major component (20%) from the irradiation was identified as *cis*-2,4,5-triphenyl-Δ^3-oxazoline (**30**): mp 30–31°; ir (neat film) 6.18 (C=N), 9.40, and 9.76 μ; nmr ($CDCl_3$) τ 2.22–2.87 (m, 15 H), 3.15 (d, 1 H, J = 4.7 Hz), and 3.87 (d, 1 H, J = 4.7 Hz).

Photoaddition of Acetone with Diphenylazirine.—A solution of 0.3 g of diphenylazirine in 150 ml of a 2:1 benzene–acetone mixture was irradiated for 1.5 hr under a nitrogen atmosphere using a 550-W Hanovia lamp equipped with a Pyrex filter. Removal of the solvent left a dark oil which was purified by preparative thick layer chromatography using a 2:1 benzene–cyclohexane mixture. The major component isolated from the preparative thick layer plate amounted to 130 mg (39%) of a colorless oil whose structure is assigned as 2,4-diphenyl-5,5-dimethyl-Δ^3-oxazoline (**31**) on the basis of the following data: m/e 251 (parent) and 193 (P − acetone); ir (neat film) 6.14 (C=N), 9.1, and 9.65 μ (CO); nmr τ 8.35 (s, 6 H), 3.43 (s, 1 H), 2.10–3.10 (m, 10 H). The low-field position of proton H_2 supports this orientation of addition.

Photoaddition of Styrene with Diphenylazirine.—A solution of 0.5 g of diphenylazirine and 0.5 g of styrene in 500 ml of benzene was irradiated for 22 hr under a nitrogen atmosphere using a 450-W Hanovia lamp equipped with a Pyrex filter. The nmr spectrum of the crude reaction mixture revealed the presence of two major photoadducts in a ratio of 1.5:1 (combined yield 50%). The two components could not be separated by chromatography on all columns tried. Characterization was accomplished by nmr spectroscopy. The major adduct showed a doublet at τ 4.71 while the minor component had a doublet at τ 4.42 (1 H). The remaining portion of the spectrum was essentially identical with the spectrum of the adducts obtained from the reaction of *N*-(*p*-nitrobenzyl)benzimidoyl chloride with triethylamine and styrene.[20]

Photoaddition of Norbornene with Diphenylazirine.—A solution containing 579 mg of diphenylazirine and 5.8 g of norbornene in 500 ml of benzene was irradiated for 22 hr through a Pyrex filter using a 450-W Hanovia immersion lamp. Removal of the solvent and excess norbornene under reduced pressure left a yellow oil. The crude reaction mixture contained two major photoadducts as evidenced by vpc analysis (combined yield 36%). The mixture could be partially separated by liquid–liquid partition chromatography. The trans tricyclic -Δ^1-pyrroline (**34**) was a crystalline solid: mp 141–143°; ir (KBr) 6.15 μ (C=N); nmr ($CDCl_3$) τ 8.6 (6 H, m), 7.9 (1 H, m), 7.68 (2 H, m), 6.7 (1 H, m), 5.3 (1 H, m), and 2.0–3.0 (10 H, m); uv (95% ethanol) 246 nm (ϵ 10,700); m/e 287 (base), 246, 193, 168, 130, 105, 91, and 77. The *cis*-Δ^1-pyrroline (**35**) could not be completely separated from the trans isomer. The nmr spectra of both **34** and **35** were essentially identical with the spectra of the adducts obtained by Huisgen from the reaction of *N*-(*p*-nitrobenzyl)benzimidoyl chloride with triethylamine and norbornene.[20]

Registry No.—**3**, 37428-95-8; **4**, 37428-96-9; **5**, 37428-97-0; **7**, 37428-98-1; **8**, 37428-99-2; **9**, 16205-14-4; **10**, 14491-02-2; **11**, 36879-68-2; **12**, 36879-69-3; **13**, 38202-09-4; **14**, 38202-10-7; **16**, 38202-11-8; **17**, 38215-47-3; **18**, 38215-48-4; **20**, 16340-36-6; **21**, 38202-13-0; **23**, 38202-14-1; **24**, 38202-15-2; **25**, 38202-16-3; **27**, 38215-49-5; **28**, 38215-50-8; **29**, 36879-78-4; **30**, 36879-77-3; **31**, 38202-17-4; **34**, 38215-53-1; **35**, 38215-54-2; 2-phenylazirine, 7654-06-0; 2,3-diphenylazirine, 16483-98-0; 3,6-dihydro-2,4,5-triphenylpyrimidine, 38202-18-5; methyl dithiobenzoate, 2168-78-7; benzaldehyde, 100-52-7; acetone, 67-64-1; norbornene, 498-66-8.

Acknowledgment.—We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-24449) and the National Institutes of Health (Grant No. CA-12195-06). We also thank Dr. David Dean for carrying out some of the photocycloaddition experiments.

