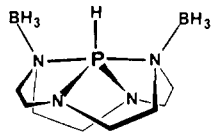
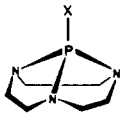


4

°C, absence of air-sensitivity, and absence of evolution of B_2H_6 on dissolution. The elemental analysis and mass spectrum, which exhibits the molecular peak, support its formulation.

The ^{31}P NMR spectrum of **4** in $CDCl_3$ solution exhibits a single sharp doublet at −28 ppm, characteristic of 5-connected phosphorus, with J_{P-H} = 790 Hz, confirming that the proton has not undergone the expected tautomeric shift to the nitrogen atom with concomitant P–N bond opening. The ^{11}B NMR spectrum consists of a quartet at −15.7 ppm (J_{B-H} = 100 Hz), a position usually found for N-coordinated BH_3 groups.[7] The ^{13}C NMR spectrum consists only of two signals of equal intensity, at +41.2 and +50.2 ppm; this can only be consistent with the presence of the two BH_3 groups on two nitrogen atoms symmetrically located in the macrocycle. The available structural data on fluorocyclenphosphorane,[8] bis(cyclenphosphorane),[2d] and molybdenum cyclamphosphoranide[4] all show the tendency of the pentavalent phosphorus atom to adopt a nearly perfect trigonal bipyramidal arrangement, in spite of the constraint imposed by the cycles; there is therefore a strong precedent to proposing that **4** adopts a similar arrangement. The BH_3 groups are then likely, both on kinetic and thermodynamic grounds, to be coordinated to the apical nitrogen atoms: these have been shown to undergo less $p\pi$–$d\pi$ interaction with phosphorus than those in equatorial positions[9] and hence are likely to manifest the greater basicity;[2e] then, even if the attack of the BH_3 groups were to occur on the equatorial nitrogen atoms, we would expect the structure to rearrange itself so as to bring the uncoordinated nitrogen atoms into the equatorial plane in which $p\pi$–$d\pi$ interactions are favored and the BH_3 coordinated nitrogen atoms, which have no electron left for back donation, into the apical positions.

Compound **4** is to our knowledge the first for which the BH_3–N–P–N–BH_3 pattern is established. Of two close analogues of **1a**, one, the tricyclic triaminophosphane **5**, was reported not

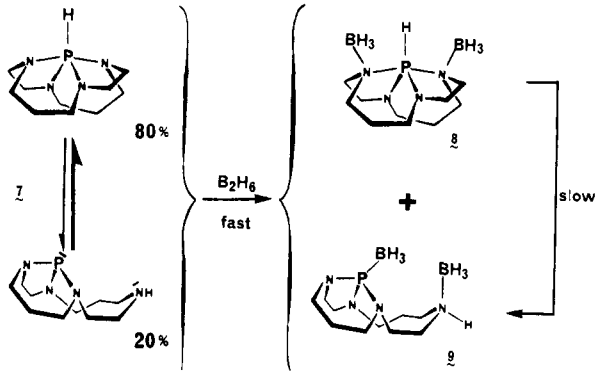


5: X = lone pair
6: X = S

to react with diborane; a solution of the other, **6**, the sulfide of **5**, was observed to absorb 1.85 equiv of BH_3; however, the nature of the crude insoluble (soluble but unstable in dimethylformamide) product isolated could not be established.[10] The gross difference in behavior of **1a** and **2** can probably be assigned both to a strong macrocyclic effect,[11] which in the former case favors the closed form, and to the presence in **1a** of apical N atoms, which are more basic in character.

The mono(borane) adduct of **1a** was not detected. Only the bis(borane) adduct **4** is formed even if only 0.5 mol equiv of B_2H_6 is used; half of the starting material is then recovered unreacted.

Preliminary investigations on cyclamphosphorane **7**, which is known to be in equilibrium with an open form in solution, reveal a more complex behavior: in comparable working conditions the addition of 1 mol equiv of B_2H_6 leads to a mixture from which 40% of closed bis(borane)–cyclamphosphorane **8**, analogous to **4**, and 15% of *open* bis(borane)–cyclamphosphane **9**, were isolated.



