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Fluorenylidene and 2,7-Dibromofluorenylidene[1]

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Photolysis of 9-diazofluorene or 2,7-dibromo-9-diazofluorene in diethyl maleate or diethyl fumarate was found to give cyclopropane derivatives nonstereospecifically. Irradiation of 9-diazofluorene in 1,2-dichloroethylene gave no addition product, but did 9-chlorofluorene in 85–89% yield. The same reaction in carbon tetrachloride gave 9,9′-dichloro-9,9′-bifluorenyl in 48% yield. Thus fluorenylidene has strong abstraction character. These chemical results suggest that fluorenylidene and 2,7-dibromofluorenylidene react in triplet state. Furthermore the ground states of these carbenes were confirmed to be triplet by ESR spectra. Concerning to zero-field parameter little effect of bromine substituent was observed in 2,7-dibromofluorenylidene.

Photolysis of diphenyldiazomethane in olefin was found to give cyclopropanes nonstereospecifically,[2,3] and it was inferred that the divalent carbon intermediate must be reacting in the triplet state.[4] Moreover this triplet nature of diphenyl methylene was attributed to the resonance stabilization of sp-hydridization (D_{2d}).[2] However, ESR data show that diphenylmethylene has not simple D_{2d}.[5] The chemical evidence also indicates that dimesitylmethylene has a bent structure.[6] Furthermore, we reported in short communication that fluorenylidene adds to olefin nonstereospecifically.[1] This result

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[1] Part of this work was reported in preliminary communication. E. Funakubo, I. Moritani, T. Nagai, S. Nishida and S. Murahashi, *Tetrahedron Letters*, **1963**, 1069.

[2] R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

[3] G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

[4] W. Kirmse, " Carbene Chemistry," Academic Press Inc., New York, N.Y. (1964).

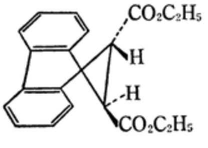
[5] R. W. Murray, A. M. Trozzolo, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962), see also A. M. Trozzolo, E. Wasserman and W. A. Yager, *ibid.*, **87**, 129 (1965).

[6] H. E. Zimmerman and D. H. Paskovich, *ibid.* **86**, 2149 (1964).

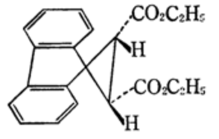
also excludes the Skell's hypothesis. Recently, it was found that fluorenylidene consisted of two distinct species, singlet state and triplet state.[7] Since the interconversion between singlet state and triplet state is catalyzed by heavy atom,[8] the chemical behavior of 2,7-dibromofluorenylidene which has heavy atoms in a molecule was investigated. In addition to this the details of preliminary communication and the results of ESR spectra of these carbenes are described.

Results and Discussion

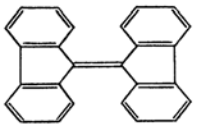
The Chemical Reactivity of Fluorenylidene and 2,7-Dibromofluorenylidene. Photolysis of 9-diazofluorene(I) in diethyl maleate (*cis*-olefin) gave *trans*-2, 3-dicarbethoxyspiro [cyclopropane-1, 9′-fluorene] (II) (65%), *cis*-2,3-dicarbethoxyspiro[cyclopropane-1,9′-fluorene] (III) (2%) and traces of bifluorenylidene (IV) and fluorenone ketazine (V).



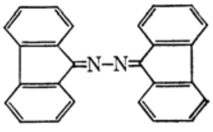
II



III



IV

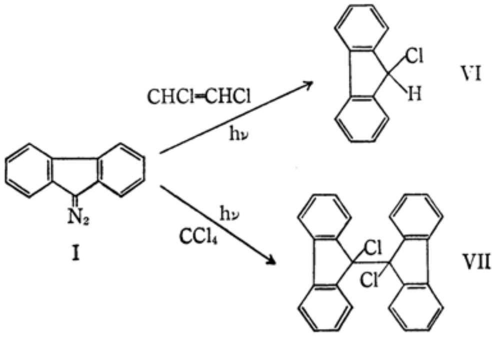


V

Assignment of the *cis* and *trans* configuration to cyclopropane derivatives was made on the basis of the NMR spectra. The NMR spectrum of II consists of a triplet at τ 8.88 (methyl protons), a quartet at τ 5.95 (methylene protons) and a singlet at τ 6.65 (cyclopropyl protons), while that of III consists of a triplet at τ 8.77 (methyl protons), a quartet at τ 5.86 (methylene protons) and a singlet at τ 7.12 (cyclopropyl protons). In the *cis* isomer the methyl and methylene protons are deshielded by the anisotropy of the carbonyl groups, while in the *trans* isomer the cyclopropyl protons are deshielded owing to the same effect. Additional support for the configurational assignment was made by synthesizing III by an independent route.[9]