The Preparation and Photolytic Decomposition of Tetrabromodiazocyclopentadiene[1]

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Received August 8, 1972

Tetrabromodiazocyclopentadiene (**3**) was prepared in a 45% yield from hexabromocyclopentadiene. Photolysis of **3** in a variety of olefins produced spiro[2.4]heptadienes in good yields. The products were heat and light sensitive and several were isolated as viscous liquids. Products due to insertion into C–H bonds were not detected by nmr analysis of the crude reaction mixtures. Photolysis in *trans*-4-methyl-2-pentene produced only the trans addition product, while photolysis in *cis*-4-methyl-2-pentene produced a mixture of the trans (55%) and the cis adducts (45%). It is concluded that the carbene adds to olefins while in the triplet spin state.

The photolytic decomposition of diazocyclopentadiene is known to yield a carbene which has a triplet ground state,[2] but which reacts in solution while in the singlet state.[3,4] In fact, the carbene is so reactive that attempts to produce the triplet state in solution by collisional deactivation were unsuccessful.[4]

We studied the decomposition of tetrachlorodiazocyclopentadiene and found that the carbene also reacted primarily while in the singlet state.[5,6] However, the presence of the four chlorine atoms allowed facile study of the triplet state by collisional deactivation with hexafluorobenzene.[6,7]

Tetrabromodiazocyclopentadiene (**3**) had been previously prepared,[8] but its decomposition to the carbene had not been studied. We thought that it would be of interest to study what effect four large bromine atoms would have on the reactions of the carbene. Thus, we now wish to report a new synthesis of **3** and a study of its photolytic decomposition in the presence of olefins.

Synthesis of Tetrabromodiazocyclopentadiene (3).—In 1963, a small amount of **3** was prepared in 15% yield from cyclopentadiene.[8] We devised an alternate synthesis to avoid the preparation of large quantities of diazocyclopentadiene, which has reportedly undergone

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[1] Taken in part from the Ph.D. Thesis of K. J. Sienkowski, Purdue University, 1972. Acknowledgment is made to the Stauffer Chemical Co. and the Viol Memorial Fellowship Fund for partial support of this research.

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

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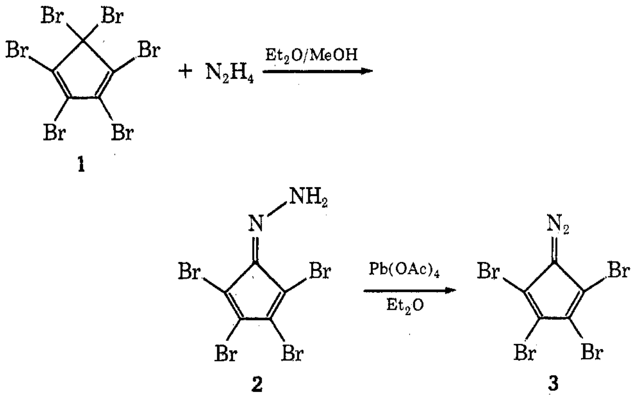
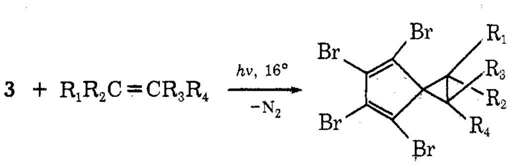
explosive decomposition.[9-11] **3** was successfully prepared in 45% yield in two steps from hexabromocyclopentadiene (**1**).[12,13] The nucleophilic addition of hydrazine to **1** produced tetrabromocyclopentadienone hydrazone (**2**) in 50% yield. This is only the second reported nucleophilic attack on **1**.[14] **2** is a fluffy, reddish-brown solid which be easily dehydrogenated with lead tetraacetate to produce **3** in greater than 80% yield.



3 is a very stable, orange solid which can be stored indefinitely in the dark at room temperature, but which can be decomposed readily when photolyzed. The infrared spectrum was identical with that reported by Cram, displaying intense diazo absorptions at 4.75 and 4.82 μ.[8]

Synthesis and Identification of 1,2,3,4-Tetrabromospiro[2,4]heptadienes.—The photolysis of **3** in a variety of olefins at 16° liberated nitrogen and produced the expected spirocyclopropanes (**4a–h**) in good yields.



4a, $R_1 = H;\ R_2 = R_3 = R_4 = CH_3$
b, $R_1 = R_2 = R_3 = H;\ R_4 = n\text{-}C_4H_9$
c, $R_1 = R_2 = R_3 = H;\ R_4 = t\text{-}C_4H_9$
d, $R_1 = R_2 = R_3 = H;\ R_4 = CH_2Cl$
e, $R_1 = R_2 = R_3 = H;\ R_4 = C_6H_5$
f, $R_1 = R_2 = R_3 = H;\ R_4 = C_2H_3$
g, $R_1 = R_2 = H;\ R_3 = CH_3;\ R_4 = C_6H_5$
h, $R_1 = R_3 = H;\ R_2R_4 = -(CH_2)_4-$

The crude reaction mixtures were carefully studied by nmr, with special attention to the vinylic region, to ensure that any insertion products would be detected. However, no insertion product for any of the olefins was observed.[15]

In general, the crude materials were quite viscous and heat-sensitive liquids, thus preventing their purification by distillation or gas chromatography. However, purification was readily effected by column chromatography on either Florisil or Florisil PR.