7 8 9

Their mass and NMR spectra support these formulations unambiguously [**8**, ^{31}P δ −45 (J_{P-H} = 780 Hz), ^{11}B δ −14.5; **9**, ^{31}P δ +115 (J_{P-B} = 95 Hz), ^{11}B δ −14.5, 43.0 Hz (J_{B-P} = 95 Hz)]. Both compounds are quite stable, as evidenced by their melting points: 117 °C for **8** and 147 °C, with decomposition, for **9**. Both compounds can be stored in the solid state for months without noticeable changes, but when **8** is left at room temperature in a sealed tube in CD_2Cl_2 solution, it converts, slowly but totally, to **9** in a matter of a few weeks.

Acknowledgment. We are grateful to Prof. J. E. Richman for a sample of cyclen.

Registry No. 1a, 64317-97-1; **4**, 84237-90-1; **7** (isomer 1), 64317-99-3; **7** (isomer 2), 71089-76-4; **8**, 84237-91-2; **9**, 84237-92-3; diborane, 19287-45-7.

1,1-Bis(benzenesulfonyl)cyclopropane: A Synthon for a Propylene 1,3-Dipole

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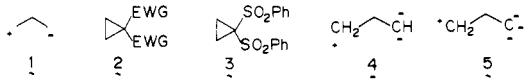
The development of 1,3-dipoles as basic building blocks have mainly focused on unsaturated systems. Trimethylenemethane[1] and oxatrimethylenemethane[2] synthons have been particularly fruitful. Their success stems from their inhibition toward self-annihilation either because of great strain or by π complexation to transition metals. The development of saturated analogues such as **1** becomes more devious since steric inhibition for closure to



a cyclopropane does not exist nor is stabilization by metal complexation easily available. Introduction of electron-withdrawing groups on the cyclopropane (i.e., **2**) facilitates the opening of this closed form of the dipole by nucleophiles[3-5]—thus making C(2)

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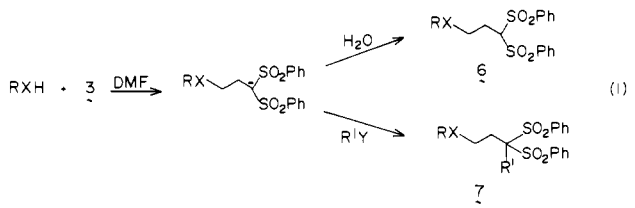
Table I. Ring Opening of 3 by Heteroatom Nucleophiles

entry	nucleophile	base	temp, °C	electrophile	product,[8] R, R′	mp, °C	yield,[a] %
1	PhSH	NaH	rt[b]	H_2O	6, PhS, H	114–116	95 (72)
2	PhSH	NaH	rt	CH_3I	7, PhS, CH_3	140–142	(91)
3	PhSH	NaH	rt	$H_2C{=}CHCH_2Br$	7, PhS, $CH_2CH{=}CH_2$	116–117	(47)
4	$PhCH_2OH$	KH	65	H_2O	6, $PhCH_2O$, H	92–93	(60)
5	$(C_2H_5)_2NH$	None	80	H_2O	6, $(C_2H_5)_2N$, H	94–95.5	(84)

[a] Number in parentheses represents yield of recrystallized product. [b] Room temperature.

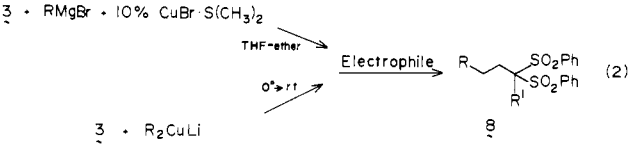
of **2** equivalent to a carbocationic center. Simultaneously, an anionic center is created at C(1) for further elaboration. The pioneering work of Danishefsky on developing 1,1-dicarboalkoxycyclopropanes takes advantage of the carbocationic character of **2**[5] but does not provide facile manipulation of the anionic enter since removal of the carboalkoxy groups is not a simple matter. Indeed, Danishefsky utilizes mainly the carboalkoxy group as his second point of attachment rather than C(1). Use of cyclopropylphosphonium salts combines nucleophilic opening of the cyclopropane ring with olefination to create a cyclopentene annulation.[6] We report that choosing EWG=$PhSO_2$ (i.e., **3**) provides a convenient synthon for **1**. Furthermore, since each sulfone can be cleaved to create a new carbanionic center, this new conjunctive reagent can serve as the equivalent of species such as **4** and **5**.

