pended in 10% NaOH in H_2O, and an ether layer was added. When the solid had disappeared the ether was collected and the aqueous solution re-extracted. The infrared spectrum of the residue after removal of the ether revealed that it consisted of an essentially pure **benzylidene desoxybenzoin** (IX); when crystallized from ethanol it furnished the compound, m.p. 101–102°, identical with that of the authentic high-melting isomer prepared according to the procedure of Knoevenagel.[10] The mixed melting point was undepressed. The highly characteristic infrared spectrum of our sample was identical with that of the authentic material in every detail, as was its ultraviolet spectrum.

sym-Triphenylcyclopropenyl fluoroborate–hydroxyfluoroborate (200 mg.) was dissolved in methanol (50 ml.) and then 2 ml. of 10% Na_2CO_3 solution was added, followed by 20 ml. of water. The excess methanol was removed *in vacuo* and the neutral material isolated by ether extraction. Trituration of the residue, after evaporation of the ether, with methanol afforded **1,2,3-triphenylcyclopropenyl methyl ether** (VII), m.p. 69–70° after recrystallization from warm methanol; yield 120 mg. (99%).

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.55; H, 6.08. Found: C, 88.65, 88.70; H, 6.16, 6.14.

The methyl ether is very soluble in ether, benzene and chloroform.

A solution of the above compound in diethyl ether was treated with gaseous HBr. A white solid precipitated immediately, which could be purified by crystallization from methanol–ether with the addition of HBr. *sym*-**Triphenylcyclopropenyl bromide**, m.p. 269–271° dec., is a colorless salt-like crystalline compound, insoluble in ether, benzene (hot or cold) and chloroform, whose solution in methanol gives an instantaneous precipitate with $AgNO_3$ solution.

Anal. Calcd. for $C_{21}H_{15}Br$: C, 72.64; H, 4.36; Br, 23.01. Found: C, 72.30; H, 4.46; Br, 23.05.

Ultraviolet Spectra.—The fluoroborate–hydroxyfluoroborate, the methyl ether, and the bromide all show, in ethanol solvent, essentially the same spectrum (due to the covalent ether): λ_{max} 317 mμ (27,000), 302 mμ (30,000) (23,000), 230 mμ (29,000) and 223 mμ (30,000) (Fig. 1,A). The picrate shows an additional band at 360 mμ (17,600) due to picrate ion, and higher intensity at the 230 and 223 mμ bands.

In acetonitrile containing ethanol (10%) the spectra are as above, as they are when HCl is added up to a concentration of 10^{-5} *N*. At greater than 10^{-4} *N* HCl in 10% ethanol–acetonitrile the methyl ether, bromide, fluoroborate–hydroxyfluoroborate, and picrate show a change to 320 mμ (42,000) and 307 mμ (47,000). The band at 287 mμ is not evident, and the two bands at 230 and 223 mμ are replaced by strong end absorption. In addition, a new band at 255 mμ (16,000) appears. The same spectrum (Fig. 1,B) is found for solutions in concentrated H_2SO_4. In the picrate the band at 360 mμ is suppressed, and the strong absorption of covalent picric acid at lower wave lengths is added to the cation spectrum. The same change from picrate ion to covalent picric acid is found, at 10^{-4} *N* HCl in 10% ethanol–acetonitrile, for authentic solutions of picric acid. Except in the region of 10^{-4} *N* acid these spectra are not affected by added acid or base. In ethanol solvent the same spectroscopic behavior is observed, except that the transition now occurs at about 1 *N* acid (as does that for the picrate ion). The spectrum of trityl methyl ether is unchanged in 10% ethanol in acetonitrile on addition of HCl or H_2SO_4 to a concentration of 1 *N*.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Studies in Organic Peroxides. XXII. The Thermal Decomposition of *t*-Butylperoxy Isobutyrate

BY NICHOLAS A. MILAS AND ALEKSANDAR GOLUBOVIĆ[1]

RECEIVED MAY 29, 1958

The purification and study of the decomposition of *t*-butylperoxy isobutyrate in the pure state, in benzene and in water are reported. The decomposition of this peroxyester is a first-order reaction and is unique in that it produced mainly a polymeric compound (dimethylpolyglycolid) the formation of which can be explained on the basis of an intermediate diradical which is stabilized by the charge distribution between two carbon and two oxygen atoms. Tentative structures of the polyglycolids have been proposed and compared with that of the dimethyldiglycolid.

