

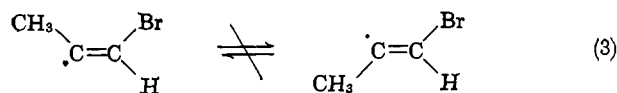
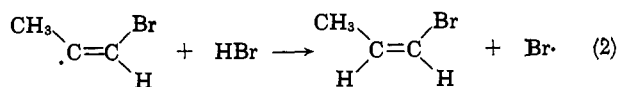
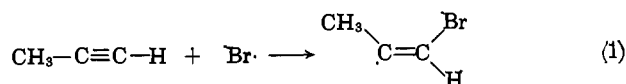
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNSYLVANIA]

***cis-trans* Isomerization in Vinyl Radicals. Gas Phase Radical-Chain Addition of Hydrogen Bromide to Propyne<sup>1</sup>**BY PHILIP S. SKELL AND RICHARD G. ALLEN<sup>2,3</sup>

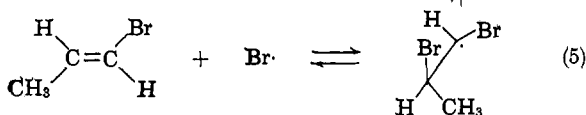
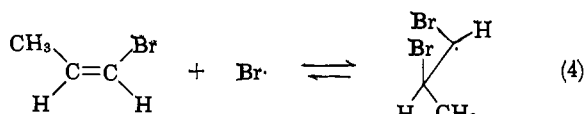
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Radical-chain addition of hydrogen bromide in the gas phase occurs by a stereospecific *trans* process. *cis-trans* Isomerization of the intermediate radical  $\text{CH}_3\text{C}(\text{Br})\text{C}\cdot\text{H}$  is an activated process,  $E_{\text{act}} \geq 17$  kcal./mole, and the half-life for this *cis-trans* isomerization is  $\geq 3 \times 10^{-7}$  sec.

In liquid phase at  $-78$  to  $-60^\circ$ , propyne and hydrogen bromide react by a stereospecific *trans* radical chain addition process, producing *cis*-1-bromo-1-propene.<sup>4</sup> These results can best be rationalized by assuming stereospecificity in both chain steps.

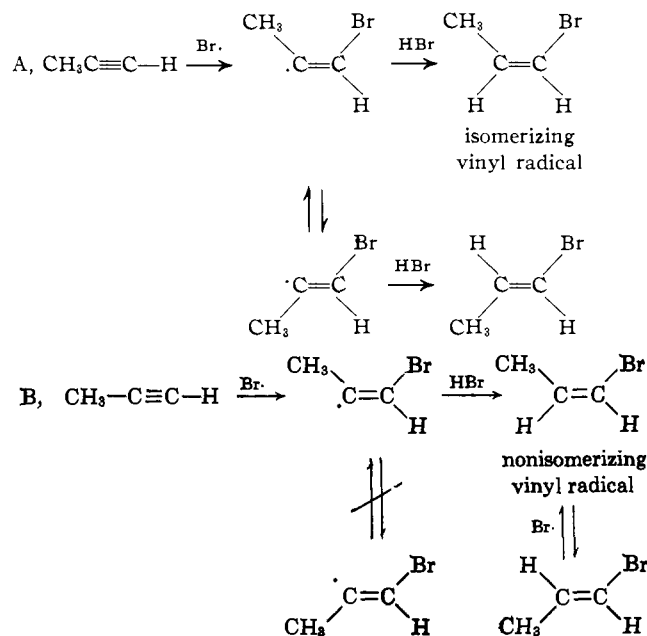


At room temperature *cis*- and *trans*-1-bromo-1-propenes are produced in equilibrium or near equilibrium mixtures in both gas<sup>4</sup> and liquid phase reactions. Since these conditions have been demonstrated<sup>4</sup> to be those required for *cis-trans* isomerizations of the 1-bromo-1-propenes, reactions 1, 2, 4, and 5 can account for the observations, but reaction 3 is not necessarily eliminated as a competing process.



