employing a frequency of 9080 Mc./sec. Resonance absorptions were observed at these magnetic fields[6]: 1227, 1619, 1978, 4588, 5272, and 7522 gauss. A broad line at the free spin value (3239 gauss; $g = 2.0027$) also was observed. (This latter line presumably is due to doublet radicals resulting from further reaction). The intensities of the absorptions were not diminished appreciably when irradiation ceased,[7] as long as the temperature of the sample did not rise above $-150°$. However, warming to $-130°$ caused the lines to disappear rapidly. Measurements also were carried out at a series of temperatures by using the Varian variable-temperature insert instead of the Dewar insert. The intensity of the various lines decreased at essentially the same rate when the temperature of the sample was raised from -186 to $-133°$, with the exception that the line at 1619 gauss may decay more slowly and the broad line at $g \approx 2$ did not diminish appreciably. Some difficulty was experienced in observing the spin resonance absorptions when less viscous matrices such as ethyl ether–isopentane or methylcyclohexane–isopentane were used.[8]

The absorption lines can be grouped in the following manner: (1) the line at 1619 gauss corresponds to a $|\Delta m|$ equal to transition, occurring at one-half the free-spin value; and (2) the lines at 1227, 1978, 4588, 5272, and 7522 gauss are associated with $|\Delta m| = 1$ transition. The line 4 has a much larger deviation from the free spin value than any known for a phosphorescent triplet.[1,2,3] Much larger interactions occur here, as the divalent carbon has two orbitals with unpaired spins with a concomitant smaller average distance between the magnetic dipoles.

Diphenylmethylene has been described by Skell as a triplet species because it adds to olefins in a non-stereospecific manner.[9] Also diphenylmethylene reacts with oxygen to give benzophenone,[10] unlike singlet, electrophilic carbenes which do not react with oxygen. In addition, diphenylmethylene is apparently able to abstract hydrogen atoms from a variety of substrates.[10,11] Herzberg[12] has shown that the ground state of CH_2 (obtained from photolysis of diazomethane) is a triplet which has an approximately linear structure. Our results indicate that the ground state of diphenylmethylene is a triplet which is stable in rigid media. The position and number of the absorption lines indicate that we are not observing a *single* species having D_{2d} symmetry[13] such as the one proposed by Skell.[9]

Recently, we have learned that Brandon, Closs and Hutchison have observed e.p.r. absorptions in an irradiated dilute single crystal solid solution of diphenyldiazomethane. Their observations indicate the presence of an oriented ground state triplet molecule.[14]

Further work with isotopically substituted samples is in progress to obtain more information on the number and structure of the species which are present in diphenylmethylene and other carbenes.

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(6) Magnetic fields were determined from proton resonance frequencies. Treatment of absorption curves is that given in ref. 3.

(7) Overnight storage at 77°K caused no substantial change in the intensities of the absorption lines.

(8) Recent experiments involving the photolysis of diphenyldiazomethane in fluorocarbon glasses at 77°K. indicate that the diphenylmethylene which is produced can undergo diffusion readily in the matrices used. See W. B. DeMore, H. O. Pritchard and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959). However, when we irradiated benzophenone azine, which might be formed by such a process, in the quartz Dewar, no absorptions were detected.

(9) R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

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(11) (a) W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 935 (1954); (b) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4675 (1952).

(12) G. Herzberg, *Proc. Roy. Soc.* (London), **Ser. A.**, **262**, 291 (1961).

(13) The spin Hamiltonian (see K. W. H. Stevens, *Proc. Roy. Soc.* (London), **Ser. A.**, **214**, 237 (1952) and Hutchison[1]) which is appropriate in this case would require only two pairs of lines for a single species having D_{2d} symmetry.

(14) The authors wish to thank Professor Hutchison for communicating his observations prior to publication.

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RECEIVED JUNE 21, 1962

PHOTOLYSIS OF CARBON-2-$^{14}C_1$-SUBOXIDE IN ETHYLENE[1]

Sir:

In a recent communication, Bayes[2] reported on the photolysis of mixtures of C_3O_2 and ethylene, propylene and other hydrocarbons. The considerable yield of allene from ethylene and methylallene from propylene suggested to Bayes that atomic carbon might be the intermediate responsible for these products, although ketocarbene was not excluded.

Since one might expect some discrimination between double bond addition and carbon hydrogen insertion, if indeed a carbene-like species is involved, we felt it of value to investigate this discrimination ratio in ethylene. To this end carbon-2-$^{14}C_1$-suboxide (I) was photolyzed in the presence of ethylene. The allene-$^{14}C_1$ (II) produced was degraded.