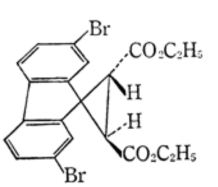
Photolysis of I in diethyl fumalate (*trans*-olefin) gave *trans* cyclopropane derivative III (85%) and traces of IV and V. Pyrolysis of I in *cis*- and *trans*-olefin at 100°C also gave *trans*-cyclopropane derivative mainly. Thus fluorenylidene adds to olefin in a nonstereospecific fashion. It has been noted that *cis*- and *trans*-2,3-dimethylspiro[cyclopropane-1,9′-fluorene] are interconverted when subjected to ultraviolet irradiation.[10] However, the possibility of such a photoisomerization occuring with II and III as well was excluded. After irradiation of II in diethyl maleate II was mostly recovered and small amount of II was converted to olefinic compounds.

Photolysis of I in *cis*- or *trans*-1,2-dichloroethylene produced 9-chlorofluorene (VI) (85% from *cis*, and 89% from *trans*) and small amounts of IV and fluorenone. The cyclopropane derivative was not detected. Furthermore, photolysis of I in carbon tetrachloride gave 9,9′-dichloro-9,9′-bifluorenyl (VII) (48%) and fluorenone (19%).

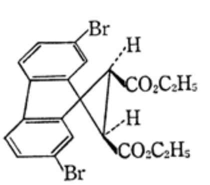


These reactions might be completed by abstraction of chlorine atom by fluorenylidene followed by further abstraction of hydrogen atom or dimerization. Irradiation of a solution of I in the mixture of diethyl maleate and carbon tetrachloride (1 : 1) yielded VII. Thus fluorenylidene may possess strong biradical character, and could abstract chlorine from even chlorovinyl group.

9-Diazo-2,7-dibromofluorene (VIII) was prepared by oxidation of the corresponding hydrazone with yellow mercuric oxide in 65% yield. Photolysis of VIII in diethyl fumarate gave small amounts of two benzene insoluble compounds, 2,7-dibromofluorenone ketazine (IX) and 2,2′,7,7′-tetrabromobifluorenylidene (X). On the other hand, recrystallization of the benzene soluble fraction from ethanol gave *trans*-2,3-dicarbethoxyspiro[cyclopropane-1,9′-(2′,7′-dibromofluorene)] (XI) in 66% yield.



XI



XII

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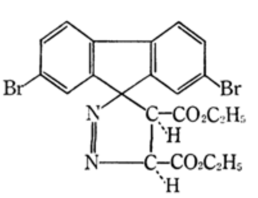
[7] M. Jones, Jr., and K. R. Rettig, *ibid.*, **87**, 4013, 4015 (1965).

[8] a) D. S. McClure, N. W. Blake and P. L. Hanst, *J. Chem. Phys.*, **22**, 255 (1954). b) M. Kasha, *Discussions Faraday Soc.*, **9**, 14 (1950).

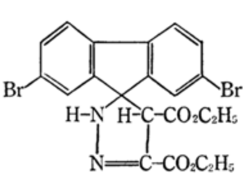
[9] L. Horner and E. Lingnau, *Ann.*, **591**, 21 (1955).

[10] W. von E. Doering and M. Jones, Jr., *Tetrahedron Letters*, **1963**, 791.

