Table I. Ring Currents<sup>a</sup> and <sup>1</sup>H NMR Chemical Shifts<sup>b</sup> for Hydrocarbons 7, 8, and 6



<sup>a</sup> Benzene = +1.00. This work; see ref 13a. <sup>b</sup> In ppm downfield from Me<sub>4</sub>Si. 300-MHz spectra taken in CDCl<sub>3</sub>, Me<sub>4</sub>Si internal reference. Multiplets analyzed by LAOCOON III (ref 10).  $^{c}$  Assignments given here assume a slightly paratropic ring current for A ring of 6. For an explanation of possible ambiguity, see ref 13b,c,d.

benzenoid protons in 6 show an upfield shift of 2.41 ppm relative to 5, while the  $\alpha$  and  $\beta$  cycloocta protons are shifted upfield by 3.15 and 1.73 ppm, respectively. The observed magnetotropism for this and similar compounds<sup>11</sup> appears to be well described by an iterative Hückel-McWeeny ring current model<sup>12-14</sup> (see Table I).

It is worthwhile to consider the qualitative origin of benzenoid atropism in 6. In addition to three rings of [4n] type, compound 6 has a coronoid topology with a central ring of  $[4]\pi$  and a periphery of  $[16]\pi$ . While the importance of peripheral circuits has been shown for some systems,<sup>8,15</sup> the perturbation by the central substructure may be so great as to remove any simple predictive capability based solely upon the periphery.<sup>16</sup> Such peripheral analyses are, to some degree, implicit in the consideration of all conjugated circuits, as in the approaches of Randič<sup>17</sup> and Gomes.<sup>18</sup> According to these methods, benzenoid atropism in 6 arises from the net cancellation of numerous Hückel and anti-Hückel conjugated circuits, as opposed to the situation encountered in the Clar-Robinson "nonsextet" rings of polycyclic aromatics,<sup>19</sup> wherein reduced diatropism results from the virtual

(12) McWeeny, R. Mol. Phys. 1958, 1, 311.

(13) (a) Ring currents were calculated by a self-consistent HMO technique used previously (ref llb). For an excellent discussion of ring currents in paratropic systems, see the following references. (b) Coulson, C. A.; Mallion, R. B. J. Am. Chem. Soc. 1976, 98, 592-598. (c) Gomes, J. A. N. F.; Mallion, R. B. J. Org. Chem. 1981, 46, 719-727. (d) Mallion, R. B. Pure Appl. Chem. 1980, 52, 1541-1548

(14) Several more highly fused derivatives of 6 and 8 have now been prepared, and the observed proton chemical shifts correlated with ring current calculations. Complete synthetic, spectroscopic, and theoretical details will be presented in a full paper. (15) (a) Platt, J. R. J. Chem. Phys. **1954**, 22, 1448–1458. (b) Müllen, K.

Helv. Chim. Acta 1978, 61, 2307. (c) Minsky, A.; Meyer, A. Y.; Hafner, K.; Rabinovitz, M. J. Am. Chem. Soc. 1983, 105, 3975-3981.

(16) This point is particularly evident in the case of cycloocta[def]biphenylene 8

(17) (a) Randić, M. J. Am. Chem. Soc. 1977, 99, 444-450; (b) Pure Appl. Chem. 1980, 52, 1587-1596.

(18) Gomes, J. A. N. F. *Theor. Chim. Acta* 1981, 59, 333-356.
(19) (a) Clar, E. "The Aromatic Sextet"; Wiley: London and New York, 1972. (b) Clar, E. "Polycyclic Hydrocarbons"; Academic Press: London and New York; Springer-Verlag: Berlin, 1964; Vol. 1.

or complete absence of conjugated circuits involving the affected ring.176

Registry No. 1, 63548-78-7; 2, 87729-44-0; 3, 87739-06-8; 4, 87729-45-1; 5, 87729-46-2; 6, 64074-44-8; 7, 259-79-0; 8, 36230-20-3.