In the industrial production of *t*-butylperoxy isobutyrate using essentially the method published from this Laboratory[2a] it was observed[2b] that under certain conditions this perester decomposed slowly into a white, non-peroxidic solid, the structure of which was unknown. We undertook to study the thermal decomposition of pure *t*-butylperoxy isobutyrate and to attempt to elucidate the structure of the solid formed during the decomposition.

Since this peroxyester has not been reported previously in the literature it was necessary to prepare it in the pure state and study its decomposition under specified conditions. The commercial product,[2] containing about 75% of the peroxyester, was purified using special methods which are described in the Experimental part. Pure *t*-butylperoxy isobutyrate is a clear colorless liquid, m.p. −45.7°.

The stability of this peroxyester was studied at various temperatures by following the peroxide content iodimetrically. At 0° the peroxyester is stable for an indefinite period of time and even at room temperature its decomposition is imperceptibly small. The pure peroxyester decomposes at 40° to the extent of 1.26% in 5 hours and at 50°, 9.12% in 4 hours. At 70° the rate of decomposition seems to be approximately of the first order as shown in Table I. At 80° the decomposition is very rapid and reaches 76.66% in 1 hour, while at 90° it proceeds explosively.

TABLE I

DECOMPOSITION OF *t*-BUTYLPEROXY ISOBUTYRATE AT 70°

Time, hr.	Decomposition, %	*k*
1	13.37	0.1436
2	27.77	.1627
3	37.97	.1592
4	44.77	.1485
5	47.05	.1272
	Mean	0.1482

The decomposition also was measured in boiling benzene under an efficient reflux and the results are shown in Table II.

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[1] Lucidol Research Assistant.

[2] (a) N. A. Milas and D. Surgenor, THIS JOURNAL, **68**, 642 (1946); N. A. Milas, U. S. Patent 2,567,615, Sept. 11, 1951; (b) Lucidol Division. Wallace and Tiernan, Inc.

TABLE II

DECOMPOSITION OF *t*-BUTYLPEROXY ISOBUTYRATE IN BOILING BENZENE (INITIAL CONCN., 6.25%)

Time, hr.	Decomposition, %	*k*
2	21.90	0.1238
4	43.68	.1436
6	52.60	.1431
8	65.34	.1329
	Mean	0.1358

Whether the decomposition of the peroxyester was carried out in benzene or in the pure state the products of decomposition were the same. In a typical experiment in which the decomposition of the pure peroxyester at 85° was allowed to go to completion, the products obtained are listed in Table III. It may be noted that the amount of carbon dioxide produced in this case is small as compared to nearly quantitative yields reported in the thermal decomposition of other *t*-butylperoxyesters.[3]

TABLE III

DECOMPOSITION PRODUCTS OF *t*-BUTYLPEROXY ISOBUTYRATE AT 85°

Product		Wt. %
Solid		39.9
Liquid	CH_3COCH_3 (main prod.) $(CH_3)_3COH$ (*ca.* 3%)	39.4
Gases by difference	CO_2 (4.14%) O_2 (1.96%) CH_4, $CH_3CH_2CH_3$, etc. (14.60%)	20.7
		100.00

The white solid obtained by the decomposition of the peroxyester either in the pure state or in boiling benzene was identical in all of its physical and chemical properties (m.p. 170–171°, mol. wt. 1536). However, when the peroxyester was allowed to decompose in boiling water the solid obtained had a lower m.p. 148–149° and a much lower mol. wt., 890, and was identical with the solid supplied to us by Lucidol.[2] In addition we were able to isolate from water solution small amounts of α-hydroxyisobutyric acid.

Both solids were insoluble in either cold or hot aqueous alkalies. However, when they were refluxed with 0.1 *N* alcoholic potassium hydroxide, the lower melting solid had a saponification equivalent of 88.87 and the higher melting 88.14. Both solids, on saponification, yielded about 80% α-hydroxyisobutyric acid. Furthermore, their carbon and hydrogen analyses were essentially the same as shown in Table IV.

