(ϵ, uncertain background). These are lower wavelengths than found for $(CF_3P)_4$, suggesting a more restricted delocalization of lone-pair electrons than in $(CF_3P)_4$.[7]

Chemical Behavior. The tetramer $(CF_3As)_4$ is sensitive to basic impurities; for example, failure to eliminate water from the container (such as an infrared cell) may lead to a change back to the original solid–liquid mixture. By analogy to the better known $(CF_3P)_n$ system,[7] we assume the slightly less volatile liquid to be the pentamer $(CF_3As)_5$. The action of air upon $(CF_3As)_4$ seems like that of oxygen on $(CF_3P)_4$; a nonvolatile white solid is formed. We have not made a monomer complex analogous to $(CH_3)_3P \cdot PCF_3$,[8] for $(CH_3)_3As$ only dissolves $(CF_3As)_4$, whereas $(CH_3)_3P$ colors it yellow and soon converts it to a nonvolatile brown solid. Basic hydrolysis destroys $(CF_3As)_4$ with nonstoichiometric formation of HCF_3, as might be expected from the behavior of CF_3–As–H compounds.[9]

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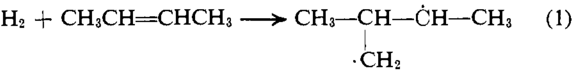
1,2 Shifts of Methyl Groups in Alkyl Diradicals. Formation of Pentenes in Triplet Methylene Reactions with 2-Butene

Sir:

Photolytically formed methylene reacts with *trans*-2-butene in the gas phase to form a variety of C_5 products, including several pentenes and both 1,2-dimethylcyclopropanes.[1–3] Direct stereospecific insertion by singlet methylene into the C=C bond or into one of the C–H bonds accounts for the formation of *trans*-1,2-dimethylcyclopropane, 2-methyl-2-butene, and *trans*-2-pentene, and isomerization of the excited *trans*-dimethylcyclopropane produces the *cis* isomer and several pentenes in reactions carried out at low gas pressures. At higher pressures, however, pentene products are still observed[4] which cannot readily be rationalized through singlet methylene mechanisms. These products, including *cis*-2-pentene, 2-methyl-1-butene, and 3-methyl-1-butene, have been attributed to the reactions of triplet methylene, both as a lesser contributor in the direct photolysis of ketene or diazomethane and as the major reactant in the presence of inert gases[5–7] or in Hg-photosensitized decompositions of methylene precursors.[8]

One initial step suggested for the reaction of triplet methylene with *trans*-2-butene is reaction 1, with subsequent rearrangement of this diradical required for the formation of the pentenes.



$$^3CH_2 + CH_3CH{=}CHCH_3 \longrightarrow CH_3{-}\underset{\displaystyle \cdot CH_2}{\underset{|}{CH}}{-}\dot{C}H{-}CH_3 \quad (1)$$

No agreement has existed concerning the nature of such rearrangements, and several possible mechanisms have been suggested,[4] including (a) 1,4-hydrogen shift; (b) 1,2-hydrogen shift; (c) 1,2-methyl shift; and (d) the closing of the diradical to the substituted cyclopropane, followed by reopening of a different ring C–C bond and a 1,2-hydrogen shift. An alternate mechanism for pentene formation involves an initial abstraction reaction by the triplet methylene, followed by methyl–butenyl radical combination.[9]

Additional information about these possible mechanisms can be obtained through tritium labeling of the original methylene and subsequent determination of the intramolecular location of the tritium label. In this situation, the diradical formed in (1) is $CH_3CH(\dot{C}HT)\dot{C}HCH_3$, and the various rearrangements lead to different locations for the tritium atom originally in the methylene group. In our initial experiments we have utilized CHT from the photolysis of CHT=C=O at 3660 A, and have analyzed the C_5 olefinic products for their intramolecular tritium location through the techniques of isotopic radio gas chromatography.[10,11] The reacting methylene is approximately 30% triplet under these conditions.

Two important products for mechanism determination in this system are 3-methyl-1-butene and *cis*-2-pentene. The shift of a methyl group in the triplet diradical would lead to $(CH_3)_2CHCH{=}CHT$ and *cis*-$CH_3CHTCH{=}CHCH_3$, while $CH_3CH(CH_2T)CH{=}CH_2$ would be formed by 1,4-hydrogen shift. The ring-closure and reopening mechanism (d) would produce $CH_3\dot{C}HCHT\dot{C}HCH_3$, and the rearrangement would give both $CH_3CH_2CT{=}CHCH_3$ and $CH_3CHTCH{=}CHCH_3$.[12] The initial abstraction of H by CHT would lead only to alkyl-tritiated forms of 3-methyl-1-butene and *cis*-2-pentene in the subsequent CH_2T–butenyl combination.[13] The intramolecular distribution of tritium between alkyl and olefinic positions is summarized in Table I for 3-methyl-1-butene and *cis*-2-pentene from CHT reactions with *trans*-2-butene under a variety of conditions.

The 3-methyl-1-butene contains tritium activity in both alkyl and olefinic positions, indicating more than one mechanism for its formation. The presence of an olefinic tritium component indicates that 1,2-methyl migration is an important process for the formation of this molecule. While 1,2 shifts of methyl or hydrogen

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(12) A kinetic isotope effect would be anticipated, such that $CH_3CH_2CT{=}CHCH_3$ should predominate.

(13) The ratio gas chromatographic techniques separate the tritiated olefins into an alkyl-*t* group and an olefin-*t* group, but do not distinguish isomeric forms within the two groups.