The importance of *cis-trans* isomerization in vinyl radicals, reaction 3, was assessed by examining products from propyne and hydrogen bromide at early stages of the reaction. If reaction 3 occurs in these systems at room temperature, then even at the earliest stages significant quantities of *trans*-1-bromo-1-propene should be observed (reaction scheme A). On the other hand, if (3) makes no contribution and reactions 1, 2, 4, and 5 are sufficient, *trans*-1-bromo-1-propene is obtained by isomerization of the *cis* compound (reaction scheme B). Thus at early stages *cis*-1-bromo-1-

propene should be observed, and only at later stages of conversion should the *trans* compound appear.



Earlier experiments toward the objective of choosing between A and B were not successful. Satisfactory exclusion of hypothesis A was accomplished by studying gas phase propyne-hydrogen bromide addition reactions in the 5 to 0.15% conversion regions. Hydrogen bromide and propyne in a 1:3 ratio were mixed in a dark container. The mixture obeyed Dalton's law, indicating that  $\pi$ -complexing and other condensation reactions do not occur on mixing. Samples were admitted to and irradiated in the glass coil of a gas chromatography sampling system. Without delay the irradiated sample was passed through a tube filled with sodium hydroxide pellets connected to the inlet of the gas chromatography column. The gas chromatography trace indicated that the only products were *cis*- and *trans*-1-bromo-1-propenes. The results of these experiments are summarized in Table I. At 11% conversion of reactants, the *cis-trans* ratio approaches the equilibrium value of 4.19. However, at smaller conversions, the *cis-trans* ratio increases until it exceeds  $10^2$ .

The high *cis-trans* ratio at lowest conversions leaves little doubt that reactions 1, 2, 4, and 5 are adequate to describe the system in liquid and gas phase within the temperature and concentration limits studied. Further, the experiments most dilute in hydrogen bromide defines an upper limit for the half-life of  $\text{CH}_3\text{C}(\text{Br})\text{C}\cdot\text{H}$  undergoing *cis* to *trans* isomerization as

(1) Acknowledgment is made to the Air Force Office of Scientific Research for support of this research under Contract AF 49(638)457.

(2) This work was done in partial fulfillment of requirements for Ph.D. degree, 1959.

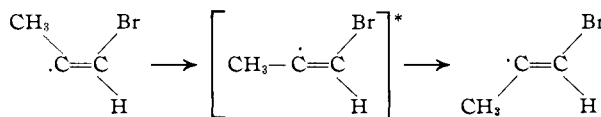
(3) Graduate Fellow, Allied Chemical Corporation, 1958-1959.

(4) P. S. Skell and R. G. Allen, *J. Am. Chem. Soc.*, **80**, 5997 (1958).

TABLE I  
RELATIVE AMOUNTS OF *cis*- AND *trans*-1-BROMO-1-PROPENES AT  
LOW CONVERSION OF HBr AND PROPYNE TO PRODUCT

% conversion to product	$\frac{cis}{trans}$
11.0	5.68
9.0	9.85
5.5	12.1
4.0	15.2
0.25	44.0
.18	53.0
.18	95.0
.15	108.0
.15	120.0

$\geq 3 \times 10^{-7}$  sec. or  $k_{cis \rightarrow trans} \leq 2 \times 10^6$  sec.<sup>-1</sup>. This number derives from the average collision frequency of a radical with hydrogen bromide molecules ( $p = 59$  mm.) of  $2 \times 10^8$  sec.<sup>-1</sup> and the observed *cis-trans* ratio of 120. This frequency ( $\leq 10^6$  sec.<sup>-1</sup>) of *cis-trans* isomerization is very small compared to in-plane bending frequencies ( $10^{13}$ - $10^{14}$  sec.<sup>-1</sup>). Thus, there is a substantial barrier to *cis-trans* isomerization of this vinyl radical. If the difference between *cis-trans* isomerization frequencies and wagging frequencies is attributed to an activation energy, its magnitude is 17 kcal./mole or greater. The only reasonable activated state for this *cis-trans* isomerization is a linear one, so that this activation energy would be closely the difference in energy of the bent and linear vinyl



