

SPIROCYCLOPROPANE FORMATION AND REARRANGEMENT IN THE THERMAL AND PHOTOCHEMICAL DECOMPOSITION OF 1-PYRAZOLINES FROM 9-DIAZOFLUORENE AND BICYCLIC[2.2.1]OLEFINS

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Abstract—The 1-pyrazolines formed by the photochemical and/or thermal cycloaddition of 9-diazofluorene to norbornadiene and norbornene were isolated and submitted to thermal and photochemical decomposition. The *exo* 1-pyrazoline from norbornadiene rearranges thermally to 2-(9-spirofluorenylidene)bicyclo[3.2.1]octadiene in high yields. Photolysis of the same pyrazoline however leads to the formation of the "normal" spirocyclopropane, which in turn can be thermally converted to the same bicyclic octadiene. The formation of the rearranged product is thought to be consistent with a mechanism involving a stabilized zwitterion and a *cis* divinylcyclopropane as intermediates. On photolysis in neat norbornadiene, 9-diazofluorene is converted in high yield to the 1,3 addition product—the 1-pyrazoline. However, when the irradiation was carried out in ether solution, in the presence of large excess of olefin, the major products isolated were 9,9'-bifluorenyl and 9,9',9''-terfluorenyl. These results add weight to the possibility of pyrazoline formation before its conversion to cyclopropane in many other analogous reactions between diazoalkanes and olefins which were widely interpreted as carbene addition to alkenes.

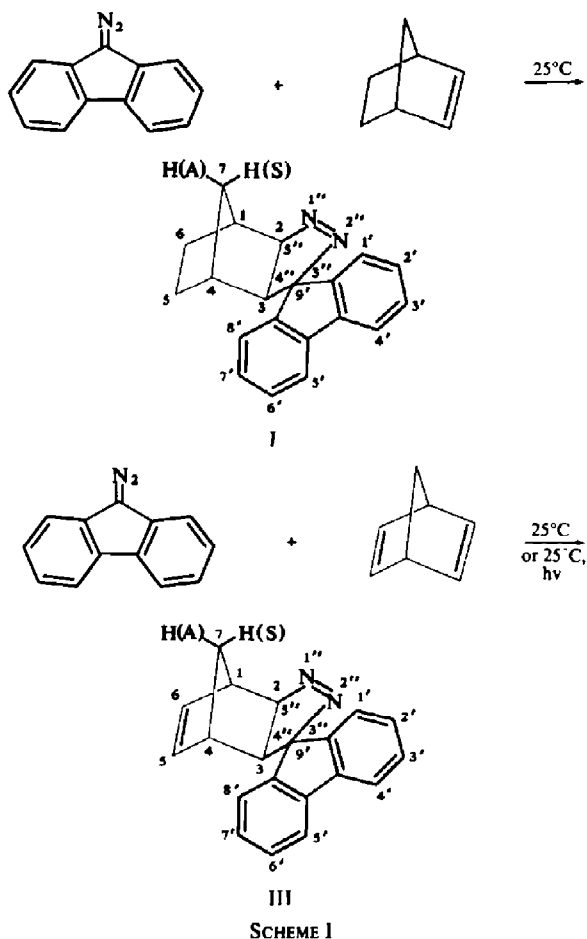
PREPARATIVE and mechanistic aspects of cyclopropane formation on pyrolysis and photolysis of diazoalkanes in the presence of olefins have received much attention.² In some cases, the initial addition product, the 1-pyrazoline, was either isolated or postulated as intermediate. More recently, the stereochemistry of the cyclopropane products from these reactions has been used as diagnosis of the spin state for the assumed transient carbene.^{2a,3} Ionic species⁴ and 1,3 diradicals^{2b,5} have been considered as intermediates in the mechanism of decomposition of 1-pyrazolines. A concerted type mechanism has also been proposed for their photolysis.^{2i,6}

The objective of this work was to isolate the 1-pyrazolines initially formed from 9-diazofluorene with norbornene and norbornadiene and to study their thermal and photochemical decomposition. In addition, the photolysis of 9-diazofluorene in solution in the presence of excess bicyclic olefin was investigated separately.

RESULTS

Addition of 9-diazofluorene to norbornylene and norbornadiene. In neat norbornadiene, the addition of 9-diazofluorene was induced either thermally or much faster photochemically to precipitate almost quantitatively a 1-pyrazoline III (Scheme I). The analogous 1-pyrazoline I from norbornene was obtained thermally in benzene.

