Table I. Reaction of Sulfoxides and Related Substrates with $W_2Cl_9^{3-}$, $Mo_2Cl_8^{4-}$, $Mo_2Cl_8H^{3-}$, and $MoCl_6^{3-}$

Registry no.	Substrate	Sulfide, %[a] $K_3W_2Cl_9$[b]	 $(NH_4)_4Mo_2Cl_8\cdot NH_4Cl\cdot H_2O$[c]	 $Cs_3Mo_2Cl_8H$[d]	 K_3MoCl_6[e]
68-68-5	Dimethyl sulfoxide	100_3[f]	75_2[f]	74_2[f]	47_2[f]
2168-93-6	Di-*n*-butyl sulfoxide	95_3	90_{18}	91_{18}	76_{18}
1193-82-4	Phenyl methyl sulfoxide	92_3	94_2	95_2	90_{72}
824-86-2	Benzyl methyl sulfoxide	92_3	72_2	92_{18}	70_{72}
19093-37-9	Allyl phenyl sulfoxide	88_3	59_{18} (63_{72})	54_{18} (60_{72})	54_{18}
4170-69-8	Isopropyl phenyl sulfoxide	97_3	94_{18}	91_{18}	72_{18}
945-51-7	Diphenyl sulfoxide	99_3	97_{22}	99_{72}	79_{72}
33840-74-3	α-Phenylsulfoxyl acetone	95_3	62_{48}	65_{48} (65_{72})	66_{72}
4381-25-3	Phenyl methyl sulfoximine	14_3	56_2	7_2	2_{72}
67-71-0	Dimethyl sulfone	$<1_6$	$<1_{72}$	$<1_{72}$	$<1_{72}$

[a] Subscript denotes reaction time (h). Unless otherwise indicated yields were determined by quantitative vapor phase chromatography and are based on sulfoxide. [b] See ref 5; reaction solvent H_2O-CH_3OH (11:1). [c] See ref 11; reaction solvent CH_3OH. [d] See ref 12; reaction solvent H_2O-CH_3OH (5:1). [e] Obtained from Climax Molybdenum; reaction solvent H_2O-CH_3OH (5:1). [f] Dimethyl sulfide was determined gravimetrically as its mercuric chloride complex: W. F. Faragher, J. C. Morell, and S. Comay, *J. Am. Chem. Soc.*, **51**, 2728 (1929).

10 ml of methanol. The resulting mixture was heated at 50 °C for 18 h, then allowed to cool before adding a known amount of tridecane (GLC internal standard). Water (25 ml) was added, the resulting mixture extracted with three 5-ml portions of chloroform, and the combined extracts dried ($MgSO_4$) and analyzed by GLC.

Reduction of Dimethyl Sulfoxide with K_3MoCl_6. Into a three-necked, 100-ml flask was placed a Teflon-coated magnetic stirrer bar, 1.29 g (3.22 mmol) of tripotassium hexamolybdate, and 30 ml of a 5:1 water–methanol mixture. A condenser was attached. The condenser and the remaining side arms were stoppered with rubber septums and the system purged briefly with nitrogen before injecting dimethyl sulfoxide (0.155 g, 2.00 mmol) by syringe. With vigorous stirring the resulting mixture was heated at 60 °C. Throughout the course of the reaction a slow stream of nitrogen was passed over the reaction mixture and allowed to ebullate through a 0.125-in. Teflon tube that terminated in 75 ml of saturated aqueous solution of mercuric chloride. When no further precipitation was observed (~2 h), the resulting solid was collected by suction filtration and dried in vacuo over P_2O_5 to a constant weight. The yield of dimethyl sulfide was determined gravimetrically as $[(CH_3)_2S]_2(HgCl_2)_3$ (see Table I, footnote *f*).

Registry No.—$W_2Cl_9^{3-}$, 23403-17-0; $(NH_4)_4Mo_2Cl_8\cdot NH_4Cl$, 40902-25-8; $Cs_3Mo_2Cl_8H$, 24436-25-7; K_3MoCl_6, 13600-82-3.

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(14) Infrared spectra were determined within sodium chloride cells on a Perkin-Elmer Model 137 spectrophotometer. NMR spectra were determined with a Varian T-60 NMR spectrometer. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-7E mass spectrometer. Analytical GLC analyses were performed on a Hewlett-Packard Model 5750 flame ionization instrument. Absolute product yields were calculated from peak areas using internal standard techniques with response factors obtained from authentic samples. All solvents were deoxygenated by purging with nitrogen for 20 min prior to use. GLC analyses were determined on a 2 ft × 0.25 in. column of 7.5% SE-30 on Chromosorb G. Unless otherwise indicated starting sulfoxides and authentic product samples were obtained from commercial sources.

