Reactions of the Ethynyl Radical

Part 2.—With Alkenes

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Ethynyl radicals, from the 2537 Å photolysis of bromoacetylene, have been reacted with C_2-C_6 monolefins with and without the addition of nitric oxide. Hydrogen abstraction occurs, and also addition of ethynyl to the π-bond followed by a displacement process giving conjugated or unconjugated enynes. The rates of these reactions have been measured relative to the formation of C_4H_2 by attack on bromoacetylene. The mechanism of the addition reaction is discussed.

In part 1 of this series [1] we reported a study of the photolysis of the bromoacetylene + nitric oxide system, and some data derived from it, including relative rate constants for hydrogen abstraction from alkanes by ethynyl radicals. Our survey of the reactions of C_2H has been extended to olefins, and the present paper describes reactions involving C_2—C_6 monolefins and butadiene-1,3.

EXPERIMENTAL

MATERIALS

Bromoacetylene and nitric oxide were prepared or purified as described previously.[1] The olefins, Phillips Research Grade (ethylene, propene, the 4 butenes, butadiene-1,3, pentene-1 and hexene-1) and American Petroleum Institute standards (pentene-2, hexene-2, hexene-3, 3-methylbutene-1 and cyclopentene) were all purer than 99·8 %, and were used after degassing and low-temperature distillation. The purities of 3,3-dimethylbutene-1 (K and K), 2-methylbutene-1 and 2-methylbutene-2 (Matheson Coleman and Bell), dimethylbutene-2 (Chemical Procurement Labs.) and methylenecyclobutane (Aldrich) were checked by gas chromatography (GLC) using a 16-ft. dimethyl sulpholane/celite column, and were improved to 99·5 %+, where necessary. C_2D_4 and CH_2CD_2 (Merck, Montreal), CD_3CHCH_2 (Volk Radiochemical), CH_3CFCH_2 and CF_3CFCF_2 (Peninsular Chemresearch) were treated similarly using a 6-ft. silica gel column. The C_2D_4 contained 3 % C_2D_3H; the isotopic purities of the other deuterated compounds were not checked.

Methylbutenyne (K and K) was purified by GLC using the dimethyl sulpholane column. 1-Pentenyne-4 and cis and trans 3-pentenyne-1 were made by esterifying 1-pentynol-4 with acetic anhydride, and pyrolyzing the acetate.[2] The three isomers (formed in similar yields) were separated by GLC using an 18-ft. tris-(cyanoethoxy)-propane/firebrick column. The remaining isomer, 1-pentenyne-3, was made [3] by bubbling butenyne into a well-stirred solution of sodium in liquid ammonia, and adding iodomethane; it was similarly purified. The structures of all five isomers were identified by n.m.r., with further confirmation by i.r. for the cis-3,1 isomer.[4] Repurified samples were used to obtain mass-spectrometric (MS) cracking patterns (see appendix).

PROCEDURE

Photolysis and analysis procedures were as described for runs with added alkane in part 1.[1] Runs without added NO contained 7·5 torr BrC_2H; the others used 15 torr of
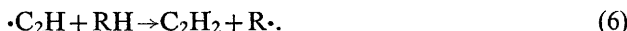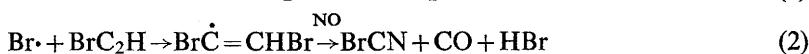
a $BrC_2H + NO$ mixture ($1:1$). Olefin pressures were 10-20 torr, and photolysis lasted 30-40 min.

The GLC detector (thermal conductivity cell) was found to have equal sensitivity to C_4H_2 and C_4H_4, so calibrations for C_5 and C_6 enynes were done using pentadiene-1,3, isoprene and hexadiene-2,4, all commercially available compounds. Errors probably do not exceed 3 %.

