mmol), giving a dark brown solution. CO_2 (1.04 mmol) was added, the solution becoming green over a period of 0.5 h. It was stirred for a further 15 h, hexane (15 cm^3) added, and the mixture filtered to remove the green precipitate of $[(Cp_2Ti)_4(CO_3)_2]$, which was washed well with hexane, yield 0.28 g (72%). The product had identical physical and chemical properties with the $[(Cp_2Ti)_4(CO_3)_2]$ obtained from the reaction of N_2O with $Cp_2Ti(CO)_2$ (see below) and with that obtained from the reaction between CO_2 and $Cp_2Ti(CO)_2$.[14]

Reaction of Dicyclopentadienyltitanium with Excess Carbon Dioxide. Tetrakis(dicyclopentadienyltitanium) Dicarbonate $[(Cp_2Ti)_4(CO_3)_2]$. A toluene solution of $(Cp_2TiH)_x$ (0.92 g, 5.1 mmol) was stirred at room temperature for 2 h, the evolved H_2 being occasionally pumped away. To the resultant dark green solution of Cp_2Ti was added CO_2 (5.4 mmol). The solution was stirred under CO_2 for 3 days, then the remaining gases were Toeplered, first through the liquid-nitrogen traps (no gas obtained), then through −78 °C traps (CO_2 obtained 1.0 mmol). The green precipitate of $[(Cp_2Ti)_4(CO_3)_2]$ was removed from the solution by filtration, yield 41% based on the equation

$$5Cp_2Ti + 4CO_2 \rightarrow [(Cp_2Ti)_4(CO_3)_2] + Cp_2Ti(CO)_2 \qquad (19)$$

The filtrate showed intense absorptions at 1900 and 1975 cm^{-1}, due to $Cp_2Ti(CO)_2$.

Reaction of Dinitrogen Oxide with Dicyclopentadienyltitanium Dicarbonyl. Tetrakis(dicyclopentadienyltitanium) Dicarbonate $[(Cp_2Ti)_4(CO_3)_2]$. In a typical experiment a solution of $Cp_2Ti(CO)_2$ (0.63 g, 2.7 mmol) in toluene (40 cm^3) was heated to 65 °C. Then N_2O (2.0 mmol) was added and the solution stirred for 12 h, after which the solution was purple-blue. The solution was cooled to −78 °C and the gases were Toeplered through liquid N_2 traps (holding back all gases except CO and N_2) into a bulb of known volume. The gases and Toepler pump were isolated from the rest of the line, and the CO and N_2 circulated over a Cu/CuO bed at 300 °C for 3 h. Trapping of the resultant CO_2 in a liquid-nitrogen bath allowed determination of N_2 (0.98 mmol) and by difference the amount of CO (1.45 mmol) produced. These gases were pumped away, and the remaining gases from the reaction (CO_2 and N_2O as shown in separate experiments by IR spectroscopy) Toeplered through −78 °C traps. Circulation of these gases over the Cu/CuO bed converted N_2O to N_2, and hence the amounts of N_2O (1.1 mmol) and CO_2 (in this case <0.15 mmol) were determined. The solvent was removed from the remaining mixture by distillation, and the excess $Cp_2Ti(CO)_2$ (1.70 mmol) sublimed onto a weighed cold finger at 45 °C and 10^{-2} Torr. There was left a pale-green solid, which was redissolved in toluene and filtered, and the filtrate was cooled at −35 °C for 48 h. The green, crystalline precipitate was removed by filtration, yield 0.25 g, 0.3 mmol (60%). Anal. Calcd for $C_{42}H_{40}Ti_4O_6$: C, 60.6; H, 4.8; N, 0; Ti, 23.0. Found: C, 59.3; H, 4.6; N, 0.1; Ti (as TiO_2), 23.7. An average of eight experiments of the type described gave the overall stoichiometry

$$1.2(\pm0.4)Cp_2Ti(CO)_2 + 1.2(\pm0.2)N_2O \rightarrow 1.0N_2 + 1.6(\pm0.1)CO + 0.0(\pm0.1)CO_2 + 0.15(\pm0.01)[(Cp_2Ti)_4(CO_3)_2]$$

