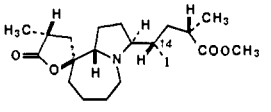
immediately submitted for Wittig olefination with the chiral phosphorane **15**,[12] producing exclusively the (Z)- alkene **16**.

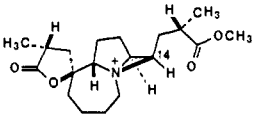
Our results, featuring sequential construction of the saturated heterocyclic system of croomine, are illustrated in Scheme II. Acid hydrolysis of the dioxepine acetal **16** (aqueous $HBF_4$; $CH_3OH$; 30 min, 72%) and basic saponification (LiOH; THF; $CH_3OH$; $H_2O$ (3:1:1 by volume) at 22 °C; 86% yield) led to the expected triol ($[\alpha]^{26.0}_D$ +10.0° (*c* 2.17, $CHCl_3$)). Slow addition of excess Jones' reagent to a tetrahydrofuran solution of triol at 0 °C with a Celite suspension (2-propanol quench) allowed for a convenient filtration to remove chromium salts. Further concentration of solvents followed by esterification with ethereal diazomethane gave a 78% yield of the butyrolactone methyl ester **17**.

Our strategy for formation of the central perhydroazepine ring has demonstrated the utility of the Staudinger reaction as a viable approach to these complex nitrogen heterocycles.[13] Removal of the benzyl ether and subsequent oxidation gave the requisite azido aldehyde **18**. Treatment of **18** with triphenylphosphine in anhydrous tetrahydrofuran led to in situ formation of an aza ylide. Subsequent intramolecular Wittig condensation afforded a seven-membered imine, which was reduced upon addition of sodium borohydride in methanol, producing a 90% yield of the perhydroazepine **19** ($[\alpha]^{25.2}_D$ +15.0° (*c* 1.54, $CH_3OH$)). The Staudinger methodology was particularly noteworthy in light of the degree of functionalization in these molecules.[14]

The final cyclizations of the C and D rings of the vicinal pyrrolidino butyrolactone segment of croomine were accomplished in a single step. Our preliminary studies of iodine-induced intramolecular cyclizations of bishomoallylic *N*-alkoxy amines were found to favor formation of trans-2,5-disubstituted pyrrolidino iodides, particularly for cases of (Z)-alkenes.[15] Furthermore, Harding had previously shown that cases of pyrrolidine formation by amidomercuration proceed with 2,5-trans stereoselectivity.[16] Treatment of our secondary amine **19** with iodide (1.1 equiv), 0 → 22 °C) afforded direct conversion to (+)-croomine (**1**).[17] This double cyclization involved formation of the initial iodoamination product **20** followed by nucleophilic anchimeric assistance by the



**20**



**21**

vicinal tertiary amine. Intramolecular capture of the intermediate aziridinium salt **21** by participation of the proximate ester resulted in net retention of carbon configuration ($C_{14}$). Synthetic (+)-croomine was compared with spectral data for the natural product.[18] An unambiguous assignment of our synthetic material was provided by X-ray crystallographic analysis of the corresponding methiodide salt of **1**.[19]

In conclusion, our route to (+)-croomine has demonstrated the utility of the Staudinger reaction for preparation of 1-azabicyclo[5.3.0]decanes. An iodine-induced cyclization of our bishomoallylic amine occurred with a stereocontrolled intramolecular nucleophilic capture of the intermediate aziridinium salt by the proximate methyl ester, providing a vicinal pyrrolidino butyrolactone. Further efforts toward the *Stemona* alkaloids are in progress.

**Acknowledgment.** We thank the National Science Foundation (Grant CHE 8618955) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also acknowledge the National Institutes of Health for partial funding of these efforts. We gratefully acknowledge the efforts of Michael Dart for large-scale preparations of many intermediates along the synthetic route.

**Supplementary Material Available:** Spectral data for key substances (5 pages). Ordering information is given on any current masthead page.

(12) Closely related phosphoranes have been examined. Bergelson, L. D.; Shemyakin, M. M. *Angew. Chem., Int. Engl. Ed.* **1964**, *3*, 250. Preparation of **15** will be available in the full account of this work.