A preparation of I in 15% yield was achieved by the P_2O_5 dehydration[3] of commercially available malonic acid-2-$^{14}C_1$. Decarboxylation of the malonic acid-2-$^{14}C_1$ proved it to be a minimum of 99.95% 2-labeled. The I was purified by gas-liquid chromatography (g.l.c.) using a silicone (GE-SF 96) column. Its identity was established by infrared analysis. Mixtures of I (pressure 0.5–0.8 mm.) and ethylene (pressure $\cong$ 50 mm.) were photolyzed in a quartz reactor using an unfiltered medium pressure mercury lamp. The two major products were allene-$^{14}C_1$ ($\sim$80%) and methylacetylene-$^{14}C_1$ ($\sim$20%).[4] Small amounts of acetylene-$^{14}C_1$ were also observed (1–2%).

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(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

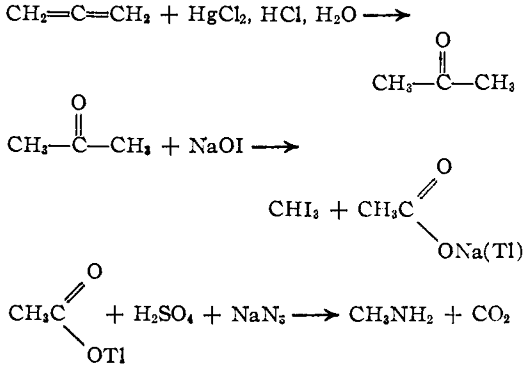
(2) K. Bayes, *J. Am. Chem. Soc.*, **83**, 3712 (1961).

(3) O. Diels and G. Meyerheim, *Ber.*, **40**, 355 (1907).

(4) These yields refer only to a 47% conversion photolysis; there is evidence that the allene to methylacetylene ratio decreases with increasing conversion. The discrepancy between our results and those of Bayes (ref. 2), who observed no methylacetylene or acetylene, may

The CO produced during photolysis assayed at less than 0.25% of the molar-specific activity of I, thereby eliminating the possibility of rearrangement of I during photolysis. The II was distilled *in vacuo* and subsequently purified by g.l.c. on a dimethylsulfolane column.

The reactions used in degrading allene are given in equations 1–3. The results of the assays are listed in Table I. Activity distribution is shown in Fig. 1.



$$CH_2{=}C{=}CH_2 + HgCl_2,\ HCl,\ H_2O \longrightarrow CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 \quad (1)^{5}$$

$$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 + NaOI \longrightarrow CHI_3 + CH_3C(=O)ONa(Tl) \quad (2)$$

$$CH_3C(=O)OTl + H_2SO_4 + NaN_3 \longrightarrow CH_3NH_2 + CO_2 \quad (3)^{6}$$

TABLE I

ACTIVITY IN PRODUCTS FROM CONVERSION AND DEGRADATION OF ALLENE-$^{14}C_1$

	47% Conversion[a] Specific activity[b]	8% Conversion Specific activity
Acetone (A)	3.23	1.02
Iodoform (B)	0.133	0.040
Thallium acetate (C)	3.10	0.942
Schmidt CO_2 (D)	3.04	0.911
Methylamine deriv. (E)	0.134	0.040
% end labeling[c]	8.20	8.02

[a] A duplicate degradation on a second portion of allene yielded results in agreement with the results listed in the Table. [b] The specific activities are given in mμ c./mg. C × C atoms/molecule. The precision of our assays is ±2%. [c] These figures represent the average of the percentage activities in the end carbons calculated in three ways

$$\frac{B+E}{B+D+E} \times 100,\ \frac{B+E}{A} \times 100,\text{ and}$$

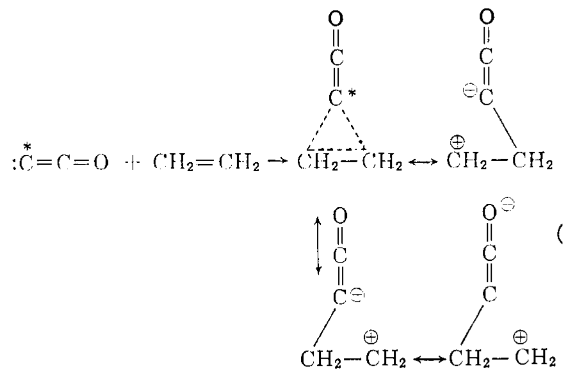
$$\frac{B+E}{C+\dfrac{B+E}{2}} \times 100$$

The low conversion run was carried out to test the possibility of a slow photolytically induced skeletal rearrangement of II. It can be inferred that such a rearrangement is unlikely since the degree of end labeling is identical under both conditions.

