3-Bromo-3-methyl-1-butyne, 1-Bromo-3-methyl-1,2-butadiene, and 1-Bromo-3-methyl-1,3-butadiene[1]

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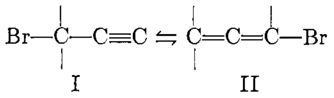
3-Bromo-3-methyl-1-butyne (IV) was obtained from 2-methyl-3-butyn-2-ol by reaction with phosphorus tribromide or thionyl bromide. It was rearranged by cuprous bromide or bromide ion to 1-bromo-3-methyl-1,2-butadiene (V). At 60–80° the latter gave 52% of *cis*- and *trans*-1-bromo-3-methyl-1,3-butadiene, 28% of the dimer *trans*-1,2-dibromo-3,4-di-isopropylidenecyclobutane, and 20% of other dimers and polymers. Displacement reactions of IV and V with iodide ion, thiophenoxide ion, and diethylamine were examined. Dehalogenation of IV, V, and the dimer by lithium aluminum hydride was also studied.

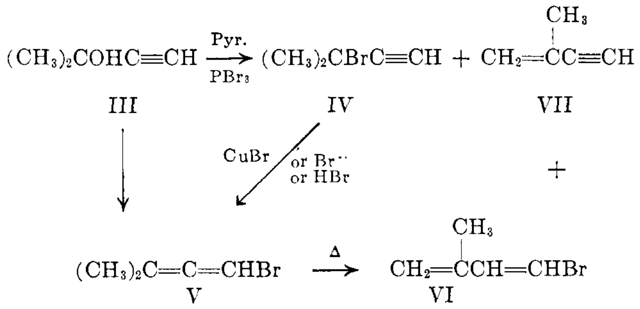
Allenic halides have been synthesized most frequently by rearrangement of the corresponding propargyl halides or from propargyl alcohols by displacement reactions which often yield rearranged halides. A number of chloroallenes are known but only two bromoallenes had been reported[2] when the present work was completed: bromoallene itself[3] and 3-bromo-5-phenyl-2,2,6,6 - tetramethyl - 3,4 - heptadiene.[4] These compounds are of interest because the anionotropic rearrangement in the acetylene–allene system I ⇌ II would be expected to occur more readily when the halogen atom is bromine instead of chlorine.



$$Br-\overset{|}{\underset{|}{C}}-C\equiv C \rightleftharpoons \overset{|}{\underset{|}{C}}=C=\overset{|}{C}-Br$$

I II

It was reported[5] that the reaction of 2-methyl-3-butyn-2-ol, with hydrobromic acid fails to yield either 3-bromo-3-methyl-1-butyne (IV) or 1-bromo-3-methyl-1,2-butadiene (V); only 1-bromo-3-methyl-1,3-butadiene (VI), which might result from the acetylene–allene rearrangement I → II followed by a prototropic rearrangement of the allene to the conjugated diene, was isolated.



Reaction of phosphorus tribromide with III was reported to yield IV which decomposed rapidly.[6] Recently a modification of Moulin's method permitted isolation of relatively pure IV, b.p. 97°, which could then be purified more completely in a vacuum train.[2] Very few other aliphatic tertiary propargyl bromides RR′CBrC≡CH have been reported and in no instance has a structure of one of these been proved. It was therefore of interest to study the synthesis and rearrangement of IV more carefully.

In our hands IV could not be obtained in higher than 30% yield by the reaction of III with phosphorus tribromide with or without pyridine. Usually enyne VII and *trans* 1-bromo-3-methyl-1,3-butadiene (VI) were also obtained and under certain conditions more completely brominated products were found. The bromoallene V appeared to be absent and no III could be recovered. The amount of polymeric material was not great and did not account for low yields of IV.

A possible explanation for these yields can be derived from the known behavior of saturated alcohols with phosphorus trihalides. It was shown[7] that trialkyl phosphites are cleaved to alkyl halides and dialkyl phosphites by hydrogen halides more rapidly than succeeding cleavages of the other alkyl groups occur. With the propargyl phosphites it may be that addition reactions take place with the primary and secondary esters more rapidly than cleavage to give the propargyl bromides. No attempt was made to isolate such addition products in the present research; they might be water soluble and would then not appear as higher boiling material. As would be predicted from this explanation, addition of III to an equimolar amount of phosphorus tribromide, which should lead to decreased yield of trialkyl phosphite as an intermediate, greatly reduced the yield of IV. It may also be mentioned that the reaction of 1-phenyl-5,9-dimethyl-9-decen-1-yn-3-ol with phosphorus tribromide was reported[8] to yield a compound containing phosphorus and more bromine than the theoretical amount for the simple bromide.