(13) For a review: Gololobor, Y. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437. For examples: Lambert, P. H.; Vaultier, M.; Carrié, R. *Chem. Commun.* **1982**, 1224. Pilard, S.; Vaultier, M. *Tetrahedron Lett.* **1984**, *25*, 1555. Ackrell, J.; Galeazzi, E.; Muchowski, J. M. *Can. J. Chem.* **1979**, *57*, 2696.

(14) Preliminary investigations of substrates leading to a primary amino group at $C_{9a}$ had demonstrated a facile intramolecular acyl transfer to form the six-membered lactam.

(15) Williams, D. R.; Osterhout, M. H.; McGill, J. M. *Tetrahedron Lett.*, in press.

(16) Harding, K. E., Burks, S. R. *J. Org. Chem.* **1984**, *49*, 40.

(17) This reaction proceeded slowly with incomplete conversion to (+)-croomine (25% yield) and reisolation of starting amine **19** (50–60%), which was readily recycled to improve the overall production of **1**. However, increased amounts of iodine and/or longer reaction times led to numerous products. Oxidation of the pyrrolidine ring of **1** to the corresponding pyrrole is well known.[2]

(18) We gratefully acknowledge Dr. Tadataka Noro (Shizuoka College of Pharmacy, Shizuoka-shi, Japan) for comparison spectra (IR, $^1H$ NMR, and $^{13}C$ NMR) of the natural product.

(19) Structure assignment of our synthetic material was unambiguously confirmed by a single-crystal X-ray diffraction study (at −145 °C) of the monohydrate of the methiodide salt of **1** (mp 187–192 °C; acetone). All atoms were located and refined to final residuals of $R_{(F)} = 0.085$ and $R_{w(F)} = 0.075$. Complete crystallographic data are available from the Indiana University Chemistry Library. Request Molecular Structure Center Report 88128.

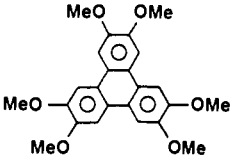
## Synthesis of an Ambient Temperature Stable, High Spin Density Organic Solid with an Anomalously Small Interspin Coupling

Long Y. Chiang,* D. C. Johnston,† D. P. Goshorn, and A. N. Bloch

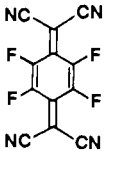
*Corporate Research Laboratory*
*Exxon Research and Engineering Company*
*Annandale, New Jersey 08801*

*Received February 16, 1988*

To date, ambient temperature stable organic ferromagnets still remain as challenging compounds to be synthesized.[1] There are two important prerequisites for the generation of room temperature magnets: ambient temperature stable high spin density in the bulk of the material and a significant ferromagnetic interaction between spins. Unfortunately, most organic solids are either diamagnetic or weakly paramagnetic with a low spin density. Recently, several ground-state triplet molecules, such as dicationic 2,3,6,7,10,11-hexamethoxytriphenylene[2] (**1** (HMT)), its derivatives, and oc-



**1**, HMT



**2**, $TCNQF_4$

†Present address: Physics Department, Ames Laboratory, USDOE, Iowa State University, Ames, IA 50011.

(1) Several theoretical models and experimental approaches have been proposed. McConnell, H. *Proc. R. A. Welch Found. Conf.* **1967**, *11*, 144. McConnell, H. *J. Chem. Phys.* **1963**, *39*, 1910. Ovchinnikov, A. A. *Dokl. Akad. Nauk SSSR* **1977**, *236*, 928. Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297. Buchachenko, A. L. *Dokl. Akad. Nauk SSSR* **1979**, *244*, 1146. Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H. *J. Am. Chem. Soc.* **1984**, *106*, 6450. Sugawara, T.; Murata, S.; Kimura, K.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 5293. Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927. Breslow, R.; Jaun, B.; Kluttz, R.; Xia, C. *Tetrahedron* **1982**, *38*, 863. Dormann, E.; Nowak, M. J.; Williams, K. A.; Angus, R. O.; Wudl, F. *J. Am. Chem. Soc.* **1987**, *109*, 2594. Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. Torrance, J. B.; Oostra, S.; Nazzal, A. *Synth. Met.* **1986**, *19*, 709.