Instruments used in this work were a Perkin-Elmer 457 IR spectrophotometer, spectra being measured as Nujol or hexachlorobutadiene mulls or in solution between KBr or CaF_2 plates; a Varian T60 NMR spectrometer; a Hitachi Perkin-Elmer RMU-60 mass spectrometer; and a locally modified version of the Varian E-4 ESR spectrometer. The vacuum line used was a much modified version of that described by Shriver.[35] Microanalyses were by A. Bernhardt, West Germany.

Acknowledgments. We thank the National Research Council of Canada, Imperial Oil Canada, and the University of New Brunswick Research Fund for financial support, Walter Brereton for technical assistance with the vacuum lines, and Dr. Colin Mailer, Department of Physics, University of New Brunswick, for assistance with the ESR spectra. The initial experiments in this work were carried out by F.B. during the tenure of an Alexander von Humboldt Fellowship at the Universität Konstanz, Federal Republic of Germany. We thank Professor Hans H. Brintzinger, Konstanz, for his hospitality, advice, and stimulating discussions during the complete course of this work.

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γ-Radiation–Oxidation of Polycyclic Aromatic Hydrocarbons: Involvement of Singlet Oxygen[1a,b]

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Abstract: Oxidation of organic compounds in the presence of high-energy radiation is generally understood in terms of organic free-radical mechanisms. We investigated the chemistry of certain polycyclic aromatic hydrocarbons in oxygenated solutions submitted to γ-radiation from a cobalt-60 source in an effort to identify and study other pathways in radiation oxidation. Products obtained could be explained either through singlet oxygen ($^1O_2$) production, through superoxide ($O_2^{-}\cdot$) production, or through a cation radical mediated reaction with O_2. Quenching experiments clearly established singlet oxygen as the intermediate involved. The oxidation products varied markedly depending on the starting compound. This resulted because the primary endoperoxide adducts were subject to radiation-induced decomposition both by retrograde O_2 expulsion and by breakdown to quinones. It was also found that certain common $^1O_2$ quenchers were ineffective in the radiation environment because of decomposition.

Introduction

Free-radical oxidation mechanisms had been known generally as the classical oxidation route for organic compounds in numerous environments. More recent investigations have brought to light other mechanisms[2] involving "activated forms" of oxygen, including excited-state singlet oxygen ($^1O_2$) and superoxide ($O_2^{-}\cdot$). The production of these intermediates in a variety of different systems has now been documented; they result,[3,4] for example, from chemical precursors, from photochemical environments, and in biological systems.

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(1) (a) This work was supported by the U.S. Department of Energy (DOE) under Contract DE-AC04-76-DP00789. (b) A preliminary account of this work was given at the Symposium on Reactive Intermediates in Ground- and Excited-State Organic Transformations, 178th National Meeting of the American Chemical Soc., Washington, DC, Sept. 1979. (c) A U.S. DOE facility.

(2) C. S. Foote, *Acc. Chem. Res.*, **1**, 102 (1968); (b) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971); (c) E. Lee-Ruff, *Chem. Soc. Rev.*, **6**, 195 (1977); (d) R. Denny and A. Nickon, *Org. React.* (*N. Y.*), **20**, 133 (1973).

(3) B. Chutny and J. Kucera, *Radiat. Res. Rev.*, **5**, 55 (1974).

(4) (a) C. S. Foote, *Free Radicals Biol.*, **2**, 85 (1976). (b) B. Ranby and J. Rabek, "Singlet Oxygen, Reactions with Organic Compounds and Polymers", Wiley, New York, 1978.