RESULTS

PRODUCTS IN THE PRESENCE OF NITRIC OXIDE

The photolysis of BrC_2H in the presence of NO and an alkane gave as products CO, C_4H_2, BrCN, HCN and acetylene, with traces of nitrogen, N_2O, cyanogen and cyanoacetylene. The mechanism proposed [1] for the formation of the major products was

$$BrC_2H \overset{h\nu}{\to} Br\cdot + \cdot C_2H \tag{1}$$

$$Br\cdot + BrC_2H \to Br\overset{.}{C} = CHBr \overset{NO}{\to} BrCN + CO + HBr \tag{2}$$

$$\cdot C_2H + BrC_2H \to C_4H_2 + Br\cdot \tag{3}$$

$$\cdot C_2H + BrC_2H \to C_2H_2 + \cdot C_2Br \tag{4}$$

$$\cdot C_2H + RH \to C_2H_2 + R\cdot. \tag{6}$$

When the alkane is replaced by an alkene the yields of CO, BrCN, HCN and cyano-acetylene are markedly reduced; with olefins other than ethylene the latter two are not detectable, while the CO yield progressively diminishes with increasing molecular weight of alkene. This change reflects a competition between reaction (2) and bromine atom scavenging by the olefin, the efficiency of which follows the order, similar to that reported by Abell [5]:

$$C_2H_4 < C_3H_6 < cis-C_4H_8 < 1-C_4H_8 < trans-C_4H_8 \simeq 1-C_5H_{10} < iso-C_4H_8.$$
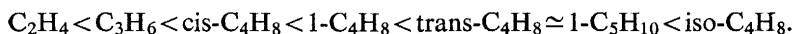
With the other olefins the CO yields were not measured. A yellow film was deposited as in the alkane experiments: it was also readily soluble in methanol.

Addition of an alkene to the $BrC_2H + NO$ photolysis decreases the yield of C_4H_2 and increases that of acetylene: hydrogen must therefore be abstracted by ethynyl from the olefin. In addition, new products are formed, characteristic of the type of olefin added. Nine such compounds have been detected by G. L. C. and identified by M. S. as C_4H_4 (1), C_5H_6 (3), and C_6H_8 (5 isomers). Higher homologues are probably formed in some cases, but could not be detected by our G.L.C. technique. Of the four possible structures for C_4H_4, one is stable (butenyne, vinyl-acetylene), which was identified as a product by its G.L.C. retention time and M.S. cracking pattern. The C_5 products were similarly identified, by comparison with synthetic samples of the five pentenynes (see Materials), as 1-pentenyne-4 and cis and trans 3-pentenyne-1. The latter pair always occurred together in a constant ratio (see table 1) similar to that obtained by synthesis.[4] No attempt was made to identify the C_6H_8 compounds, since there are 16 possible enyne structures including cis-trans isomers.

The olefins yielded enynes as follows. Ethylene and the 1-alkenes gave butenyne, while 1-alkenes with unbranched chains also formed 1-pentenyne-4. Propene also gave 3-pentenyne-1, as did the 2-alkenes. The 3-alkenes studied (pentene-2 and hexene-3) gave two of the C_6H_8 isomers, assumed (see later) to be cis and trans 3-hexenyne-1. Other enynes were formed from individual olefins; these are more conveniently shown in the table of relative rates (table 1).

To clarify the reaction mechanism some experiments were done using deuterated olefins. From ethylene-d_4 the C_4 product was C_4D_3H, indicating that a D-atom is lost in a reaction between C_2D_4 and C_2H. From CH_2CD_2 the C_4 product was 57 % $C_4D_2H_2$ and 43 % C_2DH_3; this gives a H/D isotope effect for hydrogen elimination of about 1·3. The C_4 product from CD_3CHCH_2 was $\geqslant 95$ % C_4H_4 (loss of CD_3), but the 1-pentenyne-4 from the same reaction contained 2D (D-atom