Structures **4a–h** were assigned on the basis of spectral data and elemental analyses. The mass spectra and elemental analyses showed that the products were 1:1 carbene–olefin adducts. All products had molecular ions which were observed as symmetrical five-peak clusters corresponding to the presence of four bromine atoms.[16] The adducts generally fragmented in one of two ways. Some lost bromine atoms consecutively to give peaks at M − 80, M − 160, M − 240, and M − 320. Others, which had an unsubstituted cyclopropyl carbon, fragmented to give a $C_6H_2Br_4\cdot^+$ species at m/e 390.

The infrared spectrum of all adducts shows the –BrC=CBr– stretch at ca. 6.48 μ,[13,14] and the cyclopropyl ring at ca. 9.6 μ[5,6,17] The nmr spectra feature absorptions similar to but shifted slightly downfield from the absorptions of model compounds obtained using diazo- and tetrachlorodiazocyclopentadiene with the same olefins.[3-6,18]

Although the cyclopropyl protons of spirocyclopropanes absorb between δ 0.80 and 0.25,[19-22] those of **4a–h** absorb between δ 2.0 and 3.0. This shift to lower fields is a general feature of spiro[2.4]heptadienes.[3,5,6,7,23] It has been suggested that this shift is due to delocalization of the electrons of the C–C bonds of the cyclopropanes into the proximate π system.[22]

Stereospecificity of the Addition Reaction.—A study was instituted to determine the stereospecificity of the addition of tetrabromocyclopentadienylidene (**5**) to olefins and thereby gain information regarding the spin state of the reacting carbene. Skell postulated that a singlet carbene would add in a single, concerted step, while a triplet would add in a two-step process which could destroy the stereochemical integrity of the product.[24-26] This diagnostic test for spin states has received widespread acceptance.[4,7,27-33]

Photolysis of **3** in *trans*-4-methyl-2-pentene produced a golden liquid in 89% yield which was identified by spectral means as *trans*-1,2,3,4-tetrabromo-6-methyl-7-isopropylspiro[2.4]hepta-1,3-diene (**6**). The nmr spectrum of **6** shows a complex multiplet centered at δ 2.2 which was assigned to the cyclopropyl protons and the isopropyl carbinyl proton. The cyclopropyl methyl group appears as a doublet at δ 1.55 (J = 6 Hz), while the isopropyl methyl groups were nonequivalent and

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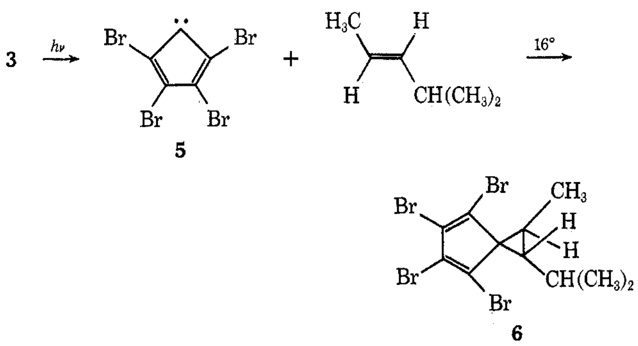
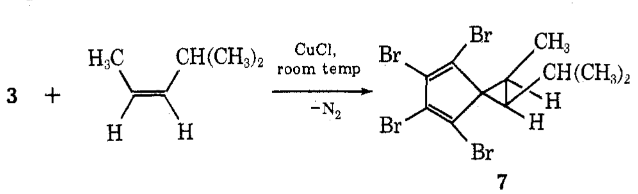


appear as two doublets at δ 0.79 (J = 6 Hz) and 1.11 (J = 6 Hz). The area ratios of the signals were correct for the assigned structure. The trans configuration for **6** was proven by preparing a sample of pure *cis*-1,2,3,4-tetrabromo-6-methyl-7-isopropylspiro[2.4]-hepta-1,3-diene (**7**) as described below and comparing



the nmr spectra of both **6** and **7**. The differences in the spectra showed conclusively that the photolysis of **3** in *trans*-4-methyl-2-pentene gave only the trans product.

The photolytic addition of **5** to the double bond of *cis*-4-methyl-2-pentene proceeded nonstereospecifically, as shown by an nmr spectrum (60% **6** and 40% **7**). However, a pure sample of **7** was obtained by the following alternate procedure. Cuprous chloride catalyzed the stereospecific addition of **3** to *cis*-4-methyl-2-pentene to produce pure **7** in 51% yield. This method of cyclopropane synthesis has been shown to produce stereospecific products.[7,34]

The nmr spectrum of **7** shows four areas of absorption which were quite similar to the absorptions of **6**. The doublets at δ 0.87 (J = 6.5 Hz) and 1.08 (J = 6.5 Hz) were assigned to the isopropyl methyl groups. A doublet at δ 1.58 (J = 6.5 Hz) was attributed to the cyclopropyl methyl group, and a complex absorption centered at δ 2.3 was assigned to the three methine protons.