Thionyl bromide was also tried for conversion of III to IV, and a yield of 39% realized; as expected[9] a tribromide was also isolated. It appears possible that the yield of IV could be markedly improved with this reagent.

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[1] This paper is taken from the Ph.D. dissertation of Walter L. Petty, UCLA, 1958, and was presented in part at the Dallas meeting of the American Chemical Society, April, 1956 (Abstracts of that meeting, p. 38-N). The research was supported by a contract with the Office of Ordnance Research, U. S. Army.

[2] Very recently V. J. Shiner, Jr., and J. W. Wilson, *J. Am. Chem. Soc.*, **84**, 2402 (1962), reported the preparation of 1-bromo-3-methyl-1,2-butadiene.

[3] T. L. Jacobs and W. F. Brill, *ibid.*, **75**, 1314 (1953).

[4] J. H. Ford, C. D. Thompson, and C. S. Marvel, *ibid.*, **57**, 2619 (1935); J. Wotiz and D. Mancuso, *J. Org. Chem.*, **22**, 207 (1957). We have found by infrared examination that the compound reported [C. Moureu, D. Dufraisse, and C. Mackall, *Bull. soc. chim. France*, (4) **33**, 934 (1923)] as 3-bromo-1,3,3-triphenylpropyne is instead 1-bromo-1,3,3-triphenyl-1,2-propadiene and believe it likely that other compounds of similar structure are likewise bromoallenes. [T. L. Jacobs and D. M. Fenton, *J. Org. Chem.*, in press; Ph.D. dissertation of D. M. Fenton, UCLA, 1958; Abstracts, 135th National meeting of the American Chemical Society, April, 1959, p. 56-O.]

[5] T. A. Favorskaya, *Zh. Obshch. Khim.*, **10**, 461 (1940).

[6] F. Moulin, *Helv. Chim. Acta*, **34**, 2416 (1951). It has been reported that this bromide can be stabilized with *t*-butylcatechol [R. F. Kleinschmidt and S. H. Pitts, Jr., U. S. Patent 3,002,029 (September 26, 1961); *Chem. Abstr.*, **56**, 2328 (1962)].

[7] W. Gerrard and H. Herbst, *J. Chem. Soc.*, 277 (1955); W. Gerrard, M. J. D. Isaacs, G. Machell, K. B. Smith, and P. L. Wyvill, *ibid.*, 1920 (1953).

[8] H. Rupe and R. Rinderknecht, *Ann.*, **442**, 61 (1925).

[9] M. J. Frazer and W. Gerrard, *J. Chem. Soc.*, 3624 (1955).

The structure of IV is indicated clearly by its infrared spectrum which shows a strong band at 3280 cm.$^{-1}$ (acetylenic hydrogen) and a weak band at 2122 cm.$^{-1}$ ($C{\equiv}C$ stretching).

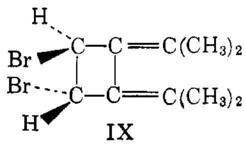
The origin of conjugated, *trans*, diene VI among the products of the phosphorus tribromide reaction is not clear. Pyridine or its hydrobromide apparently plays a role in its formation because only when pyridine was used in the reaction could any appreciable amount of VI be isolated. It seems unlikely that it arises from rearrangement of the allene (V) because the latter was never detected among the reaction products even when the reaction was carried out entirely at 0° and rearrangement of V yields both *cis* and *trans* VI (see below). No attempt was made to prove that *cis* VI would not rearrange to *trans* under the reaction conditions, so this explanation has not been ruled out. It seems more probable, however, that VI is formed by an addition–elimination mechanism. Moulin[6] showed that the action of excess hydrogen bromide on III gives a dibromide which he believed to be 1,3-dibromo-3-methyl-1-butene (VIII), $(CH_3)_2CBrCH{=}CHBr$, arising from addition to IV by a radical process. We isolated a dibromide with the same properties from III and phosphorus tribromide in the absence of pyridine. Thus VIII could be an intermediate in the formation of VI. The radical addition process would probably yield the more stable *trans* isomer. It is also possible that hydrogen bromide adds similarly to the intermediate phosphites such as $[HC{\equiv}CC(CH_3)_2]_2PHO$ to form $[BrCH{=}CHC(CH_3)_2]_2PHO$ or $[BrCH{=}CHC(CH_3)_2][HC{\equiv}CC(CH_3)_2]PHO$ which undergoes elimination and cleavage to form VI.