0002-7863/89/1511-1925$01.50/0 

tadecahydrohexaazacoronene[3] (HOC), have been synthesized for use as precursors in the preparation of high-spin solid-state organic materials. However, these dicationic triplet organics are not thermally stable. For example, the triplet state of dicationic HMT in solution was found to be stable only below the cryogenic temperature.[2a]

Here we report that triplet dicationic HMT molecules, after a reaction of HMT with certain acceptors and a doping process, can be stabilized in the solid state at ambient temperature to form novel organic charge-transfer salts possessing a high spin density with an anomalously small interspin coupling. The optimum organic acceptor for this study was found to be 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (**2** ($TCNQF_4$)). The resulting reddish purple crystalline complex possesses a molecular composition $(HMT)_2$–$TCNQF_4$ (**3**).[4,5]

Magnetic susceptibility and ESR[6] studies were performed on chemically doped samples of $(HMT)_2$–$TCNQF_4$. The undoped $(HMT)_2$–$TCNQF_4$ microcrystalline solid was studied first and proved to be only weakly paramagnetic according to ESR susceptibility measurements. In fact, the static susceptibility data indicated a spin density corresponding to only 0.1 mol % spins $^1/_2$. The doping process was carried out at the solid state of the $(HMT)_2$–$TCNQF_4$ complex with arsenic pentafluoride gas. From this process we found that the contents of arsenic fluorides varied from 27% by weight to 62% by weight, which corresponds to a molecular formula $(HMT)_2$–$TCNQF_4$–$(AsF_{5.5})_y$ (**4**, $y$ = 2.0–8.4). It was reported that the main fraction of arsenic fluorides incorporated in $AsF_5$–doped polyaromatics is a complex form of monoanionic $AsF_5$–$AsF_6$.[7] This is supported by the magnetic data of **4** at the low doping level (complex **5**) showing a matched number of spins per complex unit between calculation and an experimental and IR spectroscopic study of our doped complex, which showed two strong distinguishing bands at 400 and 700 $cm^{-1}$. However, more complicated reactions leading to other types of arsenic fluoride cannot be ruled out in this doping process.

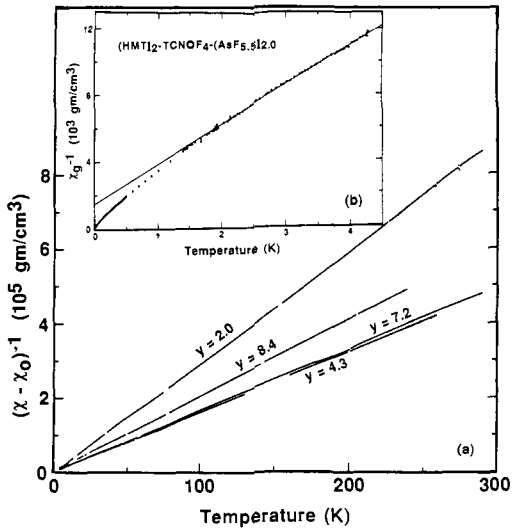



**Figure 1.** Temperature dependence of reciprocal magnetic susceptibility of (a) $(HMT)_2$–$TCNQF_4$–$(AsF_{5.5})_y$ complexes in the solid state, where $y$ = 2.0, 4.3, 7.2, and 8.4 and (b) the same complex with $y$ = 2.0 at temperatures between 0.018 and 4 K.