## A $\beta$ -Metal Ketone Strategy. Reactions of Siloxycyclopropanes with Silver(I) Tetrafluoroborate and Copper(II) Tetrafluoroborate Leading to 1,6-Diketones

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Development of new synthetic methodology for bond connection  $\beta$  to carbonyls constitutes one of the main challenging themes in modern organic synthesis.<sup>1</sup> For this purpose the use of  $\beta$ -metal-substituted ketones 1 would be most straightforward. However,



the reported result of the reaction of 1 where the metal M is an alkali metal seems discouraging because of the inevitable isomerization of 1 to more stable form 2 by internal nucleophilic addition.<sup>2,3</sup> For the efficient carbon-carbon bond formation  $\beta$ to carbonyls the use of other elements such as transition metals for M in 1 seems attractive, although in general they are hardly accessible.4,5

Our strategy for 1 is that electrophilic ring opening of siloxycyclopropane 3 by naked (or ligand free) transition-metal ions will give  $\beta$ -transition-metal ketone 1 efficiently with elimination of a trialkylsilyl moiety.<sup>6</sup> Thus, the reactions of siloxycyclopropane 3 with silver(I) tetrafluoroborate, AgBF<sub>4</sub>, and copper(II) tetrafluoroborate,  $Cu(BF_4)_2$ , have been studied. We wish to report here the new carbon-carbon bond-forming reaction in which the intervension of  $\beta$ -silver- or  $\beta$ -copper-substituted ketone as intermediates is suggested.

1-(Trimethylsiloxy)bicyclo[4.1.0]heptane(4) (5 mmol)<sup>7</sup> was added to the suspension of silver tetrafluoroborate (AgBF<sub>4</sub>, 6mmol) in anhydrous ether at -20 °C, under atmosphere of nitrogen. Over a period of 15 min the temperature was raised to 15 °C, while a silver mirror gradually appeared on the wall of the reaction vessel. After another 15 min, workup (aqueous NH<sub>4</sub>Cl and aqueous NaHCO<sub>3</sub>) and purification upon column

(3) A review for synthetic equivalent of  $\beta$ -lithio ketones; see: Werstiuk, N. H. Tetrahedron 1983, 35, 205.

(4) Stable  $\beta$ -transition-metal ketones 1; see for (a) M = Hg: DePuy, C. H.; Lanen, J. U. J. Org. Chem. 1974, 39, 3360. (b) M = Pt: Green, M.; Howard, J. A. K.; Mitrprachachon, P.; Pffefer, M.; Spencer, J. L.; Stone, F. G. A.; Woodward, P. J. Chem. Soc. Dalton Trans. 1979, 306. (c) M = Co: Wakatsuki, Y.; Aoki, K.; Yamazaki, H. J. Am. Chem. Soc. 1974, 96, 5284.
 (d) M = Mn: Bennet, W. A.; Robertson, G. B.; Watt, R.; Whimp, P. O. J. Chm. Soc., Chem. Commun. 1971, 752. (e) M = Fe: Jensen, J. E.; Campbell, L. L.; Nakanishi, S.; Flood, T. C. J. Organomet. Chem. 1983, 244, 61.

(5) Recently, Kuwajima and Nakamura have reported the aldol condensation via and isolation of  $\beta$ -titano esters; see: Nakamura, E; Kuwajima, I. J. Am. Chem. Soc. **1983**, 105, 651; **1977**, 99, 7360.

(6) Synthesis of  $\beta$ -mercuri ketones from siloxycyclopropanes and some transformations from them via transmetalation; see: Ryu, I.; Matsumoto, K.;

Ando, M.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* 1980, 21, 4283.
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<sup>(1)</sup> Seebach, D. Angew. Chem., Int. Ed. Engl. 1979, 18, 239.

<sup>(2)</sup> Hamon, D. P. G.; Sinclair, R. W. J. Chem. Soc., Chem. Commun. 1968, 890.

