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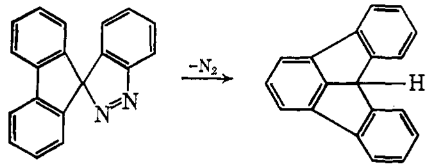
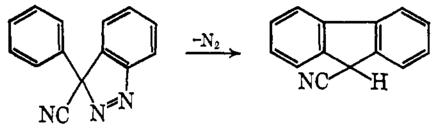
Diradical Processes in Decomposition of Spiro[fluorene-9,3′-indazole]

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.

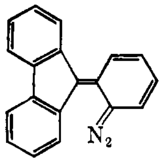


I II (1)

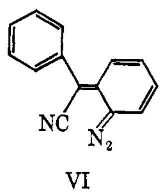


III IV (2)

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.

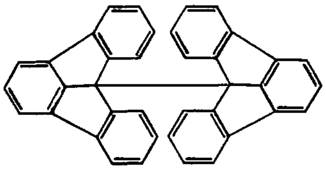


V

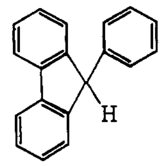


VI

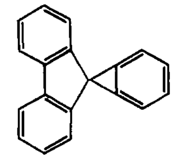
Decomposition of I (17.3 mmoles) in *o*-dichlorobenzene at 178° gives II (>80%) and <2% of 12,12′-bifluoradene (VII) and 9-phenylfluorene (VIII); IX is not isolated.[3] Thermolysis of I in concentrated solution (50 m*M*) in decalin diminishes conversion to II (9%) and increases that to VII (39%) and 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.



VII

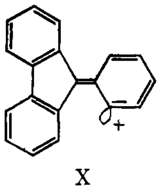


VIII

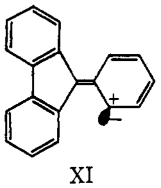


IX

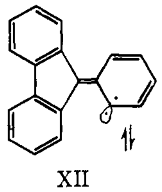
Loss of nitrogen from I can possibly give four divalent intermediates which after geometric change are represented as X–XIII.[1b] X and XI are dipolar singlets which differ in the electron distribution in their π and σ atomic orbitals; on the basis of quantum mechanical symmetry it has been argued[1b]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



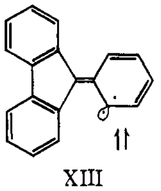
X



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).

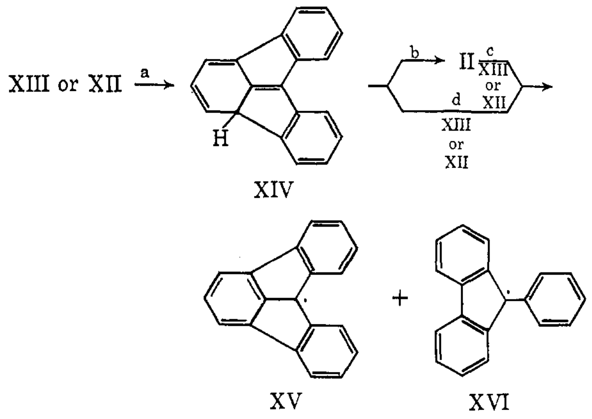
[2] L. Friedman and F. M. Logullo, *ibid.*, **85**, 1549 (1963).

[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.

undergo diradical cyclization at the 1 position of the fluorene system to give XIV which subsequently isomerizes (eq 3). Since there is extensive formation of VII and VIII from concentrated I in decalin and related solvents, a radical-like process is implied in which hydrogen is transferred from solvent and from II to give 9-phenylfluorenyl (XVI) and fluoradenyl (XV) radicals and thence VIII and VII (eq 4 and 5). Similarly generation of a diradical from solid I in the presence of effective amounts of II or its isomeric precursor(s) such as XIV yields equivalent amounts of VIII by radical transfer and subsequent coupling of XV. Rapid heating of solid I minimizes the opportunity for partitioning of hydrogen from II and XIV.