Peracetic acid oxidation of 1,1-bis(phenylthio)cyclopropane, conveniently available from acrolein and benzenethiol,[7] generates **3**,[8] a colorless crystalline solid, mp 145–146 °C. Its ^{13}C NMR spectrum [δ 58.75 (C(1)), 15.80 (C(2))] shows a considerable downfield shift of the α-carbon compared to 1,1-dicarbethoxycyclopropane [δ 41.29 (C(1)), 15.74 (C(2))]—a fact that suggests **3** would be more susceptible to nucleophilic attack than the latter. Indeed, sulfur, oxygen, and nitrogen nucleophiles smoothly open the ring as shown in eq 1 and Table I. Alkylation of the intermediate anion was demonstrated in the case of the sulfur nucleophile (entries 2 and 3).



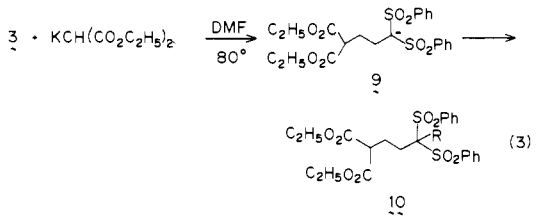
(1)

One advantage of this conjuctive reagent[9] is the inertness of its EWG toward organometallics. Thus, while cuprates were the preferred reagents for opening the ring, use of Grignard reagents in the presence of a catalytic amount of a copper salt gave the best yields [n-C_4H_9MgBr + 10 mol % of $CuBr{\cdot}S(CH_3)_2$, ether/THF, 0–10 °C, 82% vs. $(C_4H_9)_2CuLi$, ether/THF, −55 °C to room temperature, 58%]. Only the former approach succeeded in the case of an aryl transfer [4-methylenedioxyphenyl, 83%]. Quenching the intermediate with 4 equiv of methyl iodide in the presence of HMPA gave **8**[8] R′ = CH_3 and R = CH_3 (86%) or R = n-C_4H_9 (56%; eq 2).



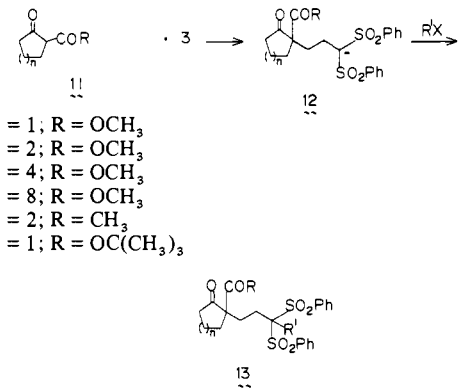
(2)

Most work focused on carbonyl-stabilized nucleophiles. Thus, malonic ester led smoothly to the intermediate anion **9**, which could be protonated (**10**,[8] R = H, 67%) or alkylated with methyl iodide (**10**,[8] R = CH_3, 64%; see eq 3). No loss of positional identity



(3)

of the carbanion occurs in **9**.[10] The β-keto esters **11a–d** smoothly effect ring opening of **3** (KOC_4H_9-t, DMF, 90 °C) to give **12**, which can be protonated or alkylated to give **13**[8] as shown in eq 4. Even the anion of a 1,3-diketone is sufficiently nucleophilic to ring open **3** (eq 4, **11e** → **13f**).



(4)

a, n = 1; R = OCH_3
b, n = 2; R = OCH_3
c, n = 4; R = OCH_3
d, n = 8; R = OCH_3
e, n = 2; R = CH_3
f, n = 1; R = $OC(CH_3)_3$

	yield, %
a, n = 1; R = OCH_3; R′ = CH_3; mp 155–156 °C	86
b, n = 2; R = OCH_3; R′ = CH_3; mp 98–98.5 °C	86
c, n = 2; R = OCH_3; R′ = $H_2C{=}CHCH_2CH_2$; mp 155–155.5 °C	64
d, n = 4; R = OCH_3; R′ = CH_3, mp 162 °C	70
e, n = 8; R = OCH_3; R′ = CH_3, mp 144–145 °C	74
f, n = 2; R = R′ = CH_3	70
g, n = 1; R = $OC(CH_3)_3$; R′ = CH_3; mp 93 °C	82