Photolysis of VIII in diethyl maleate followed by chromatography on silica gel gave, on elution with benzene, XI (54%) and *cis*-2,3-dicarbethoxyspiro-[cyclopropane-1,9′-(2′,7′-dibromofluorene)] (XII) (4.3%). Assignment of stereochemisty is made similarly as II and III. Further elution with benzene and benzene-methanol (9 : 1) gave two pyrazoline derivatives respectively, orange red crystalline material XIII, mp 118—119°C and colorless crystalline material XIV, dp 158°C. IR bands of 3, 3-(2′, 7′-dibromobiphenylenemethylene)-4, 5-*cis*-dicarbethoxy-1-pyrazoline (XIII) were observed at 1729 cm^{-1} and 1747 cm^{-1} (νC=O), 1633 cm^{-1} (νN=N), while those of 3,4-dicarbethoxy-5,5-(2′,7′-dibromobiphenylenemethylene)-2-pyrazoline (XIV) at 1714 cm^{-1} and 1728 cm^{-1} (νC=O), 3350 cm^{-1} (νN–H) and 1560 $^{-1}$ (νC=N).



XIII



XIV

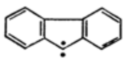
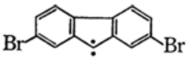
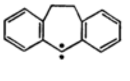
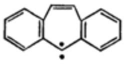
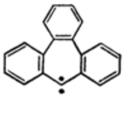
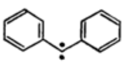
The formation of pyrazoline derivatives, XIII and XIV, suggests that cyclopropane derivatives might be formed by the photodecomposition of 1-pyrazoline. However photodecomposition of *cis*-1-pyrazoline XIII gave *cis*-cyclopropane derivatives XI stereospecifically and a small amount unidentified olefin.[11,12] This fact clearly shows that *trans*-cyclopropane derivative XII obtained from photolysis of VIII in *cis*-olefin is not formed through pyrazoline but formed from addition of 2,7-dibromofluorenylidene of triplet state to olefin.

Thus 2,7-dibromofluorenylidene adds to olefin nonstereospecifically. The ground state of this carbene was also found to be triplet state by ESR study.

Recently, the intersystem crossing from singlet fluorenylidene to triplet through collisional deactivation in solution was observed by addition of inert solvent.[7] On the other hand, high-atomic weight covalently-bonded substituents, such as halogen, might interconvert between singlet and triplet state.[8] Reaction of 2,7-dibromofluorenylidene was found to give quite similar products to those from fluorenylidene. Therefore, the heavy atom in this molecule has no effect on the interconversion between singlet and triplet state. This is also shown by ESR data that electronic state of divalent carbon of 2,7-dibromofluorenylidene is quite similar to that of fluorenylidene.

ESR Spectra. The powder of each diazo compound was irradiated with light of wavelength below 3000 Å at 77°K. The spectra were obtained with Japan Electron Optic Lab. JES-3-BX spectrometer with 100-kc modulation employing 9146 Mc/sec, which were characteristic of randomly oriented triplet of low symmetry. The spectra persisted for several hours after irradiation ceased indicating that the observed species were the ground states. Resonance absorptions of 2,7-dibromofluorenylidene (XVI) were observed at this magnetic field; 1010, 1080, 2546, 4432 and 5529 gauss. A broad line at the free spin value (3260 gauss) also observed. This latter line presumably is due to doublet radicals resulting from further reactions. These absorptions may be fitted to the Hamiltonian[13] with $D=0.4048$ cm^{-1} and $E=0.0272$ cm^{-1}. The zero-field parameters are summerized in Table 1.

TABLE 1. ZERO-FIELD PARAMETER (cm^{-1})

Carbene		D	E	Lit.
		0.4084	0.0271	
	XV	0.4078	0.0283	17
		0.4092	0.0283	14b
	XVI	0.3991	0.0279	
	XVII	0.3932	0.0170	15
	XVIII	0.3787	0.0162	15
	XIX	0.4216	0.0195	15
	XX	0.4050	0.019	14c

The observed D value which is larger than that of the phosphorescent triplet state of the aromatic hydrocarbons requires a significant one center interaction, and indicates that one of the unpaired electrons is largely localized in n-orbital at divalent carbon, and the other delocalized in π-orbital.