TABLE 1.—RELATIVE RATES FOR REACTION OF C_2H WITH OLEFINS

$C_2H + BrC_2H \rightarrow C_4H_2 + Br(3)$; $R_3 = 1·00$

type	olefin		C_2H_2	C_4H_4	C_5H_6				C_6H_8				
					c-3,1	t-3,1	1,4	'iso'	A	D	B	C	E
0	ethylene		0·55	0·78									
	ethylene-d_4		0·32	0·58									
	ethylene-1-d_2		0·5	0·8									
1	propene		0·31	1·05	·07	·06	·13	·01					
	propene-3-d_3		0·40	1·00	·06	·05	·04	·01					
	2-F-propene *		0·42	~0·2	~·1	~·1							
	butene-1		0·49	0·68			·54						
	3-Me-butene-1		0·60	0·72									·38
	3:3-diMe-butene-1		0·72	0·68									
	pentene-1		0·83	0·25			·58						
	hexene-1		1·29	0·15			·28						
	butadiene-1,3		0·18	0·15									
2A	butene-2	cis	0·51		·51	·35							
		trans	0·52		·52	·36							
	pentene-2	cis	0·8-0·95		·34	·24	·08		·06	·08			
		trans	0·8-0·95		·34	·24	·08		·06	·08			
	hexene-2	cis	1·9		·15	·12	·12						
	hexene-3	cis	0·85-0·9						·17	·21			
	cyclopentene		1·27										
2B	2-Me-propene (isobutene)		0·44					·16			·13		·16
	2-Me-butene-1		0·51					·03			·43		
	methylene-cyclobutane		0·84										
3	2 Me-butene-2		0·76									·56	
4	di-Me-butene-2		2·0										

$P_{BrC_2H} = P_{NO} = 7·5$ torr. $P_{olefin} = 10-18$ torr.   Photolysis 30 or 40 min.

* C_4 and C_5 products are C_4H_3F and C_5H_5F respectively.

loss from the CD_3 group) while the 3-pentenyne-1 was triply deuterated (loss of H from the $CHCH_2$ group).

Reaction of C_2H with 2-fluoropropene gave acetylene, C_4FH_3 and two isomeric C_5FH_5 compounds, assumed to be cis- and trans-4-fluoro-3-pentenyne-1. No C_2H-addition products were detected from cyclopentene, methylenecyclobutane, or dimethyl-butene-2; if formed, they were presumably C_7 or higher enynes. Ethylene and allene were formed in significant amounts from methylenecyclobutane (major products of its mercury-photosensitized decomposition [6]), possibly due to photosensitization by bromoacetylene. No products were detected from perfluoropropene.

In the reaction between C_2H and butadiene-1,3 trace amounts of gaseous products were obtained, including acetylene, C_4H_4 and C_6H_6 (not benzene). This was the only reaction studied which gave a polymeric deposit insoluble in methanol.

PRODUCTS FROM RUNS WITHOUT NITRIC OXIDE

Four olefins, ethylene, propene, butene-1 and cis-butene-2, were reacted with C_2H radicals, without nitric oxide. The same products were obtained as in the corresponding experiments with nitric oxide, the relative yields being somewhat different (table 2). In addition, pentyne-1 (from propene) and hexyne-1 (from butene-1) were identified as important products by their M.S. cracking patterns.

No alkynes were detected in the ethylene and butene-2 experiments. In all runs without nitric oxide a brown film was deposited, which could only be removed by hot chromic and nitric acids. Because of these polymerization difficulties, and the analysis complications introduced by the additional alkyne products, the main study was confined to the system containing nitric oxide.

TABLE 2.—YIELDS FROM ETHYNYL-ALKENE REACTIONS UNDER VARIOUS CONDITIONS

alken e	run	initial pressures, torr				yields, μmoles				
		BrC_2H	NO	alkene	N_2	C_2H_2	C_4H_2	C_4H_4	total C_5H_6	1-ynes
ethylene	1	6·5	0	31		0·42	0·38	0·33	—	—
,,	2	6·5	2·5	31		nm	0·34	1·19	—	—
,,	3	6·5	2·6	31	570	nm	0·31	0·89	—	—
propene	4	7·5	0	17·5		0·35	0·38	0·56	0·30	0·7 *
,,	5	7·5	7·5	18·3		0·41	0·31	0·77	0·16	0 *
butene-1	6	7·5	0	11·4		0·82	0·72	0·33	nm	1·5 †
	7	7·5	7·5	10·8		0·54	0·40	0·40	0·28	0 †
	8	7·5	7·5	11·4	170	0·38	0·38	0·28	0·20	—
	9	7·5	7·5	88		0·66	0·06	0·42	0·28	—
cis-butene-2	10	7·6	0	12·0		0·64	0·83	—	0·40	—
	11	7·5	7·5	11·8		0·73	0·77	—	1·04	—