Atomic Oxygen. 7. Reactions of Alkynes with Oxygen (^3P) Atoms[1]

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The reactions of oxygen atoms with alkynes can produce a wide variety of intermediates, including oxirenes, 1,3-biradicals, ketocarbenes, and excited ketenes. The existence of these intermediates is not experimentally reflected in previous studies[2] of the reactions of acetylene and propyne, which are dominated by the fragmentation of initially formed excited reaction products. On the other hand, the reaction of 2-butyne with O(^3P) produces significant amounts of an unfragmented product, 3-buten-2-one, in a pressure dependent process.[3] This pattern has its parallel in the reactions of olefins, in which ethylene and propene show large amounts of fragmentation, while the butenes yield mainly C_4H_8O products.[1,4]

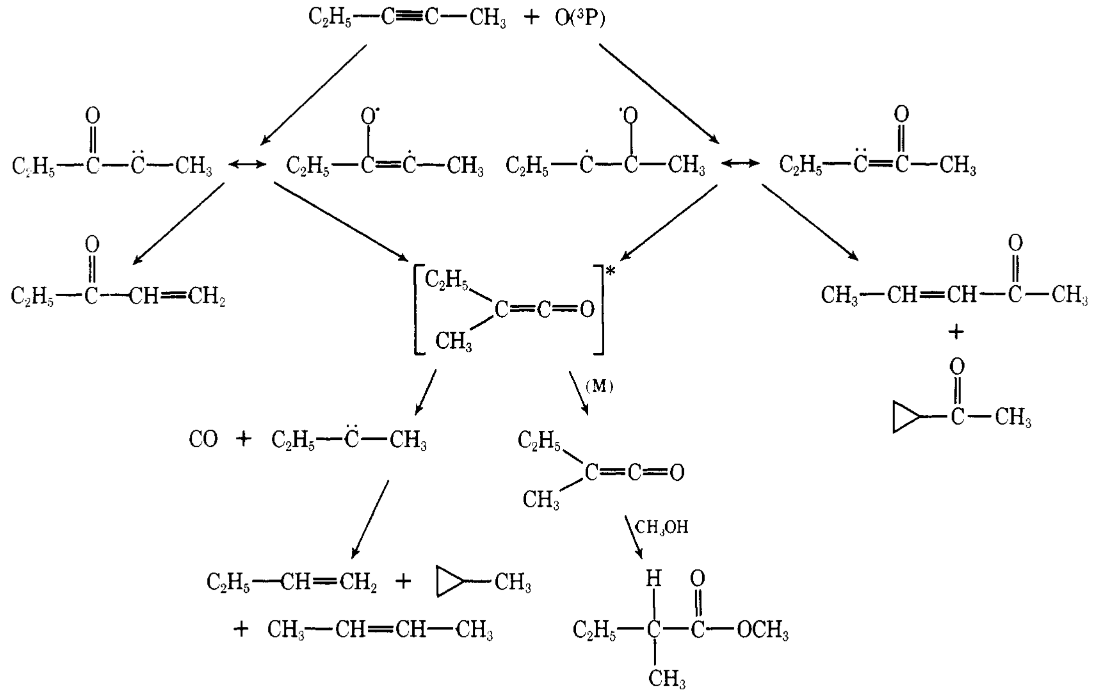
To shed further light on the reactions of O(^3P) with alkynes, we have studied the gas-phase reactions of some C_4, C_5, and C_6 acetylenes. The products of these reactions are summarized in Table I. The relatively low material balance of these reactions and the quenched reactions described below is partially due to the competing reaction of atomic oxygen with mercury.

A major portion of the isolated reaction product consisted of unfragmented carbonyl compounds. The composition of these products is reminiscent of the products obtained from the reactions of peracids with alkynes[5] and also from the decomposition of diazo ketones.[3,6,7] The fragmented products, carbon monoxide and olefins and cyclopropanes, are probably formed by the decomposition of excited ketenes to carbenes. A scheme which summarizes these transformations is shown for the 2-pentyne reaction.

Table I. Product Yields from Reactions of $O(^3P)$ with Alkynes[a]

Registry no.	Reactant	Products	Yield, %[b]
5003-17-3	2-Butyne	3-Buten-2-one	18
		Carbon monoxide	27
		Propene	18
627-19-0	1-Pentyne	*trans*-2-Pentenal	19
		trans-2-Methylcyclopropanecarboxaldehyde	2.8
		cis-2-Methylcyclopropanecarboxaldehyde	1.8
		Carbon monoxide	22
		1-Butene	15
		Methylcyclopropane	0.9
627-21-4	2-Pentyne	1-Penten-3-one	17
		trans-3-Penten-2-one	9.6
		Cyclopropyl methyl ketone	1.4
		Carbon monoxide	18
		1-Butene	4.0
		trans-2-Butene	6.0
		cis-2-Butene	3.3
		Methylcyclopropane	≤0.4
917-92-0	3,3-Dimethyl-1-butyne	2,3-Dimethyl-2-butenal	18
		2,2-Dimethylcyclopropanecarboxaldehyde	3.7
		2,2-Dimethylcyclobutanone	1.9
		Carbon monoxide	15
		1,1-Dimethylcyclopropane	7.4
		2-Methyl-2-butene	5.1
928-49-4	3-Hexyne	4-Hexen-3-one	29
		Cyclopropyl ethyl ketone	5.9
		Carbon monoxide	16
		trans-2-Pentene	7.2
		cis-2-Pentene	4.8
		Ethylcyclopropane	≤0.4

[a] Reaction conditions: temperature 25 ± 3 °C; pressure 0.8–0.9 atm; consumption of alkyne <20%; reproducibility among reactions ±13% of the stated yield. [b] Product yields are based on the measured amounts of nitrogen produced by the mercury photosensitized decomposition of nitrous oxide.