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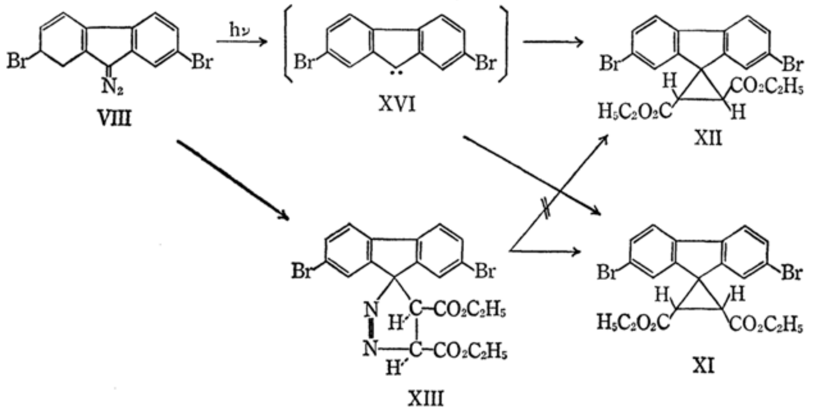
11) *cis*-Pyrazoline may be formed from the 1,3-dipolar addition of diethyl maleate with diazo compound VIII. (See R. Huisgen, *Angew. Chem.*, **75**, 604, 1741 (1963), R. Huisgen, R. Grashey and J. Sauer, " The Chemistry of Alkenes," ed. by S. Patai, Interscience Publishers, New York, N. Y. (1964)).

12) 2-Pyrazoline XIV was recovered after irradiation of XIV in diethyl maleate in the reaction condition.

13) K. W. H. Stevens, *Proc. Roy. Soc.*, **A214**, 237 (1952).

14) a) R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, Jr., B. E. Kohler and R. Silbey, *J. Chem. Phys.*, **43**, 2006 (1965); b) R. W. Brandon, G. L. Closs and C. A. Hutchison, Jr., *ibid.*, **37**, 1878 (1962).



The angle between the axes of the hybrid of divalent carbon atom for fluorenylidene was calculated to be ~135°,[16] which was supported by the examination of ^{13}C hyperfine splitting.[17] This value is greater than the internuclear angle of fluorene, which is explained by assuming that the bonds of divalent carbon in fluorenylidene are bent bond.[14c,17] The E/D value of 2,7-dibromofluorenylidene is similar to fluorenylidene, so the angle appear to be ~135° and the bond to be bent one. That the D value for XVI is smaller than that of XV suggests that bromine substituent may contribute to the π-delocalization to π-electron on divalent carbon. Recently, Hutchison and Peason calculated spin densities in the ground triplet state by electron nuclear double resonance.[18] The spin density at C_2 position shows negative value. On the basis of these data, it is likely that the contribution to the π-delocalization of bromine at C_2 position in 2,7-dibromofluorenylidene is not so large.

Because of the dominance of the one center interaction, for a given geometry about divalent carbon, D should be approximately proportional to the π-spin density at divalent carbon. Indeed, an H.M.O. calculation gives $\rho = 0.34$, 0.37, 0.40 and 0.40 for dibenzo[*a*, *d*]cycloheptenyl radical, fluorenyl radical, diphenylmethyl radical and dihydrodibenzo-[*a*,*d*]cycloheptenyl radical respectively. These π-spin densities are parallel to the D values observed of corresponding carbene. On the other hand, tribenzo[*a*,*c*,*e*]cycloheptenyl radical yields $\rho = 0.09$, while the D value of XIX is larger than the other carbenes listed in Table 1. This may be due to the substantial steric hindrance to coplanarity of XIX. Similar effect of phenyl groups is observed for pK_{R^+} value of tribenzotropylium cation.[19]

The smaller D value in XVIII is due to the delocalization of the electron on divalent carbon to the π-system of the aromatic rings. From E/D ratio, the angle for XVIII was determined to be ~150°. This value is larger than that of the internuclear angle of seven membered ring. Hence the seven membered ring is almost in plane similar to tropylium ion.[15]

Experimental

All temperatures were uncorrected. IR spectra were recorded with a Hitachi-S2 spectrophotometer. NMR spectra were recorded with a JNM-4H-100 spectrometer against internal tetramethylsilane. Electronic spectra were recorded on a Hitachi EPS-2 spectrophotometer. Petroleum ether refers to the fraction bp 40—70°C.

