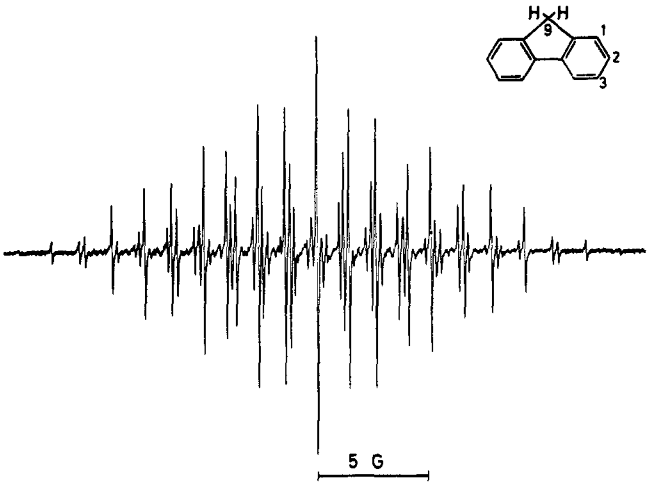

Figure 2. Esr spectrum of the fluorene radical anion in HMPA at room temperature, range 40 G, scan time 16 min, modulation frequency 100 kHz, modulation amplitude 50 mG, a_1 = 1.49 G, a_2 = 5.26 G, a_3 = 1.49 G, a_4 = 2.74 G, a_9 = 2.74 G.

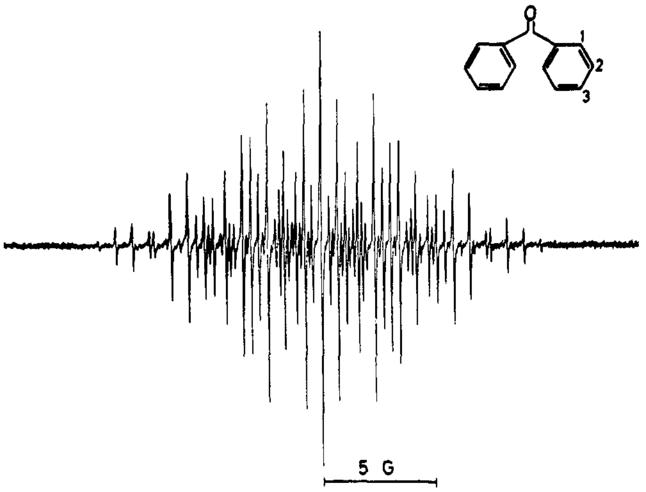

Figure 3. Esr spectrum of the benzophenone ketyl in HMPA at room temperature, range 40 G, scan time 8 min, modulation frequency 100 kHz, modulation amplitude 20 mG, a_1 = 2.38 G, a_2 = 0.73 G, a_3 = 3.49 G.

(c) Since trimethylsilylsodium can be used in large excess to substrates, essentially no neutral molecule is left in the system. Further reduction of radical anions to dianions is seemingly very slow. As a result, well-resolved, strong signals such as those in Figure 1 can usually be observed.

(d) Even though trimethylsilylsodium is very nucleophilic and basic, its rapid electron transfer dominates completely. This is illustrated by the well-resolved spectrum of the fluorene radical anion at room temperature as shown in Figure 2. Fluorene is known to react with alkali metals at room temperature to give the fluorenyl anion. The fluorene radical anion is reportedly only relatively stable at −70°.[12]

(e) For ketyl radicals such as benzophenone ketyl (Figure 3) and for radical anions from nitro compounds such as nitrobenzene,[13] the hyperfine splitting constants of ring protons and nitrogen were smaller than any recorded values. This may indicate minimum interactions of radical anions to the countercation and the solvent[14] because of a strongly basic nature of the solvent.[13,15]

Studies on the scope and limitations of this new reagent are now in progress.

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[12] D. Casson and B. J. Tabner, *J. Chem. Soc. B*, 887 (1969).

[13] G. R. Stevenson, L. Echegoyen, and L. R. Lizardi, *J. Phys. Chem.*, **76**, 1439 (1972), have recently reported the most "free" nitrobenzene radical anion in HMPA produced by metal reduction. Our spectra agreed completely with theirs.

[14] N. Hirota, "Radical Ions," E. T. Kaiser and L. Kevan, Ed., Interscience, New York, N. Y., 1968, Chapter 2.