* pentyne-1 ;   † hexyne-1 ;   nm = not measured

RELATIVE RATES

As already shown, ethynyl reacts with olefins by two processes: hydrogen abstraction giving acetylene, and addition to the double bond. In the presence of NO the only volatile products from the latter process are enynes. Relative rates for these reactions have been calculated from product yields, and referred to the rate of production of C_4H_2 ($R_3 = 1$). The same precautions were taken as in part 1, to minimize errors due to secondary reactions of C_4H_2. Two pressures of each olefin were used, and reproducibility of rate-ratios was ± 5 % with few exceptions. Table 1 gives the data, classified according to olefin type.

The hydrogen-abstraction rates of type 1 olefins (1-alkenes) show a steady increase with chain length and molecular weight, but ethylene does not fit this trend. This suggested that the acetylene yield from ethylene might be partially due to mercury photosensitization. To check this the resonance lamp was replaced by a medium-pressure lamp fitted with a 2-cm mercury-vapour filter. The results of runs with ethylene, cyclopentene or cis-pentene-2 added to the $BrC_2H + NO$ mixture indicated that photosensitization was not important in our system.

EFFECT OF REACTION CONDITIONS ON YIELDS (table 2)

PRESENCE OF NITRIC OXIDE.—The yields of acetylene and C_4H_2 are not greatly altered by the absence of nitric oxide (runs 1, 2; 4, 5; 6, 7; 10, 11). The effect on the enyne yields from the reaction of C_2H with ethylene, propene and butene-1 is also small, but it appears that nitric oxide assists enyne formation, presumably by abstraction. This effect is most noticeable in the yields of C_4H_4 from ethylene and of C_5H_6 from butene-2. It is also possible that in the absence of NO the yields of enyne are diminished by secondary reaction with radicals.

The relatively high yields of pentyne and hexyne (found in the reactions of propene and butene-1 respectively) are completely suppressed by nitric oxide. These

alkynes must arise from a radical sufficiently long-lived that it either abstracts hydrogen from the olefin or combines with NO, before it can decompose to an enyne.

INERT-GAS PRESSURE.—The addition of relatively high nitrogen pressures to the system (runs 2, 3 ; 7, 8) causes a small reduction in enyne formation, and only a slight change in the C_4H_2 yield.

ALKENE PRESSURE.—An eight-fold increase in the pressure of butene-1 (runs 7, 9) increases the acetylene and enyne yields at the expense of C_4H_2. The relative rate of enyne formation is unchanged, confirming that C_4H_2 arises from reaction (3) rather than from ethynyl radical dimerization.[1]

DISCUSSION

HYDROGEN ABSTRACTION

The relative rates of abstraction from type 1 olefins (table 1) show a steady increase with chain length. For methyl radicals abstracting from butenes [7] it is assumed that allylic hydrogens constitute the bulk of those abstracted. If this were the case for the ethynyl radical the abstraction rates for butene-, pentene- and hexene-1 should be similar, propene reacting more slowly since its allylic hydrogens are primary. Table 1 does not bear this out : the abstraction rate increases significantly as the carbon chain is lengthened. Furthermore, 3-methylbutene-1 contains a tertiary allylic hydrogen, while 3 : 3-dimethylbutene-1 has none, yet the abstraction rate increases steadily as the allylic hydrogen atoms in butene-1 are replaced by methyl groups.