McBee,[5] Jones,[7] and von E. Doering[35] have all noted the photoinstability of certain cyclopropanes. Under the photolytic conditions employed, **6** was stable while **7** completely isomerized to **6** after 1 hr. In order to prevent isomerization of **7** during the study of the stereospecificity of addition, filters were employed which prevented transmission of light below 350 nm.[36] Ultraviolet spectra shows that **7** did not absorb light above 340 nm while **3** absorbs out to 370 nm.

Using filtered light, **3** was again photolyzed in *cis*-4-methyl-2-pentene for 1 hr. Investigation of the products by nmr revealed the presence of both **6** (55%) and **7** (45%). In addition, the excess olefin was analyzed (glc) and shown to be 94.7% *cis*- and 5.3% *trans*-4-methyl-2-pentene.[39]

A possible, though unlikely, explanation for the observed nonstereospecificity of addition was that a high degree of discrimination by **5** for *trans*- rather than *cis*-4-methyl-2-pentene could give up to 55% **6**. However, when **3** was photolyzed in a mixture of *cis*- and *trans*-4-methyl-2-pentene (60:40) using filtered light, 32% of **7** was observed in the product. If the carbene discriminated to a large extent, less than 10% **7** would be produced. Therefore, the presence of 5% trans olefin observed after the photolysis does not account for the gross nonstereospecificity which was observed.

Photosensitization by **3** was also negated as a possible cause for the nonstereospecificity of the addition by irradiating equimolar amounts of **3** and **7** for 1 hr using filtered light. An nmr spectrum of the product showed that **7** was recovered unchanged.

The results of the stereospecificity study coupled with the reluctance of **5** to insert into C–H bonds[14,31] indicate that the properties of **5** can be best described as arising from the triplet state. However, being cognizant of several cautionary notes in the literature which have warned that both spin states must be observed in order to attach a high degree of certainty to a spin-state determination,[31,40] we attempted to observe chemically the singlet state of **5**. Jones and Rettig successfully accomplished such an experiment with fluorenylidene by scavenging the large triplet component with a diene, thus allowing the singlet component to become the major reacting species with *cis*-2-butene and to give stereospecific addition.[7] However, when **3** was photolyzed using filtered light in a 9:1 molar ratio of 1,3-butadiene to *cis*-4-methyl-2-pentene, the ratio of **6** to **7** was unchanged. Thus, we were unable to observe reaction due to the singlet state of **5**.

Intersystem crossing must occur quite readily for **5**. Several factors might influence the singlet to triplet conversion, such as resonance stabilization,[4] steric hindrance,[41] or a "heavy atom" effect.[42] The steric requirements of **5** are quite large compared to those of cyclopentadienylidene and tetrachlorocyclopentadienylidene, as was shown by its failure to add to the double bond of 2,3-dimethyl-2-butene.[16] This steric problem of **5** might allow many nonreactive collisions to occur, and thus give the carbene time to undergo intersystem crossing. In addition, heavy atoms are known to enhance the probability of spin-forbidden transitions through coupling of spin and orbital angular momenta. The basic requirement for the "heavy atom" effect is that the π electrons undergoing the transition spend a small amount of time on the heavy atom. This process could occur in **5** and account for the facile intersystem crossing.

This work provides chemical evidence for the formation of triplet tetrabromocyclopentadienylidene. The interesting chemical differences between cyclopentadienylidene and tetrabromocyclopentadienylidene which we have pointed out may provide the first instance of a "heavy atom" effect in carbene chemistry.

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[39] The isomerization of the olefin could be caused by acid catalysis (HBr produced in tar formation).

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Experimental Section

Procedure and Equipment.—All melting points are uncorrected Elemental analyses were determined by Dr. C. S. Yeh and her staff at Purdue University. Nuclear magnetic resonance spectra were determined using a Varian A-60A nmr spectrometer. Carbon tetrachloride was used as the solvent (unless otherwise noted) employing tetramethylsilane as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 221 infrared spectrophotometer. Ultraviolet spectra were recorded on a Bausch and Lomb Spectronic 505 spectrophotometer or a Cary 15 using spectrophotometric grade *n*-hexane. Mass spectra were determined on a Hitachi Perkin-Elmer HU-6D high-resolution mass spectrometer. Reported *m/e* values are for the monoisotopic (Br = 79) peak. Gas chromatographic analyses of the olefins were conducted using a 12 ft × 0.25 in. stainless steel column packed with 20% silver nitrate–benzyl cyanide on 60/80 mesh Chromosorb P. The light source used in the photolyses was a 400-W General Electric H400 A33-1 mercury lamp powered by a Jefferson 237-421 mercury lamp ballast transformer. Styrene and α-methylstyrene were of commercial grade and were distilled immediately before use. All other olefins were also commercial grade, but were used without further purification. The solvents utilized in column elution chromatography were distilled prior to use.