TABLE IV

PROPERTIES OF SOLID DECOMPOSITION PRODUCTS

Solid	M.p., °C.	Sapn. equiv.	Mol. wt.	C, %	H, %
1	170–171	88.14	1536	55.95	6.99
2	148–149	88.87	890	55.60	7.37

The analytical data seem to indicate that the structure of the basic unit of both solids must be the same although the number of basic units differs in the two solids. If the solids had a linear polyglycolid structure, they should not be soluble in hot aqueous alkali and both are insoluble.

Moreover, both solids had the same infrared spectrum in chloroform which showed many of the bands also present in the infrared spectrum of the original perester. However, the strong perester band at 1775 cm.$^{-1}$ was shifted to 1740 cm.$^{-1}$ and this together with a new strong band at 1300 cm.$^{-1}$ may be attributed to the glycolid group.[4] The absence of the peroxide band at 920 cm.$^{-1}$ which was present in the infrared spectrum of the peroxyester confirmed our chemical tests that our polymers were peroxide-free.

In order to obtain additional information regarding the structure of our polyglycolids, we prepared the diglycolid (I) from α-hydroxyisobutyric acid following the method of Blaise and Bagard.[5] Molecular weight determinations of this diglycolid in benzene confirmed its dimeric formula. An infrared spectrum of the diglycolid in chloroform showed two strong bands, respectively, at 1738 and 1300 cm.$^{-1}$ which were also present in the infrared spectrum of the polyglycolids. Other strong bands which were common to both appeared at 1458, 1378 and 1368 cm.$^{-1}$, respectively. A triplet occurs in the spectrum of the polyglycolids having two strong maxima at 1100 and 1180 and a weaker one at 1160 cm.$^{-1}$, respectively, and is found to be in the same region as the triplet recorded for di-isopropyl ether[6] and must therefore be attributed to the isopropyl group. A similar triplet is found in the diglycolid but shifted slightly to 1160, 1190 and 1200 cm.$^{-1}$. respectively. Two strong bands in the diglycolid spectrum at 1000–900 cm.$^{-1}$ region occur as much weaker bands in the same region of the spectrum of the polyglycolids. The infrared spectrum of the latter also shows a medium band at 850 cm.$^{-1}$ attributed to the isobutyrate group. This band appears as a shoulder in the same region of the diglycolid spectrum.

The polyglycolids may have either a linear or a cyclic structure. The linear structures II and III were considered, but since we were unable to isolate or detect any neutral end-groups in their hydrolysis products and since their calculated carbon and hydrogen values are too high as compared with the experimental analyses, we wish to propose tentatively the cyclic structures IIa and IIIa as the most reasonable structures for our two polyglycolids. Moreover, the infrared spectra of these polyglycolids seem to compare favorably with the infrared spectrum of the six-membered ring diglycolid I.

Since the thermal decomposition of *t*-butylperoxy isobutyrate is a first-order reaction it should proceed in accordance with equation 1. Moreover, since the main products of decomposition are acetone and the solid polyglycolid, it is apparent that the *t*-butoxy radical is less stable than the isobutyroxy radical. The methyl radicals formed from the decomposition of *t*-butoxy radicals and to a very small degree *t*-butoxy and isopropyl radicals ab-

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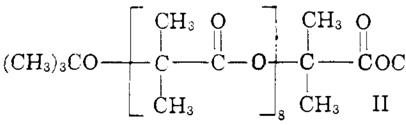
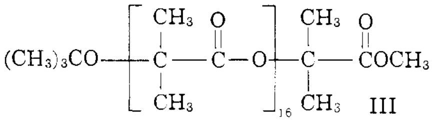
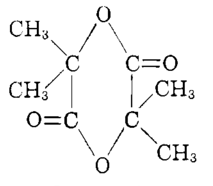


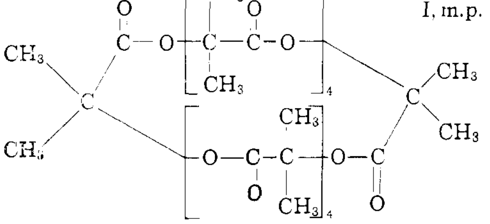
$$(CH_3)_3CO-\left[C(CH_3)_2-\overset{O}{\overset{\|}{C}}-O\right]_8-C(CH_3)_2-\overset{O}{\overset{\|}{C}}OCH_3, \quad \text{II}$$