TABLE 3.—HYDROGEN ABSTRACTION BY METHYL[8] AND ETHYNYL FROM OLEFINS ; RELATIVE RATES (K_{abs}(butene-1) $= 1$ IN EACH SYSTEM)

olefin	$R = C_2H$ K_{abs}	$R = CH_3$ K_{abs}
propene	·63	·10
butene-1	1·00	1·00
3-Me-butene-1	1·22	3·4
pentene-1	1·7	1·25
cis-butene-2	1·04	·51
trans-butene-2	1·06	·77
isobutene	·90	·33

On the basis of bond strengths, hydrogen abstraction should occur much less readily from ethylene than from propene. As our figures show to the contrary, acetylene may be formed from ethylene by an addition-decomposition process :

$$H_2\dot{C}=CH_2 + \dot{C}\equiv CH \rightarrow H_2C-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-C\equiv CH \nearrow \begin{matrix} C_4H_4 + \dot{H} & (7) \\ \searrow \\ C_2H_2 + \dot{C}_2H_3 & (8) \end{matrix}$$
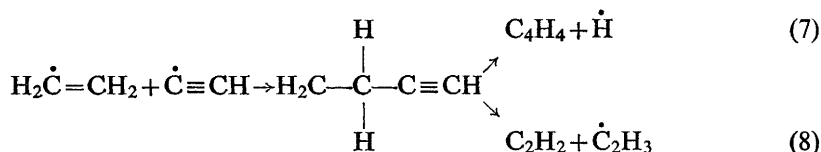
In support of this theory, the ratio $k_{C_2H_2}/k_{C_4H_4}$ is roughly constant for the three isotopic ethylenes studied. The H/D isotope effect is 1·35 for (7) and 1·7 for (8), similar to the value of 1·4-1·5 found for abstraction from alkanes.[1]

Szwarc [8] has studied the addition and abstraction reactions of methyl radicals with olefins, and has listed relative rates for these processes. It is not profitable to compare addition rates, but the abstraction figures are of interest (table 3). As

we found in the reaction of ethynyl with alkanes,[1] the general trends are similar, but are much less noticeable for ethynyl than for methyl, probably because $D(H\text{—}C_2H)$ is about 10 kcal higher than $D(H\text{—}CH_3)$.

ADDITION REACTION

Two characteristic enynes, butenyne and 1-pentenyne-4, arise from the addition of ethynyl to type 1 olefins. To explain these products we postulate addition of C_2H to the olefinic bond giving an ethynyl-substituted alkyl radical, which cleaves at the carbon atom adjacent to the radical site, i.e., at the point of attack or two carbons removed from it. This mechanism includes the reverse of the addition process, dissociation into ethynyl and olefin. The general mechanism (which involves no atom or charge migration) is, for any 1-alkene:
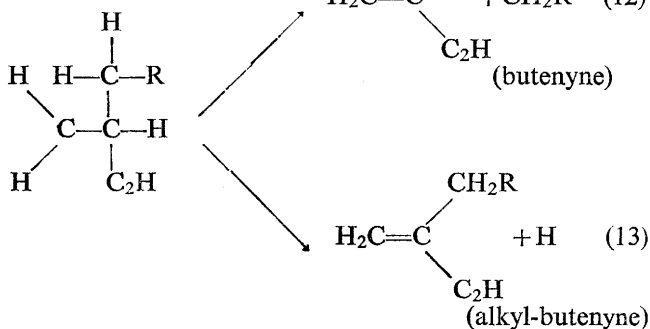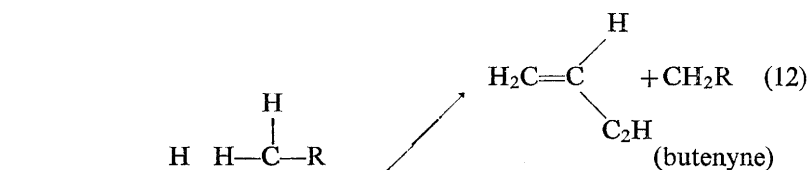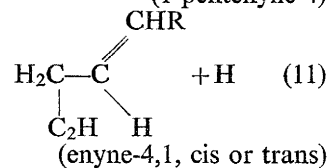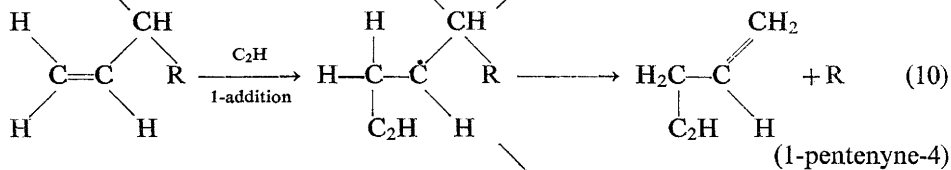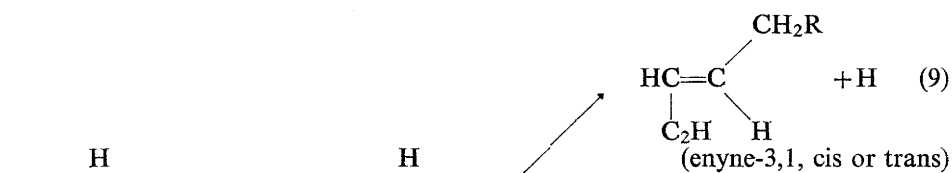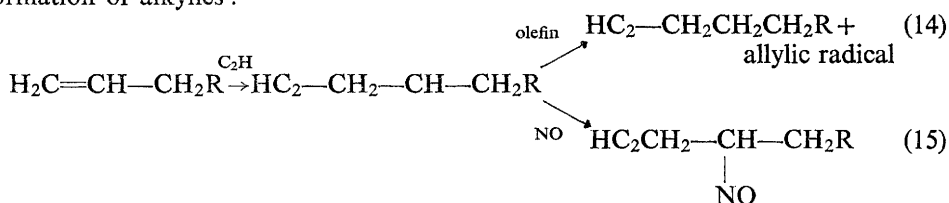