The presence of the —N=N— group was indicated by the characteristic bands in the IR spectra of both pyrazolines I and III at 1530 and 1525 cm⁻¹, respectively.²ⁱ The lack of N—H stretch in the IR, and the NMR spectra showed the absence of the



possible tautomeric 2-pyrazolines. The stereochemistry of pyrazolines I and III was determined by an analysis of the NMR spectra of compounds I, II, III, and IV (Scheme I and Table 1). As expected, the NMR spectra of I and III were very similar with the exception of the signal for the C-5 and C-6 protons. A perturbed AB pattern at 1.2–1.8 ppm was observed for the C-7 *syn* and *anti* geminal hydrogens in the spectrum of III. Such a pattern was not easily recognized for I since the four methylene protons at C-5 and C-6 also appear in the 1–2 ppm region. The upfield half of the AB multiplet is due to the 7 *anti* geminal proton since (1) the 7 *anti* protons in bicyclic[2.2.1]heptenes couple with C-2 and C-3 *endo* hydrogens to give more complex multiplets than the 7 *syn*, and (2) when an *exo* substituent is present, the 7 *syn* proton resonance is generally shifted downfield while the 7 *anti* remains relatively stationary.⁷ The fine splitting of the signal corresponding to the C-2 and C-3 hydrogens of pyrazolines I and III (Table 1) also indicates relatively strong coupling with the C-7 *anti* proton suggesting that the C-2 and C-3 hydrogens are oriented *endo*.^{7a-c} Consequently, the five member pyrazoline ring is very probably fused *exo* to the bicyclic system in products I and III.

TABLE I. NMR SPECTRA OF PRODUCTS

Compound	Chemical shift (δ)	Relative area	Multiplicity	J (c/s)	Assignment
I	0.96-1.70	6	complex		C-5,6,7
	2.05	1	doublet	6.3	C-3
	2.17	1	singlet (broad)		C-4
	3.17	1	singlet (broad)		C-1
	5.14	1	doublet (doublet)	6.3 (1.3)	C-2
	6.72-7.90	8	complex		aromatic
III	1.20-1.80	2	AB (perturbed)		C-7
	2.26	1	doublet (doublet)	6.5(1.5)	C-3
	2.77	1	singlet (broad)		C-4
	3.78	1	singlet (broad)		C-1
	5.42	1	doublet (triplet)	6.5(0.9)	C-2
	6.18	2	pentuplet	~ 2.5	C-5,6
	6.73-7.96	8	complex		aromatic
II	1.08	1	doublet (pent.)	10.9(?)	C-7 <i>anti</i>
	1.62	4	quartet		C-5,6
	1.83	2	singlet (sharp)		C-2,3
	2.39	1	doublet (pent.)	10.9(?)	C-7 <i>syn</i>
	2.73	2	singlet (broad)		C-1,4
	6.82-7.90	8	complex		aromatic
IV	1.39	1	doublet (pent.)	9.5(?)	C-7 <i>anti</i>
	2.10	2	singlet (sharp)		C-2,3
	2.58	1	doublet (pent.)	9.5(?)	C-7 <i>syn</i>
	3.33	2	singlet (broad)		C-1,4
	6.66	2	triplet	2.0	C-5,6
	6.80-8.00	8	complex		aromatic
V	2.15	1	quartet (pert.)		C-8 <i>anti</i>
	2.44	1	pentuplet	2.6	C-5
	2.78	1	doublet	9.5	C-8 <i>syn</i>
	2.89	1	pentuplet	3.0	C-1
	5.08	1	doublet (doublet)	9.5(1.8)	C-3
	5.80	1	doublet (doublet)	6.0(0.8)	C-2
	6.30-6.75	2	sextet		C-6,7
	6.90-7.80	8	complex		aromatic
VI	1.08-2.06	7	complex		
	2.06-2.77	5	complex		
	7.00-7.90	8	complex		aromatic

Chemical shifts are reported as multiplet centers unless shown otherwise.

