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Diazabenzosemibullvalene. A Precursor to the Benzoprefulvene Biradical and Indenylmethylene

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Abstract: Triplet-sensitized irradiation of the previously reported [4 + 2] photoadduct between naphthalene and N-methyltriazolinedione gave a di-π-methane rearranged urazole. The urazole was converted into diazabenzosemibullvalene by hydrazinolysis and oxidation. Solution thermolysis of the azo compound produced only small amounts of naphthalene, naphthvalene, benzofulvene, and mainly intractable material. Gas-phase pyrolysis gave only these three products cleanly. Direct irradiation of the azo compound in low-temperature matrices and at −78 °C in solution generated naphthalene, naphthvalene, and diazomethylindene. The diazo compound was characterized by IR and NMR and gave only benzofulvene on direct irradiation. Sensitized photolysis of diazabenzosemibullvalene produced only naphthalene and naphthvalene. The results of these experiments are discussed in terms of the benzoprefulvene biradical and indenylmethylene.

In 1966, Bryce-Smith and Longuet-Higgins[1,2] proposed the intermediacy of the so-called prefulvene biradical (1) in the photochemistry of benzene. This intriguing intermediate was suggested to lead to fulvene and in the presence of olefins to give the observed meta photoadducts.[1] The authors in addition proposed that 1 should also give benzvalene (2) in the irradiation of benzene, a prediction which was quickly confirmed by Wilzbach et al.[3] It has also been proposed that formation of 1 might provide an important radiationless decay pathway for excited singlet benzene.[2]


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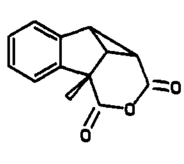
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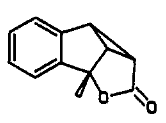
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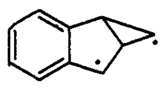
Subsequent work in a number of laboratories has weakened the case for involvement of 1 in several of the above processes. Wilzbach and Kaplan[4] showed that fulvene is not a primary photoproduct of benzene but rather is formed from catalyzed rearrangement of benzvalene (2). Extensive investigations have also shown that prefulvene-type biradicals are not involved in meta photoadditions.[5] Nevertheless, biradical 1 remains a reasonable intermediate in the formation of benzvalene. Moreover, there is evidence available which is consistent with the intermediacy of 1 in the photochemistry of benzvalene. Katz, Turro, and coworkers[6] found that specifically deuterated benzvalene undergoes scrambling of labels on direct irradiation or low-energy triplet sensitization. The mode of scrambling can be rationalized on the basis of single-bond cleavage to give 1, followed by reclosure.

We recently reported the syntheses of two molecules, 3 and 4, that are potential precursors to the benzoprefulvene biradical 5.[7] Unfortunately, these precursors require either very high temperatures or short wavelength irradiation to effect dissociation. Under these conditions, the potential naphthvalene product would not be stable. The benzo biradical 5 is of particular interest in its possible relation to the reported unusual thermal-[8] and photochemistry[9] of naphthvalene (6). Naphthvalene has been reported to eschew aromatization on thermolysis and to give instead benzofulvene (7). This is in dramatic contrast to the clean thermal isomerization of benzvalene to benzene.[10] At the onset of our work, we considered the possibility that 6 gave first biradical 5 followed by rearrangement to 7 possibly via carbene 8. Photolysis of naphthvalene has been reported to lead directly to excited triplet naphthalene.[9] The involvement of biradical 5 in this rare adiabatic rearrangement is also of considerable interest.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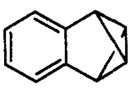
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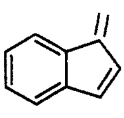
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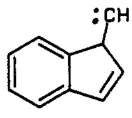
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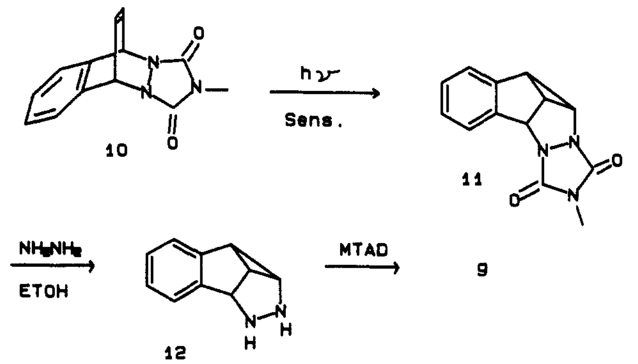
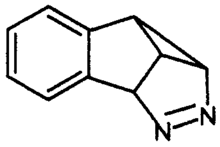
Scheme I



