Reaction with Diethylamine.—A solution of 1.5 g. (0.02 mole) of diethylamine in 10 ml. of benzene was added at once to a stirred suspension of 1.5 g. (0.01 mole) of IX in 20 ml. of benzene at room temperature. Filtration and evaporation afforded 1.39 g. (75%) of 1-(N,N-diethylcarbamoyl)-2-imidazolidinone (XII), b.p. 150° (0.5 mm.), m.p. 55–57°.

Anal. Calcd. for $C_8H_{15}N_3O_2$: C, 51.87; H, 8.16; N, 22.68. Found: C, 51.78; H, 8.19; N, 22.92.

Propyleneurea (3-Methyl-2-imidazolidinone, VIII).—To 39 g. (0.49 mole) of 1,2-diaminopropane (propylenediamine) and 80 g. (1.0 mole) of 50% sodium hydroxide in 100 ml. of water, 49.5 g. (0.5 mole) of phosgene was added at 10–20° while maintaining good agitation. The water was evaporated *in vacuo* and the residue was extracted with ethylene dichloride. Evaporation of the solvent gave 21.9 g. (43.7%) of methyl-2-imidazolidinone (VIII), m.p. 125–127°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ (infrared) 2.93, 3.13, 3.40, 5.90, 6.7, 6.95, 7.25, and 7.95 μ.

Anal. Calcd. for $C_4H_8N_2O$: C, 48.00; H, 8.06; N, 28.00. Found: C, 47.92; H, 8.32; N, 27.91.

Methyl-2-imidazolidinone-N-carbonyl Chloride (X).—A solution of 10 g. (0.1 mole) of VIII in 100 ml. of ethylene dichloride was added from a heated (60°) addition funnel simultaneously with 10 g. (0.1 mole) of phosgene to 100 ml. of ethylene dichloride at 72–77°. After purging with nitrogen fo 30 min., the reaction mixture was filtered while hot. On cooling, 9.5 g. (58.6%) of methyl-2-imidazolidinone-N-carbonyl chloride (X), m.p. 145–146°, separated.

Anal. Calcd. for $C_5H_7ClN_2O_2$: C, 36.92; H, 4.34; N, 17.23. Found: C, 36.90; H, 4.44; N, 16.42.

Acknowledgment.—The authors wish to thank Mr. B. Tucker for his valuable help with the experiments and Mr. F. Geremia for the determination of numerous infrared spectra.

Allene Chemistry. II.[1] Free-Radical Addition of Hydrogen Bromide to Allene

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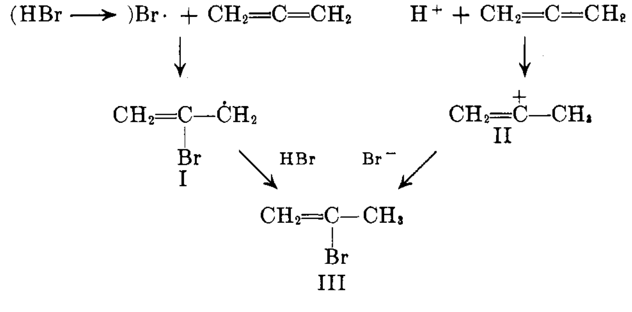
The free-radical addition of hydrogen bromide to allene was examined under different reaction conditions and the product mixtures were analyzed by capillary gas–liquid chromatography and n.m.r. spectroscopy. The ultraviolet light catalyzed gas phase reaction of equimolar amounts of the reactants at ambient temperatures yielded 2-bromopropene as the major product, along with minor amounts of 1,2-dibromopropane and 2,2-dibromopropane. No measurable terminal attack was observed. Equimolar amounts of the reactants in the liquid phase produced 2-bromopropene, 3-bromopropene, 1,2-dibromopropane, and in some cases also 1,3-dibromopropane in varying relative amounts, depending on the reaction conditions. Attack of the bromine atoms at the terminal positions of allene increased from 7% at ambient temperatures to 24% at −40° and 36% at −70°. Up to 48% of terminal attack was observed when a propane solution containing 1 mole of each of the reactants was irradiated at −70°. Reaction of excess allene with hydrogen bromide at −70° yielded mainly the monoadducts 2-bromopropene and 3-bromopropene, but none of the isomeric 1-bromopropenes, thus excluding any significant amount of isomerization of allene to methylacetylene. The amount of terminal attack decreased drastically with an increasing excess of allene. Reactions of excess hydrogen bromide with allene were complicated by competing ionic addition reactions leading to considerable amounts of 2,2-dibromopropane.