Reactions (10) and (12) are the only displacements in which an alkyl radical is lost; the remaining possibilities (9, 11, 13) involve H-atom loss. The cleavage should favour radical loss because $D(C\text{—}C) < D(C\text{—}H)$.

With propene (R = H, (10) = (11)), products from all possible displacement processes have been detected. In agreement with a radical being lost more readily than a H-atom, the predominant reaction is (12), with smaller contributions from (9) and (11), and a trace of (13) (giving " iso "-C_5H_6). The isotopic distribution in the products from CD_3CHCH_2 confirms the mechanism : the butenyne (from reaction (12)) is undeuterated, while the pentenynes (from (9) and (11)) contain three and two D atoms respectively. The radical eliminated from 3,3-dimethyl-butene-1 in process (12) is t-butyl, which was identified in the products as 2-nitroso-2-methylpropane.

For this process to occur in the presence of NO, the lifetime of the alkyl radical must be about 10^{-9} sec or less, but because the configurations of butene-2 and pentene-2 have no significant effect on the rates or configurations of the products, this lifetime also must be long enough to permit randomization by rotation, i.e., between 10^{-13} and 10^{-9}, probably about 10^{-11} sec.

The results of NO-free runs indicate two further reactions, to account for the formation of alkynes :

$$H_2C{=}CH{-}CH_2R \xrightarrow{C_2H} HC_2{-}CH_2{-}CH{-}CH_2R$$

$$\xrightarrow{\text{olefin}} HC_2{-}CH_2CH_2CH_2R + \quad (14)$$
$$\text{allylic radical}$$

$$\xrightarrow{\text{NO}} HC_2CH_2{-}\underset{\underset{NO}{|}}{CH}{-}CH_2R \quad (15)$$

The nitroso-alkyne formed by (15) probably forms part of the soluble yellow deposit.

Reactions analogous to (9-15) account for the products observed from all the olefins studied, with the exception of the 1-pentenyne-4 obtained from pentene-2 and hexene-2. Since this minor product was not definitely shown to be a C_5, it could be a low-boiling hexenyne such as ethylbutenyne, but this does not fit the mechanism either. An expected product is 3-methyl-1-pentenyne-4, but this will not have the same retention time as unsubstituted 1-pentenyne-4.