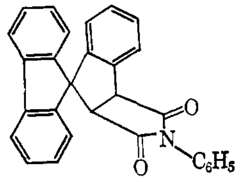


(3)

$$\text{XVI} + \text{II or XIV} \longrightarrow \text{VIII} + \text{XV} \qquad (4)$$

$$2\text{XV} \longrightarrow \text{VII} \qquad (5)$$

The geometric change in decomposition of I and the strain leading to XIV should provide real opportunity for spin inversion to XIII. Irradiation of I in 2-methyltetrahydrofuran at 77°K does provide evidence for a ground-state triplet, presumably XIII.[6] Photolysis of I in benzene containing N-phenylmaleimide gives the capture product XVII. In solution I photolyzes to II, VII, and VIII and products of incorporation of solvent and added oxygen. These results indicate that the photochemical and thermolysis reactions of I are generally similar and that intramolecular substitution in photolytic conversion of I to II possibly involves diradical processes; XV and XVI are generated in competitive reactions. Photolysis of I in toluene at 65° thus yields II (9%), VII (8%), and VIII (51%); in ethyl ether at −95° and subsequent exposure to air, 9-phenylfluorenyl peroxide (XVIII) forms in ~100% yield. The conversion to 9-phenylfluorenyl rather than fluoradenyl derivatives reflects the abilities of ethyl ether and toluene to transfer hydrogen to XII and/or XIII. Trapping of XVI by oxygen results in XVIII.



XVII

I photolyzes in benzene exposed to air to give II (12%), VII (21%), XVIII (43%), 9,9-diphenylfluorene (15%), and biphenyl. Photolysis of I results in abstraction of hydrogen from benzene to give phenyl radicals; biphenyl is apparently formed from phenyl radicals by arylation of benzene and hydrogen transfer. 9,9-Diphenylfluorene presumably results from addition of XVI to benzene and hydrogen transfer.

Decompositions of I and III differ dramatically. Thermolysis or photolysis of III yields IV (>93%) and traces of diphenylacetonitrile. The processes are not effectively partitioned to diphenylacetonitrile (<1.3%) or intercepted by the chemical techniques used for I. Decomposition of III is much more caged than I; the differences can be related to the greater rotational course from I.

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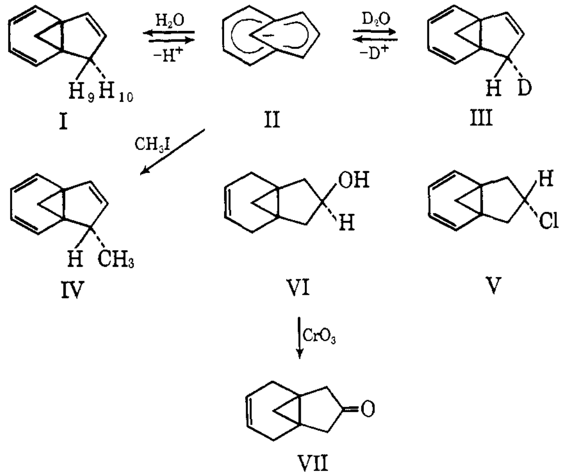
[6] The esr spectrum consists of an intense band at 3210.8 gauss (g = 2.0022), a weaker band at half-field (1618.4 gauss, A_m = 2), and poorly resolved satellite bands.

A Stereospecific Base-Catalyzed Deuterium Exchange of Tricyclo[4.3.1.0]deca-2,4,7-triene

Sir:

We have recently shown that the hydrocarbon tricyclo[4.3.1.0]deca-2,4,7-triene (I) gives rise to a ten-π-electron aromatic anion (II) when treated with sodium dimethylsulfinyl anion.[1] In this communication we report that base-catalyzed exchange of I leads to a remarkable stereospecific abstraction of proton and stereospecific incorporation of deuterium.



When a solution of II in dimethyl-d_6 sulfoxide was quenched with D_2O, the hydrocarbon isolated contained one deuterium atom at C_9. That the incorporation of the deuterium atom was stereospecific was evident from a comparison of the nmr spectrum of the deuterated hydrocarbon III at 100 MHz with that of the undeuterated I. The protons of interest in I are H_8 at τ 4.68 (double triplet, $J_{7,8}$ = 6 Hz, $J_{8,9}$ = $J_{8,10}$ = 2 Hz), H_9 at τ 7.35 (double triplet, $J_{9,10}$ = 17 Hz, $J_{8,9}$ = $J_{7,9}$ = 2 Hz), and H_{10} at τ 7.65 (double triplet, $J_{8,10}$ = $J_{7,10}$ = 2 Hz).[2] The nmr spectrum of III had H_8 at τ 4.68

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[1] P. Radlick and W. Rosen, *J. Am. Chem. Soc.*, **88**, 3461 (1966).

[2] The assignment of H_9 and H_{10} as *cis* and *trans*, respectively, to the cyclopropane ring was made on the basis that in compounds where the methylene protons on carbon adjacent to a cyclopropane ring are not