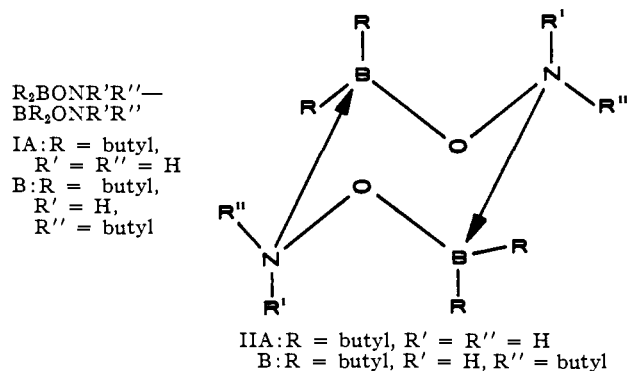formation of a crystalline solid whose analysis after recrystallization from ether is compatible with the formulation R_2BONH_2, (aminoöxy) di-n-butylborane (*Anal.* Calcd. for $C_8H_{20}BON$: C, 61.22; H, 12.75; N, 8.93; B, 6.89. Found: C, 61.44; H, 12.70; N, 8.89; B, 6.92); decomposes before melting at 130°.

Molecular weight determination of this substance in acetonitrile solution, concentration = 0.05 formal, at 35°, made with a Mechrolab osmometer indicates that it is dimeric (molecular weight of dimer, calcd.: 314, found: 300 ± 20). The dimer may be either acyclic, having the structure IA, or cyclic, having the structure IIA.

R₂BONR'R''—
BR₂ONR'R''

IA:R = butyl,
R' = R'' = H
B:R = butyl,
R' = H,
R'' = butyl

IIA:R = butyl, R' = R'' = H
B:R = butyl, R' = H, R'' = butyl

These two structures are distinguishable on the basis of their N–H bands. Structure I should have two pairs of N–H bands. The pair being due to the symmetric and antisymmetric stretching of the hydrogens on the tetracoördinated nitrogen should be found at 3200 to 3300 cm.$^{-1}$, and the pair being due to the symmetric and antisymmetric stretching of the hydrogens on the trivalent nitrogen should occur at 3400 to 3500 cm.$^{-1}$. Structure II should have only one pair of N–H bands and they should occur at 3200 to 3300 cm.$^{-1}$ since both nitrogens are equivalent and are tetracoördinated. The infrared spectrum of a dilute solution of (aminoöxy) di-n-butylborane in CCl_4 (concn. = 0.05 M, cell thickness = 1 cm.) shows only one pair of N–H bands which are at 3310 and 3270 cm.$^{-1}$, indicating the cyclic structure, IIA, is correct.

Reaction of N-n-butylhydroxylamine with di-n-butylborinic acid yields crystalline (N-butylaminoöxy) di-n-butylborane, R_2BONHR, m.p. 92–94°. (*Anal.* Calcd. for $C_{12}H_{28}BON$: C, 67.60; H, 13.14; N, 6.57; B, 5.07. Found: C, 67.69; H, 13.28; N, 6.62; B, 5.37.) Molecular weight of this compound in benzene solution showed that it too is dimeric (calcd. for dimer: 426; found: 404, by freezing point depression, and 415 ± 15 by osmometry). The infrared spectrum of a dilute solution in CCl_4 shows a single N–H band at 3210 cm.$^{-1}$ indicating the cyclic structure IIB. We propose the name Bon-Bon for this novel heterocycle represented by II. The 1,1,4,4-tetrasubstituted bon-bons which are formed by the reaction of borinic acids with hydroxylamine can be used to advantage as solid derivatives of borinic acids, since they form readily, they are stable in air (borinic acids oxidize quickly in air) and they are easily recrystallized from organic solvents.

The reaction between N,N-di-n-butylhydroxylamine and dibutylborinic acid yields the liquid product, (N,N-dibutylaminoöxy) dibutylborane, R_2BONR_2, b.p. 78° (2.5 mm.) Our product was slightly contaminated by di-n-butylborinic acid as evidenced by the weak OH band at 3627 cm.$^{-1}$ which is characteristic for borinic acids in CCl_4 solution (*Anal.* Calcd. for $C_{16}H_{36}BON$:

C, 71.37; H, 13.38; N, 5.20; B, 4.01. Found: C 71.60; H, 12.64; N, 4.89; B, 3.97.)

This compound, in contrast to the two previously described derivatives, is monomeric in 0.05 formal benzene solution (molecular weight for monomer, calcd.: 269; found: 230 ± 20). If this compound had the bon-bon structure it would have two axial butyl groups at positions 1 and 3, and two more at positions 4 and 6. Apparently the steric interference between the two pairs of axial butyl groups prevents the cyclic structure from forming and at the same time reduces the tendency to dimerize. In IIA and IIB there are no axial-axial interactions between butyl groups.