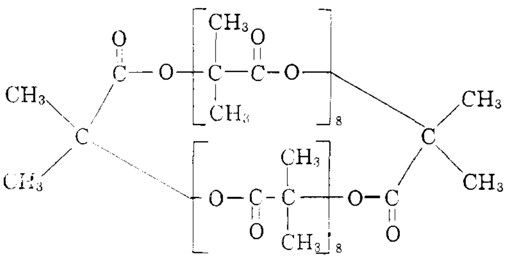
$$(CH_3)_3CO-\left[C(CH_3)_2-\overset{O}{\overset{\|}{C}}-O\right]_{16}-C(CH_3)_2-\overset{O}{\overset{\|}{C}}OCH_3 \quad \text{III}$$



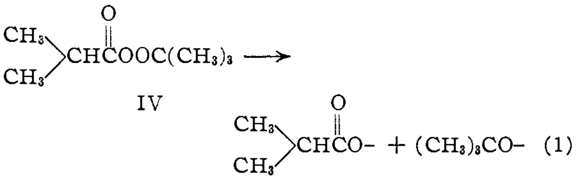
I, m.p. 80–81°



IIa, m.p. 148–149°



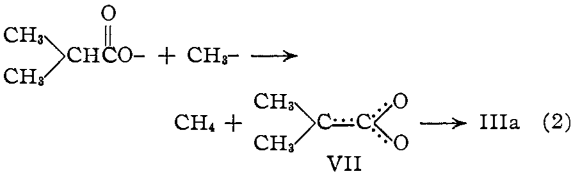
IIIa, m.p. 170–171°



$$(CH_3)_2CH\overset{O}{\overset{\|}{C}}OOC(CH_3)_3 \longrightarrow (CH_3)_2CH\overset{O}{\overset{\|}{C}}O- + (CH_3)_3CO- \quad (1)$$

IV, V, VI

stract hydrogen atoms from isobutyroxy radicals thereby forming momentarily a stabilized diradical which may have the transition formula VII. This could easily polymerize to the polyglycolids IIa and IIIa. That the methyl radicals abstracted hydro-



$$(CH_3)_2CH\overset{O}{\overset{\|}{C}}O- + CH_3- \longrightarrow CH_4 + (CH_3)_2C\cdots C\begin{smallmatrix}\cdot O\\ \cdot O\end{smallmatrix} \longrightarrow \text{IIIa} \quad (2)$$

VII

gen atoms from the isobutyroxy radicals rather than from the original peroxyester was shown by our repeated failure to isolate a derivative of tetramethylsuccinic acid.

If the peroxyester were to decompose in accordance with equations 1 and 2 with no by-products formed, the weight % yield of the polyglycolid should be 56.43. Actually the yield was 39.9% by weight, and therefore the true yield of the polymer in mole % is 70.7.

Experimental

Purification of *t*-Butylperoxy Isobutyrate.—The commercial product[2] (90 cc.) was diluted with 120 cc. of petroleum ether and the mixture cooled to 5° and shaken twice each time with 90 cc. of 5% sodium hydroxide solution also cooled to 5°. The non-aqueous layer was washed once with cold water then dried at 0° over a mixture of anhydrous magnesium sulfate and magnesium carbonate containing about 40% magnesium oxide.

The mixture was filtered and the filtrate passed through a column of silica gel maintained at 0° The solution was again passed through the column for a second time in order to remove the remaining traces of *t*-butyl hydroperoxide. The unadsorbed solution containing the pure peroxyester was subjected to a high vacuum (0.5–1.0 mm.) at 0° to remove traces of the solvent. The pale yellow residue was recrystallized several times from petroleum ether at low temperatures (−60°) and the crystalline peroxyester was again subjected to a high vacuum to remove traces of the solvent. Both the melting point and the freezing point of the pure peroxyester were determined and found to be −45.7 and −45.6°, respectively.

Anal. Calcd. for $C_8H_{16}O_3$: C, 59.97; H, 10.07; (O), 9.99. Found: C, 60.09; H, 10.34; (O), 10.00.

The active oxygen was determined iodimetrically using hydriodic acid in glacial acetic acid. When the peroxyester was run against potassium iodide in glacial acetic acid the values were 2 to 3% lower.