Hexabromocyclopentadiene (1).—This compound was prepared using several modifications of Straus' procedure.[12]

Tetrabromocyclopentadienone Hydrazone (2).—1 (54.0 g, 0.1 mol) was dissolved in 800 ml of anhydrous ethyl ether. The solution was immersed in an ice bath throughout the course of the reaction. Anhydrous hydrazine (4.8 g, 0.15 mol) was poured into 200 ml of anhydrous ethyl ether, and methanol was added until the hydrazine dissolved. The hydrazine solution was then added dropwise to the magnetically stirred solution of **1**. As the reaction proceeded, the yellow ethereal solution turned red-brown and a precipitate formed. After complete addition, the solution was filtered and evaporated to dryness. A large, fritted glass Büchner funnel was three-fourths filled with silica gel using hexane as solvent. An oversized piece of filter paper was fitted on top, and the large mass of solid was taken up in hexane as completely as possible and filtered through the silica gel. 1 (37.6 g, 0.069 mol) was recovered from the eluent. The hydrazone **2** (6.6 g, 54% yield) was insoluble in the hexane and was recovered from the top of the filter paper. This material was used without further purification. A sample purified by recrystallization from carbon tetrachloride gave pure **2**: mp 145° dec; ir (KBr) 2.95, 3.07, 3.15, 6.22, 6.44 (s), 6.56, 6.82, 7.92, 8.22, 8.30, 9.80, 13.05, 14.90 μ; uv max (methanol) 343 nm (log ϵ 4.33); *m/e* 406 (molecular ion, base ion), 377 (loss of N_2H), 327 (loss of Br), 297 (loss of BrN_2H).

Anal. Calcd for $C_5H_2Br_4N_2$: C, 14.65; H, 0.49; Br, 78.01; N, 6.84. Found: C, 14.72; H, 0.71; Br, 78.13; N, 6.94.

Tetrabromodiazocyclopentadiene (**3**).—Lead tetraacetate[43] (30 g, 67.6 mmol) was suspended in 500 ml of anhydrous ethyl ether containing magnesium sulfate (10 g). **2** (9.3 g, 22.6 mmol) was dissolved in anhydrous ethyl ether and added dropwise to the magnetically stirred lead tetraacetate solution over a 45-min period. After complete addition, stirring was continued for an additional 45 min. The solution was filtered and the solvent was evaporated under reduced pressure. The residue was dissolved in hexane and filtered through silica gel. Evaporation of the yellow fraction and recrystallization from hexane gave 7.5 g (81.3% yield) of **3**: mp 132° dec; ir (CCl_4) 4.75 (s), 4.82 (s), 6.70 (m), 6.98 (w), 7.10 (w), 7.25 (s), 7.56 (w), 8.10 (s), 9.58 μ (w); *m/e* 404 (molecular ion), 376 (base ion, loss of N_2); uv max (hexane) 310 nm (log ϵ 4.24), 318 (shoulder, 4.21).

Anal. Calcd for $C_5Br_4N_2$: C, 14.73; Br, 78.40; N, 6.87. Found: C, 14.92; Br, 78.70; N, 6.70.

1,2,3,4-Tetrabromo-6,6,7-trimethylspiro[2.4]hepta-1,3-diene (4a).—A solution of **3** (4.08 g, 10 mmol) in 2-methyl-2-butene (100 ml) was photolyzed for 17 hr at 16°. The crude oil which was obtained upon removal of the excess solvent was chromatographed on Florisil PR. Hexane eluted a light yellow oil which could not be induced to crystallize. Chromatography again on Florisil PR gave 3.55 g (79% yield) of pure **4a**: ir (neat) 6.48 (s), 9.60 μ (m); nmr δ 2.61 (1, q, J = 6.5 Hz, cyclopropyl), 1.67 (6, s, C-6 methyl groups), 1.55 (3, d, J = 6.5 Hz, C-7 methyl); *m/e* 446 (molecular ion), 366 (base ion, loss of HBr).

Anal. Calcd for $C_{10}H_{10}Br_4$: C, 26.70; H, 2.24; Br, 71.06. Found: C, 26.76; H, 2.33; Br, 70.99.

Preparation of Other Spiro[2.4]heptadienes.—These were prepared as described for **4a** except that 50 ml of the olefin was generally used and the photolyses were from 1 to 3 hr. All purifications were effected by column elution chromatography using Florisil or Florisil PR as the support and eluting with hexane.