We now wish to report the synthesis and investigation of a potential precursor to the benzoprefulvene biradical (5), diazabenzosemibullvalene (9). Besides its possible utility in sorting out the chemistry of 5, azo compound 9 represents an extremely high-energy precursor to naphthalene and thus holds considerable intrinsic interest.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Results and Discussion

We have previously reported the synthesis of the naphthalene–triazolinedione adduct **10**.[11] This fairly unstable molecule can be conveniently generated by the visible irradiation of 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) and naphthalene. Triplet-sensitized irradiation (xanthone) of **10**, followed by silica column chromatography, gives rearranged urazole **11** in ca. 40% yield (Scheme I). The yield is hampered somewhat by the thermal lability of **10**. This crystalline di-π-methane material was completely characterized spectroscopically. In particular, the ^{1}H NMR spectrum exhibits one-proton signals at 5.56, 3.36, 2.74, and 2.68 ppm. The coupling pattern is quite similar to those observed previously in our studies of other benzobicyclo[3.1.0]hexene systems.[7]

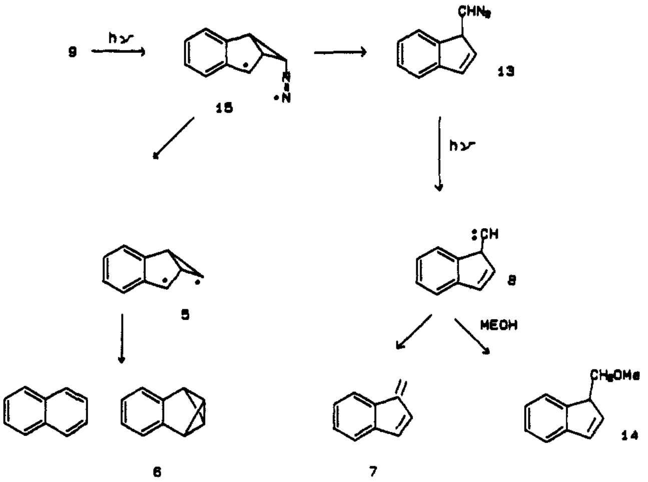
Classical base deprotection–oxidation failed to give the desired azo compound. Although monodeprotection to a semicarbazide could be effected with KOH in the usual fashion, Cu^{2+} or MnO_2 oxidation gave only formation of intractable material. Deprotection using hydrazine hydrate,[12] however, gave a new compound tentatively identified as hydrazine **12**. This compound could not be isolated, but spectroscopic evidence and subsequent chemical transformation supported the structure assignment. Although surprisingly this material did not oxidize with O_2, reaction with 1 equiv of MTAD[13] in benzene cleanly produced diazabenzosemibullvalene **9** (Scheme I). This novel azo compound, which could be purified most easily by sublimation, was completely characterized by NMR, IR, and UV (ca. 50% from **11**). The ^{1}H NMR spectrum is quite similar to that of urazole **11**, with some reasonable shifting of absorptions. The azo compound shows, in addition to the aromatic region, four one-proton signals at 6.23, 5.50, 3.52, and 3.37 ppm, with appropriate couplings. In addition, the UV spectrum exhibited a λ_{max} at 337 nm ($\epsilon = 280$) consistent with the azo functionality.

Intuition suggests that generation of naphthalene and N_2 from **9** should be extremely exothermic. This possibility is supported by simple group additivity calculations which indicate an ΔH° of -71 kcal/mol for cycloreversion of **9**.[14] Remarkably, in solution **9** gives only small amounts of naphthalene on thermolysis at 150 °C (benzene-d_6, 1 min destroys all starting material). Naphthvalene and benzofulvene are also produced, but the thermolysis mainly produces uncharacterizable material. The juxtaposition of functionality may render **9** particularly sensitive to acid-catalyzed or free-radical-catalyzed polymerization, however. We previously observed similar behavior with the "naphthalene + CO_2" molecule **4**.[7] Vapor-phase thermolysis (160 °C tube, 0.1 torr), in contrast, cleanly gave a mixture of naphthalene, naphthvalene, and benzofulvene in a ratio of 1:3:10 by ^{1}H NMR. Naphthvalene and benzofulvene were stable to these conditions.