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The oxidation of organic materials in an environment of high-energy radiation is presently described almost exclusively in terms of induced homolytic bond scission followed by radical addition to (ground-state) oxygen, leading to peroxide formation.[3] However, the interaction of radiation with organic molecules can also generate free electrons, ions, and excited states, leading potentially to a variety of possible reaction pathways.[5,6] To observe possible radiation-oxidation pathways other than those involving organic free radicals, we examined polycyclic aromatic hydrocarbons. Radiation-induced radical formation is suppressed in aromatic materials,[7] and we anticipated that these aromatic molecules could participate in potential nonradical pathways.

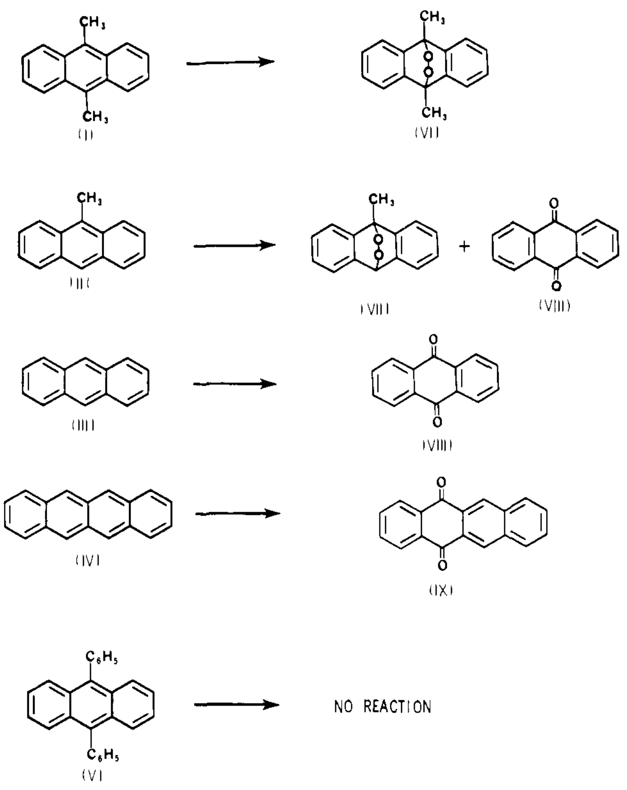
We report here on the radiation-oxidation products of these compounds, which include endoperoxides. Several mechanisms would be consistent with the products obtained. Singlet oxygen addition is one possibility.[4d,8] Alternatively, since radiation induces ionization by electron ejection from organic molecules, endoperoxides could conceivably arise from reaction of organic radical cation with superoxide ($O_2^-\cdot$) generated by scavenging an electron.[9] Foote[10] and Schaap[11] have described the reactions of $O_2^-\cdot$ with organic radical cations in a system which utilizes dicyanoanthracene to effect photosensitized electron transfer. Products obtained corresponded to singlet-oxygen-like addition of $O_2^-\cdot$ across double bonds. A third mechanism which could account for endoperoxides is an organic cation radical addition with O_2. Tang[12] recently presented evidence for such a mechanism in the oxidation of ergosterol acetate to the corresponding endoperoxide (the organic cation radical was generated chemically).

Results

Benzene solutions of polycyclic aromatic hydrocarbons were purged with O_2 while irradiated at 24 °C in a ^{60}Co γ source (0.8 Mrad/h). Reactions were monitored spectroscopically and oxidation products isolated at varying times of partial conversion.

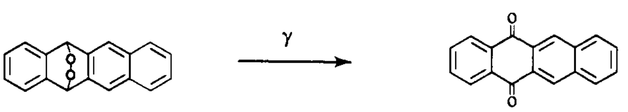
γ-Irradiation of 9,10-dimethylanthracene (I) readily gave the 9,10-endoperoxide product VI, which could be isolated in substantial yields (up to 41%). Quenching experiments were carried out on I by using the singlet oxygen quencher 1,4-diazabicyclo[2.2.2]octane (Dabco).[4b,13] Photolysis experiments were performed first, and the Dabco concentration necessary for quenching 50% of the $^1O_2$-mediated photooxidation was determined. A corresponding set of γ-radiation-oxidation experiments was run; these exhibited Dabco quenching to the extent of 50% by using the same concentrations, indicating the same mechanism as for photooxidation: singlet oxygen addition.