The samples used in the magnetic susceptibility study were prepared by a 3-min doping, a 1-h doping, a 3-h doping, and a 9-h doping to give complexes **5** ($y$ = 2.0 of **4**), **6** ($y$ = 4.3 of **4**), **7** ($y$ = 7.2 of **4**), and **8** ($y$ = 8.4 of **4**), respectively. The inverse susceptibilities per gram of $(HMT)_2$–$TCNQF_4$ are shown in Figure 1a, corrected for the ferromagnetic impurities and the temperature-independent diamagnetic susceptibilities ($\chi_0$). These constants, as well as the Curie constants $C$ and Weiss temperatures $\Theta$ were determined from least-squares fits of the data above ~4 K to the relation $\chi = \chi_0 + C/(T - \Theta)$. As seen in Figure 1a, the data follow this relation very well. The Curie constants $C_M$ ($(cm^3\ K)/mol$) for complexes **5**, **6**, **7**, and **8** were found to be 0.366, 0.677, 0.661, and 0.534, respectively. They are large, corresponding to large spin densities ($n$) of 1.0, 1.55, 1.52, and 1.31 spins $^1/_2$ per formula unit, respectively. The magnetic interactions between the spins, as indicated by the magnitudes of $\Theta$, are anomalously small (only −0.6 K for complexes **5** and **6** and −0.7 K for complexes **7** and **8**) for an organic compound with such a high spin density, and the negative sign of $\Theta$ indicates that the interactions are antiferromagnetic in nature (but see below).

The fact that $\Theta$ is nonzero for these complexes and the presence of large spin densities suggest that cooperative magnetic transitions may occur below 1 K. The susceptibility measurements were, therefore, extended to 0.02 K using a dilution refrigerator. The results for complex **4** are shown in Figure 1b (0.02–1.6 K), along with data obtained with the vibrating-sampling magnetometer above 1.3 K. In contrast to the Curie–Weiss behavior above 3 K, the inverse susceptibility at lower temperatures tends toward a Curie law with $\Theta$ = 0. This interesting behavior below 1 K could result from a number of mechanisms; e.g., the sample could contain different magnetic species with different Weiss temperatures, $\Theta_1 \sim 0$ and $\Theta_2 \sim -0.5$ K. At the lowest temperatures, the former species would dominate the susceptibility. Alternatively, the behavior in Figure 1b could be a "single-ion" effect, in which case the parameter $\Theta$ would not be viewed as reflecting an interaction between the spins.

For complex **5** with the lowest doping level, the spin density $n$ = 1 spin per $(HMT)_2$–$TCNQF_4$ complex. With increasing doping level, $n$ reaches a maximum of 1.6 spins $^1/_2$ per $(HMT)_2$–$TCNQF_4$ complex at $y$ = 4.3 but then decreases. These decreases in $n$ with increasing doping level evidently indicate that nonmagnetic charged states are becoming occupied. Finally, for $n > 1$ it seems plausible that $S$ = 1 triplet states might form and be occupied in the $(HMT)_2$–$TCNQF_4$ complex, in view of the mixed-stack structure of the compound. Magnetization isotherms up to 65 kG at 1.3 and 4.2 K, coupled with the results of the above

(2) (a) Bechgaard, K.; Parker, V. D. *J. Am. Chem. Soc.* **1972**, *94*, 4749. (b) Musgrave, O. C.; Webster, C. J. *J. Chem. Soc.* **1971**, 1397. Chiang, L. Y.; Johnston, D. C.; Stokes, J. P.; Bloch, A. N. *Synth. Met.* **1987**, *19*, 697.

(3) Breslow, R.; Maslak, P.; Thomaides, J. *J. Am. Chem. Soc.* **1984**, *106*, 6453. LePage, T. J.; Breslow, R. *J. Am. Chem. Soc.* **1987**, *109*, 6412. Thomaides, J.; Maslak, P.; Breslow, R. *J. Am. Chem. Soc.* **1988**, *110*, 3970.

(4) The oscillation Weissenberg photograph of crystal **3** gave unit cell parameters $a$ = 30 Å (roughly twice the HMT molecular diameter), $b$ (stacking direction along the needle axis of crystal) = 9.9 Å, and $c$ (very disordered). The $b$-axis lattice constant is 3 times the thickness of an aromatic molecule. This indicates that two HMT molecules alternate with one $TCNQF_4$ molecule in a one-dimensional array along the needle axis in a structure of ...DADDAD... The large disorder along the $c$-axis possibly results from the fact that HMT and $TCNQF_4$ are quite different in size and symmetry. In this particular combination of molecular ratio and stacking nature, the order in two dimensions favors disorder in the third dimension.