The problem of terminal *vs.* center attack in free-radical addition reactions to allene was outlined in our previous paper dealing with thiol addition reactions.[1] We proposed there that the observed preference of thiyl radicals for the terminal positions of allene may be a consequence of the particular geometry of the allene molecule. It was pointed out that, owing to perpendicular arrangement of its π-orbitals, the incipient radical derived from a center attack will not be resonance stabilized and its formation may, therefore, require a higher activation energy than does the formation of the vinylic radical derived from a terminal attack. A similar idea was advanced independently by Jacobs and Illingworth.[2] The exclusive terminal attack of CF_3 radicals, reported by Haszeldine and co-workers[3] in the photoaddition of trifluoroiodomethane to allene, seems also to agree with this concept.

Kovachic and Leitch[4] arrived at the opposite conclusion in interpreting the homolytic addition of hydrogen bromide to allene. They isolated 2-bromopropene (III) as the major reaction product and reasoned that the reaction should proceed *via* the resonance-stabilized 2-bromopropenyl radical (I). However, the homolytic conditions claimed were not supported by control experiments. Thus, an ionic reaction path *via* the carbonium ion intermediate II was not ruled out. Such a path would be analogous to the addition of hydrogen chloride[5] and hydrogen fluoride[6] to allene, both of which occur in the usual Markownikoff manner to yield the corresponding 2-halopropenes and/or 2,2-dihalopropanes. Furthermore, Kovachic and Leitch's experiments were apparently carried out in the gas phase and, therefore, cannot be directly related to the previously reported radical additions to allene which were generally carried out in the liquid phase.



In view of our continued interest in allene chemistry, we investigated the free-radical addition of hydrogen bromide to allene in detail.

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[1] Part I: K. Griesbaum, A. A. Oswald, E. R. Quiram, and W. Naegele, *J. Org. Chem.*, **28**, 1952 (1963).

[2] T. L. Jacobs and G. E. Illingworth, Jr., *ibid.*, **28**, 2692 (1963).

[3] R. N. Haszeldine, K. Leedham, and R. B. Steele, *J. Chem. Soc.*, 2020 (1954).

[4] D. Kovachic and L. C. Leitch, *Can. J. Chem.*, **39**, 3636 (1961).

[5] T. L. Jacobs and R. N. Johnson, *J. Am. Chem. Soc.*, **82**, 6397 (1960).

[6] P. R. Austin, U. S. Patent 2,585,529 (1952).

Results

Hydrogen bromide and allene were allowed to react under different reaction conditions, varying reaction temperature, type of initiation, reaction medium, relative reactant ratios, and reaction phase. The crude reaction products were in each case analyzed by capillary gas–liquid chromatography (Fig. 1) and semiquantitative n.m.r. spectroscopy (Fig. 2). The predominantly free-radical character of these reactions was supported by the marked enhancement of their reaction rates over those of the corresponding "dark" reactions (Table I).

Reaction in the Gas Phase.—The ultraviolet light induced reaction of an equimolar mixture of allene and hydrogen bromide in the gas phase at ambient temperatures proceeded at a fast rate. Within 3 hr. a conversion of 88% was achieved, while the corresponding "dark" reaction reached only 8% conversion in the same time. The major reaction product was 2-bromopropene, along with some 1,2-dibromopropane and very little 2,2-dibromopropane (Table I). The latter may even have been formed during work-up of the reaction mixture. No product derived from an apparent terminal attack of bromine on allene could be detected with the analytical tools used. This is in good agreement with the findings of Kovachic and Leitch.[4]

Reactions in the Liquid Phase.—Most of the previously reported free-radical additions to allene[1-3] had been carried out either with equimolar amounts of reactants or with a slight excess of one reactant over the other. As it was the objective of this work to provide data comparable with that of the reported thiol[1,2] and trifluoroiodomethane[3] additions, the major part of our studies was carried out with equimolar mixtures of hydrogen bromide and allene and, unless mentioned otherwise, without a diluent.

