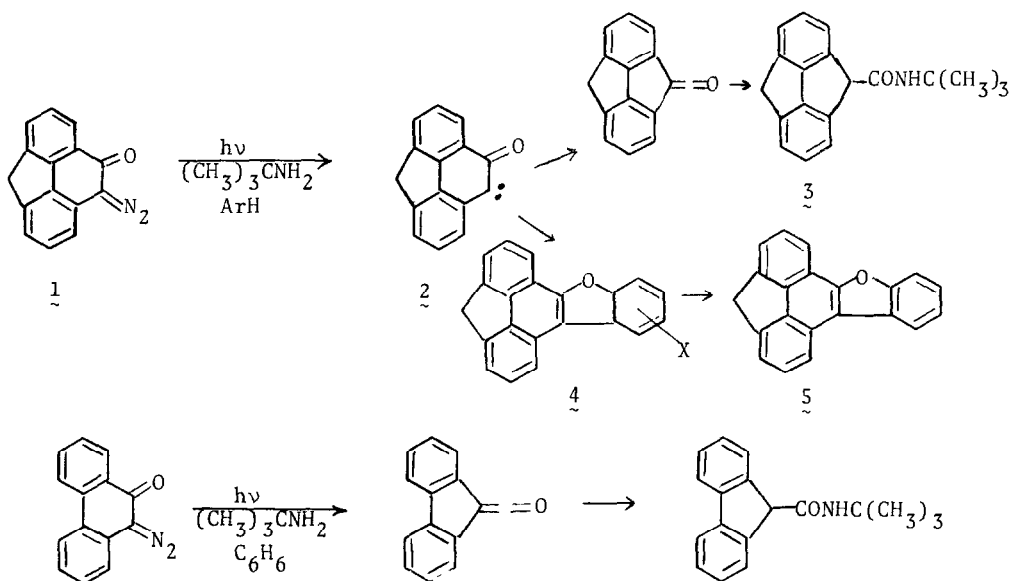


Scheme 2.  Rationale for Formation of 4 and/or 5
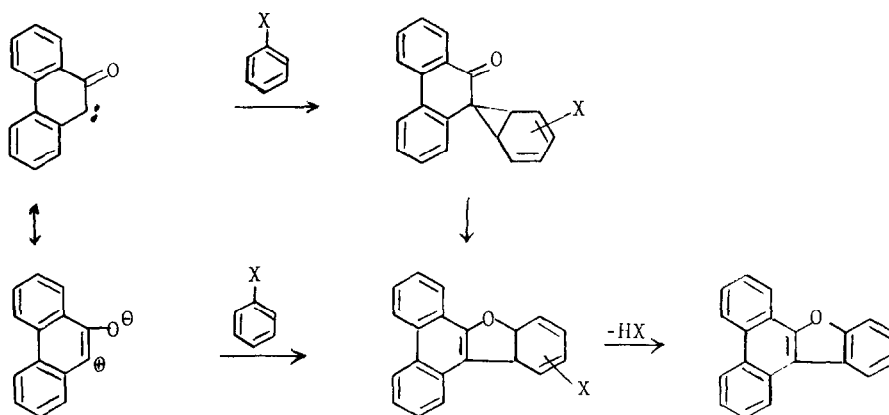
(2.94); mass spec m/e (rel %) 282(100), 281(30), 280(63), 279(27), 254(5), 253(15), 252(10), 251(7), 250(11); calcd. for $C_{21}H_{14}O$: 282.1045, found 282.1045. Compound $\underset{\sim}{5}$: ir $(CCl_4)$ cm$^{-1}$ 1631, 1592, and 1504; nmr $(CDCl_3)$ δ8.16-7.17 (10H, m) and 4.00 (2H, s); uv (95% $C_2H_5OH$) $\lambda_{max}^{nm}$ (log ε) 243 sh (4.58), 248 (4.67), 254 (4.68), 261 sh (4.65), 269 sh (4.55), 281 sh (4.17), 297 (4.12), 306 sh (4.16), 313 (4.33), 321 (4.24), 329 (4.45), 334 sh (3.88), 343 sh (3.44), and 353 (3.47); mass spec m/e (rel %) 280(100), 279(31); calcd. for $C_{21}H_{12}O$: 280.0888, found 280.0888.