Pyrolysis and photolysis of pyrazolines. Both the thermal and photochemical decomposition of pyrazoline I yield the same hydrocarbon II. However, as shown in Scheme II, on photolysis, pyrazoline III, yields a product IV different from that obtained pyrolytically (V). The cyclopropane derivative IV was obtained in high yield from the photochemical decomposition of the parent pyrazoline III. Hydrocarbons II and IV displayed characteristic spirofluorene-cyclopropane^{3c} infrared bands at 1028 and 1026 cm^{-1} , respectively. Compound IV also showed olefinic absorption bands at 3040, 1630, 725 and 677 cm^{-1} . The fluorene chromophore was preserved throughout

the decomposition reactions as shown by the UV absorption spectra of products II and IV. The *exo* orientation of the fused cyclopropane ring in both spiro compounds was established by the chemical shifts of the geminally coupled C-7 *syn* and *anti* protons.⁸ Molecular models (Dreiding) indicate that when the cyclopropane ring is oriented *exo*, the 7 *syn* hydrogen is placed directly in the plane of the aromatic nucleus of fluorene, within the Van der Waals radius of the proton position 1'. Consequently, a strong paramagnetic shift of the 7-*syn* proton signal is observed for both II and IV, as expected.^{8c,9} The fine structure of the C-7 proton signal indicates that they both are couples to the C-1 and C-4 bridgehead protons, in addition to long range coupling of C-7 *anti* proton with *endo* C-2 and C-3 hydrogens.^{3c,4} The lack of coupling between C-1 and C-4 hydrogens with the those in the C-2 and C-3 position also suggests that the cyclopropane ring in II and IV is fused *exo*.¹⁰ That only *exo*-cyclopropane products were isolated suggests that the orientation of the original 5-member pyrazoline rings of I and III were also fused *exo*.

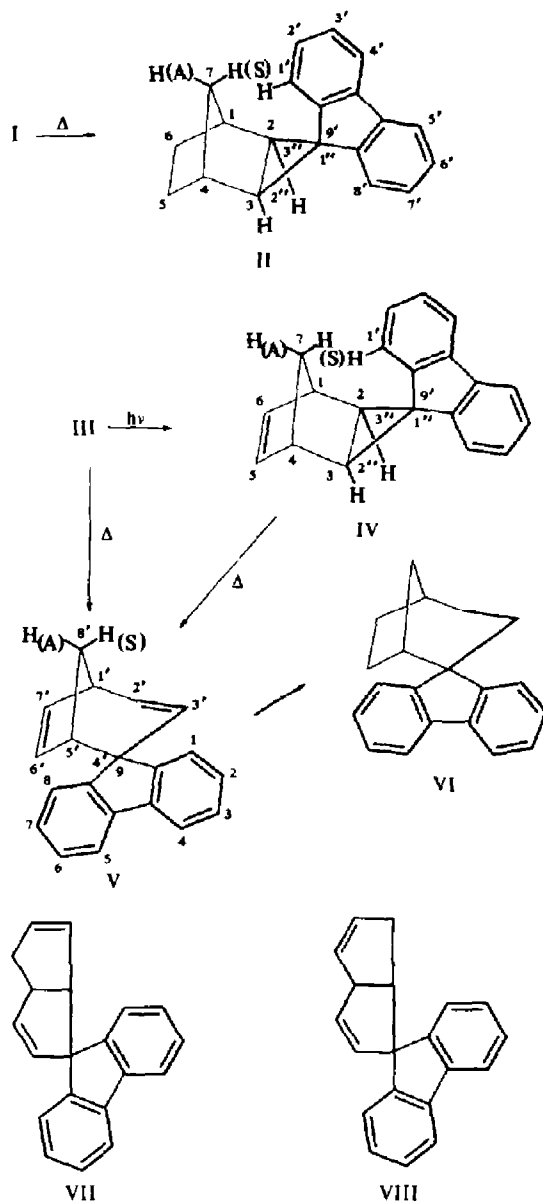
Rearranged product in the thermal decomposition of pyrazoline III. The thermolysis of pyrazoline III in diglyme gave high yields of the rearranged bicyclooctadiene V (Scheme II). It has peaks at 3100, 3040, 3005, 1630, 1570, 728 and 694 cm^{-1} in the infrared which correspond to non-aromatic C-H and C=C stretching and bending deformations. This indicates more double bonds than in the expected cyclopropane derivative IV. Typical fluorene bands were observed in the infrared and ultraviolet absorption spectra of V. The NMR spectrum of hydrocarbon V displays individual resonance for the C-1, C-4, and C-8 protons in the 2.15 to 5.80 ppm region (Table 1). Molecular models (Dreiding) suggest that the C-8 *syn* proton is in the plane of the fluorene moiety and, as expected, is shifted downfield relative to C-8 *anti* hydrogen.^{7c,9} The C-8 *anti* proton gives a quarter due to geminal coupling with C-8 *syn* and long range coupling with the C-3 proton. The non-equivalent olefinic protons C-2 and C-3 each yield a doublet of doublets.¹¹ Molecular models also suggest that the C-3 hydrogen is located directly above the plane of the fluorene π -cloud. Thus, the NMR signal of the C-3 proton should be shifted upfield with respect to C-2, as observed.⁹ Other possible structures such as hydrocarbons VII and VIII are discounted since the sextet centered at 6.5 ppm is characteristic of C-5 and C-6 protons in bicyclooctadienes.¹¹ The catalytic reduction of hydrocarbon V yields bicyclooctane VI. Both the IR and NMR spectra show the absence of non-aromatic unsaturation. Its NMR spectrum is composed of two large complex multiplets corresponding to 12 protons in the 1-4 ppm region.