Equimolar Amounts of Reactants.—The ultraviolet light catalyzed reaction at ambient temperatures produced 2-bromopropene (III) as the major reaction product, along with some 3-bromopropene (V) and little 1,2-dibromopropane (VII). The amount of formal terminal attack of bromine on allene, as represented by the occurrence of 3-bromopropene at 25°, was 7%. At −40° the same adducts were formed; however, their relative ratios were changed. More of the diadduct VII was observed and the amount of the terminal-attack product V had increased to 24%. At −70° the symmetrical diadduct 1,3-dibromopropane (VIII) was formed in addition to the three adducts III, V, and VII. The two diadducts VII and VIII now comprised 27% of the adduct mixture as compared with the formation of only 4% diadduct at ambient temperatures and 13% at −40°. The amount of terminal attack products (*viz.*, V and VIII) had increased to 36%.

Combined initiation by 2,2′-azobisisobutyronitrile (AIBN) and ultraviolet light at −70° caused an approximately threefold rate enhancement over the merely ultraviolet light catalyzed reaction. The products formed were the same and their distribution was similar to that of the ultraviolet light catalyzed addition. The amount of terminal attack products (V and VIII) had increased to 43%.

Ultraviolet light irradiation of a propane solution which was one molar for each of the reactants again produced the four adducts III, V, VII, and VIII at −70°. The amount of terminal attack products (V and VIII) was 48%.

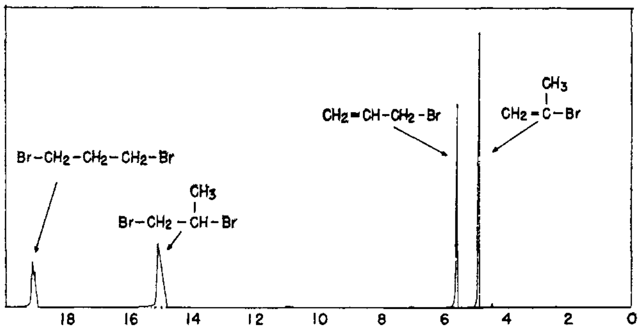

Fig. 1.—Gas chromatogram of a crude hydrogen bromide–allene adduct mixture.

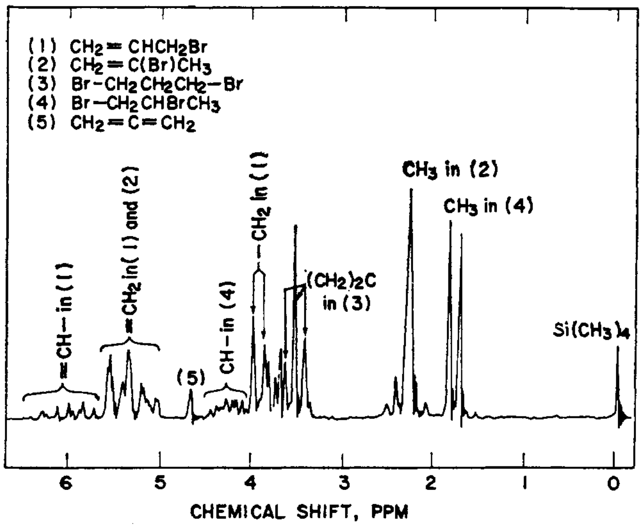

Fig. 2.—N.m.r. spectrum of hydrogen bromide–allene adduct mixture.

Excess of Allene.—The ultraviolet light induced reaction of hydrogen bromide with an excess of allene at −70° resulted in the formation of the monoadducts III and, to a much lesser extent, V, along with only minor amounts (2–3%) of the diadduct VII. The amount of the terminal attack products decreased from 36% in the reaction of equimolar amounts of the reactants to 30% with a fivefold excess of allene and 8% with a tenfold excess.