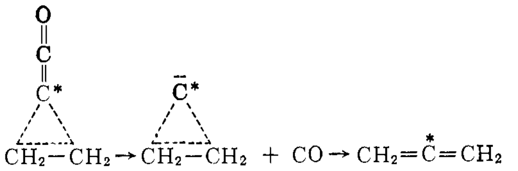
$CH_2{=}C{=}CH_2$
4% 92% 4%

Fig. 1.—Activity distribution in allene-$^{14}C_1$.

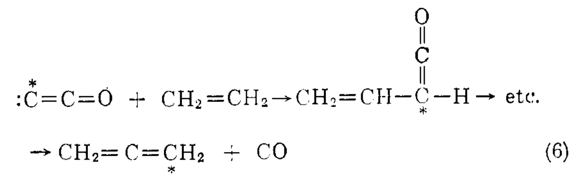
Thermochemical arguments favor C_2O as the first formed intermediate,[7] and a mechanism (equations 4–6) involving C_2O can be written to explain our results.[8]



(4)[9]



(5)



$$:\overset{*}{C}{=}C{=}O + CH_2{=}CH_2 \rightarrow CH_2{=}CH{-}\underset{*}{\overset{\overset{\overset{\displaystyle O}{\|}}{\overset{C}{\|}}}{C}}{-}H \rightarrow \text{etc.}$$

$$\rightarrow CH_2{=}\underset{*}{C}{=}CH_2 + CO \quad (6)$$

It is nevertheless possible to form atomic carbon in a ^1D state[10] by subsequent absorption of radiation by C_2O (*cf.* references 2 and 7a), and a mechanism similar to that given in equations 4–6 could be written for carbon atom reactions. The above analysis of our data leads to a discrimination ratio (double bond *versus* carbon hydrogen bond attack) of 46/1,[11] which is consistent with the expected stability of C_2O relative to atomic carbon. One might expect the latter in its ^1D state to be a voracious electrophile.

The question of atomic carbon *versus* C_2O nevertheless remains unresolved, although the weight

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be due to radiation below 2537 Å. in our case or to ^3P Hg sensitization in our system (*cf.* footnote 11 for further comment).

(5) W. Lossen, F. Moeschock and C. Dorno, *Ann.*, **342**, 163 (1905). There is no mechanistic reason to assume skeletal rearrangement at this stage but a control run with specifically labeled allene-2-$^{14}C_1$ was not carried out.

(6) R. C. Anderson and A. P. Wolf, Brookhaven National Laboratory Report BNL-3222. The methylamine was assayed as the methyl phenylthiourea.

(7) (a) H. B. Palmer and T. J. Hirt, *J. Am. Chem. Soc.*, **84**, 113 (1962). *Cf.* (b) C. MacKay, P. Polak, H. E. Rosenberg and R. Wolfgang, *J. Am. Chem. Soc.*, **84**, 308 (1962).

(8) We do not suggest that equations 4–6 constitute a unique explanation of the results.

(9) *Cf.* W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **83**, 1989 (1961).

(10) The first excited singlet state is suggested because of spin conservation in the splitting of C_2O and because we would find the insensitivity[3] to added O_2 or NO difficult to explain if it were in its triplet ground state.

(11) The distribution of activity in the methylacetylene-$^{14}C_1$ could not be determined in this series of experiments. The role its activity distribution might play in modifying the discrimination ratio is complicated by the fact that allene alone has been observed by us to photolytically isomerize to methylacetylene at a rate which would account for at least one-third of the methylacetylene-$^{14}C_1^*$ produced in the C_3O_2–C_2H_4 photolysis under the same conditions.

of the argument favors C_2O if one considers only the major products.

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TUNGSTEN TRIBROMIDE AND TUNGSTEN TETRABROMIDE

Sir:

The preparations of tungsten dibromide,[1,2,3] tungsten pentabromide,[1,4,5,6,7] and tungsten hexabromide[2,7] are well known. However, conspicuous for their absence among the known halides of tungsten are those of tungsten(III). Others[3] have attempted to prepare anhydrous tungsten trihalides but were unsuccessful. We wish to report the preparation of the first simple trihalide of tungsten, tungsten tribromide, and the preparation of tungsten tetrabromide.

