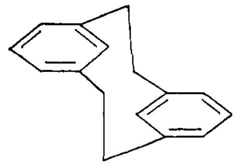
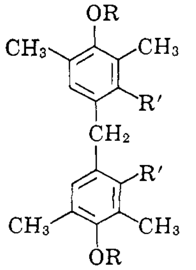
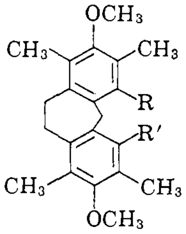


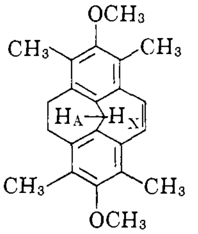
I



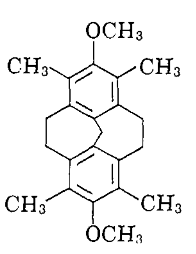
IIa, R = R' = H
b, R = CH3; R' = H
c, R = CH3; R' = CH2Cl



IIIa, R = R' = H
b, R = CH2Cl; R' = H
c, R = CH2Cl; R' = CHO
d, R = CH2P+ (Ph)3Cl−; R' = CHO



IV



V

methyl) compound IIc, mp 137–138°, 75%. The methyl groups in IIb serve to block the undesired introduction of chloromethyl groups *ortho* to the ether functions. Transformation of IIc into the 5H[*a*,*d*]-dibenzocycloheptene IIIa, mp 140–141°, 47%, was accomplished *via* a modified Wurtz procedure[4a,7] using sodium sand with tetraphenylethylene as catalyst. A second halomethylation carried out as above on IIIa yielded the monochloromethyl compound IIIb, mp 220–221°, 52%, as major product. Formylation of IIIb with dichloromethyl butyl ether[8] and stannic chloride occurred smoothly over a 24-hr period at room temperature with the formation in 76% yield of the chloromethyl aldehyde IIIc, mp 204–205° (1680 cm^{-1}, CHO).[9] The phosphonium salt IIId, mp 220–221° (1670 cm^{-1}, CHO), is obtained in 85% yield from the chloromethyl aldehyde by displacement with triphenylphosphine in refluxing toluene. Generation of the phosphorane[10] in anhydrous ethanol by addition of sodium ethoxide at reflux temperature forms the 8,16-methano-*cis*-[2.2]metacyclophane monoolefin IV, mp 184–185°, 85% ($\lambda_{\max}^{\text{cyclohexane}}$ 212 (ϵ 35,500), 256 (23,100), 286 (9300), and 298 mμ (8900)). The nmr spectrum[11] of IV shows resonances at τ 6.43 (singlet, two OCH$_3$), 6.75 (A$_2$B$_2$ multiplet, –CH$_2$CH$_2$–), 7.78 and 7.90 (equivalent singlets, four CH$_3$), *and importantly:* a two-proton singlet at 2.70 (–CH=CH–) and two widely separated doublets of an AX spin system at 5.95 and 7.70 (J_{AX} = 10 cps). These last resonances are assigned to the protons of the 8,16-methylene bridge; strong diamagnetic shielding of H$_X$ (IV) by the adjacent bridge double bond[12] produces an upfield shift of 1.80 ppm.

The mass spectrum of IV shows the correct molecular weight, M$^+$ 334 (base peak), indicating intramolecular Wittig olefin formation from IIId. Other fragmentations seen at M$^+$ − 14 (19% of base peak), M$^+$ − 15 (25%), M$^+$ − 30 (30%), and M$^+$ − 31 (49%) are presumably due to loss of CH$_2$, CH$_3$, two CH$_3$, and two CH$_3$ + H$^+$, respectively.