The reactions of excess allene with hydrogen bromide permit some conclusions with regard to the possible isomerization of allene to methylacetylene under the free-radical conditions employed. We have shown in independent experiments that at −70° hydrogen bromide adds approximately three times as fast to methylacetylene as it does to allene. Any methylacetylene formed should, therefore, show up in the form of its respective free-radical mono- (IV) and/or diadduct (VII).[7] However, we could demonstrate by g.l.c. retention times (*cf.* Tables I and II)[8] and n.m.r. analy-

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[7] The photochemical addition of hydrogen bromide to methylacetylene at −78° had been previously reported to yield mainly *cis*-1-bromopropene, along with some 1,2-dibromopropane; see P. S. Skell and R. G. Allen, *J. Am. Chem. Soc.*, **80**, 5997 (1958).

[8] G.l.c. analysis of a synthetic blend, containing 2-bromopropene, 3-bromopropene, and the isomeric 1-bromopropenes gave a complete resolution. As one would anticipate on the basis of the individual retention times, the peaks for the isomeric 1-bromopropenes appeared between those of 2-bromopropene and 3-bromopropene.

TABLE I

EXPERIMENTAL AND ANALYTICAL DATA OF HYDROGEN BROMIDE–ALLENE ADDITIONS

Ratio of HBr–C_3H_4	Type of initiation	Temp., °C.	Time, hr.	Yield, %	Relative amounts of components in mixture,[a] mole %					
					$BrCH_2CH{=}CH_2$[g]	$Br(CH_2)_3Br$[h]	$CH_2{=}$ $CBrCH_3$[i]	CH_3 | $BrCHCH_2Br$[j]	$CH_3CBr_2CH_3$[k]	Terminal attack on allene, %[l]
1[b]	ultraviolet	ambient	3	88[c]	trace		85	13	2	<1
1	ultraviolet	ambient	8.5	93	7	trace	89	4	trace	7
1	ultraviolet	−40	21	83	24	trace	63	13		24
1	ultraviolet	−70	18.5	92[d]	27	9	46	18		36
1	ultraviolet, AIBN	−70	6	88[d]	30	13	33	24		43
1[e]	ultraviolet	−70	19	82	37	11	28	24		48
10	ultraviolet	−70	21	99		43		34	23	43
0.5	ultraviolet	−70	19	81	30		68	3		30
0.1	ultraviolet	−70	69	63[f]	8		89	2		8

[a] Based on g.l.c. analysis. [b] Gas phase reaction. [c] Compared with 8% yield in the corresponding "dark" reaction. [d] A "dark" reaction gave only 13% yield in 25 hr. [e] Reaction carried out in 1 *M* propane solution. [f] The gas chromatogram in this case showed some peaks of intermediate and higher retention times, suggesting that telomerization may have occurred. [g] Retention time 5.6 min. [h] Retention time 19.1 min. [i] Retention time 4.8 min. [j] Retention time 15.1 min. [k] Retention time 9.5 min. [l] Calculated as the sum of the mole % of 3-bromopropene and 1,3-dibromopropane.

TABLE II

EXPERIMENTAL AND ANALYTICAL DATA OF HYDROGEN BROMIDE ADDITIONS TO METHYLACETYLENE, 2-BROMOPROPENE, AND 3-BROMOPROPENE

Unsaturate used, mole %		HBr, mole %	Type of initiation	Temp., °C.	Time, hr.	Yield, %	Relative amounts of products formed,[a] mole %				
							$BrCH{=}CHCH_3$[b] *cis*[c]	 *trans*[d]	$Br(CH_2)_3Br$	CH_3 | $BrCHCH_2Br$	$CH_3CBr_2CH_3$
$HC{\equiv}CCH_3$	0.1	0.1	ultraviolet	−70	5	80	74	23		3	
$HC{\equiv}CCH_3$	0.05	0.5	ultraviolet	−70	2:40	68	35	12		49	4
$CH_2{=}CHCH_2Br$	0.1	0.1	ultraviolet	−70	29	94			100		
$CH_2{=}CHCH_2Br$	0.1	0.1	ultraviolet AIBN	−70	19	92			100		
$CH_2{=}CBrCH_3$	0.1	0.1	ultraviolet	−70	21	89				45	55
$CH_2{=}CBrCH_3$	0.1	0.1	ultraviolet. AIBN	−70	20	87				86	14