Table I. γ-Radiation Oxidation Products of Polycyclic Aromatic Hydrocarbons

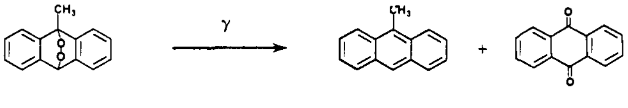


A diversity of products resulted from the radiation oxidation of the other polycyclic aromatics investigated (Table I). Both endoperoxides and quinones appeared in some instances, whereas in one case no oxidation products were obtained. In contrast, photooxidation of these hydrocarbons readily yields the singlet oxygen mediated endoperoxide adduct in each case.

γ-Irradiation experiments on the nonsubstituted hydrocarbons anthracene and naphthacene gave only quinones along with recovered starting material. The naphthacene reaction was further investigated and found to be quenched by Dabco, with 50% inhibition achieved at similar quencher concentrations for radiolysis and photolysis. Naphthacene endoperoxide (X), which was synthesized photochemically, was rapidly converted to naphthacenequinone when subjected to γ-radiation.



On γ-irradiation of 9-methylanthracene (II), both endoperoxide and quinone could be readily isolated. Quenching experiments on II established that the Dabco concentration for 50% quenching was the same for photolysis and radiolysis. γ-Irradiation of endoperoxide (VII) yielded substantial amounts of both anthracenequinone and 9-methylanthracene.



No oxidation products were isolated following γ-irradiation of solutions of 9,10-diphenylanthracene.[14] γ-Irradiation of 9,10-diphenylanthracene endoperoxide (XI) resulted in facile conversion to 9,10-diphenylanthracene.[15]

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(5) (a) A. Singh, *Radiat. Res. Rev.*, 4, 1 (1972); (b) A. Chapiro, "Radiation Chemistry of Polymeric Systems", Wiley, New York, 1962, p 42. (c) J. Hunt, *Adv. Radiat. Chem.* **5**, 185 (1976).

(6) The occurrence and potential role of activated oxygen intermediates (particularly $O_2^-\cdot$) in radiation damage in biological and organic systems have been discussed before: (a) A. Singh, *Photochem. Photobiol.*, **28**, 429 (1978); (b) A. Chapiro, "Radiation Chemistry of Polymeric Systems", Wiley, New York, 1962, p 43; (c) K. Altman, G. Gerber, and S. Okada, "Radiation Biochemistry", Vol. 1, Academic Press, New York, 1970, p 28; (d) B. Bielski and J. Gebicki, *Adv. Radiat. Chem.*, **2**, 177 (1970); (e) J. Wilson, "Radiation Chemistry of Monomers, Polymers and Plastics", Marcel Dekker, New York, 1974, pp 128, 147; (f) G. Czapski, *Annu. Rev. Phys. Chem.*, **22**, 171 (1971).

(7) A. Chapiro, "Radiation Chemistry of Polymeric Systems," Wiley, New York, 1962, pp 91, 95.

(8) (a) C. S. Foote and S. Wexler, *J. Am. Chem. Soc.*, **86**, 3880 (1964); (b) E. J. Corey and W. C. Taylor, *ibid*, **86**, 3881 (1964).

(9) A similar mechanism involving formation of benzene radical cation and fumarodinitrile radical anion during the γ-irradiation of benzene solutions of fumarodinitrile has been proposed to account for product formation in that system. The radiation products observed were phenylsuccinodinitrile along with the adduct corresponding to sequential 2 + 2 and 2 + 4 cycloaddition of succinodinitrile to benzene [H. Heusinger and P. Schuler in "Proceedings of the Fourth Tihany Symposium on Radiation Chemistry", P. Hedvig and R. Schiller, Eds., Akademiai Kiado, Budapest, 1977, p 201].