To gain more information on possible intermediates in these processes, the photochemistry of **9** was investigated. Irradiation of **9** in an argon matrix at 10 K (band-pass filter, 340–380 nm) gave by IR naphthalene, naphthvalene (**6**), and a new compound whose most intense absorption was at 2060 cm^{-1}. The three compounds appeared to be formed in comparable amounts. No benzofulvene (**7**) was observed. Subsequent irradiation of the matrix with visible light (>340 nm) destroyed the unknown compound with concomitant formation of benzofulvene only. The IR spectrum and photochemistry suggest that the unknown photoproduct is the diazo compound **13**.

Irradiation in solution at low temperature confirmed the identity of **13**. Photolysis of **9** was carried out in CD_2Cl_2 at -78 °C with a band-pass filter as above. Proton NMR at -78 °C revealed the formation of naphthalene, naphthvalene, and a new compound whose absorptions were consistent with the diazo compound **13** (3:1:4 ratio). The ^{1}H NMR spectrum for **13** showed one-proton absorptions at 6.85, 6.50, 4.13, and 3.80 ppm. The proton at 3.8 ppm is similar to those observed by others for diazomethyl absorptions.[15] This signal is also a doublet as expected. Reirradiation with visible light at this temperature destroyed the diazo compound and gave benzofulvene only. The diazo compound was too unstable for isolation but could be trapped. Addition of MeOH to the cold solution containing **13**, followed by visible irradiation, gave complete conversion of **13** to the known ether **14**.[16] Benzofulvene was independently shown to be stable to these conditions.

Scheme II



Triplet-sensitized (xanthone) irradiation of **9** at 20 or -78 °C gave only naphthalene and naphthvalene (**6**) in approximately equal amounts. Integration, with the sensitizer as an internal standard, indicated that these products accounted for 70% of the azo destroyed. No other products were discernible by ^{1}H NMR. Addition of camphorquinone or fluorenone to -78 °C solutions of **13** as prepared above, followed by irradiation at wavelengths where only sensitizer absorbed, destroyed the diazo compound but gave no increase in naphthalene or naphthvalene by NMR.[17] Benzofulvene (**7**) could not be observed by NMR, although independent experiments showed this product to be unstable to the sensitization conditions giving polymeric products.[17]

The photochemical results suggest the mechanistic picture shown in Scheme II. Formation of naphthalene and naphthvalene suggest the intermediacy of the benzoprefulvene biradical **5**. Stepwise cleavage of the azo would give diazenyl biradical **15**, which could cleave to either **5** or **13**.[18]

Schneider and Csacsko[19] have suggested that a number of substituted 2,3-diazabicyclo[3.1.0]hex-2-enes undergo only ring cleavage to the corresponding diazo compounds on irradiation. Our results, however, clearly indicate that diazo formation from **9** competes with biradical generation. Our results are reminiscent of a previous report of Gassman and Greenlee,[20] who showed that irradiation of the diphenyl azo compound **16** at -78 °C produced a mixture of the diazo **17** and bicyclobutane **18**. Further photolysis of the diazo compound gave only dienes via hydrogen shifts. It is not obvious why these results and ours differ from those of Schneider and Csacsko.[19] The common feature of aryl substitution suggests a reasonable solution, however. It may be that reasonance stabilization of the carbon-centered radical in intermediate **15** permits denitrogenation to compete with C–C bond cleavage.

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(17) Triplet-sensitized irradiation of diazo compound **13** or benzvalene **7** gave only unreproducible, featureless humps in the proton NMR.

(18) We cannot rule out the possibility that diazenyl biradical **15** directly gives either naphthalene or naphthvalene, rather than cleaving to **5**. Both processes are without precedent, however.