That IV is the correct structure of the internal Wittig product is shown by its ready catalytic absorption of 1 mole of hydrogen to yield the saturated 5,13-dimethoxy-4,6,12,14-tetramethyl-8,16-methano-*cis*-[2.2]-metacyclophane,[2] V, mp 155° ($\lambda_{\max}^{\text{cyclohexane}}$ 220 (ϵ 36,700) and 264 mμ (8100), 90%, the nmr spectrum of which, in addition to resonances at τ 6.50 (singlet, two OCH$_3$), 6.88 (A$_2$B$_2$ multiplet, two –CH$_2$CH$_2$–), and 7.95 (singlet, four CH$_3$), shows a two-proton singlet at 6.36. This singlet corresponds to the now-equivalent protons of the methylene bridge and appears in proximity to the H$_A$ resonance of IV, showing the similarity of environments. Mass spectral analysis[13] of V confirms the molecular weight, M$^+$ 336 (base peak), and shows important fragmentations at M$^+$ − 15 (76% of base peak) and M$^+$ − 30 (49% of base peak) which are tentatively assigned to successive losses of the methoxyl methyls. Loss of the 8,16-methylene group does not appear to be an important fragmentation pathway.

The *cis* geometry of V is required by the 8,16-bridging methano group. The chemistry of this new metacyclophane and its monoolefin IV will be reported at a later date.[14,15]

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[7] E. Müller and G. Röscheisen, *Chem. Ber.*, **90**, 543 (1957).

[8] H. Gross, A. Rieche, and E. Höft, *Chem. Ber.*, **94**, 544 (1961).

[9] Infrared spectra for all reported compounds were taken with KBr disks and are consistent with assigned structures.

[10] A. Maercker, *Org. Reactions*, **14**, 270 (1965).

[11] Nmr spectra were obtained in deuteriochloroform on a Varian A-60A using TMS as internal standard.

[12] R. C. Cookson, T. A. Crabbe, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, **7**, 355 (1966), and references cited therein.

[13] Mass spectra were obtained by Dr. Paul Nicholson of these laboratories on a C.E.C. Model 21-103C instrument using a heated inlet operating at 180°; ionization potential 70 e.v.

[14] Satisfactory analyses were obtained for all new compounds.

[15] V. Boekelheide, B. A. Hess, and A. S. Bailey have recently reported the preparation of 8,16-oxido[2.2]metacyclophane, which must also possess *cis* or *syn* geometry (*cf. J. Am. Chem. Soc.*, **89**, 2746 (1967)). We wish to thank Professor Boekelheide for informing us of their results prior to publication.

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Received June 13, 1967

Quantitative Evidence Concerning the Relative Stabilities of Cycloalkynes and Arynes[1]

Sir:

Cyclooctyne is the cycloalkyne of smallest ring size to have been isolated; it is air sensitive and rearranges and polymerizes easily.[2] Considerable evidence has accumulated which suggests that cycloheptyne, cyclohexyne, and cyclopentyne can exist as short-lived reac-

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[1] This research was supported in part by National Science Foundation Grant No. GP-7423.

[2] (a) A. T. Blomquist and L. H. Liu, *J. Am. Chem. Soc.*, **75**, 2153 (1953); (b) G. Wittig and A. Krebs, *Ber.*, **94**, 3260 (1961).

tion intermediates.[3] We wish to report the results of a series of experiments designed to obtain a quantitative estimate of the relative stabilities of cyclooctyne, the transient cycloalkynes, and several aryne intermediates.

It has been found that cycloalkynes can be conveniently generated near room temperature by the dehydrochlorination of 1-chlorocycloalkenes with lithium piperidide.[4] Moreover, if phenyllithium is present, lithium piperidide adds to the cycloalkynes (**2** → **4**) in competition with the phenyllithium (**2** → **3**). Depending upon how the reaction products are processed, either enamines or ketones can be obtained from adduct **4**. These findings make it possible to extend the competition method which Huisgen has used to assess aryne stabilities[5] to explore the stabilities of cycloalkynes. The Huisgen method consists of measuring rate constant ratios (k_1/k_2) for the competitive addition of phenyllithium and lithium piperidide to aryne intermediates. Aryne stabilities are inferred from the ratios, assuming that the stabilities of the various intermediates parallel their selectivities. In Table I competition ratios are reported for cyclooctyne, cycloheptyne, cyclohexyne, and cyclopentyne which were generated from appropriate 1-chlorocycloalkenes. In addition, a value of k_1/k_2 was determined for cyclooctyne which had been synthesized independently. Several aryne ratios are included for comparison purposes.