radicals.<sup>5</sup>

The reported<sup>6</sup> elegant analysis of spectroscopic data for formyl radical suggests a bent ground state,  $\text{H}-\dot{\text{C}}=\text{O}$ , and a linear excited state,  $\text{H}-\dot{\text{C}}=\text{O}$ , lying 23 kcal. above the ground state. The minimum value adduced for the analogous transition in  $\text{CH}_3\dot{\text{C}}=\text{CHBr}$

(5) Alternatively, the postulate of a bridged radical ( $\text{CH}_3-\text{C}=\text{C}-\text{H}$ )  
Br

instead of a stable *cis*-vinyl radical, could explain the observations, since the bridged species would require donation of a hydrogen atom *trans* to the bromine atom.

(6) D. A. Ramsey, *Ann. N. Y. Acad. Sci.*, **67**, 485 (1957).

is consistent with this value, and one might anticipate that the activation energy for all *cis-trans* isomerizations at double bonded carbon radicals  $\text{Z}-\dot{\text{C}}=\text{X}$  might approximate 23 kcal./mole.

Two instances of nonstereospecific radical-chain additions to acetylenes are reported in the literature.<sup>7a,b</sup> Since at present there is some doubt regarding the meaning of these observations,<sup>7a,b</sup> the stereospecific additions reported here may indeed be general as suggested above.

### Experimental

Hydrogen bromide and propyne were introduced into the evacuated and darkened reaction flask to partial pressures of 100 and 300 mm., respectively. The gases were mixed thoroughly by means of a Teflon covered magnet in the reaction flask. Samples of the reaction mixture were let into the evacuated vapor phase chromatographic gas sampling coil (Pyrex) and irradiated with a medium pressure mercury arc as shown in Table II. After irradiation, the reaction mixture was swept through a solid sodium hydroxide tube and into the gas chromatograph. The *cis-trans* 1-bromo-1-propene peak heights were determined as well as the approximate per cent conversion to products.

TABLE II  
*cis*- TO *trans*-1-BROMO-1-PROPENE RATIO AT LOW CONVERSIONS  
OF HYDROGEN BROMIDE AND PROPYNE TO PRODUCT

Run	Pressure, mm.	Irradiation	Time, sec.	<i>cis/trans</i> height	% conversion
1	355	Ultraviolet	300	5.68	11.0
2	330	Ultraviolet	45	9.85	9.0
3	305	Ultraviolet	12	12.1	5.5
4	285	Ultraviolet	5	15.2	4.0
5	238	Ultraviolet	4	44.0	0.25
6	204	Room light	15	53.0	.18
7	174	Room light	15	95.0	.18
8	280	Dark		108.0	.15
9	237	Dark		120.0	.15

*cis*- and *trans*-1-bromo-1-propene were the only product peaks seen by vapor phase chromatography.

(7) (a) R. A. Benseker and co-workers, *J. Am. Chem. Soc.*, **83**, 4385 (1961) (benzoyl peroxide catalyzed additions of trichlorosilane to acetylenes). Since isomerizations of the olefinic products were demonstrated to accompany the addition reactions, scheme B is probably correctly applied in this case, and scheme A may be incorrect. (b) L. D. Bergelson [*Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 1235 (1960)] reports that peroxide catalyzed additions of hydrogen bromide to 1-bromo-1-alkynes produce *trans*-1,2-dibromo-1-alkenes, presumably by *cis* addition of hydrogen bromide. Alternatively, positive halogen compounds such as 1-bromo-1-alkynes may react with hydrogen bromide to yield bromine and the 1-alkyne, which would react with one another in a *trans* electrophilic addition to yield the *trans*-1,2-dibromo-1-alkenes.