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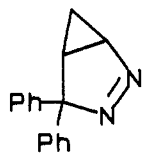

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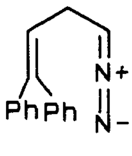

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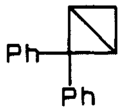

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Adam and co-workers[15] have recently reported several examples of azo compound rearrangements to diazo compounds. In the reported cases, only direct photolyses led to diazo formation and consequently to carbene-type products; thermolyses and triplet-sensitized irradiations gave only biradical-derived products. Lower temperatures in the direct photolyses led, in general, to less diazo compound. These results have been rationalized on the basis of Salem-type orbital correlation diagrams applied to intermediate diazenyl biradicals.[15] In contrast, we observe the greatest amounts of carbene product, benzofulvene (**7**), on vapor-phase thermolysis of **9**. The most economical hypothesis is that diazo compound **13** is also formed thermally to a major extent, although the experimental conditions do not permit us to observe this intermediate directly. We also do not observe a substantial difference in the relative amount of diazo compound formed photochemically over the wide temperature range of 10–195 K. The differences between our results and those of Adam and co-workers[15] are difficult to rationalize on the basis of these limited experiments. The large difference in stability of the benzylic radical and the incipient cyclopropyl radical and the potential for strain release should however certainly predispose diazenyl diradical **15** toward diazo formation.[21]

Since both diazo compound **13** and the carbene product benzofulvene (**7**) give only polymeric products on triplet sensitization,[17] it is more difficult to discuss the triplet chemistry of azo compound **9**. Approximately 30% of azo compound is unaccounted for by ^{1}H NMR integration of the crude triplet-sensitized experiments. It is thus possible that triplet azo compound also gives diazo. The sensitization experiments clearly indicate the following, however: (1) triplet azo **9** primarily produces naphthalene and naphthvalene, and (2) triplet diazo **13** does not give either of these products.[22]

Biradical **5** and carbene **8** are potential intermediates in the unusual thermal conversion of naphthvalene to benzofulvene.[8] Additionally, the carbene has recently been proposed as an intermediate in the thermal automerization of naphthalene.[24] Our results may help clarify these issues. Since benzofulvene is not produced as a primary photoproduct from azo compound **9**, the biradical **5** does not appear to cleave to carbene **8**. In view of this result, we have reinvestigated the thermal rearrangements of naphthvalene. Our experiments, reported elsewhere, indicate that solution formation of benzofulvene from naphthvalene is a catalyzed process[25] and that naphthalene is formed thermally in the gas phase.

Formation of only benzofulvene from diazo compound **13** indicates that carbene **8** shifts only hydrogen and not phenyl or vinyl groups. This is, perhaps, not unexpected because of the low activation barrier for H shifts in carbenes. These results contradict conclusions of Burger and co-workers,[26] however, who have suggested that this carbene gives naphthalene and naphthvalene. It should be noted, however, that these workers' results were obtained under carbenoid conditions, and it is likely that the organolithium compounds behave differently than the free carbene. Our results pose no conflict with the contention that **8** is an intermediate in the automerization of naphthalene since, as pointed out by Scott,[24] benzofulvene rearranges to naphthalene at higher temperatures.

In summary, we have for the first time synthesized diazabenzosemibullvalene **9**, a naphthalene + N_2 molecule. Gas-phase thermolysis of this compound gives naphthalene, naphthvalene, and benzofulvene; low-temperature irradiation gives naphthalene, naphthvalene, and the previously unknown diazomethylindene **13**. Irradiation of the diazo compound in turn produces benzofulvene. These results suggest that the benzoprefulvene biradical **5** only opens to give naphthalene or closes to give naphthvalene. The carbene **8**, on the other hand, only undergoes a hydrogen shift to give benzofulvene. We are continuing to study the chemistry of this interesting azo compound, in particular with respect to the chemistry of naphthvalene and as a highly energetic aromatic precursor.

Experimental Section

General. Dichloromethane was distilled from calcium hydride. Benzene was stirred over H_2SO_4 for 24 h, washed with water, dried, and distilled from P_2O_5. Flash chromatography was performed as specified by Still,[27] on silica gel 60, 230–400 mesh from EM Reagents. Infrared spectra were recorded on a Beckman IR 4250. UV spectra were taken on a Cary 118 spectrometer. Proton NMR were recorded on a Bruker WP-200 (200 MHz) or Bruker WP-270 (270 MHz) as indicated. Carbon-13 spectra were recorded on a JEOLCO FX-200 at 50 MHz. Carbon multiplicities were determined by an Ernst-Doddrell pulse sequence.[28] Chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were obtained on an AEI-902 instrument at 70 eV unless otherwise specified. Details of the matrix isolation apparatus are described elsewhere.[29] MTAD was synthesized according to the procedure in ref 31.