Scheme I



chromatography (SiO<sub>2</sub>/n-hexane-Et<sub>2</sub>O) afforded a 1,6-diketone, 1,2-dicyclohexan-2-on-1-ylethane (7) (70% GLC yield).8

The desilylative dimerization of the siloxycyclopropane 4 to the 1,6-diketone 7 occurred with site-selective cleavage of the cyclopropane ring at the bond a shown in Scheme I, and no product arising from bond b scission was obtained.<sup>9</sup> This dimerization  $\beta$  to carbonyls may be well accounted for by the intervension of  $\beta$ -silver ketone intermediate 6 (Scheme I). The electrophilic attack of Ag<sup>+</sup> at the least sterically crowded site of 4 followed by elimination of  $(CH_3)_3SiF^{10}$  via 5 would give 6 which then would undergo dimerization to afford 7.<sup>11</sup> The well-documented fact that primary alkyl silver(I) dimerizes to bis(alkane) is consistent with above postulation.<sup>12</sup> Electrophilic ring opening of cyclopropanes by Ag<sup>+</sup> has also ample precedents.<sup>13</sup> The reaction of some other siloxycyclopropanes with AgBF<sub>4</sub> are shown in Table I.

Interestingly, copper(II) tetrafluoroborate  $(Cu(BF_4)_2)^{14}$  (7) mmol), less expensive and less hygroscopic than  $AgBF_4$ , also reacted with 4 (5 mmol) at 15 °C in  $Et_2O$  (5 mL) to give even higher yield of the same product, 7 (87% GLC and 80% isolated yields). Again the reaction was site selective at a in 4. Table I also contains the results of the reaction of siloxycyclopropanes with  $Cu(BF_4)_2$  in  $Et_2O$  at 15 °C.

Some characteristics of the present  $Cu(BF_4)_{2}$ -induced coupling may deserve comments. The diketone 7 was obtained in good yield in CH<sub>3</sub>COOEt (86%) and even in protic solvents, such as EtOH (86%), t-BuOH (89%), and MeOH (37%).<sup>15</sup> When the reaction of 4 (1 mmol) was carried out using 1/2 molar equiv of Cu(BF<sub>4</sub>)<sub>2</sub> (0.5 mmol) in Et<sub>2</sub>O (1 mL), a clean copper mirror gradually

(9) It appears general that the ring opening of 4 occurs at the least hin-dered site; see for (a) bromination: Murai, S.; Seki, Y.; Sonoda, N. J. Chem. Soc., Chem. Commun. 1974, 1032. (b) Isomerization with ZnI2: Murai, S.; Aya, T.; Renge, T.; Ryu, I.; Sonoda, N. J. Org. Chem. 1974, 39, 858. Ryu, ; Murai, S.; Otani, S.; Sonoda, N. Tetrahedron Lett. 1977, 1995. (c) Mercuration: ref 6

(10) Distilled out directly from the reaction mixture; <sup>1</sup>H NMR  $\delta$  0.21 (d,

 $J_{HF} = 7$  Hz). (11) Alternatively, the (CH<sub>3</sub>)<sub>3</sub>Si group in 4 might be converted to five coordinated  $F(CH_3)_3Si^-$  group before the attack of Ag<sup>+</sup>. At the present stage we can not eliminate the possibility that the reaction might proceed via prior

We call not enhance the possionity that the reaction might proceed via prior formation of cyclopropoxy metal intermediates.
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(14) Durchased from Ventron Co. Prior to use dried and stored over P.0.

(14) Purchased from Ventron Co. Prior to use, dried and stored over P2O5 under reduced pressure.

Table I. Reaction of Siloxycyclopropanes with  $AgBF_4$  and  $Cu(BF_4)$ ,<sup>*a*</sup>