Tungsten tribromide was prepared by the reaction between WBr_2 and excess liquid bromine in a sealed tube at 50° for two weeks. On removal of the excess bromine *in vacuo*, a black powder remained. An X-ray diffraction powder pattern of the resulting compound did not indicate the presence of any of the known tungsten bromides. Chemical analyses on several samples of the product indicated the formula WBr_3 (calcd. for WBr_3: W, 43.40; Br, 56.60. Found: W, 43.22 ± 0.07; Br, 56.30 ± 0.56). The preparation of other trihalides of tungsten by similar methods or by using WBr_3 as a starting material is being investigated.

From the available information on the tungsten halides Brewer, *et al.*,[8] estimated that the tungsten trihalides should not be thermally stable compounds. An examination of the effect of heat on WBr_3 confirmed this estimate. At about 80° *in vacuo* decomposition into WBr_2 and bromine became noticeable. The decomposition at this temperature was very slow, but accelerated with increasing temperature. At 300° the decomposition was rapid and complete; only at the latter temperature was a relatively small amount of a volatile higher bromide formed. X-Ray diffraction powder patterns of this volatile fraction showed that the major constituent was WBr_5.

In its inertness to water, concentrated hydrochloric acid, and air WBr_3 closely resembles $MoBr_3$. Attempts to prepare chloride or bromide complexes from WBr_3 and the aqueous hydrogen halides were unsuccessful because of the low solubility of the solid. This apparent low solubility in water and relative stability in air suggests that the solid WBr_3 exists in a polymerized form rather than a form of simple structure. The solid is slightly soluble in some polar organic solvents, *e.g.*, nitroethane, nitrobenzene and acetonitrile, producing wine-red solutions. Molecular weight determinations and identification of the species in these solutions are in progress.

An examination also is being made of the oxidation state of tungsten in WBr_3. The possibility of WBr_3 containing trivalent tungsten is of special interest since the only trivalent tungsten compounds known at the present time are confined to the anion complexes of tungsten(III), *e.g.*, $W_2Cl_9^{3-}$. The latter ion has been shown to have a dimeric structure[9,10] and is considered to be a derivative of the hypothetical dimer W_2Cl_6.

Although the tungsten tetrahalides WF_4, WCl_4, and WI_4 are known, the preparation of WBr_4 has not been reported. This compound was prepared by reducing WBr_5 with tungsten metal. The starting materials were placed in opposite ends of a Vycor tube along which a uniform temperature gradient was maintained: 630° at the tungsten end and 340° at the WBr_5 end. Upon cooling the tube after ten days a crystalline deposit was observed near the center of the tube. Analysis of this deposit indicated a compound having the formula WBr_4 (calcd. for WBr_4: W, 36.52; Br, 63.48. Found: W, 36.63; Br, 63.45). The X-ray diffraction powder pattern of this compound was similar to those[11] of $MoBr_4$, $NbBr_4$, and $TaBr_4$. The available data indicate the existence of an isomorphous series for these tetrabromides.

The magnetic susceptibilities and structural relationships of WBr_3 and WBr_4 with other tri- and tetrahalides of niobium, tantalum, and molybdenum are presently under consideration. In addition, a study is being made on the stability relations among the complete series of tungsten bromides, WBr_2 through WBr_6.

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[9] C. Brosset, *Nature*, **135**, 874 (1935).

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[11] R. E. McCarley, P. J. H. Carnell, B. A. Torp and J. C. Boatman, to be published.

[12] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

CONTRIBUTION No. 1162[12]

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RECEIVED JUNE 2, 1962

CHEMISTRY OF THE NEOMYCINS. XI.[1] N.M.R. ASSIGNMENT OF THE GLYCOSIDIC LINKAGES

Sir:

In the accompanying communication[1] the gross structures of neomycins B and C were completed. In the present report the stereochemistry of the ribose-neamine linkage is established by n.m.r. spectroscopy, thus completing the stereochemistry of neomycin C (except for the absolute stereochemistry of the substituted deoxystreptamine)[2]

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[1] Paper X in this series: K. L. Rinehart, Jr., M. Hichens, A. D. Argoudelis, W. S. Chilton, H. E. Carter, M. Georgiadis, C. P. Schaffner and R. T. Sebillings, *J. Am. Chem. Soc.*, **84**, 3218 (1962).