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THE REACTIONS OF SULFUR ATOMS. II. SULFUR ATOM INSERTION IN CARBON-HYDROGEN BONDS. THE FORMATION OF CYCLOPROPYL MERCAPTAN IN THE REACTION WITH CYCLOPROPANE

Sir:

Recent investigations in this Laboratory on the reactions of S-atoms with olefins[1] are currently being extended to include paraffinic hydrocarbons. Here evidence has been found for the first time that sulfur atoms, in the (^1D) state from the photolysis of gaseous carbonyl sulfide, undergo an insertion reaction into carbon–hydrogen bonds. While a quantitiative kinetic treatment of a series of such substrates[2] will be forthcoming shortly, the results obtained with cyclopropane are being reported here since they are illustrative of the general behavior of the sulfur atom–paraffin systems under investigation. In addition, the present reaction is of special interest in that the expected isomerization of the cyclopropyl compound to the allyl isomer does not occur. Finally, the insertion reaction represents a relatively simple method for preparing cyclopropyl and other mercaptans from the corresponding paraffins.

When carbonyl sulfide and cyclopropane, at partial pressures of 50–300 and 70–1100 mm., respectively, were irradiated in a static system at 25°, in the wave length region 2290–2550 Å., using a suitably filtered mercury arc, the major products were CO, sulfur, and cyclopropyl mercaptan. Carbon monoxide was removed by pumping at −196°, while unreacted COS and cyclopropane were removed by distillation at −130°. The remaining fraction, analyzed by gas chromatography on an 8-ft. 15% silicone 550 (with 2% stearic acid) on Celite column at 25° with H_2 carrier at 65 ml./min., was found to be at least 95% cyclopropyl mercaptan. The remainder was CS_2 and a trace of unknown. Identification analyses were performed on mercaptan samples trapped from the chromatographic effluent.
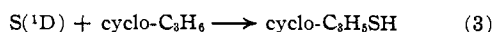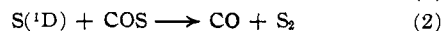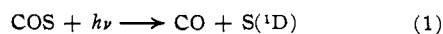
The identity of the mercaptan was confirmed by mass spectrometric, infrared and n.m.r. analysis. The mass spectrum showed a molecular weight of 74, and the infrared spectrum was consistent with that expected for cyclopropyl mercaptan. The n.m.r. spectrum exhibited four complex multiplets centered on τ values of A, 8.05; B, 8.23; C, 9.26; and D, 9.53; with integrated areas being in the ratio 1:1:2:2. Peaks C and D may be assigned to the methylene protons on the cyclopropyl ring since the occurrence of such signals at high fields has been observed for cyclopropylamine and methyl cyclopropyl carboxylate.[3] Peak B resembles that observed for the methine proton in the

(1) O. P. Strausz and H. E. Gunning, *J. Am. Chem. Soc.*, **84**, 4080 (1962).
(2) A. R. Knight, O. P. Strausz and H. E. Gunning, to be published.
(3) Varian Associates, "N.M.R. Spectra Catalog," Palo Alto, California, 1962.

latter compound, and if a similar assignment is made here, peak A could be ascribed to the mercapto proton.

All of the C_3H_5SH isomers were considered as possible reaction products, and to this end the various spectra and other properties were determined directly or obtained from published reports. Comparison of the data permitted elimination of all isomers except cyclopropyl mercaptan. The ultraviolet spectrum of the mercaptan vapor showed absorption beginning at ca. 2600 Å., with a maximum at 2300 Å., followed by the onset of strong absorption at ca. 2200 Å. The compound eluted in 10.5 min. on both the silicone 550 column described above and on an 8-ft. 20% tricresyl phosphate on Kromat column operating at 25°, with H_2 carrier at 60 ml./min. The boiling point (extrapolated) was 60.0 ± 1.3° and the vapor pressure was 175 mm. at 25°. The compound is a colorless liquid with characteristic mercaptan odor. We have been unable to find previously published data on the synthesis or properties of cyclopropyl mercaptan.

A simple mechanism, similar to that already proposed for the reaction of S-atoms with olefins,[1] and which accounts qualitatively for the observed results here, is

$$COS + h\nu \longrightarrow CO + S(^1D) \qquad (1)$$

$$S(^1D) + COS \longrightarrow CO + S_2 \qquad (2)$$

$$S(^1D) + \text{cyclo-}C_3H_6 \longrightarrow \text{cyclo-}C_3H_5SH \qquad (3)$$

$$nS_2 \longrightarrow S_{2n} \qquad (4)$$

The insertion reaction (3) is dictated by the fact that cyclo-C_3H_5SH is the only significant product arising from S-atom attack on cyclopropane. The S-atom involved in (3) is likely in the initially-formed (^1D) metastable state[1]; otherwise the ground-state cyclopropane singlet would have to be converted to a triplet level of the mercaptan, for the spin to be conserved in reaction with $S(^3P)$ atoms. By analogy with alcohols and other mercaptans, a low-lying triplet state of the mercaptan product is unlikely.