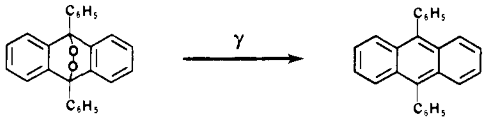
(10) J. Ericksen, C. S. Foote, and T. L. Parker, *J. Am. Chem. Soc.*, **99**, 6455 (1977).

(11) A. P. Schaap, K. Zaklika, B. Kaskar, and S. Gagnon, "Electron Transfer Mechanisms in Photooxygenation and Chemiluminescence", presented at the 178th National Meeting of the American Chemical Society, Washington, DC, Sept. 1979.

(12) C. R. Tang, H. Yue, J. F. Wolf, and F. Mares, *J. Am. Chem. Soc.*, **100**, 5248 (1978).

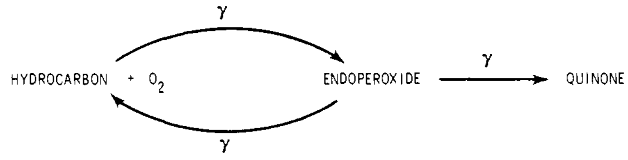
(13) D. Bellus, *Adv. Photochem.*, **11**, 105 (1979).

(14) Production of endoperoxide was apparently not zero; some evidence for small amounts in the reaction mixtures was obtained by liquid chromatography, but no product could be isolated by our standard workup procedure of column chromatography.



Discussion and Conclusions

It is found that polycyclic aromatic hydrocarbons are subject to γ-radiation-induced oxidation due to attack by singlet oxygen, as supported by quenching experiments. The variation in oxidation products is derived from the susceptibility found for the endoperoxide adducts toward further radiation-induced reaction, in terms of both retrograde expulsion of O_2 and decomposition leading to quinones; which reaction products are obtained is governed for each hydrocarbon by the *relative* rates of the three radiation-induced reactions.



This is to our knowledge the first direct evidence of $^1O_2$ chemistry in a γ-radiation environment.[16] The singlet oxygen presumably is produced by sensitization from triplet aromatic molecules generated by the radiation.

It is interesting that $^1O_2$ oxidation dominates the chemistry of this system. This requires not only production of substantial amounts of $^1O_2$ but also means that the lifetime of $^1O_2$ in this γ environment is not prohibitively short for subsequent reaction; that is, the $^1O_2$ produced is not summarily quenched by ions or other species produced simultaneously during irradiation.[17] γ-Irradiation induces initial excitation into the system nonselectively, generating a distribution of excited-state molecules; the retrograde reaction which regenerates starting material is most likely unimolecular cycloreversion from excited-state endoperoxide.

Behavior of Other $^1O_2$ Quenchers in a Radiation Environment. β-Carotene (believed to be a natural biological $^1O_2$ quencher)[5a] and bis(2-butene-2,3-dithiolato)nickel (II) (XII) (used as an oxidative stabilizer in certain polyolefin formulations)[13,18] are highly efficient $^1O_2$ quenchers,[4b,5a,13,19] and have been employed as diagnostic tools for $^1O_2$ determination in numerous systems. We find that in contrast to the Dabco results, addition of β-carotene or XII gave no detectable inhibition of the radiooxidation reaction. This failure to quench resulted because both β-carotene and XII undergo rapid γ-radiation-induced decomposition, as could be seen spectroscopically.[20] γ-Irradiated quencher solutions were inactive when subsequently employed in photochemical quenching experiments.