The reluctance of the ketocarbene to undergo the Wolff rearrangement led to the virtually unprecedented reaction with the aromatic solvent to produce dihydrobenzofuran.[3] To determine whether the aromatic solvent was unusually reactive toward this ketocarbene, various solvents were explored. Aqueous acidic dioxane and acidic methanol, common solvents for closely related systems,[4] led to 0.3 to 0.5% yields of ring contraction product. Decreasing the reactivity of the aromatic solvent by going to chlorobenzene or hexafluorobenzene does improve the yield but only to 3-5%. In chlorobenzene, a 50% yield of $\underset{\sim}{5}$ was isolated directly from the reaction. To rule out electronic factors as the cause, the contraction of 9-diazo-10-ketophenanthrene[5] was examined. Utilizing the standard conditions (see Scheme 1), an 80% yield of ring contracted product was obtained. Clearly, the low yield of ring contraction in the case of $\underset{\sim}{1}$ reflects a steric inhibition because of increasing ring strain in the product. The generation of compounds of higher total strain energy than $\underset{\sim}{3}$ (such as the propellanes[6]) by this method rules out total strain energy as a contributing factor. However, unlike the propellanes in which the incremental increase in strain in the Wolff rearrangement step is only 20-30 kcal/mol, in the rearrangement of $\underset{\sim}{2} \rightarrow \underset{\sim}{3}$, approximately 45-51 kcal/mol of additional strain energy is created. Therefore, these results suggest that the Wolff rearrangement as a synthetic approach will be applicable only in those cases in which the strain created in a single step is lower than approximately 50 kcal/mol.

The formation of dihydrobenzofurans as the major products indicates the exceedingly high reactivity of this ketocarbene--a fact which precludes unusual stability as the cause for lack of rearrangement. While two reasonable mechanisms may be postulated (see Scheme 2), the intriguing possibility of a 1,3-dipolar addition to a simple aromatic would be un-precedented.[8]

## References

1. For a recent revidw see W. Kirmse, "Carbene Chemistry," Academic Press, New York, 1971, pp 475-503.

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3. The only report of benzene reacting with a photolytically generated α-ketocarbene is that obtained from ethyl diazoacetate. See G. O. Schenel and H. Ziegler, Ann., 584, 221 (1953); F.J.L. Sixma and E. Detilleux, Rec. Trav. Chim. Pays Bas, 72, 173 (1953). Benzenes substituted with electron withdrawing groups have not been reported to react.

4. See for example a) O. Süs and K. Müller, Ann., 593, 91 (1955); 612, 153 (1958); b) L. Horner, W. Kirmse, and K. Muth, Chem. Ber., 91, 430 (1958); c) L. Horner, K. Muth, and H. G. Schmelzer, ibid., 92, 2953 (1959); d) L. Horner, H. G. Schmelzer, H. V. van der Eltz, and K. Habig, Ann., 661, 44 (1963); e) P. Eilbracht and K. Hafner, Ang. Chem. Internat. Ed., 10, 751 (1971).

5. M. P. Cava, R. L. Little, and P. R. Napier, J. Amer. Chem. Soc., 80, 2257 (1958).

6. P. E. Eaton and K. Nyi, ibid., 93, 2786 (1971).

7. This estimate arises from the difference in strain energies of 4,8-dihydrodibenzo[cd,gh]pentalene (66 kcal/mol) and 4,5-methylene-phenanthrene (15-20 kcal/mol).

8. For α-ketocarbenes probably serving in a 1,3-dipolar addition, see J. Novak, J. Ratusky, V. Sneberk, and F. Sorm, Collect. Czech. Chem. Commun., 22, 1836 (1957). For a 1,3-dipolar addition to simple benzenes, see W. J. Linn and R. E. Benson, J. Amer. Chem. Soc., 87, 3657 (1965).