siloxycyclo- propane	reagent	product	yield, <b>6</b> %
Me <sub>3</sub> SiO Ph	AgBF <sub>4</sub> Cu(BF <sub>4</sub> ) <sub>2</sub>	Phr Ph	42 78
Me3Si0	Cu(BF <sub>4</sub> ) <sub>2</sub>	Ks June 25	ŝl
Me <sub>3</sub> Si0	AgBF <sub>4</sub>	Jerry K	68
Me <sub>3</sub> Si0	AgBF <sub>4</sub> Cu(BF <sub>4</sub> ) <sub>2</sub>	Ŝ~~Ţ	68 77
Me <sub>3</sub> Si0	AgBF <sub>4</sub> Cu(BF <sub>4</sub> ) <sub>2</sub>		70 87, <u>80</u>
Me <sub>3</sub> Si0	AgBF <sub>4</sub> Cu(BF <sub>4</sub> ) <sub>2</sub>		<u>68</u> 74
Me <sub>3</sub> Si0	Cu(3F <sub>4</sub> ) <sub>2</sub>		69
Me <sub>3</sub> S10	Cu(BF <sub>4</sub> ) <sub>2</sub>	j~?	70
Me <sub>3</sub> Si0	Cu(BF <sub>4</sub> ) <sub>2</sub>	$\langle \rangle$	63

<sup>*a*</sup> Reactions were performed on 1–5 mmol scale according to the procedure described in the text (for AgBF<sub>4</sub>, -20 to ~15 °C, 0.5-1 h; for  $Cu(BF_4)_2$ , 15 °C, 0.5–1 h) with  $Et_2O$  as solvent. No efforts were made to establish the ratio of meso and racemic isomers concerning the products obtainable from bicyclic substrates. <sup>b</sup> Determined by GLC. Isolated yields are underlined.

appeared on the surface of the reaction vessel, and 7 was obtained in 83% GLC yield. This implies that the Cu(II) salt can serve as two electron-oxidizing species through the overall process.

These results may be explained by assuming  $\beta$ -copper ketone 8 in a similar way as Scheme I.<sup>16</sup> Coupling of 8 would lead to



the formation of 7 and CuBF<sub>4</sub>, which in turn would disproportionate to  $Cu(BF_4)_2$  and Cu(0). Any ideas that the cleavage of the C-C bond in 4 by Ag<sup>+</sup> or Cu<sup>++</sup> would give free radical or cationic species seem unattractive, since such a process would give rise to more stable radical or cationic intermediate 9 as the results of central bond fission (cleave b in Scheme I).<sup>17,18</sup>

<sup>(8)</sup> Obtained as a mixture of meso and racemic isomers: mp 74-79 °C; ms, m/e 222 (M<sup>+</sup>), 204 (M<sup>+</sup> – H<sub>2</sub>O); <sup>1</sup>H NMR (CCl<sub>3</sub>, Me<sub>4</sub>Si)  $\delta$  1.94–2.60 (m); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  213.06 (s, C=O), 50.91, 50.58 (each d, methine C  $\alpha$  to C=O); IR (Nujol) 1700 cm<sup>-1</sup>. A multistep and low overall yield synthesis of 7 has previously been reported. See: Ghera, E.; Gibson, M.; Sondheimer, F. J. Am. Chem. Soc. 1962, 84, 2953.

<sup>(15)</sup> The reaction of 4 with AgBF<sub>4</sub> can be also conducted by using protic solvent such as MeOH (-20 to ~15 °C, 0.5 h, 50% yield). For examples of silver salt induced coupling of alkyl moieties that proceeded in protic solvents (MeOH or H<sub>2</sub>O), see: Brown, H. C.; Hebert, N. C.; Synder, C. H. J. Am. Chem. Soc. **1961**, 83, 1001. Theile, H. Z. Electrochem. **1974**, 49, 426.

<sup>(16)</sup> To our knowledge the related alkylcopper(II) species (RCu(II)X) analogous to that postulated here seem rare and have been postulated in the reaction of CuX<sub>2</sub> with organometallics (R<sub>4</sub>Pb or RHgX). See: (a) Clinton, N. A.; Kochi, J. K. J. Organomet. Chem. **1972**, 42, 241; Ibid. **1973**, 56, 243. (b) Beletskaya, I. P.; Artamkina, Y. A.; Reutov, O. A. Ibid. 1975, 99, 343. An alternative mechanism via  $\beta$ -acylalkylcopper(I) may also be envisioned.  $Cu(BF_4)_2$  could effect oxidative dimerization of  $\beta$ -acylalkylcopper(I) inter-Bediates, if formed, from a siloxycyclopropane and Cu(I)BF<sub>4</sub> obtainable from Cu(BF<sub>4</sub>)<sub>2</sub> and Cu(0). See: (a) Whitesides, G. M.; Stedronsky, E. R.; Casey, C. P.; Filippo, J. S., Jr., J. Am. Chem. Soc. 1978, 92, 1426. (b) Tamura, M.; Kochi, J. K. J. Organomet. Chem. 1972, 42, 205. (c) Reference 12b. (17) (a) Ito, Y.; Fujii, S.; Saegusa, T. J. Org. Chem. 1976, 41, 2073; Org. Such 2004, 2014; Constant Const