(5) The indirect evidence of the mixed-stack structure of **3** is derived from its transport properties. The four-probe room temperature resistivity of crystal **3** along the needle axis was found to be $10^{10}$ Ω cm. If complex **3** has a segregated-stack structure, with a partial charge transfer (0.2 charge per $TCNQF_4$) between HMT and $TCNQF_4$, it should give an appreciable conductivity such as that of an organic metal or semiconductor. Therefore, the observed high resistivity of complex **3** in the insulating region along the stacking direction is consistent with the mixed-stack structure nature of the crystal. In addition, to date nearly all the Mott–Hubbard insulating segregated-stack $TCNQF_4$ salts have a full charge transfer between D and A, such as the HMTSF–$TCNQF_4$, HMTTF–$TCNQF_4$, TTF–$TCNQF_4$, TMTTF–$TCNQF_4$, and TMTSF–$TCNQF_4$ salts (references in: Chappell, J. S.; Cowan, D. O.; Bryden, W. A.; Stokes, J. P.; Bloch, A. N. *J. Am. Chem. Soc.* **1981**, *103*, 2442).

(6) Chiang, L. Y.; Thomann, H. The triplet resonances of dicationic HMT in the solid state of doped complex **4** ($y$ = 8.4), stable at temperatures from 5 to 298 K, was observed in the ESR study. The triplet spectrum shows the zero-field splitting parameters $D$ = 0.038 $cm^{-1}$ and $E \approx 0$, consistent with the trigonal symmetry of the parent molecule and with previous measurements of the triplet state of HMT in solution.[2a] The measured magnetic susceptibilities of this complex as described in this report, showing linear relationships between the inverse susceptibilities vs temperature and following the Curie–Weiss law from room temperature to near 1 K, reflect that the observed triplet state of dicationic HMT in the solid is a ground state. In addition, without the $TCNQF_4$ complexation, no triplet resonances of dicationic HMT were detected in the solid of HMT–$(AsF_{5.5})_{4.1}$, which has a segregated structure (...DDD...) and was prepared by the same method as that for complex **4**.

(7) Ebert, L. B.; Mills, D. R.; Scanlon, J. C. *Mater. Res. Bull.* **1979**, *14*, 1369. Ebert, L. B.; Selig, H. *Synth. Met.* **1981**, *3*, 53. Ebert, L. B.; Mills, D. R.; Scanlon, J. C.; Selig, H. *Mater. Res. Bull.* **1981**, *16*, 831.

low-field susceptibility measurements, are consistent with this possibility. These data suggest that up to ~50% of the magnetization at low temperatures may arise from $S = 1$ spin triplets, the remainder coming from $S = {}^1/_2$ doublets. Our recent ESR measurements do, in fact, conclusively demonstrate the occurrence and evolution of spin triplets with increasing doping level.[6]

In conclusion, we describe for the first time a synthetic method to introduce low-spin $TCNQF_4$ as molecular spacers in the solid state of $(HMT)_2$-$TCNQF_4$-$(AsF_{5.5})_y$ to separate high-spin HMT molecules into molecular domains that avoids the spin pairing between adjacent HMT radicals. This synthetic manipulation results in stabilization of the triplet state of dicationic HMT and ambient temperature stable organic solids possessing a high spin density on the order of 1.0-1.6 spins ${}^1/_2$ per formula unit with an anomalously small interspin coupling. Since stable ground-state high-spin organics are thought to be essential components in the design of organic ferromagnetic solids, the results suggest that $(HMT)_2$-$TCNQF_4$ may be a good model complex for the study of organic ferromagnets. Also the observation encourages us to study further the conditions necessary to achieve ferromagnetism in this type of organic material system.[8]

(8) Cowan, D. O.; Wiygul, F. M. *C&EN* July 21, 1986, 28-45.