8,9-Benzo-4-methyl-2,4,6-triazatricyclo[5.2.2.0^{2,6}]undeca-8,10-diene-3,5-dione (10). Naphthalene (0.54 g, 4.4 mmol) and 4-methyl-1,2,4-triazoline-3,5-dione (MTAD, 0.5 g, 4.4 mmol) were dissolved in dichloromethane (200 mL) and placed in a water-jacketed flask equipped with a stir bar. The solution was deaerated with N_2 and placed under positive nitrogen pressure. The solution was irradiated with a 1000-W incandescent lamp with stirring (aluminum foil was loosely wrapped around the flask and bulb) until the solution decolorized (ca. 4 h). The volume was reduced by careful rotary evaporation (bath temperature less than 40 °C) to ca. 10 mL. The concentrated solution was purified via rapid flash chromatography (30% ethyl acetate in hexane), giving white prisms (0.4–0.75 g, ca. 40–70% yields): ^{1}H NMR (200 MHz, $CDCl_3$) ArAA′BB′ δ_A 7.34, δ_B 7.23 (2 H each, $J_{AB} = 5.4$, $J_{AB'} = 1.2$, $J_{BB'} = 6.0$ Hz), olefin/bridgehead AA′BB′ δ_A 5.82, δ_B 6.82 (2 H each, $J_{AB} = 4.2$, $J_{AB'} = 1.6$, $J_{BB'} = 5.3$ Hz), δ 2.9 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$, −20 °C) δ 158.0 (s), 136.8 (s), 134.5 (d), 127.6 (d), 123.5 (d), 56.8 (d), 25.3 (q); IR (KBr) 1760, 1710, 1700 cm^{-1}; MS (30 eV), *m/e* calcd 241.0852, measd 241.0852, base peak 128.

9,10-Benzo-5-methyl-3,5,7-triazatricyclo[6.3.0^{2,11}.0^{3,7}]undeca-9-ene-4,6-dione (11). The adduct **10** (0.45 g, 1.87 mmol) and xanthone (0.15 g, 0.76 mmol) were dissolved in 200 mL of benzene in a water-jacketed flask. The solution was deaerated with nitrogen and photolyzed with stirring under positive nitrogen pressure using Rayonet 300-nm bulbs. The photolysis was stopped after NMR analysis of aliquots showed no further product formation (10–24 h). The solution was filtered, and the solvent was removed in vacuo. The residue was purified by chromatography on a 4- × 15-cm silica gel column eluted with 30% ethyl acetate in hexane, giving white prisms after solvent removal (0.15 g, 30%): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.38–7.08 (m, 4 H), 5.56 (d, 1 H, $J = 4.7$ Hz), 3.93 (dd, 1 H, $J = 7.0, 6.5$ Hz), 3.64 (ddd, 1 H, $J = 7.0, 5.8, 4.7$ Hz), 2.74 (dd, 1 H, $J = 6.5, 5.8$ Hz), 2.68 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$ δ 155.9 (s), 154.7 (s), 139.5 (s), 139.4 (s), 129.4 (d), 127.0 (d), 125.0 (d), 124.3 (d), 67.5 (d), 43.9 (d), 38.3 (d), 35.4 (d), 24.9 (q); IR

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(21) It is possible that the added strain in our system increases the likelihood of concerted 1,3-dipolar cycloreversion of **9** to **13**. It also may be that formation of diazo **13** occurs thermally in solution leading to the intractable material formed. We do not observe products by ^{1}H NMR on warming solutions containing **13**.

(22) Our experiments do not permit us to address the multiplicity of biradical **5**. Calculations by Oikawa and co-workers[23] (MINDO/3) suggest that biradical **1** may be a ground-state triplet.

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($CDCl_3$) 1760, 1700 cm^{-1}; MS, *m/e* calcd 241.0852, measd 241.0846.