Table I. Intramolecular Distribution of Tritium in Pentenes from CHT Reactions with *trans*-2-Butene

Pressure, torr	Butene/ketene ratio	Wave-length, A	Total C_5 yield, %	Alkyl-tritium, %
		Product 3-Methyl-1-butene		
25	30	3660	3.9 ± 0.3	52 ± 3
150	30	3660	2.0 ± 0.5	71 ± 2
294	49	Mixed[a]	2.5 ± 0.1	75 ± 3
294	49	3660	1.6 ± 0.1	85 ± 4
400	49	3660	1.0 ± 0.1	88 ± 3
		Product *cis*-2-Pentene		
25	30	3660	2.5 ± 0.3	97 ± 3
150	30	3660	1.3 ± 0.2	100 ± 2
294	49	3660	0.9 ± 0.2	99 ± 2
400	75	3660	0.7 ± 0.3	100 ± 2

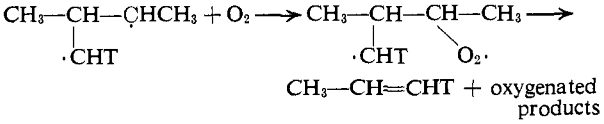
[a] Major bands are 3130 and 3660 A.

have not been unequivocably confirmed in alkyl monoradical reactions,[14] the additional driving force of the formation of the double bond should more readily permit such shifts for 1,3-diradicals. The increase in yield at lower pressures for the $(CH_3)_2CHCH{=}CHT$ may indicate that the 1,2 shift occurs more readily for the diradical still excited from the exothermic reaction (1).[15]

cis-2-Pentene shows no olefinic tritium activity in this pressure range within the limits of measurement, and therefore shows no evidence for the ring-closure–reopening mechanism.

The alkyl-*t* activity in *cis*-2-pentene is consistent with the 1,2-methyl shift mechanism, but could also be formed by radical combination. Similarly, the alkyl-*t* activity in 3-methyl-1-butene has two possible sources, and cannot be definitely assigned to a particular mechanism.

When oxygen is present, 3-methyl-1-butene is not observed and propylene appears as a product.[1] These changes can occur through the oxygenation of the diradical from reaction 1 and its subsequent decomposition, as shown in (2). The propylene-*t* formed by



$$CH_3{-}\underset{\cdot CHT}{\underset{|}{CH}}{-}\dot{C}HCH_3 + O_2 \longrightarrow CH_3{-}\underset{\cdot CHT}{\underset{|}{CH}}{-}\underset{O_2\cdot}{\underset{\diagdown}{CH}}{-}CH_3 \longrightarrow CH_3{-}CH{=}CHT + \text{oxygenated products} \quad (2)$$

this sequence in triplet CHT reactions with *trans*- or *cis*-2-butene should be entirely $CH_3CH{=}CHT$, and actual observations of propylene-*t* formed in the presence of 3% oxygen indicate no alkyl-*t* activity within the limits of accuracy (about ±3%).

Propylene formation with all of the tritium activity in olefinic positions is certainly consistent with the sequence given in (2), but does not represent firm evidence for any structure of the addition product of the diradical and oxygen. It is, however, clear evidence that the oxygen does not completely scavenge the CHT itself, but instead reacts much of the time after the prior reaction of CHT with the olefinic substrate. These results indicate that the rate of reaction of triplet CHT with a double bond is competitive with its reaction with O_2, and that the 1,2-methyl shift of the diradical is slow compared to reaction of the diradical with O_2. The specific rate constant for the 1,2-methyl shift cannot exceed about 10^8 sec^{-1} in these experiments.

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[15] Measurements of the isomerization rates of excited dimethylcyclopropanes indicate that isomerization to the pentenes is negligible even at 25 mm. The yields of *cis*-1,2-dimethylcyclopropane, the highest yield isomerization product, confirm that these reactions are not important at these pressures.[3]

Nitroxides. XIX. Norpseudopelletierine-N-oxyl, a New, Stable, Unhindered Free Radical

Sir:

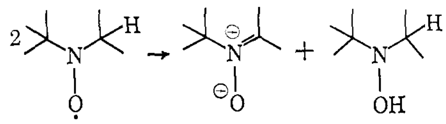
The "stability" of organic free radicals is generally considered to arise from a "delocalization" of the unpaired electron over a conjugated system or in other words from the presence of mesomeric structures.

Nitroxide radicals have recently been prepared[1,2] in which the unpaired electron is part of a two-center three-electron bond without further delocalization. Their stability has been attributed to steric hindrance,[2-4] bulky groups preventing the formation of the dimer.

However, the situation is certainly not very different from the NO or NO_2 molecules in which there is no steric hindrance to prevent dimerization. The stability of the paramagnetic monomer is then attributed to some particularities of the three-electron N–O bond.[2,5]

Organic unhindered nitroxides, such as dimethyl nitroxide[6] or diethyl nitroxide,[7] are also known, but these compounds are "unstable." This instability does not seem to be due to dimerization but rather to a decomposition of the free radical. To our knowledge, only two decompositions of nitroxide radicals have been studied (N,N-diphenyl nitroxide[8] and N-*t*-butyl-N-phenyl nitroxide[4,9]), suggesting a bimolecular dismutation of these aromatic nitroxides. On the other hand, the oxidation of hydroxylamines, known to give nitrones,[10] has been shown to involve unstable nitroxide radicals.[6,11]

This suggests that "unstable" nitroxide free radicals, *e.g.*, I, may decompose by dismutation to a nitrone (II) and a hydroxylamine (III), or, at least, that the nitrone may be an important intermediate in their decomposition.



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We wish to report the synthesis of a stable unhindered

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