Like pyrazoline III, its photoproduct, cyclopropane IV also rearranges to the same bicyclooctadiene V under identical pyrolysis conditions.

Photolysis of 9-diazafluorene in ether solution in the presence of excess bicyclic olefin. When 9-diazafluorene was irradiated in absolute ether in the presence of large excess of norbornadiene the only cross product—isolated in small yield—was pyrazoline III. The major products were 9,9'-bifluorenyl XIII (30%) and 9,9',9',9'-terfluorenyl XIV (40%) which were identified by their m.ps,¹² NMR, and mass spectra. Similar photochemical reactions in ether with or without norbornene yielded no pyrazoline or cyclopropane and only XIII and XIV could be isolated in essentially the same ratio.

DISCUSSION

Carbene versus pyrazoline. To our knowledge, this is the first time a pyrazoline

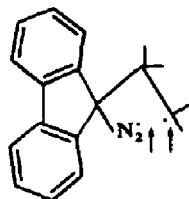


SCHEME II

was prepared photochemically, in practically quantitative yields, by the addition of a diazo alkane to an olefin.

This finding is significant in the context of the discussion of stereospecificity of singlet or triplet carbene addition to olefins versus diazoalkane addition followed by loss of nitrogen and ring closure.^{2a, 3a-c, 13} It has been reported that diphenylmethylene and fluorenylidene add stereoselectively when the parent diazo alkane is irradiated in pure *cis*- or *trans*-2-butene.^{3a-c, 14} Upon adding hexafluorobenzene—a

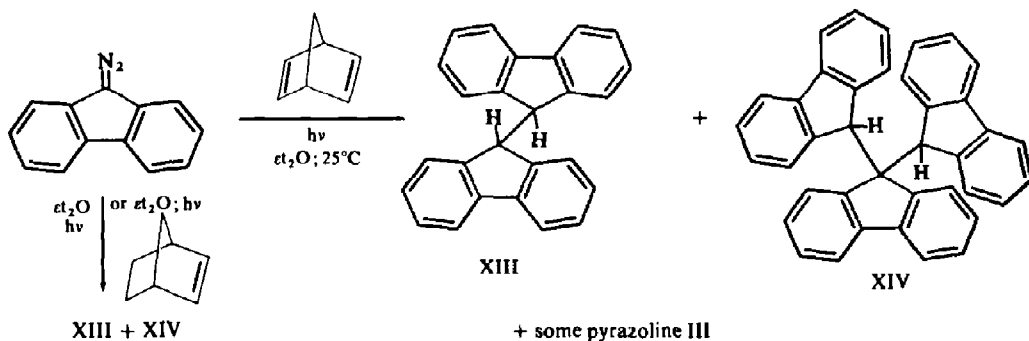
solvent inert to fluorenylidene—to the olefin-diazoalkane mixture undergoing photolysis, Jones and Rettig^{3a,b} proposed that the collisional deactivation of the singlet fluorenylidene to the ground triplet is responsible for the decrease in its stereoselectivity. However, they also consider two other alternatives. First, they point out the possibility that some or even all of non-stereospecific additions observed may result from the addition of the diazoalkane in the lowest triplet state to the olefin with the formation of a diradical intermediate XV in which the rate of loss of nitrogen



XV

is greater than that of the ring closure. Second, if the pyrazoline is initially formed, the stereochemistry of the cyclopropane final products may depend on the structure of the pyrazolines, since these are known to decompose photolytically in a stereoselective fashion.^{2f}

Our present results certainly add weight to the possibility of intermediate pyrazoline formation before loss of nitrogen takes place. Even more, it shows that the pyrazoline III is formed *photochemically*, probably from the short lived excited singlet of the diazoalkane since in the presence of a solvent such as ether, the pyrazoline is isolated only in less than 8% (see below).