6,7-Benzo-3,4-diazabicyclo[3.3.0]octa-3,6-diene (9). (a) Cleavage of Urazole 11 to Hydrazine 12. The urazole **11** (0.54 g, 2.2 mmol) was suspended in 50 mL of absolute methanol. Hydrazine hydrate (5.0 mL, 100 mmol) was added, the mixture was stirred for 3 days at room temperature, and the solvent was removed in vacuo. The intermediate hydrazine **12** could not be purified but could be observed by ^{1}H NMR: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.26–7.08 (m, 4 H), 4.80 (d, 1 H, J = 5.0 Hz), 3.46 (dd, 1 H, J = 6.0, 4.6 (Hz), 3.26 (ddd, 1 H, J = 5.0, 4.7, 4.6 Hz), 2.51 (dd, 1 H, J = 6.0, 4.7 Hz).

(b) Oxidation of 12 to 9. The crude hydrazine **12**, from above, was dissolved in 50 mL of benzene. MTAD (0.25 g, 2.2 mmol) was added in small portions to the stirred solution. The solution was filtered, and solvent was removed in vacuo. The crude yield was essentially quantitative by weight and NMR. The residue was purified by sublimation (ca. 0.1 torr, −78 °C cold finger, 40 °C bath). The desired compound was collected as nearly colorless crystals (0.15 g, 0.96 mmol, 44% from **11**): ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.5–7.05 (m, 4 H), 6.23 (d, 1 H, J = 5.4 Hz), 5.50 (dd, 1 H, J = 6.0, 4.5 Hz), 3.52 (ddd, 1 H, J = 5.4, 4.5, 4.5 Hz), 3.37 (dd, 1 H, J = 6.0, 4.5 Hz); UV (CH_3CN) λ_{max} 337 (ϵ 280); IR (KBr) 2950, 2920, 2850, 1490, 1468, 1458, 1300, 1270, 1255, 1215, 1175, 1155, 1145, 1080, 1020, 1010, 980, 895, 795, 770, 765, 750, 730, 700, 670 cm^{-1}.

Naphthvalene (6).[8] Indene (freshly distilled, 14 g, 120 mmol) and anhydrous ethyl ether (1250 mL) were placed in a 2-L three-necked flask equipped with two dropping funnels, a low-temperature thermometer, and a nitrogen inlet. The entire apparatus had been dried in an oven and cooled under a N_2 stream. The solution was cooled to less than 10 °C with an ice bath, and *n*-BuLi (50 mL of 2.5 N in hexane, 125 mmol) was added dropwise under N_2 via one of the funnels so that the temperature remained <10 °C (ca. 0.5 h). After the addition, the solution was stirred an additional 0.5 h at 10 °C and then the temperature was lowered to −60 °C with a dry ice/acetone bath. A solution of dichloromethane (17 mL, 22 g, 250 mmol) in dry ether (100 mL) was added dropwise via the other funnel over ca. 1 h such that the temperature remained at −60 °C, and the mixture was allowed to stir for an additional 15 min. A second aliquot of *n*-BuLi (100 mL, 250 mmol) was added so that the temperature remained at ca. −60 °C. Water (500 mL) was cautiously added dropwise, and the cooling bath was removed. The organic layer was washed once with brine (500 mL), dried over $CaCl_2$, and the solvent was removed in vacuo. The volatiles were separated via bulb-to-bulb distillation at 0.1 torr with gentle heating. The volatile fraction was taken up in a minimum amount of hexane (ca. 5 mL) and cooled to −78 °C until naphthalene crystallized. The solution was decanted, and the naphthalene removal process was repeated at least 5 times. The solvent was removed, and the material was taken up in HPLC-grade acetonitrile. Naphthvalene was purified by preparative reverse-phase HPLC (ODS ultrasphere, Beckman), eluting with acetonitrile. The spectral properties of **6** were consistent with those reported in the literature.[8]

Benzofulvene (7). Naphthvalene (ca. 0.1 g, 0.8 mmol in an enriched mixture was naphthalene) was placed in a 10-mL flask, and a small piece of copper wire was added. Dry benzene was added, and the solution was refluxed for 0.5 h. The volume was reduced in vacuo, and the benzofulvene was purified by preparative VPC (OV 101). The spectra of **7** were consistent with those reported in the literature.[30]