An infrared spectrum of the pure peroxyester (10% in CCl_4) showed prominent bands at 1775 cm.$^{-1}$, due to the peroxyester group; 1465, 1360, 1380 and 1190–1240 cm.$^{-1}$, due to isopropyl and *t*-butyl groups; 1060 and 920 cm.$^{-1}$, due to the peroxide group; and 858 cm.$^{-1}$, due to the isobutyrate group.

Decomposition of *t*-Butylperoxy Isobutyrate.—The rate of decomposition of this peroxyester was determined at various temperatures in a thermostatically controlled oven (±0.5°). Samples of the pure peroxyester (0.05–0.07 g.) were placed in a series of long tubes, each of which was protected from atmospheric moisture with a calcium chloride tube. Individual tubes were withdrawn at the end of a definite period of time and the total undecomposed peroxyester determined iodimetrically.

For the isolation of the decomposition products a larger sample (0.9381 g.) of the peroxyester was heated at 85° in a closed system connected to an apparatus designed to collect the liquid as well as gaseous products separately. Although all of the gaseous products were formed during the first 4 hr. the peroxyester was heated for 72 hr. at the above temperature to ensure complete decomposition. The products from this experiment are shown in Table III.

The liquid was mainly acetone from which was prepared the 2,4-dinitrophenylhydrazone, m.p. 125°; mixed m.p. with an authentic sample gave no depression. A portion of the liquid was treated in a benzene–pyridine mixture with 3,5-dinitrobenzoyl chloride and the ester formed recrystallized from petroleum ether, m.p. 141°, mixed m.p. with an authentic sample prepared from *t*-butyl alcohol gave no depression.

An analysis of the gaseous products showed the presence of 4.14% carbon dioxide, 1.96% oxygen and the remaining 14.6% was a mixture of hydrocarbon gases, the infrared spectrum of which showed the following characteristic bands: 3000–2800 cm.$^{-1}$. (strong) attributed to methane and ethane, 1460–1450 cm.$^{-1}$ (strong) due to CH_3C- and $-CH_2-$, a doublet at 1352–1340 cm.$^{-1}$ (strong) attributed to isopropyl group or the presence of propane, 1295–1260 cm.$^{-1}$ (strong) attributed to *t*-butyl group or the presence of isobutane. In addition, two weak bands at 1635 and 1662 cm.$^{-1}$, respectively, are due to the presence of small amounts of an olefinic hydrocarbon.

The solid residue was recrystallized from ethanol and the crystals (fine, white) were subjected to a high vacuum for 72 hr. at the temperature of boiling acetone, m.p. 170–171°. The infrared spectrum of this polyglycolid (10% in $CHCl_3$) is discussed elsewhere.

Anal. Calcd. for $(C_4H_6O_2)_{18}$: C, 55.81; H, 7.02; mol. wt., 1549; sapn. equiv., 86.09. Found: C, 55.95; H, 6.99; mol. wt., 1536 (Rast); sapn. equiv., 88.14.

When a larger sample of the above dimethylpolyglycolid was saponified by refluxing it with 0.1 *N* alcoholic potassium hydroxide, a solid acid was recovered which was recrystallized from chloroform, yield 80%, m.p. 79.5°; mixed m.p. with an authentic sample of α-hydroxyisobutyric acid gave no depression; neut. equiv. 104.8, calcd. for α-hydroxyisobutyric acid 104.1.

Lucidol Polymer.[2b]—This was recrystallized several times from ethanol and the crystals subjected to a high vacuum for 48 hr. at the temp. of boiling acetone, m.p. 148–149°. The infrared spectrum of this solid (10% in $CHCl_3$) was identical with that of our dimethylpolyglycolid, m.p. 170–171°.

Anal. Calcd. for $(C_4H_6O_2)_{10}$: C, 55.81; H, 7.02; mol. wt., 861; sapn. equiv. 86.09. Found: C, 55.60; H, 7.37; mol. wt., 890 (Rast); sapn. equiv., 88.87.

Saponification of this solid with alcoholic potassium hydroxide gave about 80% α-hydroxyisobutyric acid.

Decomposition of *t*-Butylperoxy Isobutyrate in Boiling Water.—When 1 g. of pure *t*-butylperoxy isobutyrate was allowed to decompose under reflux of 50 cc. of water, a white solid appeared floating on the surface of the water after 3 hr. of heating. Refluxing was continued for 24 hr., then the mixture cooled, the solid separated and recrystallized from ethanol, m.p. 148–149°; mixed m.p. with the purified solid obtained from Lucidol gave no depression.