Photolysis of 9-Diazofluorene (I) in Diethyl Maleate. Photolysis of a solution of 1.24 g of 9-diazofluorene (6.35 mmol) in 40 m*l* diethyl maleate was carried out by a low pressure mercury lamp (2537 A) for 9 hr. After removal of the diethyl maleate (bp 91.5°C/10 mmHg), which showed a single peak by vpc, yellow solid was obtained. Chromatography of the residue on silica gel (40 g) gave, on elution with a mixture of petroleum ether-benzene (5: 1), 40 mg of red needles, bifluorenylidene (IV), mp 188.5—189°C (lit.[20] mp 189°C). Further elution with benzene gave 30 mg of dark red crystalline material, fluorenone ketazine (V), mp 265—266°C (lit.[21] mp 266°C).

Found: C, 87.74; H, 4.45; N, 7.75%. Calcd for $C_{26}H_{16}N_2$: C, 87.64; H, 4.50; N, 7.86%.
Continued elution with benzene-methanol (9: 1) gave oil. The oil was again chromatographed on silica gel. Elution with benzene gave 944 mg (63%) of *trans*-2,3-dicarbethoxyspiro[cyclopropane-1,9′-fluorene] (II), mp 100.5—101.0°C.

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[15] I. Moritani, S. Murahashi, M. Nishino, Y. Yamanoto, K. Itoh and N. Mataga, *J. Am. Chem. Soc.*, **89**, 1259 (1967).

[16] J. Higuchi, *J. Chem. Phys.*, **39**, 1339 (1963).

[17] E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 2304 (1964).

[18] C. A. Hutchison, Jr., and G. A. Peason, *J. Chem. Phys.*, **43**, 2545 (1965).

[19] a) D. Meuche, H. Strauss and E. Heilbronner, *ibid.*, **43**, 1221 (1960), and see also A. Streitwieser, Jr., "Molecular Orbital Theory," John Wily and Sons, Inc., New York (1961), p. 362.

[20] J. R. Sawpey and E. E. Reid, *J. Am. Chem. Soc.*, **69**, 234 (1947).

[21] H. Wieland and A. Roseeu, *Ann.*, **381**, 229 (1911).

Found: C, 74.97; H, 6.06%. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99%.

Further elution with benzene gave 34 mg of *cis*-dicarbethoxyspiro[cyclopropane-1,9′-fluorene](III), mp 88°C.

Found: C, 74.88; H, 6.05%. Calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99%.

This was confirmed by mixed mp with an authentic sample.[9]

Photolysis of 9-Diazofluorene (I) in Diethyl Fumarate. Photolysis of a solution of 9-diazofluorene in diethyl fumarate similar to the photolysis in diethyl maleate. Besides of traces of bifluorenylidene and fluorenone ketazine, II was obtained in 85% yield.

Pyrolysis of 9-Diazofluorene (I) in Diethyl Maleate or Diethyl Fumarate. Pyrolysis of a solution of 9-diazofluorene in diethyl maleate or diethyl fumarate carried out at 100°C until the cease of evolution of nitrogen. Besides a trace of fluorenone ketazine, *trans*-cyclopropane derivative II was obtained in 75% or 85% yield respectively.

Photolysis of 9-Diazofluorene (I) in *cis*- or *trans*-1,2-Dichloroethylene. A solution of 900 mg of 9-diazofluorene (4.68 mmol) in 28 m*l* of *cis*-1,2-dichloroethylene was photolyzed until the cease of evolution of nitrogen. After removal of *cis*-1,2-dichloroethylene the residue was subjected to column chromatography on silica gel. Elution with benzene-petroleum ether (1:9) gave 83 mg of 9-chlorofluorene (VI) (89%), mp 89.5—90.2°C. λ_{max}^{EtOH} 275 mμ (log ε 4.13). The NMR spectrum showed multiplets at 2.48—2.57 τ (H_1, H_4), 2.72—2.82 τ (H_2, H_3) and a singlet at 4.38 τ (H_9).

Found: C, 77.70; H, 4.48%. Calcd for $C_{13}H_9Cl$: C, 77.81; H, 4.52%.

Further elution with the same solvent gave trace of bifluorenylidene and fluorenone (mp 80—81°C). On the other hand, photolysis of a solution of 9-diazofluorene in *trans*-1,2-dichloroethylene gave 9-chlorofluorene in 85% yield together with trace amounts of IV and fluorenone.