## Calibration of the Bicyclo[2.1.0]pent-2-yl Radical Ring Opening and an Oxygen Rebound Rate Constant for Cytochrome P-450†

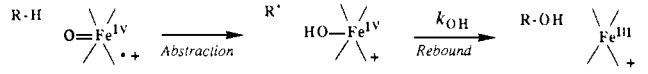
Vincent W. Bowry,‡ Janusz Lusztyk, and K. U. Ingold*

*Division of Chemistry*
*National Research Council of Canada*
*Ottawa K1A 0R6, Canada*
*Received October 6, 1988*

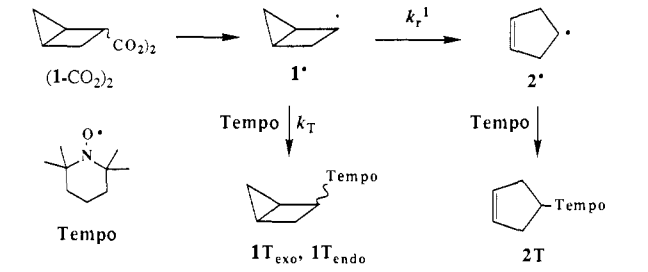
Cytochrome P-450 catalyzed oxidation (hydroxylation) of hydrocarbons[1] is believed to occur by a mechanism involving hydrogen atom abstraction from the substrate (R-H) followed by rapid transfer of HO• to the resulting alkyl radical (R•). This so-called *oxygen rebound mechanism*[1] is consistent with reports of allylic and stereo- and regiochemical scrambling and of large *intrinsic* or *intramolecular* deuterium kinetic isotope effects in P-450 oxidations. *Oxygen rebound* has supplanted an earlier concerted mechanism[2] which was proposed to account for the (then) preponderance of regio- and stereoselectivity and for the small *intermolecular* deuterium kinetic isotope effect.[1]

In an exciting and incisive investigation, Ortiz de Montellano and Stearns[3] have used the *radical-clock* method[4] to probe the mechanism and kinetics of the hydroxylation process at the in vivo temperature of 37 °C: methylcyclopropane, which would be hydroxylated via the cyclopropylmethyl (CPM) radical,[5,6] afforded only the unrearranged alcohol, viz. cyclopropanemethanol; bicyclo[2.1.0]pentane, on the other hand, afforded a mixture of both the corresponding unrearranged *and* rearranged alcohols in ca. 7:1 molar ratio. The latter result indicates that ring-opening of the intermediate bicyclo[2.1.0]pent-2-yl radical (**1**•) competes with the hydroxyl radical transfer or *rebound* step, and, since these processes are in direct competition, the implication[7-9] is that $k_{OH}$

**Scheme I**




**Scheme II**




*Pseudo-first-order Kinetic Equation:* $k_r^1/k_T = [\text{Tempo}].[2T]/([1T_{exo}]+[1T_{endo}])$

$\approx 7k_r^1 \gg k_r^{CPM}$. We report herein the first measurement of $k_r^1$ which, when combined with Ortiz de Montellano's P-450 data, provides the first estimate of $k_{OH}$ for this species.

Both EPR spectroscopy[10-12] and Ortiz de Montellano's P-450 work[3] show that the rearrangement of **1**• → **2**• must be extremely rapid relative to the cyclopropylmethyl ring-opening, and only a chemical trapping procedure using a superbly efficient trap for carbon radicals seemed likely to provide a reliable value for $k_r^1$. Various considerations, including in particular the fact that trapping rate constants have been reliably measured and been found to be almost diffusion controlled,[13,14] do not depend significantly on alkyl radical structure,[6,13,14] and the fact that at 37 °C the trapping agent could, if necessary, be used as the neat liquid (6 M) led us to choose Tempo as our trap. Typically, the neat diacyl peroxide[15,16] $(1\text{-}CO_2)_2$ was added to a stirred, preheated (37 °C) solution of Tempo (30-fold excess) in chlorobenzene (for 1-5 M Tempo) or 2,2,4-trimethylpentane (<1 M Tempo). Nitroxide-induced decomposition[18] of the peroxide afforded reaction

† Issued as NRCC No. 29981.