The above mechanism predicts that in the pressure region where $R(CO)$ and $R(\text{cyclo-}C_3H_5SH)$ are constant $(P(\text{total}) > 300 \text{ mm.})$ the ratio $R(CO)/R(\text{cyclo-}C_3H_5SH)$ should be unity; in fact, this ratio = 2.7 at $P(\text{total}) = 560$ mm. Collisional deactivation of $S(^1D)$ atoms to $S(^3P)$ is therefore indicated, as previously observed in the olefin system.[1] Triplet sulfur may then disappear via the reactions

$$S(^3P) + COS \longrightarrow CO + S_2 \qquad (2a)$$

$$S(^3P) + S(^3P) \xrightarrow{M} S_2 \qquad (4a)$$
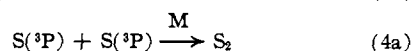
Thus any singlet → triplet conversion occurring will have the dual effect of decreasing the mercaptan yield and increasing that of carbon monoxide. The importance of electronic relaxation is also substantiated by recent investigations in this Laboratory on the reaction of S-atoms with cis- and trans-butene-2.[4] Here it was shown that the cyclic sulfide product arose from the addition of triplet sulfur to the olefin despite the fact that $S(^1D)$ atoms are initially formed in (1), and, as a result, the sulfide yield was essentially quantitative.

The insertion of sulfur atoms into the C–H bond in paraffinic hydrocarbons, as exemplified in this communication by the formation of cyclopropyl mercaptan from cyclopropane substrate, would appear to be an excellent model for the detailed investigation of atomic insertion reactions because of the simplicity of the technique, the absence of complicating side reactions, and

(4) E. M. Beatty, J. A. Poole, O. P. Strausz and H. E. Gunning, to be published.

the remarkable stability of the products formed in the reaction.

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PHOTOREARRANGEMENT OF A 4-PYRONE TO A FURAN DERIVATIVE

Sir:

Ultraviolet irradiation of 2,6-dimethyl-4-pyrone (I) in either the solid state or in solution has been found to result in dimerization.[1] Investigation of the products formed on irradiation of I in aqueous solution at high dilution, i.e., under conditions chosen to retard dimerization, has now led to the observation of a novel rearrangement of the 4-pyrone to a furan derivative.

An aqueous 0.2% solution of I was irradiated in a quartz apparatus in the absence of air with a Hanovia high-pressure mercury-vapor 450-w. lamp for 36 hr. Fractionation of the crude product by extraction and chromatography gave, in addition to photodimer, an oil (ca. 1%), $\lambda_{max}^{CCl_4}$ 3.52 3.62 (shoulder), 5.93, 6.20, 6.60 μ, τ 0.54, 3.07, 7.68, 7.99 p.p.m. (intensities ca. 1:1:3:3). This was characterized by means of the following derivatives: oxime, m.p. 79.5–81°, $\lambda_{max}^{CHCl_3}$ 2.78, 3.05 (broad), 6.10 (shoulder), 6.18, 6.6 μ, $\lambda_{max}^{CH_3OH}$ 218 mμ (log ϵ 3.62), 284 mμ (log ϵ 4.24) (Anal. Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.81; H, 6.65; N, 9.90); 2,4-dinitrophenylhydrazone, red needles, m.p. 224–225°, $\lambda_{max}^{CHCl_3}$ 393 mμ (Anal. Calcd. for $C_{13}H_{12}N_4O_5$: C, 51.31; H, 3.98. Found: C, 51.50; H, 4.16); semicarbazone, m.p. 217° dec., $\lambda_{max}^{CH_3OH}$ 306 mμ (log ϵ 4.34). On the basis of these data and its origin, the product was considered to be 4,5-dimethyl-2-furaldehyde (II).
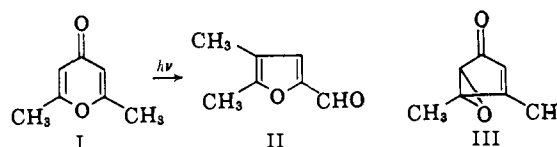
An authentic sample of II was synthesized by a modification of the method of Mndzhoyan, et al.[2] The bands in the infrared and nuclear magnetic resonance of this compound were identical in position with those in the spectra of the photochemical product, although some differences in relative intensities in the infrared spectra indicated that the latter product was impure. Comparison of derivatives fully established the formation of II in the photochemical reaction. The derivatives obtained from the authentic sample of II were: oxime, m.p. 79–81°, mixture m.p. 79–81°, infrared spectrum identical with that of the oxime of the photochemical product (Anal. Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.62; H, 6.68; N, 9.94); 2,4-dinitrophenylhydrazone, red needles, m.p. 226–227° (Anal. Calcd. for $C_{13}H_{12}N_4O_5$: C, 51.31; H, 3.98; N, 18.42. Found: C, 51.30; H, 4.06; N, 18.40); semi-

(1) E. Paternò, Gazz. chim. ital., 44, 151 (1914); P. Yates and M. J. Jorgenson, J. Am. Chem. Soc., 80, 6150 (1958).
(2) A. L. Mndzhoyan, V. G. Afrikyan, M. T. Grigoryan, and E. A. Markaryan, Dokl. Akad. Nauk Arm. SSR, 25, 277 (1957); 27, 301 (1958) [Chem. Abstr., 52, 12835 (1958); 54, 481 (1960)].