Photolysis of 9-Diazofluorene (I) in Carbon Tetrachloride. A solution of 600 mg of 9-diazofluorene (3.12 mmol) in 50 m*l* of carbon tetrachloride was photolyzed by low pressure mercury lamp for 9.5 hr. After removal of carbon tetrachloride, the residue was subjected to chromatography on silica gel. Elution with benzene gave 602 mg of 9,9′-dichloro-9,9′-bifluorenyl (VII) (48%), which was assigned by comparison with authentic sample, mp 230—231°C (lit.[22] mp 230°C).

Found: C, 77.91; H, 4.20%. Calcd for $C_{26}H_{16}Cl_2$: C, 78.20; H, 4.04%.

Further elution with benzene 107 mg of fluorenone were obtained in 19% yield.

Synthesis of 2,7-Dibromo-9-diazofluorene (VIII). 2,7-Dibromofluorenone was obtained from oxidation of 2,7-dibromofluorene (mp 164°C, λ_{max}^{EtOH} 256 mμ (log ε 4.41), 299 mμ (3.74), 310 mμ (3.89)) by chromium oxide-acetic acid in 85% yield, mp 198°C. λ_{max}^{EtOH} 256 mμ (log ε 4.23), 266.5 mμ (5.20), 299 mμ (4.39), 310 mμ (4.36) and 415 mμ (2.64).

Hydrazone was prepared by heating 1.5 molar equivalents of 100% hydrazine hydrate in *n*-propyl alcohol at reflux for 3 hr in 85% yield, mp 360°C. λ_{max}^{EtOH} 245 mμ (log ε 4.81), 299 mμ (4.38), 310 mμ (4.40) and 338 mμ (4.17).

Found: N, 7.93%. Calcd for $C_{13}H_8Br_2N_2$: N, 7.96%. This hydrazone and 1.2 molar equivalents of mercuric oxide (yellow) were suspended in dry ether and added several drops of alcoholic potassium hydroxide. After the mixture was mechanically stirred for 4 hr, the reaction mixture was filtered off. Evapolation of the solvent in vacuum gave 9-diazo-2,7-dibromofluorene in 65% yield, mp 145°C (decomp.) (recrystallized from ether). λ_{max}^{EtOH} 242 mμ (log ε 2.92), 255 mμ (4.55), 269 mμ (4.39), 292 mμ (4.53), 310 mμ (4.64), 336 mμ (4.13) and 350 mμ (4.14).

Found: C, 44.64; H, 1.70; N, 8.05%. Calcd for $C_{26}H_{12}Br_4N_2$: C, 44.61; H, 1.73; N, 8.00%.

Photolysis of 9-Diazo-2,7-dibromofluorene (VIII) in Diethyl Fumarate. A solution of 5.0 g of 9-diazo-2,7-dibromofluorene (13.5 mmol) in diethyl fumarate (55 g) was photolyzed until the cease of evolution of nitrogen. After removal of diethyl fumarate in vacuum (bp 64.5°C/1 mmHg), the residue was recrystallized twice from ethanol to give *trans*-2,3-dicarbethoxyspiro-[cyclopropane-1,9′-(2′, 7′-dibromofluorene)] (XI) (4.4 g, 66%), mp 177.5—178.5°C. ν_{max}^{Nujol} 1721 cm^{-1} and 1732 cm^{-1} (νC=O). λ_{max}^{EtOH} 219 mμ (log ε 4.41), 240 mμ (4.35), 286 mμ (4.22) and 295 mμ (4.17).

Found: C, 51.06; H, 3.67%. Calcd for $C_{21}H_{18}O_4Br_2$: C, 51.03; H, 3.69%.

