stereospecific addition could be easily explained by assuming that all addition proceeds through the singlet state while hydrogen abstraction is a triplet-state reaction,[20] since stereospecific addition is usually interpreted in terms of singlet-state reaction. This is in agreement with a triplet ground state as it is well known that methylene addition in solution is stereospecific although methylene also has a triplet ground state.[21]

Another explanation might be advanced. The hydrogen abstraction products, **5–8** and **12**, are obtained together with the addition products. This result strongly suggests that a considerable amount of triplet state is involved in these reactions. This triplet carbene may possibly add to olefin to give cyclopropane as well as other arylcarbenes.[1-3] Since the present results show the stereospecific addition, triplet carbene might add to olefin stereospecifically.

pounds **1d** and **2d** with 2-butene, and abstraction products, **5–8** and **12**, were obtained.

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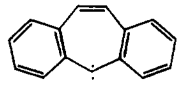
The Electron Spin Resonance of Triplet Dihydrodibenzo[*a*,*d*]cycloheptenylidene, Dibenzo[*a*,*d*]cycloheptenylidene, and Tribenzo[*a*,*c*,*e*]cycloheptenylidene

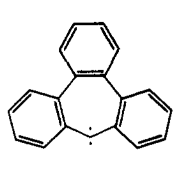
Sir:

In the preceding communication[1] we reported that dibenzo[*a*,*d*]cycloheptenylidene (**1**) and tribenzo[*a*,*c*,*e*]cycloheptenylidene (**2**) added to olefins stereospecifically to give cyclopropanes. Generally, carbenes which have a π-benzene system next to the divalent carbon show ground-state triplet and would add to olefins in a nonstereospecific fashion.[2,3] It is interesting to know whether the ground state of **1** or **2** is a triplet or not. Dihydrodibenzo[*a*,*d*]cycloheptenylidene (**3**) was also investigated and compared with **1**, **2**, and diphenylmethylene (**4**).

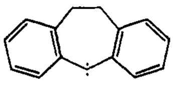
These carbenes (**1–3**) showed a triplet ground state. The corresponding diazo compounds were irradiated with ultraviolet light of wavelength below 3000 A at 77°K. The spectra were obtained with a Japan Electron Optics Lab JES-3BX spectrometer with 100-kc field modulation, and showed characteristics of randomly oriented triplets of low symmetry. The spectra persisted for hours after irradiation ceased, indicating that the observed species were in the ground states. The spectra can be described by the Hamiltonian[4]



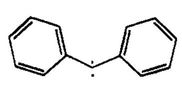
1



2



3



4

$$\mathcal{H} = g\beta\vec{H}\vec{S} + DS_{z2} + E(S_{x2} - S_{y2})$$

where $S = 1$. The zero-field parameters obtained from these observations were: for **1**, $D = 0.3787$ cm^{-1}, $E = 0.0162$ cm^{-1}; for **2**, $D = 0.4216$ cm^{-1}, $E = 0.0195$ cm^{-1}; and for **3**, $D = 0.3932$ cm^{-1}, $E = 0.0170$ cm^{-1}. The larger D value observed, compared to that of the phosphorescent triplet state of the aromatic hydrocarbons, requires a significant one-center interaction and indicates one unpaired electron largely localized in an n orbital at C-1, the divalent carbon atom, and another delocalized in a π orbital.

It is interesting to compare carbene **3** with diphenylmethylene (**4**; $D = 0.405$ cm^{-1}, $E = 0.019$ cm^{-1}).[5-9] The nonzero value of E for **4** eliminates[5] a structure of D_{2d} symmetry[3] (the aromatic rings are perpendicular to each other and bound to the central carbon). The angle between the axes of the C-1 hybrids for **4** and phenylcarbene were calculated to be ~150°,[10] a value supported by the examination of the ^{13}C hyperfine splittings.[11] For **3**, the value of E/D is similar to that of diphenylmethylene, so the angle formed by the axes of the hybrids at C-1 appears to be ~150°. This value is greater than the internuclear angle of the seven-membered ring, which is presumably due to the fact that the bonds to C-1 in **3** are bent bonds.[6,11]

If the C-1 hybrids of **3** are sp^2, similar to ketone, it is clear that the π orbital on C-1 is almost perpendicular to the π orbitals of both benzene rings. Such a model is clearly inconsistent with the observed D value. On the other hand, the enlargement of the angle of the axes of the hybrids at C-1 increases the s character of the bonds of the carbon and the planarity of the seven-membered ring, which contributes to the delocalization of the π electron of the C-1 atom with both benzene rings. The above consideration also suggests the bent bond of C-1 in **3**.

The D value for **3** is smaller than that of **4**. Greater opportunity for π delocalization should reduce the density of the π electron on the C-1 atom, and, thus, reduce the value of D. Recently we reported the ab-

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sorption spectra of **3** and **4** at 77°K.[12–14] Both spectra showed similar characteristics and suggested both carbenes had the similar π-electronic configuration. Carbene **3** (468 mμ) absorbed at longer wavelengths than did **4** (486 mμ), consistent with the smaller D value of **3** than that of **4**.

The smaller D value in **1** is due to the delocalization of the electron on C-1 with the π system of the aromatic rings. From the E/D ratio, the angle for **1** was also determined to be $\sim$150°; this value is larger than that of the internuclear angle of the seven-membered ring.[15] This suggests that the seven-membered ring is almost in a plane similar to that of tropylium ion.

