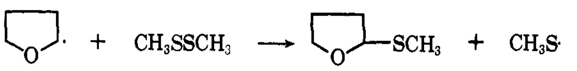
In THF a minor reaction with solvent occurs, resulting in the formation of methyl 2-tetrahydrofuryl sulfide (**3**). (Bp 66–67° (21 mm); n^{20}D 1.4868. *Anal.* Calcd for $C_5H_{10}OS$: C, 50.80; H, 8.53; S, 27.12. Found: C, 50.86; H, 8.60; S, 27.00.) This presumably arises through hydrogen abstraction from the α position and reaction of the radical thus formed with methyl disulfide (eq 9). The side product did not interfere seriously with the reaction.



3 (9)

Since THF is a common solvent for hydroboration,[9] it is most convenient to carry out organoborane reactions in this solvent. However, the production of **3** could be easily avoided by adopting *n*-hexane as the solvent. In this solvent the rates are approximately the same with the yields being somewhat higher.

The photochemical reactions are even faster than the air-induced reaction, being complete in about 2 hr. However, reactions carried out in THF give somewhat lower yields and increased formation of **3**. Thus *n*-hexane was preferred for the photochemical reactions.

Both the air-induced and photochemical reactions are synthetically useful. The reaction was applied to a representative series of olefins. The results are summarized in Table I.

Table I. The Reaction of Trialkylboranes with Methyl Disulfide

Trialkylborane	Oxygen initiated[a] Time, hr	RSCH₃,[c] %	**3**, %	Photochemical[b] Time, hr	RSCH₃,[c] %
Tri-*n*-butyl-	24	71[d]	8	2	91[d]
Triisobutyl-	20	68	30	3	91
Tri-*sec*-butyl-	10	83	13	2	95
Tri-*n*-octyl-	24	84 (75)[e]	11	2	95[c]
Tricyclopentyl-	12	81 (74)	Tr	3	93
Tricyclohexyl-	5	88 (77)	Tr	2	93
Tri-*exo*-norbornyl-	5	78 (75)	6	2	95

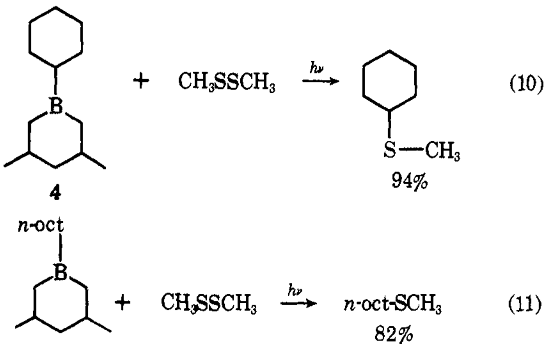
[a] In THF solution. [b] In *n*-hexane solution. [c] Yield based on methyl disulfide by gc. Isolated yields are in parentheses. [d] The product contained 15% of the *sec*-butyl isomer. [e] The product contained 10% of the *sec*-octyl isomer.

The following procedure for the preparation of methyl norbornyl sulfide is representative. A dry 200-ml flask equipped with a septum inlet and a magnetic stirrer was flushed with nitrogen. The flask was charged with 82 ml of dry THF and 14.1 g of norbornene (150 mmol) and cooled to 0°. Hydroboration was achieved by the dropwise addition of 18.6 ml of a 2.68 *M* solution of borane in THF (150 mmol of hydride) at 0° followed by stirring at room temperature for 1 hr. Methyl disulfide, 9.4 g (100 mmol), was then added. Air was introduced through a syringe needle above the THF solution at 1 ml/min. The THF solution was stirred at room temperature overnight (10 hr, 5 hr on 10-mmol scale for gc analysis) and then distilled directly. Methyl norbornyl sulfide, 10.6 g, 75%, was collected, bp 90–92° (23 mm), n^{20}D 1.5115, sulfone mp 74.5–75° (lit.[10] bp 82° (18 mm), n^{20}D 1.5118, sulfone mp 75°).

For the photochemical reactions, the THF was removed with a water aspirator after hydroboration and replaced with *n*-hexane. The methyl disulfide was then added and the resulting solution illuminated with an external ultraviolet sunlamp.[5] The *n*-hexane was allowed to reflux.