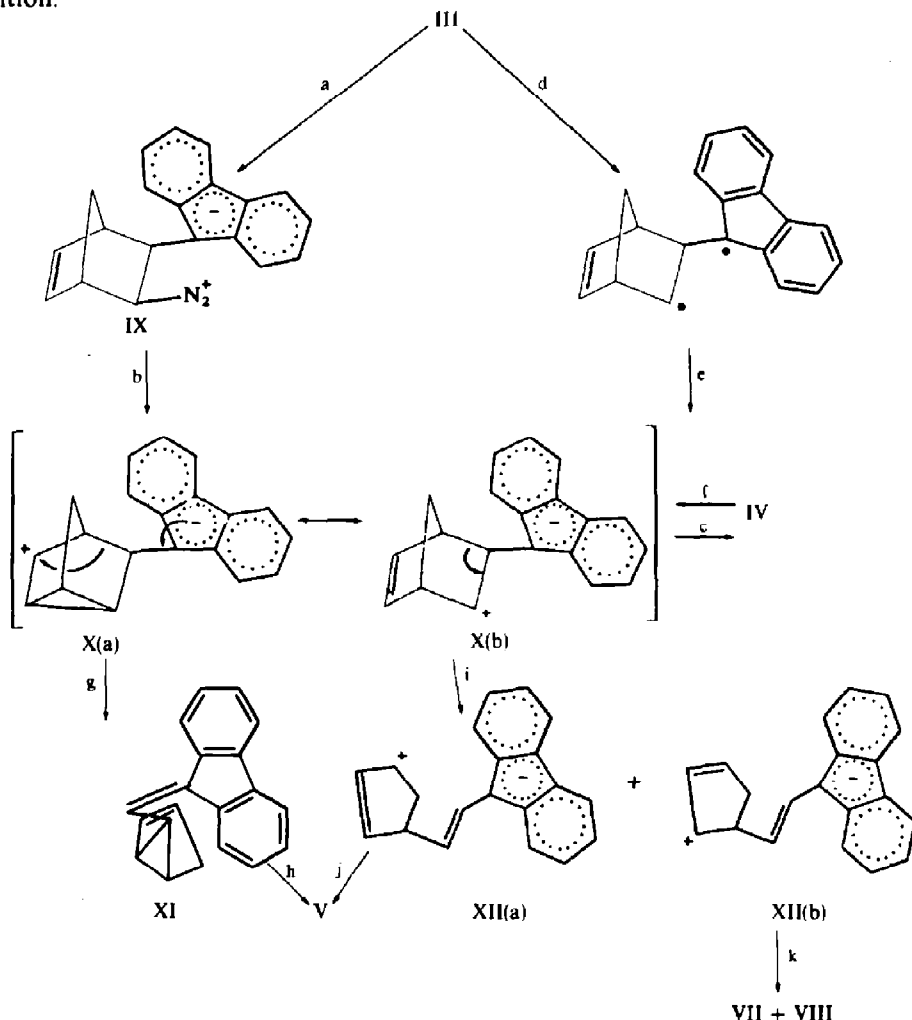


SCHEME III

It is conceivable that the excited lowest singlet state of the diazoalkane adds stereospecifically to olefins and that the configuration is maintained in the final cyclopropane product, formed upon absorption of a second photon by the pyrazoline. If however—as in our case—the pyrazoline happens to be very insoluble in the pure olefin (but not photochemically stable) it can be isolated quantitatively. On the other hand, it seems that in solvents other than hexafluorobenzene, the singlet carbene formed by loss of nitrogen from the excited singlet state of the diazoalkane will preferentially abstract an atom from the solvent host or insert^{13a, 15} before it undergoes

intersystem crossing to a triplet carbene. In our opinion, there seems to be no other acceptable alternative to explain the absence of cyclopropane derivatives or difluorenylidene among the products of photolysis of 9-diazo fluorene in ether solution in the presence of large excess of olefins such as norbornylene or norbornadiene.* If this is the general case, many previous non-stereospecific additions which were attributed to triplet carbene reacting with the olefin must be reinterpreted as either nonstereospecific pyrazoline formation due to a greater rate of rotation than ring closure in XV or absence of stereospecific pyrazoline \rightarrow cyclopropane photochemical conversion.