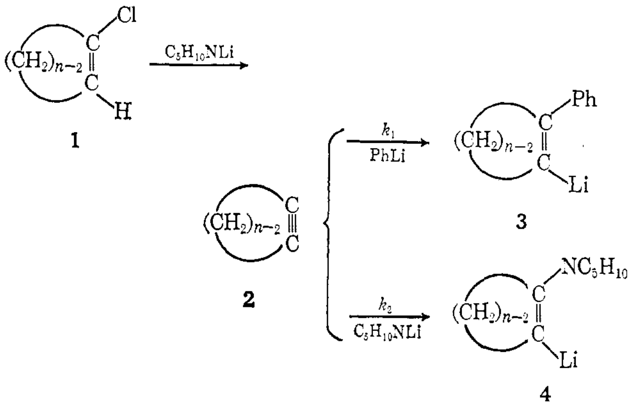


Table I. Cycloalkyne and Aryne Competition Ratios[a]

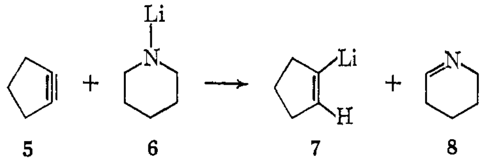
Intermediate	k_1/k_2[b]
Cyclooctyne (generated *in situ*)	20.8 ± 2
Cyclooctyne (synthetic)	21[e]
Cycloheptyne	21 ± 3
Cyclohexyne	5.2 ± 0.5
Cyclopentyne	2.6 ± 0.3[c] (10.8[b])
Benzyne	4.4[d]
1-Naphthyne	5.8[d]
9-Phenanthryne	12.8[d]

[a] Reactions carried out in ether in ampoules at 35° using salt-free phenyllithium and lithium piperidide. [b] Ratios based on the yields of 1-phenylcycloalkenes and cycloalkanones as determined by gas-liquid partition chromatography. Method otherwise generally the same as in ref 5. [c] Rate constant k_2 based on the sum of cyclopentanone and phenylpiperidine. [d] Reference 5. [e] Based on only two measurements.

The competition ratios for authentic cyclooctyne and *in situ* generated cyclooctyne are the same, which they should be if the substitution products from 1-chlorocyclooctene are actually produced from a cyclooctyne intermediate. Within experimental error, the cycloheptyne ratio is equal to that for cyclooctyne. It is unquestionably clear from other studies[6] that cycloheptyne is less stable than cyclooctyne. The inability of the competition method to detect this difference is not surprising. The large k_1/k_2 ratios are difficult to measure experimentally. Moreover, large differences in reactivity are compressed into the relatively short competition ratio scale. This point is vividly illustrated by comparing the competition ratios of cyclooctyne (21) and benzyne (4.4). A 0.1 *M* solution of benzyne would have a dimerization half-life of approximately 10^{-8} sec.[7]

The stability of cyclohexyne appears to lie much closer to benzyne than to cycloheptyne. It is tempting to conclude that cyclohexyne is more stable than benzyne. Until the competition method has been critically examined, however, it is doubtful whether such a subtle comparison ought to be attempted. The positioning of 9-phenanthryne relative to benzyne and cycloheptyne is noteworthy. Although 9-phenanthryne is surprisingly more stable than benzyne, it is not close to the stability of cycloheptyne, which can be synthesized and manipulated to a limited extent at −80°.[6b]

1-Chlorocyclopentene afforded 1-phenylpiperidine, 2-phenylpiperidine, and cyclopentene in addition to 1-phenylcyclopentene and cyclopentanone. The abnormal products most likely arise from the reduction of cyclopentyne by lithium piperidide (**5** + **6** → **7** + **8**).