The photochemical reactions proceed faster and give higher yields but involve the extra step of solvent removal. If the alkyl group contains light-sensitive functional groups, the air-induced reaction gives satisfactory results.

It was recently pointed out that the use of *B*-alkyl-3,5-dimethylborinanes (**4**, **5**) can offer advantages in achieving high utilization of a particular alkyl group which may be a valuable intermediate in a synthesis.[11] This was tested for the present reaction. Excellent results were realized (eq 10, 11).



These results establish that organoboranes readily undergo a reaction with disulfides *via* a free-radical chain mechanism. The reaction provides a new convenient synthesis of mixed sulfides.

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(9) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(10) D. I. Davies, L. T. Parfitt, C. K. Alden, and J. A. Claisse, *J. Chem. Soc. C*, 1585 (1969).

(11) H. C. Brown and E. Negishi, *J. Amer. Chem. Soc.*, in press.

(12) National Science Foundation Predoctoral Fellow.

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Received March 10, 1971

Phosphabenzene and Arsabenzene

Sir:

The close resemblance of benzene and its nitrogen analog, pyridine **1**, is familiar to all chemists. This resemblance in terms of structure and overall stability clearly demonstrates that the isoelectronic nitrogen atom replaces a methine group of benzene without disrupting its "aromaticity." While a formal replacement of the nitrogen of pyridine by its congeners, phosphorus and arsenic, gives phosphabenzene (phosphorin) (**2**) and arsabenzene (arsenin) (**3**), it is less clear that these materials would show aromatic properties.[1] Heavily substituted derivatives of **2**, such as

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(1) This is rather difficult to predict since there are extremely few stable compounds of trivalent phosphorus and arsenic which are dicoordinated: see K. Dimroth and P. Hoffmann, *Chem. Ber.*, **99**, 1325 (1966); G. Märkl and F. Lieb, *Tetrahedron Lett.*, 3489 (1967); and ref **2** and **3**.

(2) G. Märkl, *Angew. Chem., Int. Ed. Engl.*, **5**, 846 (1966); G. Märkl, F. Lieb, and A. Merz, *ibid.*, 6, 458, 944 (1967); P. deKoe and F. Bickelhaupt, *ibid.*, 6, 567 (1967); P. deKoe, R. VanVeen, and F. Bickelhaupt, *ibid.*, **7**, 465 (1968); K. Dimroth and W. Mach, *ibid.*, **7**, 460 (1968); G. Märkl and A. Merz, *Tetrahedron Lett.*, 1231 (1969); A. I. Tolmachev and E. S. Kozlov, *J. Gen. Chem. USSR*, 37, 1826 (1967).

(3) P. Jutzi and K. Deuchert, *Angew. Chem., Int. Ed. Engl.*, **8**, 991 (1969); H. Vermeer and F. Bickelhaupt, *ibid.*, **8**, 992 (1969).

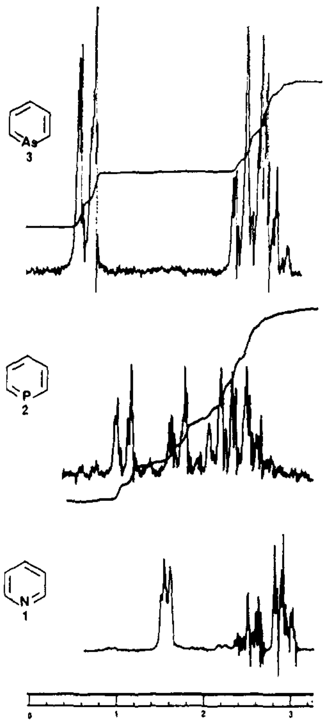
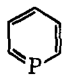


Figure 1. Proton magnetic resonance spectra of arsabenzene (**3**), phosphabenzene (**2**), and pyridine (**1**). The spectra were determined at 60 MHz. τ values are in parts per million relative to internal TMS.

4, have been prepared by Märkl and others.[2] Most of these materials are reasonably stable. On the other hand, the only arsenin which has been reported, although not isolated, is the highly reactive 9-arsaanthracene (**5**).[3] Since the substitution in **4** and **5** may mask the properties of the parent ring compounds, an examination of the unsubstituted **2** and **3** would be a valuable addition to the study of conjugation of arsenic and phosphorus with carbon.