Because of the dominance of the one-center interaction, for a given geometry about C-1, D should be approximately proportional to the π spin density at C-1, ρ_1.[16] A HMO calculation gives 0.34, 0.37, 0.40, and 0.40 for the dibenzo[*a,d*]cycloheptenyl, fluorenyl, diphenylmethyl, and dihydrodibenzo[*a,d*]cycloheptenyl radicals, respectively. These π spin densities are parallel to the D values of corresponding carbenes. On the other hand, tribenzo[*a,c,e*]heptenyl radical yields $\rho_1 = 0.09$, while the D value of **2** is larger than those of **1**, **3**, and **4**. This may be due to the substantial steric hindrance to coplanarity of **2**. A similar effect of phenyl groups was observed for the pK_{R^+} of tribenzotropylium cation. Generally, a plot of pK_{R^+} values *vs.* the π-energy difference between a model of the carbinol and that of the cation gives a linear correlation. However, a deviation is observed for tribenzotropylium cation.[17]

The carbenes **1** and **2** added to olefins in a stereospecific manner, although the ground state of these carbenes is triplet. The mechanistic discussion of these interesting results will be reported in full in a forthcoming paper.

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The Structure of Fomannosin, a Novel Sesquiterpene Metabolite of the Fungus *Fomes annosus*

Sir:

We wish to report the structure of a biologically active sesquiterpene metabolite of the wood-rotting fungus *Fomes annosus* (Fr.) Karst. This material, which has been named fomannosin (I), has been shown to be toxic toward 2-year-old *Pinus tadea* seedlings, *Chlorella pyrenoidosa*, and some bacteria.[1] The novel ring structure of this unusual sesquiterpene is of special interest since, to our knowledge, this is the first reported example of a sesquiterpene containing the cyclobutene moiety. Although fomannosin follows the isoprene rule, the isoprene units are not connected in the usual head-to-tail sequence.

Fomannosin was isolated by chloroform extraction of a still culture of *Fomes annosus* which was at least 6 weeks old. The chloroform extracts were purified by column chromatography, followed by preparative thin layer chromatography (ptlc), giving the pure toxin as a noncrystalline semisolid. Attempts to crystallize the toxin were unsuccessful. However, the material purified as above was homogeneous by thin layer chromatography in three dissimilar solvent systems. Fomannosin is unstable, and consequently we were unable to obtain a satisfactory elemental analysis. We also found it necessary to use freshly purified material (ptlc) for experimentation and spectral analysis.

Fomannosin ($C_{15}H_{18}O_4$)[2] has $\nu_{\max}^{CS_2}$ 3450 (OH), 1745 and 1715 cm^{-1} (C=O) and $\lambda_{\max}^{C_2H_5OH}$ 261 mμ (ϵ 9400). The 100-Mc nmr spectrum of fomannosin is shown in Figure 1A.

A dihydro derivative of fomannosin was obtained by catalytic hydrogenation. Dihydrofomannosin (II) ($C_{15}H_{20}O_4$),[3] mp 71–72°, has $\nu_{\max}^{CS_2}$ at 1745 and 1720 cm^{-1} and a plateau in the ultraviolet spectrum, $\lambda^{C_2H_5OH}$ 205–217 mμ (ϵ 6230). The 1745-cm^{-1} band in the infrared spectrum of II was attributed to a five-membered-ring nonconjugated ketone on the basis of the following evidence. Dihydrofomannosin formed a 2,4-dinitrophenylhydrazone derivative[3] [mp 220–225°, m/e 444.1635 ($C_{21}H_{24}N_4O_7$ requires mass 444.1645] which did not contain the 1745-cm^{-1} band but did have $\nu_{\max}^{CS_2}$ 1725 cm^{-1}. The ultraviolet spectrum of the dinitrophenylhydrazone, $\lambda_{\max}^{C_2H_5OH}$ 360 (ϵ 2.35 × 10^4), 274 (ϵ 1.15 × 10^4), and 232 mμ (ϵ 2.36 × 10^4), indicated that the ketone with which the 2,4-dinitrophenylhydrazine had reacted was not conjugated.

The assignment of the 1720-cm^{-1} band exhibited by II to a conjugated δ-lactone was based on the following data. Attempts to prepare a bis-2,4-dinitrophenylhydrazone of II were not successful. Allowing II to react with a second mole of hydrogen gave a tetrahydro derivative which had only one carbonyl band in the infrared (1740 cm^{-1}) and no appreciable ultraviolet absorption. Treatment of II with 1 equiv of base at room temperature afforded an acid which gave a noncrystalline ester upon reaction with diazomethane. Dihydrofomannosin could be regenerated from the ester by acid catalysis.

Furthermore, the spectral and hydrogenation data indicated that the chromophore in I was a diene lactone. The more easily reduced double bond must be disubstituted and the double bond α to the lactone must be tetrasubstituted since the two olefinic proton resonances in the nmr spectrum of I are absent in the nmr spectrum of II (Figure 1A, B).

Dihydrofomannosin formed a monoacetate ($C_{17}H_{22}O_5$),[3] $\nu_{\max}^{CS_2}$ 1740 cm^{-1}. It was inferred that a primary alcohol had been acetylated since a two-proton singlet at δ = 4.28 ppm in the nmr spectrum of dihydrofomannosin had shifted to δ = 4.78 ppm upon forma-

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(1) C. Bassett, R. T. Sherwood, J. A. Kepler, and P. B. Hamilton, submitted for publication.

(2) The molecular formula of fomannosin is inferred from elemental analyses, from high-resolution mass spectra of the dihydro derivatives, and from the integration of its nmr spectrum.

(3) A satisfactory elemental analysis was obtained for this material.