The filtrate was treated with sodium bicarbonate and extracted with ether. Acetone was identified in the ether layer *via* its 2,4-dinitrophenylhydrazone. The sodium bicarbonate layer was acidified with hydrochloric acid and extracted with chloroform from which was obtained α-hydroxyisobutyric acid, m.p. 79–80°; mixed m.p. with an authentic sample showed no depression.

Dimethyldiglycolid (I).—This diglycolid was synthesized in accordance with the method of Blaise and Bagard[8] and purified by fractional distillation under reduced pressure and recrystallization from pentane, m.p. 80–81°, mixed m.p. with α-hydroxyisobutyric acid 60–62°; sapn. equiv. 86.12, calcd. for the diglycolid (I) 86.09; mol. wt. 167 (cryoscopic in benzene), calcd. for (I) 172.18. The infrared spectrum (10% in $CHCl_3$) of this diglycolid is compared (*vide infra*) with the infrared spectra of the polyglycolids.

Acknowledgment.—The authors are indebted to Dr. Nagy for all the analyses, to Dr. Nelson and Mrs. Taylor for the infrared spectra and to Lucidol Division of Wallace and Tiernan, Inc., for financial support of this investigation.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE PENNSYLVANIA STATE UNIVERSITY]

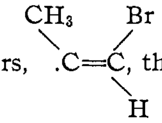
Stereochemistry of Radical Processes. Stereospecific *trans* Addition of HBr to Propyne

BY PHILIP S. SKELL AND RICHARD G. ALLEN

RECEIVED JUNE 12, 1958

Under illumination propyne and HBr react rapidly in the liquid phase (−78 to −60°) in a stereospecific *trans* radical process, producing *cis*-1-bromo-1-propene. Gas phase reactions are markedly accelerated by light and oxygen. The stereochemistry of the gas phase addition is obscured by the rapid equilibration of the 1-bromo-1-propenes. In the gas phase, at equilibrium, the *cis* to *trans* ratio is 4.14.

Introduction

With rare exceptions radical–olefin addition reactions have been reported to be non-stereospecific.[1] Walling, Kharasch and Mayo[2] described a noteworthy exception in the addition of HBr to 2-butyne. The reaction was carried to completion with excess HBr and the product was *d,l*-2,3-dibromobutane contaminated by a small amount of 2,2-dibromobutane (from competing ionic addition). The *d,l*-2,3-dibromobutane could have resulted from two successive *trans* (or *cis*) additions.[3] However, reflecting the then current concepts of configurational instability of free radicals the authors dismissed the possibility that the successive steps were stereospecific.[4] Subsequent reports by Epstein[5] and Goering and Larsen[6] indicated that *cis*-2-bromo-2-butene yields *meso*-2,3-dibromobutane and *trans*-2-bromo-2-butene yields *d,l*-2,3-dibromobutane. Since the latter are *trans* additions, by inference the addition of HBr to 2-butyne produces *trans*-2-bromo-2-butene by *trans* addition of HBr to the acetylenic bond. However, it does not follow from the evidence that the observed addition to an acetylene was exclusively a radical process, for an ionic reaction could equally well account for the conversion of 2-butyne to *trans*-2-bromo-2-butene, this followed by a radical sequence for addition of the second HBr. Since the interpretation of the stereochemistry of the first step in the HBr–acetylene reaction stems from circumstantial evidence, the radical HBr–propyne reaction was re-examined. Propyne was chosen because *trans* addition would involve the most sterically compressed of the radical pairs,  $\overset{\mathrm{CH_3}}{\cdot\mathrm{C}}{=}\underset{\mathrm{H}}{\overset{\mathrm{Br}}{\mathrm{C}}}$, thus providing a firmer base for a rationale of the steric course of the reaction and the stability of the intermediate radical.

There appears to be agreement in the literature that addition of HBr to terminal acetylenes in the presence of radical inhibitors and/or Lewis-type acids produces $RCBr{=}CH_2$ and $RCBr_2CH_3$.[7-12]

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[4] Reference 2, footnote 4; see also ref. 8, footnote 4.

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