The existence of fragmentation products attributable to excited ketenes brought up the possibility of trapping these ketenes as their methanol adducts, methyl esters.[8] The reaction of $O(^3P)$ with 50:50 mixtures of methanol and alkyne did indeed produce significant quantities of the methyl esters derived from the corresponding ketenes. The yields of methyl esters from the various alkynes follow: 2-butyne, 10%; 1-pentyne, 15%; 2-pentyne, 16%; 3,3-dimethyl-1-butyne, 22%; and 3-hexyne, 20%. Interestingly, the formation of these methyl esters was not accompanied by decreases in the yields of either the fragmentation products or the carbonyl products. Furthermore, when methanol was added to the alkyne–atomic oxygen product mixture (after photolysis but before workup and distillation), the isolated yield of methyl ester decreased by no more than 8% of its original value. This observation means that the fragmentation products are predominantly formed by decomposition of an excited adduct in the O(^{3}P) reaction pathway, rather than by the formation and subsequent photolysis of an isolable ketene. While spin conservation dictates that the initial adduct be a triplet, intersystem crossing to the singlet ketocarbene may precede product formation.

The reaction of atomic oxygen with a 50:50 mixture of 2-pentyne and methanol produced no detectable amounts of methyl 2-ethylbutyrate or methyl 2-methylpropionate and only traces of C_3 and C_5 hydrocarbons. This result indicates that the ketene-forming rearrangement of the O(^{3}P)–alkyne adduct is intramolecular, in that it proceeds without the migrating group becoming detached from the adduct. This pattern is in contrast to that of O(^{3}P) plus olefin reactions, in which migrating alkyl radicals become detached from the molecule during rearrangement.[4] The Wolff rearrangement of α-diazo ketones is also intramolecular.[10]

Experimental Section

Reaction Technique. Procedures for the reaction of atomic oxygen, generated in situ by the mercury photosensitized decomposition of nitrous oxide, have been described previously.[11] The alkynes were obtained commercially and distilled before use. Relative rate constants of the alkynes vs. cyclopentene were determined by the method of Cvetanovic and converted to the usual standard, 2-methylpropene, using the figure $k_{\text{cyclopentene}}/k_{\text{2-methylpropene}} = 1.19$.[4]

Product Analysis. The VPC substrates most often used were noncondensable gases, 5A molecular sieves; hydrocarbon products, DC710; and carbonyl and ester products, dinonyl phthalate. Authentic samples of 3-buten-2-one, 1-penten-3-one, *trans*-3-penten-2-one, cyclopropyl methyl ketone, methyl 2-methylpropionate, and the hydrocarbon products were obtained commercially for comparison of spectra and VPC retention times. Cyclopropyl ethyl ketone and 4-hexen-3-one were prepared by reaction of diethylcadmium with the appropriate acid chloride.[12] Spectra of the other carbonyl and ester products were routinely predictable or available from the literature.[13]

trans-2-Methylcyclopropanecarboxaldehyde was prepared by reaction of 2-butenal with diiodomethane and zinc–silver couple.[14] The published NMR spectrum of this compound contains uncorrected errata. We found the spectrum (in CCl_4) to be δ 0.9–1.4 (m, 6 H), 1.9 (m, 1 H), and 9.08 (d, 1 H).

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Registry No.—Atomic oxygen, 17778-80-2; *trans*-2-methylcyclopropanecarboxaldehyde, 50991-21-4.

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Oxidation of *p*-Toluenesulfonylhydrazide to 1,2-Di(*p*-toluenesulfonyl)hydrazine

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p-Toluenesulfonylhydrazide (**1**) and catalytic amounts of cobalt salts in solution react with aqueous hydrogen peroxide to give 1,2-di(*p*-toluenesulfonyl)hydrazine (**4**) (or its tautomer **5**) as the major product. The same reactants in the presence of stoichiometric amounts of cobalt salts produce the more complete oxidation products of cobalt sulfonate and cobalt sulfinate salts. A reaction (Scheme I) patterned after the Haber–Weiss decomposition scheme is expected to produce the free radicals which subsequently oxidize the sulfonhydrazide.[2-4]

Scheme I

$$\mathrm{HOOH} + \mathrm{Co}^{2+} \longrightarrow \mathrm{HO}\cdot + \bar{\mathrm{O}}\mathrm{H} + \mathrm{Co}^{3+}$$
$$\mathrm{HOOH} + \mathrm{Co}^{3+} \longrightarrow \mathrm{HOO}\cdot + \mathrm{H}^{+} + \mathrm{Co}^{2+}$$

The isolation of **4** or **5** as the major product strongly suggests that *p*-toluenesulfonylhydrazide (**1**) undergoes reactions (Scheme II) similar to those of primary alkyl and aryl hydra-

Scheme II