While reductive cleavage of the sulfone in protic media simply effects desulfonylation,[11] such cleavage in aprotic media offers the opportunity to pursue further carbanionic behavior of the type represented by **4** or **5**. No fruitful results derived from use of low-valent titanium[12] or samarium iodide.[13] On the other hand, the lithium arylides in THF transformed **13b** into a product whose yield depended upon the reduction potential of the arylide—the yield increasing as the reduction potential decreased (biphenylide, 34%, naphthalenide, 42%; phenanthrenide, 88%). All subsequent reactions consequently employed lithium phenanthrenide (5 equiv, 0.5 M, THF, −78 °C). Most surprising, the incipient nucleophile

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(8) All new compounds have been fully characterized by spectroscopic analysis. Elemental compositions have been determined by combustion analysis and/or high-resolution mass spectroscopy.
(9) Trost, B. M. *Acc. Chem. Res.* **1978**, *11*, 453.
(10) The estimated pK_a of 10 for a disulfonylmethane compared to 14 for a malonic ester allows prediction of such an observation.
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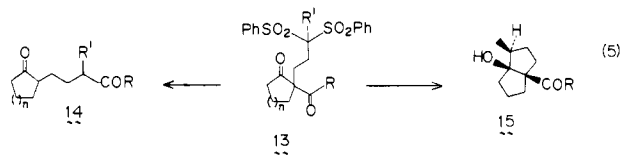
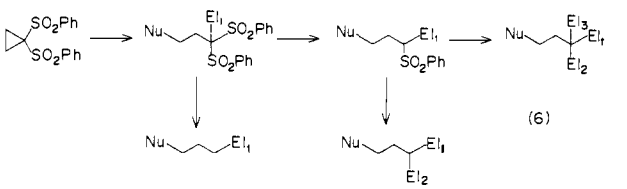
attacked the ester group preferentially to give **14**[8] (n = 2, R = OCH_3, R′ = CH_3), whose structure was proven by comparison to an authentic sample. This novel three-carbon chain extension of β-keto esters proceeds with equal facility for **13b,d,e** to give the corresponding products in 69%, 80%, and 74% yields, respectively (eq 5).[14]



(5)

In contrast to these results, the five-membered ring analogue **13a** gave the chain extended product **14** (n = 1, R = OCH_3, R′ = CH_3) in 33% yield and the product of attack at the ketone carobonyl group **15** (R = OCH_3) in 45% as a single diastereomer as shown by TLC and ^1H and ^{13}C NMR spectroscopy. On the basis of the ^{13}C shift for the methyl group[15] it is assigned the exo configuration. Sterically retarding the attack at the ester carbonyl group as in **13g** permits shifting the reaction exclusively to this latter process, i.e., to give **15** [R = $OC(CH_3)_3$] in 69% yield.

The 1,1-bis(benzenesulfonyl)cyclopropane appears to fulfill the requirements for a propylene 1,3-dipole. As summarized in eq 6, the fact that the sulfones can be sequentially removed permits



(6)

selective introduction of between one and three electrophiles. In the case of β-keto esters such versatility created a novel three-carbon insertion between the ester group and the ketone or a cyclopentane annulation. Such flexibility offers new opportunities for developing synthetic strategy toward complex targets.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs. J.C. gratefully acknowledges support by the CNRS and for a NATO postdoctoral fellowship for a portion of her stay, and J.B. acknowledges an NSF postdoctoral fellowship.