Synth. 1980, 59, 113. (b) Schaafsma, S. E.; Jorritsma, R.; Steinberg, H.; de Boer, T. S. Tetrahedron Lett. 1973, 827.

<sup>(18)</sup> The free radical pathway seems incompatible with the following observations: When the reaction was conducted in the presence of styrene or 2,3-dimethylbutadiene, any significant products with incorporation of these olefins were not formed. Furthermore, the reaction in the presence of pcymene, a good hydrogen donor, did not affect the product distribution.

Studies on the further use of intermediate 6 and 8 in synthesis as well as application of the  $\beta$ -metal ketone strategy to other naked (or ligand free) metal cations are in progress.

Acknowledgment. This work was supported in part by Grant-in-Aid for Special Project Research No. 57118002 provided by the Ministry of Education, Science, and Culture, Japan. We thank Shin-Etsu Chemical Industry Ltd. for the gift of trimethylchlorosilane.

Supplementary Material Available: Spectral data of products listed in Table I (7 pages). Ordering information is given on any current masthead page.

## (Iminomethylidene)phosphines (RP=C=NR)

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There has been much recent interest in compounds incorporating  $P=C^{2,3}$  and  $P=P^4$  double bonds. Furthermore, the stable (2,2dimethylpropylidyne)phosphine,  $(CH_3)_3CC \equiv P$ , featuring a PC triple bond has been prepared.<sup>5</sup> However, previous attempts to isolate cumulenes possessing a two-coordinate phosphorus atom, RP=C=X, have failed,  $^{2,3,6}$  except in a single case, the preparation of the stable and sterically protected  $(CH_3)_3CP = C = NC(CH_3)_3$ . We now wish to report a general method of preparation of unstable (iminomethylidene)phosphines (monophosphorus analogues of carbodiimides), their direct observation by IR and mass spectrometry, and their initial chemical reactions.

The required starting materials, (iminomethyl)phosphines 1, exist in equilibrium with carbamoylphosphines [(CH<sub>3</sub>)<sub>3</sub>SiP(R)- $CON(Ph)Si(CH_3)_3$  and smaller amounts of alkylidenephosphines  $RP=C(OSi(CH_3)_3)N(Ph)Si(CH_3)_3$ <sup>8</sup> In analogy with the reaction used in the preparation of  $(CH_3)_3CC = P_5^5$  the compounds 1 could be expected to eliminate hexamethyldisiloxane and thus give rise to the desired (iminomethylidene)phosphines, RP= C=NPh (Scheme I).

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In the event, the treatment of 1 with a catalytic amount of solid NaOH led only to the isolation of the dimers 3.9 3b and 3e were also obtained by spontaneous decomposition of the adducts 2b and

<sup>(1) (</sup>a) University of Marburg. (b) Present address: University of Stuttgart. (c) University of Mons. (2) Appel, R.; Knoll, F.; Ruppert, I. Angew. Chem. 1981, 93, 771; Angew.

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<sup>(9) (</sup>a) Satisfactory elemental analyses (C, H, N, P) were obtained for these compounds. (b) X-ray crystallographic determinations of 3c and 3d confirm the structure assignments. The two exocyclic phosphorus ligands are trans oriented. Full crystallographic data will be published: Becker, G.; Härer, J.; Riffel, H.; Uhl, G.; Wessely, H.-J., in preparation.