γ-Irradiation under Inert Atmosphere. Historically, formation of endoperoxide adducts of anthracene compounds was linked with the observation that without oxygen but under similar UV exposure these same hydrocarbons readily dimerized,[21] bridging the 9,10 ring positions. Having observed endoperoxide formation in a γ environment, we looked for dimer formation upon γ-irradiation of 9-methylanthracene under nitrogen, but did not find evidence for its formation. However, the 9-methylanthracene dimer (which was readily prepared photochemically) underwent rapid conversion to the monomer on γ-irradiation. Presumably, the radiation generates excited states of both monomer and dimer, with the overall radiostationary state, at least under these conditions, favoring monomer.[22]

Experimental Section

γ-Irradiation was carried out in a ^{60}Co source consisting of a circular array of cobalt pencils about a central cavity. A dose rate of 0.8 Mrad/h was determined by thermoluminescence dosimetry by using CaF_2 wafers. Ambient temperature in the cavity was 24 °C. The source was equipped for O_2 purging of solutions. Photolysis experiments utilized a water-jacketed Sylvania DWT tungsten-halogen lamp operated at 60 V.

Spectrometers used were: UV and visible, Cary 14; IR, Perkin-Elmer 21; mass, Finnigan 1015 with Data system 6000; NMR, Varian XL-100 (CW mode). Elemental analysis was performed by Spang Labs (Eagle Harbor, MI).

Liquid chromatography was carried out on a Waters chromatograph equipped for UV and RI detection. Experiments were performed with a Waters μ-Porasil silica column by using 10:1 isooctane/ether. Column chromatography utilized silica gel, with 5:1 hexane/ether as eluant.

Endoperoxides VI, VII, X, and XI were synthesized by photolysis of oxygenated solutions of the hydrocarbons in accord with published procedures;[23,24] identities were verified spectroscopically and by CH analysis.

γ-Irradiation of 9,10-dimethylanthracene in benzene (2.5 mg/mL) was carried out for 14 h with continuous O_2 purging. Column chromatography gave VI in 41% yield (mp 198–202 °C). The IR and NMR spectra matched those of photochemically prepared VI.

O_2-purged solutions of I in benzene (7 mg/mL) were photolyzed for 6 min, and the conversion was determined by NMR. Without quencher, conversion was 24%; addition of 0.36 mg/mL of Dabco reduced conversion to 13%. γ-Irradiation of similar solutions for 2.25 h gave 14% conversion without quencher and 7% conversion with 0.36 mg/mL of Dabco.

γ-Irradiation of 9-methylanthracene (II) in benzene (7.5 mg/mL) for 24 h with O_2 purging gave two products on column chromatography along with starting material (34% recovered). The product eluted first (mp 273–275 °C) had an IR spectrum identical with that of commerical VIII (yield 8%). The second product eluted (mp 129–131 °C dec) had IR and NMR spectra that were superimposable on those of photolytically synthesized VII (yield 15%).

On γ-irradiation of equimolar solutions of VII and II for 3 h, liquid chromatography showed 4% and 0.45% quinone production, respectively, consistent with formation of VIII from II via VII.

Quenching experiments were performed with 10 mg/mL of II in benzene. Photolysis of O_2-purged mixtures for 20 min gave 22% conversion by NMR; 0.057 mg/mL of Dabco reduced conversion to 11%. γ-Irradiation for 5 h gave 11% conversion to endoperoxide in the absence of quencher and 6.5% conversion with 0.057 mg/mL of added Dabco.

Naphthacene (IV) was γ-irradiated in O_2-purged benzene (0.7 mg/mL) for 17 h. Column chromatography afforded a 36% yield of IX (mp 286–288 °C, lit.[25] mp 294 °C), identified by comparison of the IR and visible spectra with those of a commerical sample. Quenching experiments were carried out on O_2-purged solutions of IV in benzene (0.05 mg/mL), with disappearance of IV monitored by the absorbance at 475 nm. Photolysis for 30 s gave 45% naphthacene loss; addition of 0.04 mg/mL of Dabco reduced conversion to 18%. γ-Irradiation for 15 min gave 32% naphthacene loss without quencher and 18% loss with 0.04 mg/mL of Dabco.

When naphthacene endoperoxide (0.63 mg/mL) in benzene was γ-irradiated for 16 h and submitted to column chromatography, a yield of 43% of IX was obtained.