[a] Based on g.l.c. analysis. [b] The configuration has been assigned based on Skell's experience that under similar conditions the *cis* compound was produced in a larger ratio (see ref. 7). [c] Retention time 5.1 min. [d] Retention time 5.3 min.

sis[9] that neither of the isomeric 1-bromopropenes (IV) was present in our adduct mixtures which were derived from reactions of excess allene with hydrogen bromide. These observations place, therefore, an upper limit of 2–3% (*i.e.*, the amount of the diadduct VII formed) for for the amount of isomerization of allene to methylacetylene under the prevailing reaction conditions.

Excess of Hydrogen Bromide.—The ultraviolet light induced reaction of excess hydrogen bromide with allene produced the diadducts 1,2-dibromopropane (VII), 1,3-dibromopropane (VIII), and 2,2-dibromopropane (VI). The latter probably arose through competing ionic addition reactions, which are known to be favored in halogen acid media.[10a]

Model experiments showed that even in an equimolar mixture of hydrogen bromide and 2-bromopropene at −70° ionic reaction took place to a considerable extent.[11] Thus, the merely ultraviolet light catalyzed addition yielded a mixture consisting of 45% of 1,2-dibromopropane and 55% of 2,2-dibromopropane. The combined initiation by ultraviolet light and AIBN, on the other hand, apparently greatly favored the free-radical reaction, yielding 86% of 1,2-dibromopropane and 14% of 2,2-dibromopropane (Table II).

No complicating ionic reaction was observed in either the ultraviolet light catalyzed or the ultraviolet–AIBN catalyzed reaction of equimolar amounts of hydrogen bromide and 3-bromopropene. The reaction yielded 1,3-dibromopropane as the only detectable product, in agreement with previous findings[12] (Table II).

Discussion

On the basis of all of our results, we believe that the free-radical addition of hydrogen bromide to allene in the liquid phase generally follows the reaction paths indicated by the solid arrows and not the theoretically also possible alternate routes indicated by the dotted arrows.

The selectivity of the addition varies characteristically with such conditions as reaction temperature or relative reactant ratios. Increasing reaction temperature and increasing excess of allene over hydrogen bromide cause a decrease in the formation of terminal attack products. It seems, therefore, that the previously reported strong preference for the formation of center attack products[4] is restricted to reactions at elevated temperatures or with an excess of allene, while reactions at lower temperatures and with equimolar

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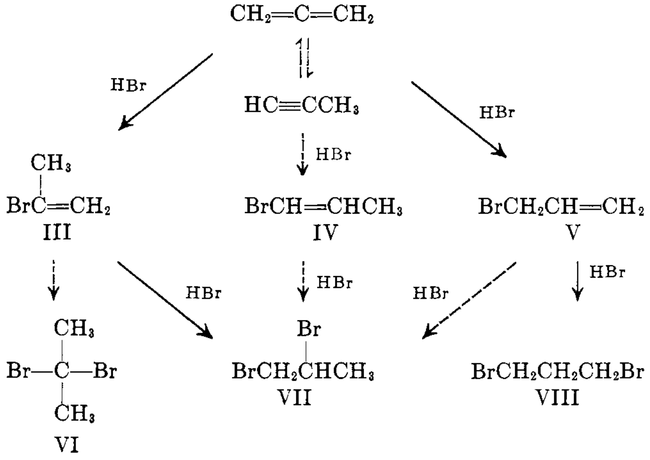
(9) The n.m.r. spectrum of a mixture of the isomeric 1-bromopropenes exhibited two methyl doublets (further split by remote coupling with the vinylic proton at C-1), centered at 1.65 and 1.73 p.p.m., respectively. These signals were absent in the spectrum of the reaction mixture derived from reaction of excess allene with hydrogen bromide.