[15] A. Cserhegyi, J. Chaudhuri, E. Franta, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, **89**, 7129 (1967).

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Synthesis of a Bridged [18]Annulene

Sir:

It has been predicted that the delocalization energy per double bond will decrease with increasing ring size until, somewhere in the range of 22–30 members, such annulenes will become simple polyolefins.[1-3] Sondheimer and his colleagues have demonstrated that both [22]annulene[4] and monodehydro[26]annulene[5] sustain a dimagnetic ring current, thus providing qualitative evidence for delocalization of the π electrons in rings of 22 and 26 members. However, as has been shown in such a striking fashion for [18]annulene,[6] the simple annulenes are subject to conformational flipping which undoubtedly decreases the effective delocalization energy. To test the upper limit for the delocalization energy of $4n + 2$ hydrocarbons it is highly desirable to use as a test molecule one with a rigid, planar annulene skeleton. In the present communication we describe an approach of possibly general application leading to bridged molecules with a rigid, planar annulene skeleton.

Treatment of 2,8-dibromodibenzothiophene[7] (**1**) with *n*-butyllithium followed by *N*,*N*-dimethylformamide gave the corresponding dialdehyde **2**, mp 233–234°, in 68% yield.[8] Reduction of **2** with sodium borohydride proceeded in quantitative yield to give the diol **3**, mp 159–160°. Treatment of **3** with hydrogen bromide in glacial acetic acid then afforded 2,8-bis(bromomethyl)dibenzothiophene (**4**) in 93% yield as white needles, mp 217–218°. When **4** was treated with 1,4-bis(mercaptomethyl)benzene (**5**) in ethanolic base, the paracyclophane **6**, mp 260–261°, formed in 88%

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[1] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc., Ser. A*, **251**, 172 (1959); **257**, 445 (1960).

[2] C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215 (1962).

[3] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965).

[4] R. M. McQuilken, B. W. Metcalf, and F. Sondheimer, *Chem. Commun.*, 338 (1971).

[5] B. W. Metcalf and F. Sondheimer, *J. Amer. Chem. Soc.*, **93**, 5271 (1971).

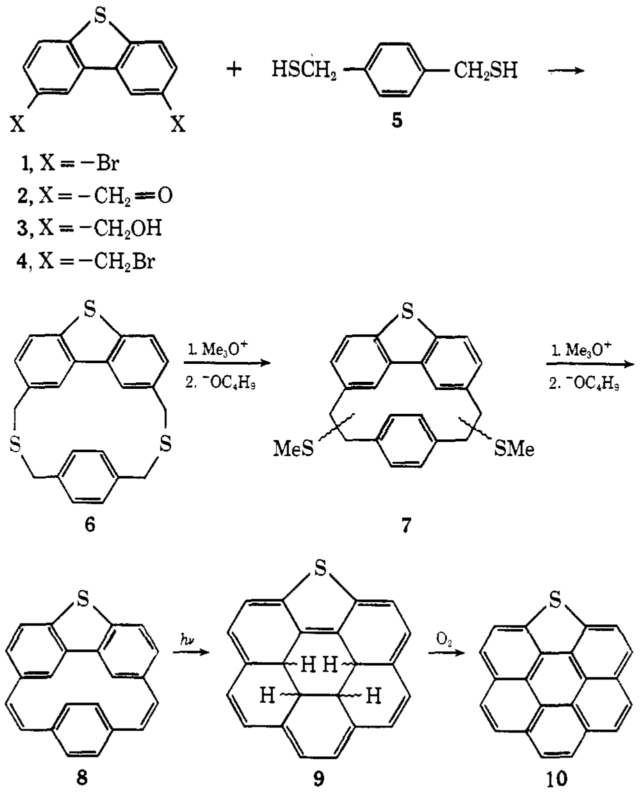
[6] J.-M. Gilles, J. F. M. Oth, F. Sondheimer, and E. P. Woo, *J. Chem. Soc. B*, 2177 (1971).

[7] C. Neumoyer and E. Amstutz, *J. Amer. Chem. Soc.*, **69**, 1920 (1947).

[8] Satisfactory elemental analyses are available for all new compounds being reported except thiacoronene, for which a satisfactory high-resolution mass spectrum is available.

yield. Methylation of **6** followed by reaction with potassium *tert*-butoxide in tetrahydrofuran gave the Stevens rearrangement product **7**, as a mixture of isomers, in 22% yield. Remethylation of **7** followed by treatment again with potassium *tert*-butoxide in tetrahydrofuran effected a double Hofmann elimination to give the diene **8**, mp 220–221°, in 19% yield (Scheme I).