As 1-pentenyne-4 is the major enyne product of terminal addition of C_2H to a 1-alkene, conjugation does not appear to be an important factor in the decomposition of the intermediate radical. The data for propene substantiate this view : terminal addition can result in 3-pentenyne-1 (isomers) by reaction (9) or 1-pentenyne-4 by reaction (10), the processes involving loss of secondary and primary hydrogen respectively. Conjugation and the lower secondary C—H bond strength favour the former, the only factor in favour of the 1,4 product being the statistical 3 : 2 ratio. The yields found are 0·13 and 0·13. This equivalence suggests that the intermediate is a hot radical.

From our mechanism the radical formed by terminal addition of C_2H to a 1-alkene has two fates : trapping by NO (or abstraction of hydrogen to give a 1-alkyne), and decomposition into enyne. If enynes arise from hot radicals, while thermalized radicals abstract hydrogen, we should expect a greater pressure effect than we in fact observe (table 2). It is possible that enynes are formed in a pressure-independent fragmentation of the radical.[9]

In the absence of NO we have detected abstraction products only of radicals formed by terminal addition of C_2H : no branched-chain alkynes have been found, even from butene-2, although enynes have been detected from both types of addition. The unbranched radical must therefore have a longer lifetime, probably because of the mechanism of enyne formation. The radical formed in 1-addition (reactions 9, 10, 11) generally forms an enyne by group-loss two carbons distant

from the point of attack, while in the radical formed by (12) or (13) group-loss is only possible at the point of attack. The decomposition of the former radical therefore requires transfer of energy along the carbon chain. An energy-distribution effect is apparent in the data : the proportion of hexyne formed from butene-1 is higher than that of pentyne from propene (table 2), and enyne yields generally diminish with increasing chain length (table 1).

If we assume that the pentyne and enynes obtained from propene represent all the radicals formed by ethynyl addition to propene, and we also neglect secondary loss of these products, the proportion of terminal addition to propene (pentyne + C_5H_6/C_4H_4) is about 2 : 1, or 65 %. The corresponding figure for butene-1 is about 80 %. Addition of hydrogen atoms to propene,[10] and of methyl radicals to propene [11] and butene-1,[7] is 88-92 % terminal, so these assumptions are probably unjustified. Tedder's proposal,[12] that the orientation of free-radical addition to olefins is governed primarily by the strength of the initial radical-olefin bond, would indicate a lower activation energy and stronger bond for the 1-addition. However, this should lead to higher internal energy and more rapid decomposition to enynes. This effect must be more than offset by the energy distribution restrictions mentioned above.

Enyne formation, which is adversely affected by the addition of nitrogen, is enhanced by nitric oxide, hydrogen-loss processes being more affected than methyl loss. This assistance of nitric oxide in removal of an atom or group from a radical, which is tantamount to an abstraction, has not previously been observed at room temperature. The order of efficiency that we observe would be expected if $D(\text{H—NO}) > D(\text{R—NO})$.[13]

From three olefins (pentene-1, hexene-1 and 3-methylbutene-1) capable of losing a propyl radical by (10) or (12), a peak corresponding to propene was observed in G.L.C. analysis. The n-propyl radical decomposes to ethylene and CH_3 more readily than to propene+H ; in any case it will first be trapped by NO.[14] Propene may arise from reactions of nitrosopropane or its isomeric oximes ; or by analogy with other NO-inhibited systems,[15]

$$C_3H_7 + C_3H_7NO \rightarrow C_3H_6 + C_3H_8 + NO.$$
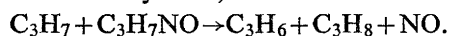
We therefore conclude that steps analogous to (9)-(15) occur in the reaction of ethynyl with olefins, and that the fission of the radical formed in the addition process is dictated by the strengths of the bonds involving the carbon atom(s) adjacent to the transient radical site. Where alternative reaction paths exist, the product yields illustrate the relative occurrence of fission in the various bonds (table 4). With pentene-2 we are assuming equal rates of addition at the olefinic C atoms, which may be incorrect.