‡ NRCC Research Associate, 1988-89.

(1) For a detailed discussion and leading reference, see: Ortiz de Montellano, P. R. In *Cytochrome P-450: Structure, Mechanism, and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986; pp 217-271. See, also: McMurry, T. J.; Groves, J. T. on pp 3-5.

(2) Hamberg, M.; Bjorkhem, I. *J. Biol. Chem.* **1971**, *246*, 7411-7416.

(3) Ortiz de Montellano, P. R.; Stearns, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 3415-3420.

(4) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317-323.

(5) Cyclopropylmethyl radical ring opens with a rate constant[6] $k_r^{CPM} = 1.2 \times 10^8\ M^{-1}\ s^{-1}$ at 37 °C.

(6) Beckwith, A. L. J.; Bowry, V. W.; Moad, G. *J. Org. Chem.* **1988**, *53*, 1632-1641.

(7) A word of caution: in making use of the alcohol product ratios to calculate $k_{OH}$ we have assumed that rearranged radicals are efficiently converted into alcohols. However, many species which rearrange during hydroxylation are known to destroy the P-450 catalyst, presumably without formation of the alcohol.[8] The (kinetic) effect of this and of other possible non-alcohol-forming reactions[9] of the rearranged substrate radical may need to be investigated.

(8) Catalyst turnover vs P-450 destruction data[3] indicate that this would only have a minor effect on kinetic data for bicyclopentane since the rearranged alcohol is formed about six times more rapidly than P-450 destruction. On the other hand, if one assumes **1**• and CPM have the same *rebound* rate constant, viz. $2 \times 10^{10}\ s^{-1}$, one may readily calculate that 3-buten-1-ol *should* be formed at about the same rate that P-450 is being destroyed by cyclopropylmethane!

(9) For example, there is evidence for radical diffusion from model catalysts, see: Groves, J. T.; Nemo, T. E. *J. Am. Chem. Soc.* **1983**, *105*, 6243-6248. However, this is less likely for P-450.

(10) Whereas CPM may be observed by EPR at temperatures up to -120 °C,[11] Jamieson et al.[12] found that **1**• had completely rearranged to 3-cyclopentenyl radical, **2**, even as low as -160 °C, which indicates that $k_r^1 \gg k_r^{CPM}$ at low temperature. From the experimental conditions the authors estimated $k_r^1 \geq 10^2\ s^{-1}$ at -160 °C and $E_A \leq 5.7$ kcal/mol with log $A = 13.0$ ($\therefore k_r^1 \geq 10^9\ s^{-1}$ at 37 °C).

(11) Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1978**, *98*, 7024-7026.

(12) Jamieson, C.; Walton, J. C.; Ingold, K. U. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1366-1371.

(13) Radical clock calibrations[6] indicate $k_T^{1°\text{-alkyl}} \approx k_T^{2°\text{-alkyl}}$, and time-resolved radical quenching data[14] indicate that even 3°-alkyl and benzylic radicals are trapped nearly as rapidly.

(14) Chateauneuf, J.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1988**, *53*, 1629-1632.

(15) Bis(bicyclo[2.1.0]pentane-2-carbonyl) peroxide $(1\text{-}CO_2)_2$ and bis(cyclopent-3-enecarbonyl) peroxide $(2\text{-}CO_2)_2$ were prepared by standard procedures[6] from the corresponding acids.[16,17]

(16) Brooks, P. R.; Brophy, B. V.; Bernard, V. *J. Chem. Soc., Perkin Trans 1* **1985**, 2509-2513.

(17) Cremer, S. E.; Blankenship, C. *J. Org. Chem.* **1982**, *47*, 1629-1632.

(18) Moad, G.; Rizzardo, E.; Soloman, D. H. *Tetrahedron Lett.* **1981**, *22*, 1165-1168.

0002-7863/89/1511-1927$01.50/0 Published 1989 by the American Chemical Society