Scheme I



Since we had previously shown that irradiation of [2.2]metacyclophane-1,9-diene gives *trans*-15,16-dihydropyrene,[9] which is stable in degassed solution but is quickly oxidized by air to pyrene, we expected **8** to behave similarly. Irradiation of **8** in degassed perdeuteriobenzene gave a deep orange solution. When the reaction was followed by nmr, it could be seen that the signals for the photoproduct were arising both at higher and lower field than the starting material. The nmr spectrum of the photoproduct is presented in Figure 1. Its striking feature is the signal in the high-field range of τ 15.0–15.69. Furthermore, the integrated area of this region corresponds to four protons, whereas the region of τ 1.16–1.54 corresponds to ten protons, as expected. The only reasonable structure to account for such high-field protons is a bridged [18]annulene such as **9** where the high-field protons are the interior protons.

Although the splitting patterns of the low-field protons of the photoproduct are readily interpretable in terms of the perimeter protons of **9**, the splitting pattern of the upfield protons cannot be interpreted readily in terms of a single stereoisomer. It would appear that the double photocyclization may occur stepwise and, after the first ring closure, conformational flipping is possible so that the second photocyclization can lead to more than one stereoisomer. Alternatively, the initial photoproduct from **8** may undergo a subsequent irradiation-induced stereoisomerization or tautomerization, possibly involving isomers where the interior double bond has shifted. The overall structure of **9** seems quite certain, but the exact assignment for the internal protons as well as the interior ring is not yet clear.

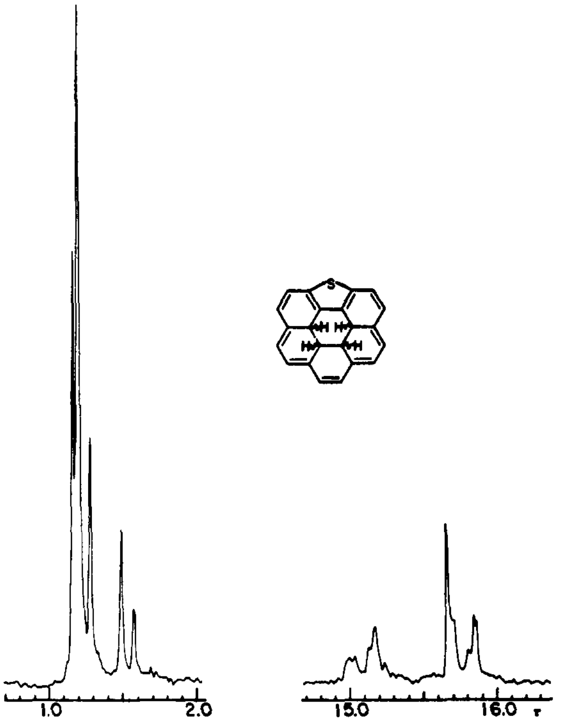


Figure 1. The nmr spectrum of **9** in degassed perdeuteriobenzene as measured using a Varian XL-100-Hz instrument with Fourier transform. Chemical shift values are in τ.

When the irradiated solution of **9** was exposed to air, oxidative removal of the internal hydrogens occurred and thiacoronene (**10**) was formed. The ultraviolet and visible spectrum of **10** corresponds very closely to that of coronene itself, and the nmr spectrum of **10** is in full accord with its assigned structure.

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(9) R. H. Mitchell and V. Boekelheide, *J. Amer. Chem. Soc.*, **92**, 3510 (1970).

A Stereoselective Method for the Synthesis of Both Olefinic Isomers from a Single Precursor. The Conjugate Reduction of α,β-Unsaturated Epoxides

Sir:

The need for stereoselective methods for the synthesis of olefins that are convenient and of general applicability is attested to by numerous recent publications in this area.[1] The available methods generally have sought to optimize stereoselectivity but as a consequence have suffered a loss of generality, *viz.*, only

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(1) Recent reviews include: D. J. Faulkner, *Synthesis*, 175 (1971); J. Reucroft and P. J. Sammes, *Quart. Rev., Chem. Soc.*, **25**, 135 (1971).