Photolysis of 9-Diazo-2,7-dibromofluorene (VIII) in Diethyl Maleate. A solution of 5.0 g (13.5 mmol) of 9-diazo-2,7-dibromofluorene in diethyl maleate (85 g) was photolyzed for 18 hr. Nitrogen evolved was 110 cc (28°C). After removal of diethyl maleate in vacuum (bp 64.5°C/1 mmHg), the residue was dissolved in 100 m*l* of benzene, and 35 mg of insoluble red material was filtered off, which was identified as the mixture of 2,7-dibromofluorenone ketazine (IX) and 2,2′,7,7′-tetrabromobifluorenylidene (X) (4:1) by IR spectrum. The benzene solution was subjected to chromatography on silica gel (100 g). Elution with benzene-petroleum ether gave 98 mg of yellow crystalline material, which was identified as 2,7-dibromofluorenone by comparison with IR spectrum and mixed mp with an authentic specimen, mp 198°C. Further elution with benzene gave 2.58 g of colorless compound. Recrystallization from ethyl acetate and benzene provided *cis*-2,3-dicarbethoxyspiro-[cyclopropane-1,9′-(2′,7′-dibromofluorene)] (X), mp 204—205°C, which was identified by comparison with an authentic sample prepared from independent route. Continued elution with additional benzene gave 581 mg of orange-red crystalline material, which was identified to be 3,3-(2′,7′-dibromobiphenylenemethylene)-4,5-*cis*-dicarboxy-1-pyrazoline (XIII) by NMR and IR spectra, mp 118—119°C (from petroleum ether). ν_{max}^{Nujol} 1729 cm^{-1}, 1745 cm^{-1} (νC=O), 1633 cm^{-1} (νN=N). λ_{max}^{EtOH} 215 mμ (log ε 4.79), 262 mμ (4.86), 271 mμ (5.02), 310 mμ (4.27), 440 mμ (3.42). The NMR spectrum of XIII consists of triplets at 8.93 τ and 8.53 τ (the methyl protons), quartets at 5.61 τ and 5.58 τ (the methylene protons) and a singlet at 6.23 τ (the methine proton).

Found: C, 48.43; H, 3.57; Br, 30.85%. Calcd for $C_{21}H_{18}N_2O_4Br_2$: C, 48.30; H, 3.47; Br, 30.61%.

Finally, elution with benzene-methanol (9:1) gave 1350 mg of material, which was recrystallized from petroleum ether, ethyl acetate and ethanol, dp 158°C. ν_{max}^{Nujol} 1714 cm^{-1} and 1728 cm^{-1} (νC=O), 3350 cm^{-1}

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22) J. Schmidt and H. Wagner, *Ber.*, **43**, 1796 (1910).

(νN–H) and 1560 cm^{-1} (νC=N). The NMR spectrum of XIV consists of triplets at 9.10 τ and 8.62 τ (the methyl protons), quartets at 6.18 τ and 5.62 τ (the methylene protons), a singlet at 5.72 τ (methine proton) and a singlet at 3.70 τ (N–H proton). Thus, this compound was identified as 3,4-dicarbethoxy-5,5-(2′,7′-dibromobiphenylenemethylene)-2-pyrazoline (XIV).

Preparaion of *cis*-2,3-Carbethoxyspiro[cyclopropane-1,9′-(2′,7′-dibromofluorene)] (X). A mixture of maleic acid anhydride (1.3 g, 13.2 mmol) and 9-diazo-2,7-dibromofluorene (4.6 g, 13.2 mmol) in 40 m*l* of xylene was heated at reflux for one hour. The hot homogeneous solution was allowed to cool slowly, leading to crystallization of the product. Filtration gave 3.6 g of 1,1-(2′,7′-dibromobiphenylenemethylene) cyclopropane-2,3-*cis*-dicarboxylic acid anhydride. Recrystallization from tetrahydrofuran-benzene (1 : 1) gave a sample, mp 171°C with decomposition and 0.45 g of ketazine (IX). A solution of 3.6 g of the above obtained acid anhydride in 20 m*l* of ethanol containing 2 m*l* of sulfuric acid was heated at reflux for 2 hr. The reaction mixture was poured into water. After filtration, compound X was obtained in 85% yield, mp 204—205°C (recrystallized from ethyl acetate). $\nu_{max}^{\mathrm{Nujol}}$ 1857 cm^{-1} and 1786 cm^{-1} (νC=O).

Preparation of 2,7-Dibromofluorenone Ketazine (IX). 2,7-Dibromofluorenone hydrazone was heated at 150°C in vacuum for 2 hr and red colored ketazine was obtained in 90% yield, mp>300°C.

Found: C, 46.19; H, 1.85; N, 4.13%. Calcd for $C_{26}H_{13}Br_4N_2$: C, 46.47; H, 1.80; N, 4.17%.

Preparation of 2,2′,7,7′-Tetrabromobifluorenylidene (X). It was prepared from 2,7,9-tribromofluorene according to the procedure of Wittig.[23]

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[23] G. Wittig and W. Lange, *Ann.*, **536**, 266 (1938).