(10) (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957: (a) p. 294; (b) p. 292.

(11) M. S. Kharasch, H. Engelmann, and F. R. Mayo [*J. Org. Chem.*, **2**, 288 (1937)] apparently did not obtain a complete selectivity in this reaction either.

(12) M. S. Kharasch and F. R. Mayo, *J. Am. Chem. Soc.*, **55**, 2468 (1933).



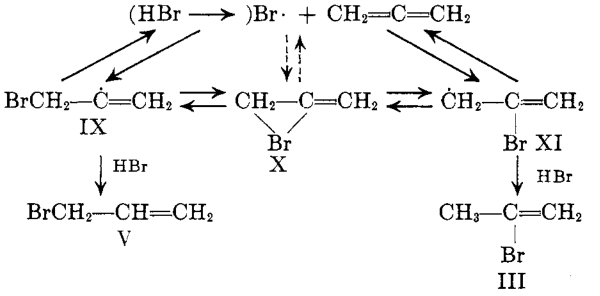
amounts of the reactants lead to almost equal amounts of terminal and center attack products.

The observed increase of terminal attack products with decreasing reaction temperature parallels our previous experience in the addition of methanethiol to allene.[1] Although this effect is more pronounced in the hydrogen bromide–allene additions (*viz.*, 29 *vs.* 6% in methanethiol reactions), it may well represent a common feature of free-radical additions to allene in general. The reported lower amounts of terminal attack products in the free-radical addition of thiols to allene at elevated temperatures[13] (approximately 80°) may also be indicative of such a correlation.

A consideration of the known free-radical additions to allene may suggest a similar correlation between the rate of the second propagation step and the course of the reaction; it seems that slower chain transfer leads to more terminal attack. Thus, under comparable conditions (ambient temperatures, ultraviolet irradiation) increasing terminal attack has been reported in this sequence: HBr (7%), C_6H_5SH[1] (83%), CH_3SH[1] (90%), H_2S[14] (98%), and CF_3I[3] ("exclusively"). Whether this observed trend is real or merely coincidental can, however, not be decided on the basis of the sparse data available.

While the present work describes the gross results of the free-radical addition of hydrogen bromide to allene, this question of the point of initial attack of bromine on allene remains unanswered. Skell and co-workers[15] reported recently that α-bromoalkyl radicals, the postulated first intermediates in free-radical additions of hydrogen bromide to olefins[10b] (*e.g.*, IX or XI in the case of allene), undergo fast rearrangements, possibly *via* bridged-radical intermediates[16] (*e.g.*, X in the case of allene).

On the basis of this argument, 2-bromopropene (III) can be envisaged to be derived from an initial terminal attack of bromine on allene to form the vinylic radical IX, which then rearranges to the more stable allylic radical XI. In other words, the preferential formation of the "center attack product" 2-bromopropene does not necessarily reflect a preferential attack of the bromine atom at the center position of allene, but may



equally well be due to the greater migratory aptitude of bromine compared with, *e.g.*, thiyl groups.

To complicate matters even more, Abell and Piette[17] reported recently that the initial attack of a bromine atom in free-radical hydrogen bromide additions leads directly to a bridged radical, *e.g.*, of type X.[18] If this is so, it would render any discussion on the point of initial attack immaterial, since the problem would then be one of a selective ring opening of this bridged radical in the second propagation step.

In view of these complications the observed product distributions in our hydrogen bromide–allene additions do not necessarily reflect the selectivities of the initial attack of bromine on allene. Additional work on this aspect of the problem is under way.

Experimental

Materials.—The allene used was pure according to g.l.c. analysis. Hydrogen bromide of 99.8% minimum purity, propane of 99.99% purity, and methylacetylene of 96% minimum purity were purchased from Matheson. The g.l.c. and n.m.r. reference samples of 3-bromopropene, 1,2-dibromopropane, and 1,3-dibromopropane were Matheson products; 2-bromopropene was purchased from Chemicals Procurement Laboratories. The samples were all redistilled before use.