Flash-Vacuum Pyrolysis of 9. The azo compound **9** (5–10 mg) in dichloromethane solution was placed in a 5-mL pear-shaped flask, and the solvent was removed by careful rotary evaporation so that the material coated the walls of the flask. The flask was connect via a 14/20 distillation adaptor to a 25-cm Vigreux column, a vacuum adaptor, and a receiving flask. The Vigreux column was wrapped with Nichrome wire connected to a variable-voltage source, was covered with a Fiberglas sleeve, and was heated to 160 °C. The temperature of the column was monitored with a thermometer slipped inside the insulation. A vacuum was applied to the system, and the delivery flask was warmed to 60 °C in an oil bath. Products were collected at −78 °C and were analyzed by NMR.

Photolysis of 9 in an Argon Matrix. The azo compound **9** was deposited in an argon matrix by sublimation from −20 °C with concurrent condensation of Ar onto a CsI window cooled to 25 K. The sample was irradiated with a xenon arc lamp (300 W) filtered through a combination of Corning 0-52 and 7-37 filters (≃340–380 nm) for 1 h. The IR spectrum showed complete destruction of **9**, and formation of naphthalene and naphthvalene (by comparison to authentic samples), and a set of absorptions at 2060, 1360, 873, 831, 765, and 730 cm^{-1}. Subsequent irradiation through a corning 0-52 filter (λ > 340 nm) for 90 min destroyed the unknown's absorptions and gave rise to absorptions of benzofulvene (by comparison to an authentic sample).

Photolysis of 9 at −78 °C. Generation of 13 in Solution. A solution of **9** in CD_2Cl_2 was prepared and deaerated in a 5-mm NMR tube. The tube was suspended in an unsilvered Dewar filled with an ethanol/dry ice slurry and irradiated in a Rayonet photoreactor at 350 nm for 1.5 h. ^{1}H NMR at −78 °C or rapidly at room temperature showed the destruction of starting material and the presence of naphthalene, naphthvalene, and diazo compound **13**: ^{1}H NMR (CD_2Cl_2, 200 MHz) δ 6.85 (m, 1 H), 6.50 (m, 1 H), 4.13 (m, 1 H), 3.80 (d, 1 H, J = 4 Hz), aromatic protons obscured by other products.

Warming the solution containing **13** to room temperature for several hours caused complete destruction of **13**, but no discernible products by NMR. Reirradiation of the solution containing **13** at −78 °C with a xenon arc lamp through a Corning 3-73 filter (>380 nm) for 2 h caused complete conversion of **13** to **7** by NMR.

Conversion of 13 to 14 by MeOH Trapping. Methanol (0.1 mL) was added to a solution of **13**, prepared as above, cooled to −78 °C. Irradiation at this temperature with λ > 380 nm gave complete conversion of **13** to **14**[16] by NMR. Benzofulvene was stable to these conditions.

Triplet-Sensitized Irradiations. In all experiments the sensitizer was calculated to absorb more than 99% of the irradiation wavelengths.

(a) Sensitized Decomposition of Azo 9. A solution of **9** (5 mg) and xanthone (10 mg) was prepared in 0.3 mL of CD_2Cl_2 in a 5-mm NMR tube and deaerated with N_2. The tube was irradiated at −78 °C at 300 nm. ^{1}H NMR indicated 50% consumption of **9** and formation of approximately equal amounts of naphthalene and naphthvalene. Integration of the sample against xanthone as the internal standard showed that azo **9** and the two products accounted for 70% of the starting material.

(b) Sensitized Decomposition of Diazo 13. Solutions containing **13** were prepared by the method described above. Fluorenone, thioxanthone, camphorquinone, or biacetyl (0.01 g) were added, and the solutions were irradiated at −78 °C at wavelengths where the sensitizer received all the light (>360, 350, >430, and >430 nm, respectively). In all cases, NMR indicated consumption of **13** with no concomitant formation of any $C_{10}H_8$ isomer.

(c) Sensitized Decomposition of Benzofulvene (7). Benzofulvene was subjected to the same triplet sensitization conditions as indicated above for **13**. In all cases, ^{1}H NMR indicated consumption of benzofulvene and production of broad, structureless absorbances at varying chemical shifts.

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