It should be pointed out, however, that the isolation of the pyrazolines I and III may be primarily due to the ideal reactivity of these bicyclic olefins toward 1,3 dipolar addition.



* The photolysis of 9-diazo fluorene in ether yielded difluorenyl XII and terfluorenyl XIV as major products, and no cyclopropanes or difluorenylidene—the expected products from triplet fluorenylidene.

Thermal rearrangement of unsaturated pyrazoline III and cyclopropane IV. Apparently the presence of the 5,6 olefinic bond is necessary for the rearrangement of III and IV to the bicyclic octadiene V, since the saturated analogs I and II do not rearrange thermally to bicyclic octenes. The formation of V from the thermal decomposition of 1-pyrazoline III or cyclopropane IV, is consistent with the mechanism proposed in Scheme IV.

Both 1,3 diradicals^{2c,5} and zwitterions⁶ have been proposed as intermediates in the pyrolysis of 1-pyrazolines to cyclopropanes and olefins. Recently reported kinetic evidence indicates that both carbon nitrogen bonds of certain 1-pyrazolines are broken simultaneously in the transition state with the formation of a diradical.^{2c} Rearrangements and solvent effects in the decomposition of other 1-pyrazolines have tended to indicate that highly polar transition states are involved.⁶ Thus, spirocyclopropane IV can be formed either through dipolar intermediates (route a-b-c, Scheme IV) or a diradical species (route d-e).

Spirocyclopropane IV, the product (82%) obtained in the photolysis of pyrazoline III, could not be isolated in the thermal decomposition of the same pyrazoline III. However, the existence of IV as an intermediate in the pyrolysis reaction cannot be ruled out, since the thermolysis of photoproduct IV yields rearranged bicyclo-octadiene V, identical to the product from the pyrolysis of III. The intermediate X can therefore be formed either by heterolytic opening of cyclopropane IV or via diazonium fluorene zwitterion IX by loss of molecular nitrogen.

The rearrangement of intermediate X shown in step g produces *cis*-divinylcyclopropane XI, which subsequently undergoes a Cope rearrangement^{11,16} in step h. A multicenter XI → V rearrangement is thermally allowed but photochemically forbidden¹⁷ and since product V is formed thermally in high yield but could not be isolated from the photolysis of III or IV, steps g and h do reflect the probable mechanism.

The other possibility for the X → V transformation, route i-j (Scheme IV) is considered less probable because in this case some amounts of tetrahydropentalene derivatives 7 and 8 would be expected to form (step k). No such byproducts could be identified.

EXPERIMENTAL

General. Mps were determined on a Thomas Hoover Model 6406 K apparatus and are uncorrected. IR spectra were recorded from samples in CCl₄ or KBr pellets in double beam with either a Perkin-Elmer Model 221 or Beckmann IR5A spectrophotometer. UV spectra were determined in double beam on a Cary Model 15 spectrophotometer. NMR spectra were recorded on a Varian Model A-60 spectrometer in CDCl₃ (or as specified) with TMS as internal standard. Mass spectra were obtained from an Atlas CH4 mass spectrometer. Elemental analysis were performed in our laboratory with an Aminco C & H analyzer. Mol wts were determined with a Mechrolab Vapor Pressure Osmometer Model 301A. All photochemical reactions were carried out in a 520 ml or 250 ml capacity conventional immersion well reactor provided with a Pyrex sleeve, magnetic stirrer, and a 450 watt medium pressure Hanovia Mercury Arc lamp.