1,2,3,4-Tetrabromo-6-*n*-butylspiro[2.4]hepta-1,3-diene (4b).—The yield of viscous liquid identified as **4b** was 97%: nmr δ 0.88 (3.2, m), 1.26 (4.3, m), 1.93 (5.0, m); ir (neat) 6.47 (s), 9.61 μ (m); *m/e* 460 (molecular ion), 390 (base ion, loss of C_5H_{10}).

Anal. Calcd for $C_{11}H_{12}Br_4$: C, 28.48; H, 2.61. Found: C, 29.26; H, 2.66.

1,2,3,4-Tetrabromo-6-*tert*-butylspiro[2.4]hepta-1,3-diene (4c).—Recrystallization from hexane gave a 95% yield of **4c**: mp 66–66.5°; ir (CCl_4) 3.35 (m), 6.44 (m), 8.11 (s), 8.23 (s), 9.21 (m), 9.60 (m), 10.22 (s), 11.65 μ (m); nmr δ 1.12 (3.04, s, *tert*-butyl), 2.1 (1.0, m, cyclopropyl); *m/e* 460 (molecular ion), 390 (base ion, loss of C_5H_{10}); uv max (hexane) 253 nm (log ϵ 3.90), 286 (3.55).

Anal. Calcd for $C_{11}H_{12}Br_4$: C, 28.48; H, 2.61; Br, 68.91. Found: C, 28.64; H, 2.79; Br, 68.71.

1,2,3,4-Tetrabromo-6-chloromethylspiro[2.4]hepta-1,3-diene (4d).—Recrystallization from methanol gave a 95% yield of **4d**: mp 76–77.5°; ir (KBr) 6.47 (s), 8.25 (s), 8.32 (s), 9.20 (m), 9.85 (m), 10.30 (s), 11.55 (s), 14.33 μ (s); nmr δ 4.02 (2, m, methylene), 2.57 (1.1, quintet, cyclopropyl methine), 1.97 (1.9, m, cyclopropyl methylene); *m/e* 452 (molecular ion), 390 (base ion, loss of C_2H_3Cl); uv max (hexane) 249 nm (log ϵ 3.85), 290 (3.54).

Anal. Calcd for $C_8H_5Br_4Cl$: C, 21.06; H, 1.10; Br, 70.07; Cl, 7.77. Found: C, 21.24; H, 0.90; Br, 70.10; Cl, 7.67.

1,2,3,4-Tetrabromo-6-phenylspiro[2.4]hepta-1,3-diene (4e).—**4e** was isolated as a viscous, yellow liquid: ir (neat) 6.48 (m), 6.70 (s), 6.90 (s), 8.30 (s), 9.70 (m), 10.10 (s), 10.26 (s), 11.08 (s), 13.10 (s), 14.40 μ (s); nmr ($CDCl_3$) δ 7.15 (5.0, s, aromatic), 3.46 (1, t, benzyl), 2.17 (2 m, methylene); *m/e* 480 (molecular ion), 242 (base ion, loss of HBr_3).

Anal. Calcd for $C_{13}H_8Br_4$: C, 32.27; H, 1.67. Found: C, 33.00; H, 1.60.

1,2,3,4-Tetrabromo-6-vinylspiro[2.4]hepta-1,3-diene (4f).—Recrystallization from methanol provided an 87% yield of **4f**: mp 63–64°; nmr δ 2.02 (2, d, J = 9 Hz, methylene), 2.81 (1, q, cyclopropyl methine), 5.26 (2, m, vinyl), 6.23 (1, m, vinyl); *m/e* 429 (molecular ion), 271 (base ion, loss of Br_2).

Anal. Calcd for $C_9H_5Br_4$: C, 24.92; H, 1.39; Br, 73.69. Found: C, 24.64; H, 1.19; Br, 74.40.

1,2,3,4-Tetrabromo-6-methyl-6-phenylspiro[2.4]hepta-1,3-diene (4g).—Recrystallization from hexane afforded an 87% yield of **4g**: mp 134–135°; ir (CCl_4) 6.51 (s), 6.71 (s), 6.94 (s), 8.19 (s), 9.56 (m), 9.78 (w), 13.20 (s), 14.40 μ (s); nmr ($CDCl_3$) δ 1.98 (2.9, s, methyl), 2.44 (2, q, J = 5.5 Hz, cyclopropyl), 7.38 (5.1, s, aromatic); *m/e* 494 (molecular ion), 415 (base ion, loss of Br).

Anal. Calcd for $C_{14}H_{10}Br_4$: C, 33.77; H, 2.02; Br, 64.20. Found: C, 33.93; H, 2.25; Br, 63.86.

Norcarane-7-spiro-5′-(1′,2′,3′,4′-tetrabromocyclopenta-1′,3′-diene) (4h).—Recrystallization from methanol provided a 56% yield of **4h**: mp 99–99.5°; ir (CCl_4) 3.39 (s), 3.47 (s), 6.48 (s), 6.92 (s), 8.1 (s), 8.51 (m), 9.7 (w), 10.2 μ (s); nmr δ 2.5–1.5 (broad complex absorption).