TABLE 4.—RELATIVE RATES OF RADICAL LOSS FROM THE TRANSIENT SPECIES

olefin	alternative splits	products	ratio
propene	C—Me ; C—H	C_4H_4, iso-C_5H_6	~100 : 1
pentene-2	C—Et ; C—Me	C_5H_6 (−3,1) ; C_6H_8 (−3,1)	4 : 1

The five hexenynes (A-E in table 1) have been identified only by M.S. Some of the sixteen hexenyne isomers have not yet been reported in the literature. However, in view of the general applicability of our mechanism we are able to assign structures as follows.

A AND D.—These occur together as products from cis- or trans-pentene-2 or hexene-3. By analogy with the parallel C_5-products they must be cis- and trans-3-hexenyne-1 arising from methyl and ethyl loss respectively. While the equilibrium mixture for 3-pentenyne-1 is 59 % cis,[4] 3-hexenyne-1 appears to be 55 % trans.

B AND C are formed from isobutene by hydrogen loss; B also arises from 2-methylbutene-1 and C from 2-methylbutene-2 by methyl loss. The structures are therefore 2-methyl-1-pentenyne-4 (B) and 4-methyl-3-pentenyne-1 (C).

E comes only from 3-methylbutene-1, by methyl loss. This can only give 4-hexenyne-1, which should exist in cis and trans forms. The shape of the G.L.C. trace suggested the presence of a second small peak.

APPENDIX

The mass spectra of the five acyclic pentenynes (purified by G.L.C.) are given in table 5. They were taken on a Metrovick MS2 at an ionizing potential of 70 V. Agreement with available spectra of I and IV [16] is good; the samples of I and a mixture of III and IV used in the only other report [17] were obviously impure. No spectrum of II is available. Isomers

TABLE 5.—MASS-SPECTRA OF C_5 ENYNES

m/e	I methyl butenyne	II 1-pentenyne-4	III 3-pentenyne-1 cis	IV 3-pentenyne-1 trans	V 1-pentenyne-3
68	0·1		0·1	0·1	0·1
67 i	5·4	5·5	5·7	5·4	5·4
66 p	100·0	100·0	100·0	100·0	100·0
65	54·6	42·4	52·4	47·8	41·7
64	3·7	4·1	4·2	4·5	4·1
63	15·2	15·3	18·6	19·3	19·8
62	11·2	9·6	12·4	12·4	13·7
61	7·4	6·6	8·2	8·5	8·9
60	1·6	1·5	1·8	1·9	1·9
52	1·6	0·5	0·6	0·5	0·6
51	32·5	8·4	10·4	10·2	9·7
50	19·8	6·0	9·7	9·1	5·4
49	5·5	2·1	3·0	2·6	2·1
48	0·6	0·3	0·4	0·4	0·4
41	2·0	3·9	2·0	1·4	1·1
40	48·2	33·3	49·6	45·5	35·1
39	65·4	81·7	70·4	68·5	70·3
38	10·8	20·8	19·0	17·9	12·9
37	8·3	10·1	10·0	9·3	7·2
36	1·0	1·2	1·3	1·2	0·9
33 d	0	0	0·3	0·4	0·8
32·5 d	0·2	0·3	0·4	0·4	0·6
32 d	1·0	1·4	1·7	1·7	2·3
31·5 d	0·9	1·0	1·4	1·5	1·8
31 d	4·2	4·4	6·2	6·5	7·3
28	0·8	1·1	1·4	0·9	0·6
27	5·8	14·6	9·6	9·3	6·4
26	2·2	4·7	3·4	3·2	2·3
25	0·7	0·9	0·8	0·7	0·5
24	0·2	0·2	0·2	0·2	0·1
15	1·5	0·7	1·0	1·3	0·4
14	0·7	0·5	0·3	0·3	0·4

II-V are best distinguished by the ratio of their 39 and 40 peaks, which are 2·5, 1·5, 1·5 and 2·0 respectively.

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