Addition of phenyllithium to Schiff base **8** would produce the phenylpiperidines.[8] Wittig has reported a similar reduction of benzyne by lithium diethylamide.[9] The competition ratio for cyclopentyne, based on yields of 1-phenylcyclopentene and cyclopentanone, is 10.8. In complementary experiments it has been demonstrated that cyclopentyne is definitely produced in this system and that the reaction products can be analyzed for satisfactorily. Although it is possible that a reversal in stability takes place in the case of cyclopentyne, it is not likely, for there are too many qualitative indications of cyclopentyne's extreme instability.[10] A reasonable alternative is that the lithium piperidide addition and reduction reactions proceed through a common inter-

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(3) G. Wittig, *Pure Appl. Chem.*, **7**, 173 (1963).

(4) L. K. Montgomery, A. O. Clouse, A. M. Crelier, and L. E. Applegate, *J. Am. Chem. Soc.*, **89**, 3453 (1967).

(5) R. Huisgen, W. Mack, and L. Möbius, *Tetrahedron*, **9**, 29 (1960).

(6) (a) F. G. Willey, *Angew. Chem. Intern. Ed. Engl.*, **3**, 138 (1964); (b) G. Wittig, Chemistry Colloquium, Indiana University, Feb 28, 1967.

(7) M. E. Schafer and R. S. Berry, *J. Am. Chem. Soc.*, 87, 4497 (1965).

(8) The ratio of 1-phenyl to 2-phenyl isomers was ~1:5. A trace of 1-phenylpiperidine, which was not large enough to account for the observed product, was detected in a blank run (no 1-chlorocyclopentene). Fortunately, since the 2-phenyl isomer predominates, the cyclopentyne competition ratio (2.6) is not greatly influenced by the inclusion or exclusion of 1-phenylpiperidine as a reaction product.

(9) G. Wittig, H. J. Schmidt, and H. Renner, *Chem. Ber.*, **95**, 2377 (1962).

(10) See ref 3 for pertinent references.

mediate[11] or are mechanistically very similar, *e.g.*, they follow multicenter pathways where lithium attachment to cyclopentyne dominates the energetics of both reactions. Under such circumstances, the combined yields of cyclopentanone and phenylpiperidines should be used in calculating the competition ratio. A k_1/k_2 of 2.6 is obtained in this way. Finally, it is conceivable that the competition method cannot be validly applied to estimating cyclopentyne's stability. This would be the case if the electronic ground state of cyclopentyne is drastically different from that of the other cycloalkynes or the rates of its reactions with the organolithium reagents are approaching the diffusion-controlled limit. Attempts to clarify the picture concerning the stability of cyclopentyne using other nucleophile pairs have not been successful to the present.

[11] In this connection see Wittig's postulated mechanism for the reduction of benzyne by lithium diethylamide.[9]

[12] National Institutes of Health Predoctoral Fellow.

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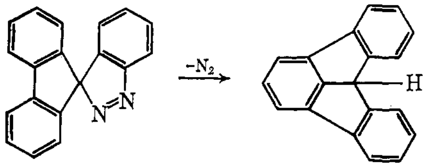
Received July 28, 1967

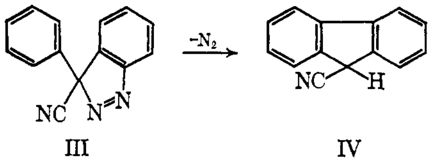
Diradical Processes in Decomposition of Spiro[fluorene-9,3′-indazole]

Sir

Carbenic reagents react thermally or photochemically with aromatic compounds to give substitution and addition products. The reactions previously investigated[1] are postulated to involve singlets of the type $Z_2C\pm$. We now describe thermolysis and photolysis of spiro[fluorene-9,3′-indazole] (I) to fluoradene (II, eq 1) and of 3-cyano-3-phenylindazole (III) to 9-cyanofluorene (IV, eq 2). Decomposition of I to II is noteworthy because the divalent aromatic substitution reaction involves a diradical process; conversion of III to IV is interesting because the mechanism is significantly different than that for I.