Anal. Calcd for $C_{11}H_{10}Br_4$: C, 28.60; H, 2.18; Br, 69.21. Found: C, 28.76; H, 2.37; Br, 68.98.

***trans*-1,2,3,4-Tetrabromo-6-methyl-7-isopropylspiro[2.4]hepta-1,3-diene (6)**.—**6** was isolated as a viscous liquid in 89% yield: nmr δ 0.79 (1, d, J = 6 Hz, isopropyl methyl), 1.11 (1, d, J = 6 Hz, isopropyl methyl), 1.55 (1, d, J = 6 Hz, cyclopropyl methyl), 2.2 (1, m, methine).

***cis*-1,2,3,4-Tetrabromo-6-methyl-7-isopropylspiro[2.4]hepta-1,3-diene (7)**.—To a solution of **3** (1.0 g, 2.45 mmol) in 25 ml of *cis*-4-methyl-2-pentene was added 0.2 g of cuprous chloride. Evolution of N_2 occurred slowly from the magnetically stirred solution. After 39.5 hr at room temperature, the olefin was distilled off and was shown to be pure *cis*-4-methyl-2-pentene (glc). The dark mass was chromatographed on Florisil PR using cyclohexane and gave 0.58 g of a light, viscous liquid (51% yield) identified as **7**: nmr δ 0.87 (d, J = 6.5 Hz), 1.08 (d, J = 6.5 Hz) 1.58 (d, J = 6.5 Hz), 2.3 (m); uv max (hexane) 254 nm (log ϵ 3.97), 286 (3.61).

Photolysis of 3 in *cis*-4-Methyl-2-pentene.—*cis*-4-Methyl-2-pentene (50 ml, 99.5% cis) containing **3** (1.9 g, 4.65 mmol) was deoxygenated for 20 min by bubbling dry nitrogen through the

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[43] 2,3,4,5-Tetrachlorocyclopentadienone hydrazone was readily oxidized to tetrachlorodiazocyclopentadiene using mercuric oxide or silver oxide.[5,6] However, **2** was inert to these reagents.

solution. The olefin was checked at this point and it was found that no isomerization had yet occurred (glc). The olefin (at 16°) was not able to dissolve the entire quantity of **3**. Both the amount of nitrogen released and the olefin composition were monitored during the photolysis. The photolysis was stopped after 75 ml of nitrogen had evolved, indicating that *ca.* three-fourths of **3** had decomposed. The olefin composition at this point was 92.6% *cis-* and 7.4% *trans*-4-methyl-2-pentene. The isolated material, having a total weight of 1.9 g, consisted of crystals (**3**) and an oil. Nmr analysis of the product mixture showed that both **6** (57%) and **7** (43%) were formed.

Irradiation of 6 in Cyclohexane.—A solution of **6** (50 mg) in cyclohexane was brought to 16° and irradiated for 8 hr. The excess cyclohexane was removed under reduced pressure and the remaining oil was analyzed by nmr. Compound **6** remained unchanged. **7** was not observed under these conditions.

Irradiation of 7 in Cyclohexane.—A solution of **7** (50 mg) in cyclohexane (50 ml) was brought to 16° in a Pyrex tube and irradiated for 1 hr. The excess solvent was stripped off, leaving an oil which was analyzed by nmr. Nearly complete isomerization to **6** was found. A small peak due to **7** was visible (<5%).

Irradiation of 7 in Cyclohexane Using Filtered Light.—A solution of **7** (0.15 g, 0.325 mmol) in 100 ml of cyclohexane was irradiated for 1 hr at 16° using filtered light. The filters employed were 5 cm of $CuSO_4 \cdot 5H_2O$ in H_2O (100 g/l.)[37] and 1 cm of 2,7-dimethyldiaza-3,6-cycloheptadiene-1,6-perchlorate in H_2O (0.1 g/100 ml).[37,38] These filters cut off all light below 350 nm. All of the apparatus which remained above the aqueous copper sulfate solution was covered with aluminum foil to prevent unfiltered light from striking the solution. Analysis of the product isolated showed that pure **7** was unchanged.

Photolysis of 3 in *cis*-4-Methyl-2-pentene Using Filtering Solutions.—*cis*-4-Methyl-2-pentene (50 ml) containing **3** (1.0 g, 2.45 mmol) was irradiated for 1 hr at 16° employing both filtering solutions as previously described. The starting olefin was stripped off and was found to be 94.7% *cis-* and 5.3% *trans*-4-methyl-2-pentene (glc). Analysis of the dark oil product showed that both **6** (55%) and **7** (45%) were present (nmr analysis using peak heights of the cyclopropyl methyl absorptions).

Photolysis of 3 in a Mixture of *cis-* and *trans*-4-Methyl-2-pentene.—A mixture of *cis-* and *trans*-4-methyl-2-pentene (*ca.* 60:40) containing **3** (0.5 g, 1.22 mmol) was irradiated at 16° for 1.5 hr using filtered light. Stripping off to the excess olefins left an oil in which **6** and **7** were observed in the ratio of 68:32, respectively.