Method of Analyses.—All the adduct mixtures were analyzed by capillary g.l.c. on a Perkin-Elmer Model 226 linear programmed temperature gas chromatograph under the conditions reported for the methanethiol–allene adducts in the previous paper of this series.[1]

Allene was analyzed on a F and M Model 500 gas chromatograph using a 10-ft. column packed with 20% dimethylsulfolane on Chromosorb P. The column temperature was maintained at 30°.

N.m.r. spectra were recorded and integrated on a Varian Model A-60 proton resonance spectrometer.

Addition of HBr to Allene in the Gas Phase.—The ultraviolet light catalyzed reactions were carried out in a 2-l., one-necked, round-bottomed quartz flask; the uninitiated reactions were carried out in a darkened 2-l., one-necked Pyrex flask. The flask was arranged upside down and its neck was tightly connected to the top of a 10-ml. graduated cylinder which contained an outlet on its side. After the whole system was evacuated, 2 g. (0.05 mole) of allene and 4 g. (0.05 mole) of HBr were condensed into the graduated cylinder, which was kept at the temperature of liquid nitrogen. Then the system was closed, the cooling bath was removed, and the reactants were allowed to completely evaporate into the evacuated 2-l. flask at room temperature.

On irradiation of the flask with a 100-W Hanovia utility lamp, the reaction mixture became hazy after about 3 to 5 min. and the precipitation of a thin liquid layer, probably the adduct product, began on the inside walls. Although some reaction may have occurred in this liquid phase, the abundance of monoadduct suggests that this was not a serious complication.

After the reaction was over, the graduated cylinder was cooled to −78° and the reaction flask was gently warmed up to promote

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[13] H. J. Van der Ploeg, J. Knotnerus, and B. F. Bickel, *Rec. trav. chim.*, **81**, 775 (1962).

[14] Unpublished results from this laboratory.

[15] P. S. Skell, R. G. Allen, and N. D. Gilmour, *J. Am. Chem. Soc.*, **83**, 504 (1961).

[16] P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).

[17] P. I. Abell and L. H. Piette, *ibid.*, **84**, 916 (1962).

[18] The particular evidence presented by Abell and Piette was subsequently refuted by M. C. R. Symons [*J. Phys. Chem.*, **67**, 1566 (1963)]. However, the general concept of bridged radicals seems to be deriving increasing support from chemical evidence.

condensation of the adduct into the graduated cylinder. The product was analyzed in the same manner as described above.

Addition of HBr to Allene or Methylacetylene in the Liquid Phase.—The ultraviolet light catalyzed reactions were carried out in 100-ml. quartz tubes, which were either sealed or closed by a Teflon-tipped needle valve (obtained from Fisher and Porter Co., Clifton, N. J.) that was sealed to the top of the tube. The noninitiated reactions were carried out in Pyrex tubes which were "darkened" with a black enamel (from Krylon, Inc., Morristown, Pa.).

Allene (or methylacetylene) and HBr were condensed into the tubes at the temperature of liquid nitrogen through a vacuum system. The evacuated closed tubes were then transferred into a temperature-controlled water or "Freon" bath. A 100-W Hanau ultraviolet immersion lamp (obtained from G. W. Gates and Co., Long Island, N. Y.) was used for the initiation. If the reaction was carried out below room temperature the lamp was surrounded by a quartz mantle to insulate it against excessive cooling.

After an arbitrary period of reaction time, the tubes were transferred to a liquid nitrogen bath and opened. The unreacted gases were allowed to evaporate through a drying tube filled with anhydrous calcium sulfate ("Drierite"). The remaining adduct mixtures in the tube were slightly yellow to dark brown mobile liquids. They were analyzed as such by g.l.c. and n.m.r.

Vacuum distillation of an adduct mixture derived from the reaction of equimolar amounts of hydrogen bromide and allene produced 1,3-dibromopropane as the highest boiling component and left no residue. This indicates that, when equimolar amounts of reactants or an excess of HBr are used, telomerization is insignificant and that the g.l.c. method, therefore, can provide a complete analysis of these adduct mixtures.