2,3exo[Fluorene-9'-spiro-3"-1-pyrazoline]bicyclo[2.2.1]heptane (I)

9-Diazofluorene (5.0 g; 26.2 mmoles) was placed in a round bottom flask containing a soln of norbornylene (2.87 g; 30.5 mmole) in 30 ml benzene. The reaction mixture was stirred at reflux temp for several min and left overnight. Vacuum removal of the solvent left an oil to which 15 ml n-heptane was added and on

standing crystallization gave 6.3 g (84%) of I. Recrystallization from heptane-benzene (80:20) yielded pure I m.p. 136–137° (dec); ν^{KBr} : 3010, 2930, 2840, 1530, 1460, 1438 cm^{-1} ; NMR: see Table 1. (Found: C, 83.65; H, 6.31; N, 10.04. Calc. for $\text{C}_{20}\text{H}_{18}\text{N}_2$: C, 83.92; H, 6.29; N, 10.42%. Mol wt: Calcd. 286; Found 280).

2,3exo[Fluorene-9'-spiro-1''-cyclopropane]bicyclo[2.2.1]heptane(II)

Pyrolysis of I. 0.5 g of I was heated in xylene at reflux for 30 min. The sol was cooled and reduced to an oil. After the addition of 15 ml of hot 95% EtOH crystallization occurred on standing, to yield 0.41 g (91%) of II. Recrystallization from 95% EtOH gave white needles m.p. 139°; ν^{CCl_4} : 3020, 2940, 2850, 1470, 1440, 1028 cm^{-1} ; UV (methylcyclohexane), λ_{max} μm (ϵ): 271 (17,600), 293 (9600), 303 (8000); NMR—see Table 1 (Found: C, 92.94; H, 7.00. Calc. for $\text{C}_{20}\text{H}_{18}$: C, 92.97; H, 7.02%. Mol wt: Calc. 258, Found 247).

Photolysis of I. 0.95 g (3.68 mmole) of I was placed in the photochemical reactor containing 250 ml of abs diethyl ether. After 3 hr of irradiation under N_2 , the clear colorless sol was reduced to dryness. The residue was washed out of the flask with the minimum amount of hot 95% EtOH and recrystallized to yield 0.48 g (50.6%) of white needles. The m.p. and spectra were identical with product II above.

2,3exo[Fluorene-9'-spiro-3''-1-pyrazoline]bicyclo[2.2.1]hept-5-ene(III)

Thermal addition. 5.0 g (26.2 mmole) 9-diazafluorene was placed in a 100 ml round bottom flask containing 30 ml norbornadiene. The mixture was heated to dissolve all the diazoalkane and allowed to stand for 2 days. The yellow solid that formed was filtered off and dried, yield 6.76 g (91%). The compound was recrystallized from benzene-heptane (20:80) to give white prisms of III, m.p. 156° (dec); ν^{KBr} : 3010, 2950, 1525, 1426, 1460 cm^{-1} ; UV (dioxane) λ_{max} μm (ϵ): 231 (17,500), 255 (12,900), 271 (14,200), 302 (2220); NMR: see Table 1. (Found: C, 84.50; H, 5.63; N, 9.87. Calc. for $\text{C}_{20}\text{H}_{16}\text{N}_2$: C, 84.37; H, 5.61; N, 10.02%. Mol wt: Calc. 284, Found 282).

Photochemical addition in neat olefin. 200 ml norbornadiene containing 5.0 g (26.2 mmole) 9-diazafluorene was irradiated in the photochemical reactor at 25°. In a few min a ppt began to form. The reaction was continued for 2 hr and the solid filtered off to yield 4.48 g (60%) of light yellow powder. The product was recrystallized from benzene-heptane (20:80) mixture yielding white prisms with m.p. and spectra identical to those obtained for III.

Photochemical decomposition of 9-diazafluorene in ether solution. 5.0 g (26.2 mmole) 9-diazafluorene was irradiated in 480 ml abs ether sol containing 40.0 g (0.434 mole) norbornadiene. After 5 hr the sol was reduced to 40 ml and chromatographed through a column in 4 portions on silica gel (Brinkmann; 0.05–0.02 mm). Products XIII (1.7 g, 40%), XIV (1.39 g, 32%) and III (0.5 g, 7%) were obtained by eluting with 50:50 benzene-pet. ether (30–60°), benzene, and abs EtOH, respectively.

The crude XIII was recrystallized from acetone to yield white needles m.p. 242° (lit.¹² m.p. 243°); ν^{KBr} : 3030, 1465, 1450, 777, 753, 742, 733, and 677 cm^{-1} ; NMR (CS_2): 6.80–7.80 δ 16H (complex), 4.38 δ 2H (S); mass spec.: 330 (M^+), 165 *m/e*.