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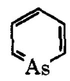

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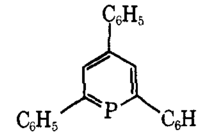

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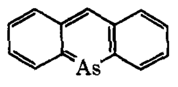
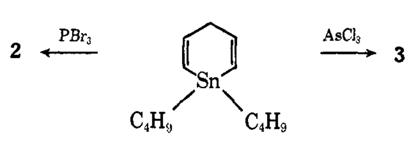


5



6

We now wish to report on a one-step synthesis of **2** and **3** and on some of their spectral properties. Treating the recently available 1,4-dihydro-1,1-dibutylstannabenzene (**6**)[4] with 0.67 mol of phosphorus tribromide gave the hydrobromide of **2** and dibutyltin dibromide.[5] **2** could be freed from its salt by adding 1,5-diazabicyclo[4.3.0]non-5-ene and purified by glpc at 110° on an Apiezon L column. Phosphabenzene is a colorless volatile liquid with a characteristic phosphine odor. It is air sensitive but appears to be quite stable under an inert atmosphere. Similarly, arsenic trichloride and **6** reacted exothermally in a THF solution. Only **3** and dibutyltin dichloride were isolated on distillation. Purification by glpc gave a liquid with a characteristic onion-like odor. **3** is very air-sensitive and brief exposure turns it bright red.

The spectra of **2** and **3** unambiguously establish their structure.[6] Pmr spectra of **1**, **2**, and **3** are shown in Figure 1. These spectra are remarkably similar in appearance. The α protons occur at lowest field. The protons at C_4 are higher while the β protons occur at highest field. The α proton of **2** is strongly coupled to ^{31}P ($J = 38$ Hz) while the $J_{H_\alpha H_\beta}$ becomes larger for **2** (10 Hz) and **3** (11 Hz) than for **1** (5.5 Hz). Surely the most interesting feature of these spectra is the shift to lower field for **3** and **2** relative to **1**. The shift is most striking for the α proton of **3**.

It seems unlikely that these effects can be explained on the basis of the charge distribution on the ring.[7] While the α protons will be strongly influenced by the magnetic anisotropy of the neighboring heteroatom,[8] this effect should be smaller for the β and γ protons. In particular, the low-field position of the relatively remote γ protons seems most consistent with an appreciable ring current for **2** and **3**.[9]

The mass spectra of pyridine, phosphabenzene, and arsabenzene show relatively intense molecular ions (Table I). For pyridine the principal fragmentation involves loss of HCN at *m/e* 52, loss of HCN, H at *m/e* 51, and loss of HCN, H_2 at *m/e* 50. Loss of C_2H_2 at *m/e* 53 is relatively less important. On the other hand, both phosphabenzene and arsabenzene fragment primarily by loss of C_2H_2. Phosphabenzene does show

Table I. Mass Spectra of Pyridine, Phosphabenzene, and Arsabenzene Showing the Major Ions and Their Relative Abundances[a]

Compd	Parent ion $(M)^{+}$[b]	$(M - C_2H_2)^{+}$[b]	$(M - HCX)^{+}$[b]	Other ions *m/e*
Pyridine (**1**)	79 (100)	53 (8)	52 (61)	$52 > 51 > 50$
Phosphabenzene (**2**)	96 (100)	70 (24)	52 (8)	$70 > 69 > 68$
Arsabenzene (**3**)	140 (100)	114 (24)	52 (<1)	$114 > 113 > 112$

[a] The mass spectra were determined on an MS-9 spectrometer at 45 eV using a gas inlet. [b] The first number is *m/e* which is followed by the relative abundance of the peak in parentheses.

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(4) A. J. Ashe, III, and P. Shu, *J. Amer. Chem. Soc.*, **93**, 1804 (1971).

(5) For a similar procedure see: L. Maier, D. Seyferth, F. G. A. Stone, and E. G. Rochow, *ibid.*, **79**, 5884 (1957), and ref 3.