Attempted Photosensitized Isomerization of 7 by 3.—A solution containing **3** (0.44 g, 1.08 mmol) and **7** (0.50 g, 1.08 mmol) in cyclohexane (100 ml) was photolyzed at 16° for 1 hr employing filtered light. After the cyclohexane was stripped off, nmr analysis of the product showed that **7** was unchanged by the conditions employed.

Photolysis of 3 in *cis*-4-Methyl-2-pentene Containing 90 Mol % 1,3-Butadiene.—*cis*-4-Methyl-2-pentene (3.46 g, 41.1 mmol) containing **3** (1.0 g, 2.45 mmol) and 1,3-butadiene (20.0 g, 270 mmol) was irradiated for 3 hr in a sealed ampoule using filtered light. The ampoule was opened, allowing the excess 1,3-butadiene to boil off. The excess cis olefin was stripped off, leaving a light yellow oil. Analysis of the mixture by nmr showed that both **6** and **7** were present. The trans product (**6**) was the major product (*ca.* 55%), but difficulties in analysis make this number less reliable than the others. It is probably good within 15%.

Registry No.—**1**, 14310-17-9; **2**, 38123-54-5; **3**, 38123-55-6; **4a**, 38123-56-7; **4b**, 38229-30-0; **4c**, 38123-57-8; **4d**, 38123-58-9; **4e**, 38123-59-0; **4f**, 38123-60-3; **4g**, 38123-61-4; **4h**, 38123-62-5; **6**, 38123-63-6; **7**, 38123-64-7.

Amidrazones. II.[1] Tautomerism and Alkylation Studies

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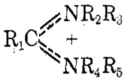
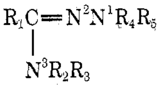
Received October 25, 1972

Amidrazone tautomers are exclusively formed from the reaction of *N*-methylbenzimidoyl chloride and 1,1-disubstituted hydrazines. A series of amidrazones and hydrazide imides have been prepared and their sites of alkylation with methyl iodide have been established. With the exception of the N^1,N^1-dimethyl substituted amidrazones **7**, **9**, and **11**, which undergo methylation at N^1, the other compounds displayed amidine-type behavior and afforded charge-delocalized cations resulting from substitution at either N^2 or N^3.

The reaction of amidines with alkyl halides results in alkylation of the imino nitrogen to give amidinium cations with the charge-delocalized structure **1**.[2] However, aside from the diverse results reported on three compounds in paper I[1] of this series, little is known of the site of alkylation in amidrazones (**2**) or hydrazide imides (**3**). The latter compounds possess three potential sites for alkylation and the position of alkylation could be expected to depend on a number of factors, including the nature of the substituents bonded to the nitrogen atoms and whether the compound reacting with the alkylating agent has structure **2** or **3**.

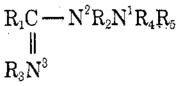


1



$$R_1C{=}N^2N^1R_4R_5 \quad | \quad N^3R_2R_3$$

2



$$R_1C{-}N^2R_2N^1R_4R_5 \quad \| \quad R_3N^3$$

3

This paper reports a study of structural effects on the site of alkylation of amidrazones and hydrazide imides with methyl iodide and some observations on amidrazone–hydrazide imide tautomerism. The recommended[3] method for numbering the nitrogen atoms in amidrazones and hydrazide imides is employed throughout and is illustrated in structures **2** and **3**.

Tautomerism Studies.—Amidrazone–hydrazide imide tautomerism is possible with appropriately substituted compounds **2** and **3** (R_2 = H). In our earlier paper,[1] we established from spectroscopic data that compound **25** exists exclusively in the hydrazide imide form. However, we have found that, when the N^3-phenyl group is replaced by N^3-methyl, the amidrazone is apparently the exclusively formed tautomer. Reaction of *N*-methylbenzimidoyl chloride with 1,1-dimethylhydrazine and 1-methyl-1-phenylhydrazine gave *N*-methylbenzamide dimethylhydrazone (**4**) and *N*-methylbenzamide methylphenylhydrazone (**5**), respectively. The nmr spectrum of both **4** and **5** displayed N^3-methyl signals that are spin coupled to NH. The observed methyl doublets (J = 4 Hz) collapsed to singlets on deuterium exchange. These results are in-

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[1] For paper I see R. F. Smith, D. S. Johnson, C. L. Hyde, T. C. Rosenthal, and A. C. Bates, *J. Org. Chem.*, **36**, 1155 (1971).

[2] For a discussion of amidinium salts, see P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. 1, W. A. Benjamin, New York, N. Y., 1966, p 181.

[3] D. G. Nielsen, R. Roger, J. W. M. Heattie, and L. R. Newlands, *Chem. Rev.*, **70**, 151 (1970).