Registry No. 3, 34782-46-2; **6** (RX = PhS), 84109-67-1; **6** (RX = $PhCH_2O$), 84109-68-2; **6** (RX = $(C_2H_5)_2N$), 84109-69-3; **7** (RX = PhS; R′ = CH_3), 84109-70-6; **7** (RX = PhS; R′ = $CH_2CH=CH_2$), 84109-71-7; **8** (R = R′ = CH_3), 84109-72-8; **8** (R = n-C_4H_9; R′ = CH_3), 84109-73-9; **10** (R = H), 84109-74-0; **10** (R = CH_3), 84109-75-1; **11a**, 10472-24-9; **11b**, 41302-34-5; **11c**, 5452-73-3; **11d**, 62939-87-1; **11e**, 874-23-7; **11f**, 84109-76-2; **13a**, 84109-77-3; **13b**, 84117-56-6; **13c**, 84109-78-4; **13d**, 84109-79-5; **13e**, 84109-80-8; **13f**, 84109-81-9; **13g**, 84109-82-0; **14a**, 84109-83-1; **14b**, 82257-46-3; **14d**, 84109-84-2; **14e**, 84109-85-3; **15** (R = OCH_3), 84109-86-4; **15** (R = $OC(CH_3)_3$), 84109-87-5; $PhCH_2OH$, 100-51-6; $(C_2H_5)_2NH$, 109-89-7; CH_3I, 74-88-4; $H_2C=CHCH_2Br$, 106-95-6; H_2O, 7732-18-5; $CuBr{\cdot}S(CH_3)_2$, 54678-23-8; $KCH(CO_2C_2H_5)_2$, 37892-24-3; PhSH, 108-98-5; n-C_4H_9MgBr, 693-03-8; lithium biphenylide, 34467-57-7; lithium naphthalenide, 7308-67-0; lithium phenanthrenide, 34509-57-4; acrolein, 107-02-8; 1,1-bis(benzenethio)cyclopropane, 69519-84-2.

(14) Alternatively, attack at the ketone carbonyl group could be followed by spontaneous retroaldolization to give the three-carbon ring enlarged 4-carbomethoxy-2-methylcycloalkanone. Thus, chemical transformations were also employed for the structural assignment. Baeyer-Villiger oxidation of **14b** led to a lactone that did not bear a methyl group at the oxygen-bearing carbon. Enol acetate formation under thermodynamically controlled conditions for **14d** and **14e** led to an enol acetate lacking a vinyl methyl group. Both of these observations rule out the intercalation process.

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Sulfur Activation of Azides toward Addition of Organometallics. Amination of Aliphatic Carbanions

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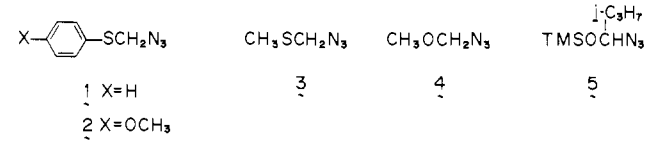
The growing importance of carbanions as reactive intermediates stimulates the search for electrophilic partners. The successful use of azidomethyl phenyl sulfide[1] as a synthon for $^+NH_2$[1-3] depends upon an understanding of the addition of organometallics to azides and the subsequent decomposition of the triazenes. We report that sulfur substitution plays a beneficial role in both processes and put forth a possible rationale.

The question of the addition of organometallics to azides appears somewhat controversial.[3-5] We undertook a systematic comparison of various heteroatom substituted azides, **1-5**. Whereas



1[1,6] reacts smoothly with phenylmagnesium bromide at −78 to 0 °C, subjection of **5**[7] to identical conditions led only to recovered azide. Phenethylmagnesium bromide smoothly forms the corresponding triazene with **1** at −78 °C, but **3**[6] requires 0 °C. Moreover, **4**[8] leads to no reaction at −78 °C and only trace amounts of any triazene at 0 °C. A direct competition between

$$3 + 4 + PhCH_2CH_2MgBr \rightarrow \underset{\mathbf{6}}{CH_3SCH_2N{=}NNHCH_2CH_2Ph} + \underset{\mathbf{7}}{CH_3OCH_2N{=}NNHCH_2CH_2Ph}$$

3 and **4** (1:1 ratio) for this Grignard reagent at −78 to 0 °C led to **6** and **7** in a 7:1 ratio as determined by the ratio of the signals at δ 4.52 and 2.00 for **6** and δ 4.79 and 3.22 for **7**. **1** was competed against **2** for a limited amount of phenyl- and phenethylmagnesium bromide in order to probe the effect of electron density in the arylthio series. In both cases, the corresponding triazenes were formed in a 1:1 ratio. These experiments clearly establish the order **1** ~ **2** > **3** > **4** ≫ **5**. This order does not correspond to either the Lewis basicity toward magnesium salts or to electron density. It clearly establishes the activating influence of sulfur compared to oxygen and of arylthio compared to alkylthio.

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