(6) The pmr spectra were taken in dilute CCl_4 solutions using TMS as an internal standard. They were recorded using a Varian T-60 instrument. The mass spectra were taken on an AEI Model MS-9 spectrometer at 45 eV using a gas inlet. The uv spectra were recorded in cyclohexane using balanced 1-cm cells on a Cary-14 spectrometer while the ir spectra were taken using a Perkin-Elmer Model 237 instrument with balanced 0.1-mm cells. Calibration was by polystyrene film and absorption maxima are quoted to the nearest 5 cm^{-1}.

(7) The chemical-shift values of protons in aromatic compounds have been found to be a function of the charge density at the adjacent carbon: T. Schafer and W. G. Schweider, *Can. J. Chem.*, 41, 966 (1963). However, the electronegativity decreases in the series N, P, and As and one might expect the protons to move upfield in 3 and 2 relative to 1 if there was much charge separation in the ring.

(8) For pyridine see: J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 303 (1961).

(9) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961), and for a brief summary see G. M. Badger, "Aromatic Character and Aromaticity," Cambridge University Press, Cambridge England, 1969, pp 61–70.

a moderate peak at m/e 52, but the intensity of this peak is very small for arsabenzene. The decreasing abundance of the $(M - HCX)^+$ peak might be understandable in terms of decreasing stability of the eliminated HCX molecules.

The uv spectrum of pyridine shows a weak peak at 270 mμ (ϵ 450) assigned to the $n \rightarrow \pi^*$ transition and three more intense peaks at 250 (ϵ 2000), 192 (ϵ 6300), and 175 mμ (ϵ 80,000), due to $\pi \rightarrow \pi^*$ transitions.[10] The spectra of **2** and **3** were taken in cyclohexane. Each shows two intense bands: at 213 (ϵ 19,000) and 246 mμ (ϵ 8500) for **2** and at 219 (ϵ 15,000) and 268 mμ (ϵ 11,000) for **3**. Each has a shoulder on the high-wavelength side of these peaks: at 290 mμ (ϵ 250) for **2** and 305 mμ (ϵ 350) for **3**. This low-intensity shoulder can probably be assigned to an $n \rightarrow \pi^*$ transition.

The infrared spectrum of pyridine has been subject to a complete analysis.[11] The ir spectra of **2** and **3** in CCl$_4$ grossly resemble that of **1**. Although there is some uncertainty in the assignment of bands for **2** and **3**, there appears to be a progressive shift to lower frequency of corresponding bands in the series **1**, **2**, and **3**. This shift is rather small from C-H bands: **1** has bands at 3083, 3054, and 3036 cm^{-1}, **2** at 3080, 3045, and 3015 cm^{-1}, and **3** at 3065, 3020, and 2995 cm^{-1}. The shift becomes rather larger for the ring modes. For example, pyridine shows two intense peaks at 1572 and 1439 cm^{-1}. **2** shows bands at 1515 and 1395 cm^{-1}, while **3** shows them at 1505 and 1375 cm^{-1}. Such shifts are in the expected direction for vibrations which involve much displacement of the heavy heteroatom. A similar shift of bands has been noted between furan and thiophene.[12]

Preliminary examination of **1**, **2**, and **3** shows considerable similarity in their spectra. Whether **2** and **3** do show other "aromatic properties" must await an elucidation of their chemistry now in progress.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research (Grant No. 5241-AC3-4) and also the National Science Foundation for a grant (GP-8345) to the University of Michigan for the purchase of an MS-9 mass spectrometer.

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[10] L. W. Pickett, L. W. Corning, M. E. Wieder, G. M. Semernov, and J. M. Buckley, *J. Amer. Chem. Soc.*, 75, 1618 (1953).

[11] C. H. Kline, Jr., and J. Turkevich, *J. Chem. Phys.*, 12, 300 (1944); L. Corrsin, B. J. Fox, and R. C. Lond, *ibid.*, 21, 1170 (1953); J. K. Wilmshurst and H. J. Bernstein, *Can. J. Chem.*, 35, 1183 (1957).

[12] A. R. Katnitzky and A. P. Ambler in "Physical Methods in Heterocyclic Chemistry," Vol. 2, Academic Press, New York N. Y., 1963, pp 199–202.