The use of stringent precautions is recommended for carrying out these reactions regardless of the reaction temperature employed. In one case a vigorous explosion occurred when an equimolar mixture of allene and HBr was irradiated at room temperature for approximately 5 min. The explosion was preceded by a yellow flash in the reaction tube. In a second case a mixture containing allene, methylacetylene, and HBr in the relative molar ratios of 1:1:2 exploded when it was irradiated at −70°. In both cases the experiments were well shielded and no one was injured. The reasons for these explosions are unknown.

Acknowledgment.—The authors thank their colleague, Dr. R. B. Long, for supplying them with samples of pure allene and Miss M. Doolan for carrying out the g.l.c. analyses. The skillful technical assistance of Mr. A. M. Palmer in carrying out experiments is particularly acknowledged.

Sodium- and Potassium-Induced Reactions of β-Methylstyrene[1,2]

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Considerable difference was observed in the reactions of β-methylstyrene (I) in nonexchanging solvents in the presence of dispersed sodium or potassium. At 100–155°, in the presence of sodium, I underwent mainly dimerization to 1,5-diphenyl-4-methyl-1-pentene (V, yield 80–87%), whereas the fastest reaction in the presence of the more electropositive potassium was hydrodimerization resulting in 1,4-diphenyl-2,3-dimethylbutane (IV, optimal yield 85–93% at 80–100°). The two reactions are mechanistically different: dimerization of I is a typical carbanion-catalyzed chain reaction, whereas hydrodimerization, which probably involves the intermediate formation of an anionic free radical, is a noncatalytic reaction requiring 2 g.-atoms of metal per mole of hydrodimer formed. Dimer V underwent a slow decomposition and recombination leading to the formation of 1,3-diphenyl-2-methylpropane (III) and to a C_{11} hydrocarbon (II) to which the structure 3-methyl-4-phenylcyclobutene was assigned. The mechanism of the reaction is discussed.

It has been reported[4,5] recently that α- and β-methylstyrene react with alkylbenzenes in the presence of dispersed potassium to form 1,3-diphenylalkanes. In the case of β-methylstyrene (I) the relative rate of aralkylation was found[5] to decrease sharply with increased size of the substituent in the alkylbenzene reactant, while, simultaneously, the dimerization and concurrent hydrodimerization of I became increasingly competitive.

As an extension of the above work the reactions of I have been separately studied in nonexchanging media. Comparative experiments were carried out employing dispersed sodium or dispersed potassium as a catalyst. The effect of temperature upon the relative rate of dimerization and upon the partial evolution of the dimer into secondary products was also studied by performing the reaction in four different alkylcyclohexane solvents at their respective boiling points: cyclohexane (80°), methylcyclohexane (100°), ethylcyclohexane (132°), and isopropylcyclohexane (155°). The course of the reaction at a given temperature was followed by plotting the product composition as a function of reaction time.

The experimental procedure was similar to that described previously.[6] The reaction products were separated and analyzed by a combination of fractional distillation, gas chromatography, hydrogenation, and ozonation, as well as by infrared, ultraviolet, and n.m.r. spectroscopy. Part of the compounds formed were identified by comparison with pure synthetic samples.

Results and Discussion

As seen from Table I there is considerable difference in the composition of products obtained in the experiments with sodium and potassium catalysts.

The main dimerization product in the presence of dispersed sodium is 1,5-diphenyl-4-methyl-1-pentene (V). The dimer is obtained in high yields (80–90%) at 100° and extended reaction time (expt. 1) or at 155° and short contact time (expt. 4); the reaction under these conditions can be conveniently employed as a preparative method.

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(1) Paper XXVII of the series "Base-Catalyzed Reactions." For paper XXVI, see E. M. Lewicki, H. Pines, and N. C. Sih, *Chem. Ind.* (London), 154 (1964).

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(3) On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel, 1959–1961.

(4) J. Shabtai and H. Pines, *J. Org. Chem.*, **26**, 4225 (1961).

(5) J. Shabtai, E. M. Lewicki, and H. Pines, *ibid.*, **27**, 2613 (1962).

(6) H. Pines and J. Shabtai, *ibid.*, **26**, 4220 (1961).