The crude XIV was recrystallized from acetone to yield a mixture (see text) of γ - and β -tribiphenylene-propane as white prisms m.p. 285° (dec) [lit.¹² m.p. γ , 257° (dec); m.p. β , 294° (dec)]; ν^{KBr} : 3000, 1468, 1434, 774, 752, 734, 668, 642 cm^{-1} ; NMR (CS_2): 6.13–8.39 δ (complex), 5.27 δ (S), 5.15 δ (S); mass spec.: 494 (M^+), 329, 165 *m/e*.

The m.p. and spectra of the product eluted with EtOH, after recrystallization from acetone, were identical with those of III.

In identical photochemical runs in ether with no olefins present the only products isolated were XIII and XIV. When norbornylene was present, no pyrazoline was obtained and only XIII and XIV were isolated.

2,3exo[Fluorene-9'-spiro-1''-cyclopropane]bicyclo[2.2.1]hept-5-ene(IV)

Compound III (1.0 g; 4.19 mmole) was stirred in 500 ml abs ether until it dissolved, followed by irradiation under N_2 for 3 hrs. After filtration the soln was reduced to an oil. The oil was placed on a silica gel column with CCl_4 and eluted with heptane. The heptane fraction was reduced to an oil and the residue taken up in acetone. The resulting soln was reduced to dryness and 0.73 g (81%) of yellow crystals of crude IV were obtained. Recrystallization from 95% EtOH gave white needles m.p. 115–116°; ν^{CCl_4} : 3040, 2970, 2885, 1630, 1470, 1440, 1026, 775, 710, 677 cm^{-1} ; UV (MeOH) λ_{max} μm (ϵ): 277 (30,700), 266 (15,500), 271 (16,000), 303 (2900); NMR: see Table 1. (Found: C, 93.59; H, 6.27. Calc. for $\text{C}_{20}\text{H}_{16}$: C, 93.75; H, 6.25%. Mol wt: Calc. 256, Found 258).

Fluorene-9'-spiro-4'-bicyclo[3.2.1]octa-2,6-diene (V)

From III. 1.33 g (4.68 mmole) of III was placed in a 100 ml round bottom flask containing 50 ml diglyme.

The mixture was heated at reflux for 1 hr. Most of the diglyme was removed to yield a green oil to which 30 ml of hot 95% EtOH was added yielding 0.63 g (52%) of yellow needles which crystallized on standing. The product was recrystallized from EtOH to give fine white needles of V m.p. 117.5°; ν^{CCl_4} : 3100, 3040, 3005, 2910, 1612, 1570, 1440, 1020, 720, 708, 694 cm^{-1} ; UV (methylcyclohexane) λ_{max} μm (ϵ): 234 (9760), 267 (16,700), 269 (17,100), 293 (5670), 304 (10,000); NMR: see Table I. (Found: C, 93.56; H, 6.33. Calc. for $\text{C}_{20}\text{H}_{16}$: C, 93.75; H, 6.25%. Mol wt: Calc. 256, Found 255).

From IV. 0.1 g (0.38 mmole) of IV was heated for 1 hr in 4 ml diglyme at reflux. After evaporation of the solvent, 50 ml hot EtOH was added to yield upon cooling 0.08 g (80%) of white needles having the m.p. and spectra identical with those of V obtained from the pyrolysis of III above.

Fluorene-9-spiro-4'-bicyclo[3.2.1]octane (VI)

Compound V (0.8 g; 3.12 mmole) was reduced with H_2 in the presence of Pt on charcoal by a procedure described by Fieser,¹⁹ except that absolute EtOH was used as solvent for both the olefin and the NaBH_4 soln. When the reaction was completed the catalyst was filtered off and the EtOH was reduced to $\frac{1}{2}$ of its volume yielding 0.7 g (87%) of white needles which crystallized on cooling. Upon recrystallization from 95% EtOH the fine white needle clusters of VI melted at 109°; ν^{CCl_4} : 3050, 2970, 2940, 2870, 1474, 1445, 728 cm^{-1} ; NMR: see Table I. (Found: C, 92.57; H, 7.31. Calc. for $\text{C}_{20}\text{H}_{18}$: C, 92.31; H, 7.68%).

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