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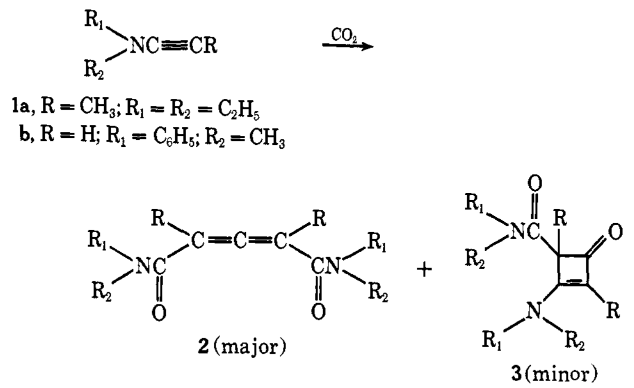
Received April 15, 1971

Cycloaddition of Ynamines with Carbon Dioxide. A Route to Diamides of Allene-1,3-dicarboxylic Acids

Sir:

The literature records only a very small number of cycloadditions involving carbon dioxide.[1] We have now observed that ynamines react with great facility with this very simple heterocumulene, and describe here the first results we have obtained on interesting cycloadditions which lead from 2 mol of ynamines (**1**) and 1 mol of carbon dioxide to allenic derivatives of type **2** accompanied by small quantities of aminocyclobutenones of type **3** (Scheme I).

Scheme I



The reaction involving diethylaminopropyne, (Et)$_2$NC≡CCH$_3$,[2] is especially fast; its reaction with a saturated solution of carbon dioxide in acetonitrile–ether is exothermic and is complete in 1 hr at −60° or 15 min at room temperature. The reaction is even more rapid under carbon dioxide pressure. Under any of these conditions the yield of the allenic diamide **2a** (ir (film) 1965, 1630 cm^{-1}; nmr[3] (CCl$_4$) 1.1 (t, 12 H), 1.9 (s, 6 H), 3.4 ppm (q, 8 H)) is practically quantitative. A small amount (less than 5%, not detectable by nmr) of aminocyclobutenone **3a** can be detected by the presence of a very weak absorption band at 1750 cm^{-1} in the reaction product.

The same aminocyclobutenone **3a** (bp 120° (0.005 mm); ir (film) 1750, 1640, 1590 cm^{-1}; nmr (CCl$_4$) δ 1.45 (s, 3 H), 1.65 ppm (s, 3 H)) is produced, however, in 24% yield, together with 76% of the allenic diamide **2a**, by the use of a less polar solvent, such as hexane (under pressure of carbon dioxide).

N-Methyl-*N*-phenylaminoacetylene (**1b**),[2a] a less reactive ynamine than diethylaminopropyne, reacts slowly with carbon dioxide in hexane, but at ordinary temperature in acetonitrile under 35 atm of carbon dioxide it gives a 40% yield of the *N*-methyl-*N*-phenyldiamide of pentadiene-2,3-dicarboxylic acid (**2b**): mp 173°; ir (CHCl$_3$) 1970, 1640 cm^{-1}; nmr (CDCl$_3$) δ 3.3 (s, 6 H), 5.7 (s, 2 H), 7.2 ppm (m, 10 H). No aminocyclobutenone can be detected in this instance.

The allenic structure of the adducts **2**, which was strongly suggested by their infrared spectra, was confirmed by chemical means: catalytic hydrogenation of the *N*-methyl-*N*-phenyldiamide of allene-1,3-dicarboxylic acid (**2b**) (platinum in acetic acid) gives an 85% yield of the *N*-methyl-*N*-phenyldiamide of glutaric acid (mp 92°) identified by comparison with an authentic sample prepared from the reaction of *N*-methylaniline with dichloroglutaric acid (mp 92°).

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[1] (a) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967, p 267. (b) In a recent review on cycloaddition (R. Gompper, *Angew. Chem., Int. Ed. Engl.*, 312 (1969)) Gompper refers to unpublished work on the reactivity of aminothioketene ketals.

[2] (a) J. Ficini and C. Barbara, *Bull. Soc. Chim. Fr.*, 2787 (1965); (b) H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, 6, 767 (1967); (c) also obtainable from Fluka Lab., Switzerland.

[3] Nmr spectra were recorded on a Varian T-60 with internal TMS reference, or on a Varian A-60.