γ-Irradiation of anthracene (4.5 mg/mL) in O_2-purged benzene for 44 h, followed by column chromatography, allowed isolation of VIII in 21% yield (mp 275 °C). Identification was made by IR. Unreacted

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[15] In previous work on the *thermal* decomposition of anthracene endoperoxides, 9,10-diphenylanthracene endoperoxide was found to stand out among other derivatives as reverting to hydrocarbon plus O_2 in very high yields (ref 21).

[16] Recently, other workers have found evidence for singlet oxygen production in organic solutions on application of bursts of electrons in pulse radiolysis experiments [A. Gorman, G. Lovering, and M. A. J. Rodgers, *J. Am. Chem. Soc.* **100**, 4527 (1978)].

[17] Ions can be very efficient singlet oxygen quenchers; for example, superoxide ($O_2^{-}\cdot$) reportedly has $k_q = 7 \times 10^9$ M^{-1} s^{-1} [H. J. Guiraud and C. S. Foote, *J. Am. Chem. Soc.*, **98**, 1984 (1976)].

[18] A. Zweig and W. Henderson, *J. Polym. Sci., Polym. Chem. Ed.*, **13** 717 (1975).

[19] C. S. Foote and R. W. Denny, *J. Am. Chem. Soc.*, **90**, 6233 (1968).

[20] Foote has recently found that these same two quenchers are destroyed in a photochemical environment in the case of a system utilizing dicyanoanthracene as a photosensitized electron-transfer agent for superoxide production (C. S. Foote, private communication).

[21] G. Badger, "The Structures and Reactions of the Aromatic Compounds", Cambridge University Press, New York, 1954, p 364.

[22] A similar scheme has been reported before. Photolysis experiments on 9-nitroanthracene showed apparent wavelength-dependent monomer–dimer interconversion, with cleavage to monomers favored at shorter wavelength [C. Depuy and O. L. Chapman, "Molecular Reactions and Photochemistry", Prentice-Hall, Englewood Cliffs, NJ, 1972, p 65; O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, *J. Am. Chem. Soc.*, **88**, 5550 (1966)].

[23] P. F. Southern and W. A. Waters, *J. Chem. Soc.*, 4340 (1960).

[24] K. Gollnick and G. Schenck, in "1,4-Cycloaddition Reactions", J. Hamer, Ed., Academic Press, New York, 1967, p 324.

[25] "Handbook of Chemistry and Physics", 46th ed., Chemical Rubber Publishing Co., Cleveland, OH, 1965, p C-414.

anthracene recovered was 54%. No endoperoxide was obtained.

γ-Irradiation of 9,10-diphenylanthracene (V) in O_2-purged benzene (2.7 mg/mL) was carried out for 18 h. On column chromatography no oxidation products were obtained.[14] When 2 mg/mL of 9,10-diphenylanthracene endoperoxide in benzene was γ-irradiated, it was seen by UV that V was produced in 24% yield after 8 h.

9-Methylanthracene Dimer. On photolysis of 0.1 g/mL of II in benzene at 0-20 °C under N_2 for 6 h, the white precipitate amounted to 21%. Recrystallization from benzene gave white crystals (mp 250-252 °C, lit.[26] mp >250 °C) of low solubility in organic solvents. Anal. ($C_{30}H_{24}$) C, H.

γ-Irradiation of II in benzene (20 mg/mL) was carried out under N_2 for 20 h. No dimer could be isolated. When 2 mg of dimer and 7 mL of benzene were sealed under N_2 and γ-irradiated, UV showed production of II in 38% yield after 6 h.

Quenching Experiments with Bis(2-butene-2,3-dithiolato)nickel(II) (XII) and β-Carotene. Complex XII was prepared by using the literature procedure.[27] Solutions of I in benzene (7.1 mg/mL) containing varying amounts of XII were purged with O_2 while photolyzed at 25 °C for periods of 6 min. It was seen by NMR spectroscopy that 0.02 mg/mL of XII quenched 50% of the reaction. In γ experiments, no quenching was observed with 0.02 mg/mL or 0.06 mg/mL of XII. When 0.06 mg/mL of XII in oxygenated benzene was γ-irradiated for short time periods, the solution lost its blue-violet color; the visible spectrum showed complete disappearance of XII (λ_{max} 770 nm). To this γ-irradiated solution was added 7.1 mg/mL of I; photolysis of this mixture showed no quenching effect.