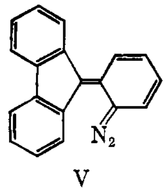
(1)



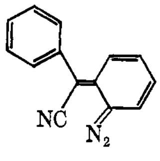
(2)

Indazoles I (mp 167°, 80%) and III (mp 75°, 22%) are prepared by cycloaddition of benzyne[2] with 9-diazofluorene and with α-phenyldiazoacetonitrile. The adducts are established as indazoles (I and III) rather than diazo compounds (V and VI) by infrared methods.

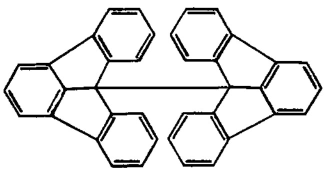
Decomposition of I (17.3 mmoles) in *o*-dichlorobenzene at 178° gives II (>80%) and <2% of 12,12′-bifluoradene (VII) and 9-phenylfluorene (VIII); IX is not isolated.[3] Thermolysis of I in concentrated solution (50 m*M*) in decalin diminishes conversion to II (9%) and increases that to VII (39%) and VIII ($\gg$14%). Heating solid I quickly (5 min) to 160° results in III (40%) and equivalent quantities of VII (19%) and VIII (22%); upon heating I slowly to 160°, the yield of II (10%) is reduced and VII (32%) and VIII (34%) become major products.



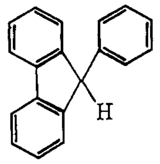
V



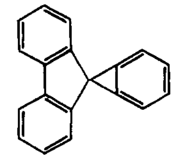
VI



VII

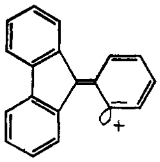


VIII

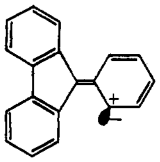


IX

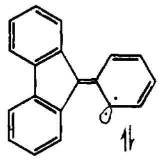
Loss of nitrogen from I can possibly give four divalent intermediates which after geometric change are represented as X–XIII.[1b] X and XI are dipolar singlets which differ in the electron distribution in their π and σ atomic orbitals; on the basis of quantum mechanical symmetry it has been argued[1b] however that intermediates similar to X and XI are resonance hybrids. XII and XIII are singlet and triplet diradicals, respectively.[4]



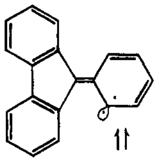
X



XI



XII



XIII

A dipolar singlet or its prior rotamer may be formed initially in thermolysis of I. The chemistry of conversion of I to II is more compatible, however, if XII and/or then XIII[5] are (eventual) major intermediates which

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[1] (a) F. Weygand, H. Dworschak, K. Koch, and S. Kontas, *Angew. Chem*, 73, 409 (1961); (b) M. J. S. Dewar and K. Narayanaswami, *J. Am. Chem. Soc.*, 86, 2422 (1964).

[2] L. Friedman and F. M. Logullo, *ibid.*, 85, 1549 (1963).

[3] Methyl 3,3-dimethylindiazene-6-carboxylate photolyzes to 1,1-dimethyl-3-carbomethoxybenzocyclopropene: R. Anet and F. A. L. Anet, *ibid.*, 86, 525 (1964).

[4] The questions as to the intermediates involved in conversion of I to II, VII, and VIII eventually apply if I isomerizes to V, if nitrogen is not expelled in initial bond breaking of I, or if IX forms and is converted to the observed products.

[5] Interconversion to XII is expected to be rapid and intersystem crossing to XIII relatively slow.