Benzene solutions (0.05 mg/mL) of IV containing varying amounts of β-carotene were photolyzed with O_2 purging, with naphthacene loss monitored spectroscopically (λ 475 nm). β-Carotene addition of 0.001 mg/mL effected 50% quenching. γ Experiments showed no quenching by 0.005 mg/mL of β-carotene. Spectroscopy (λ 459 nm) showed destruction of β-carotene on γ-irradiation for short times.

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(26) R. Calas and R. Lalande, *Bull. Soc. Chim. Fr.*, 763 (1959).

(27) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 1483 (1965).

Cooligomerizations of 3-Substituted 1,5-Hexadiynes with Bis(trimethylsilyl)acetylene Catalyzed by Cobalt. A General Synthesis of Tricyclic Ring Systems from Acyclic Precursors[1]

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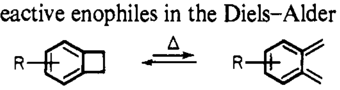
Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received January 4, 1980*

Abstract: A one-step synthesis of polycycles is described which utilizes a $CpCo(CO)_2$-catalyzed cooligomerization of substituted 1,5-hexadiynes with bis(trimethylsilyl)acetylene solvent to produce intermediate benzocyclobutenes which may be subsequently or concomitantly ring opened to furnish intermediate *o*-xylylenes. The latter dienes react intermolecularly with solvent to yield ultimately 2,3,6,7-tetrakis(trimethylsilyl)naphthalene (**6**), substrate to a variety of electrophiles. Intramolecular trapping by appended dienophiles results in the formation of tricyclic systems containing ortho-bis-silylated benzenes and a variety of heteroatoms via exo transition states leading to trans ring fused compounds. Only in one case, **31**, was a significant proportion of the cis isomer observed. Protodesilylation may be achieved with acid to give the parent systems. In the case of **17** containing an aldehyde as a dienophile the cobalt-catalyzed cyclization results in ketal **22**. A general synthetic entry into 3-alkylated 1,5-hexadiynes was found via the in situ generation of 1,3,6-trilithio-1,5-hexadiyne.

Benzocyclobutenes **1** have in the last decade been shown to be versatile building blocks in polycycle synthesis by virtue of their propensity to thermally open the four-membered ring to generate *o*-xylylenes **2**, reactive enophiles in the Diels-Alder reaction. When the four-membered ring bears a dienophile carrying side chain, intramolecular cycloaddition furnishes a tricyclic system often with good regio- and stereoselectivity. This synthetic method, first discovered by Oppolzer,[4] has recently been exploited by several groups in the construction of natural products.[5] Despite advances in approaches aimed at improving the general availability of benzocyclobutenes the most serious drawback of the above methodology has been the relative difficulty of constructing variably substituted members of the series by simple and effective reactions. We had some time ago suggested[6] as a possible solution



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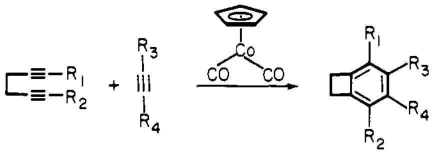
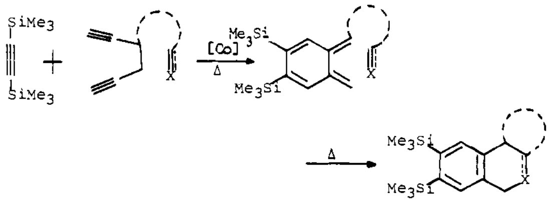
Scheme I



Scheme II



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(1) Taken in part from the Ph.D. Thesis of R. L. Funk, University of California, Berkeley, 1978.

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