IV is rearranged to V by cuprous bromide and less readily by other bromides (see Experimental for details and for isolation of pure V). V has a strong infrared peak at 1956 cm.$^{-1}$ (allene) and no absorption at 3280 cm.$^{-1}$ (acetylenic hydrogen) or 1580 and 1620 cm.$^{-1}$ (conjugated double bonds).

At 60 or 80° V undergoes isomerization to VI (approximately equal amounts of *cis* and *trans*), dimerization and polymerization (to a small extent). The isomerization appears to be catalyzed mildly by di-*t*-butyl peroxide and inhibited mildly by *t*-butylpyrocatechol. In the presence of the peroxide a typical run gave 52% VI, 28% of crystalline dimer IX, and 20% of other dimers and polymers. It is interesting that *t*-butylpyrocatechol has been patented as a stabilizer for IV.[6]

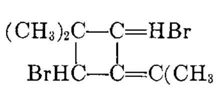
Structures were assigned to *cis* and *trans* VI on the basis of infrared spectra and confirmed by alkaline dehydrobromination (preferential attack of *cis*). The position of the bromine was established by conversion of VI to 4-methylpentanoic acid (formation of the lithium derivative, carbonation and hydrogenation).

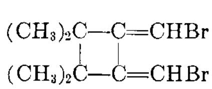
The structure of the crystalline dimer was shown to be IX by analysis, molecular weight determination, and ozonization to acetone and *dl*-dibromosuccinic acid. Infrared, ultraviolet, and n.m.r. spectra are in agreement with this structure. The bromine atoms in IX are moderately reactive toward sodium iodide in acetone and toward alcoholic silver nitrate as would be expected for allylic bromines. By contrast *trans*-1,2-dibromocyclobutane is unreactive.[10] IX does not form a maleic anhydride adduct; it reacts slowly with bromine in carbon tetrachloride and yields much hydrogen bromide.

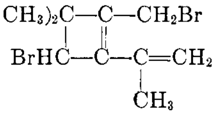

IX

Further confirmation of the carbon skeleton was obtained by debromination with lithium aluminum hydride and hydrogenation of the resulting olefin to 1,2-diisopropylcyclobutane. The physical constants of the latter were the same as for a sample prepared by dimerization[11] of dimethylallene and hydrogenation of the dimer. One attempt to isolate the intermediate olefin, possibly 3,4-diisopropylidenecyclobutene, failed when a sticky mass was obtained as soon as the solvent had been removed.

Dimerization of V might be expected to yield X and XI as well as IX by analogy with products from dimerization of 3-methyl-1,2-butadiene.[11] It was not possible to isolate a pure liquid dimer from the dimeric and polymeric material which remained after IX had been separated. Distillation under reduced pressure gave a dimer fraction which was debrominated and then hydrogenated to a saturated hydrocarbon which had the physical properties of 1,1,2-trimethyl-3-isopropylcyclobutane. The infrared spectrum is in better agreement with structure XII which can be obtained from X by a hydrogen shift analogous to that observed in V → VI.


X


XI


XII

Further work is being carried out on allene dimerization, and the nature of the products other than IX that are obtained from V will receive further attention. V is especially suitable for such a study because the dimerization occurs under such mild conditions. It is interesting that the dimerization in this instance appears to give such a large preponderance of product with *trans* bromine atoms. Allene dimerization has been discussed briefly by Roberts and Shorts.[12]

Early in this work it was thought possible that one of the volatile bromides obtained thermally from V was 2-bromo-3-methyl-1,3-butadiene (XIV). This bromide was, therefore, synthesized by the action of hydrobromic acid on 2-methyl-1-buten-3-yne (VII) in the presence of cuprous bromide. This synthesis had not been examined by others when our work was done, but it has been reported since[13]; with 62% hydrobromic acid small amounts of IV were isolated in addition to

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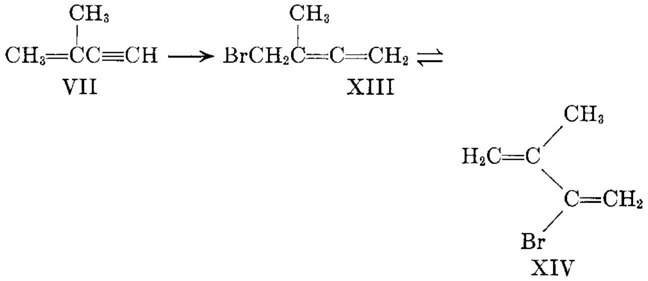
[10] J. Weinstock, S. N. Lewis, and F. G. Bordwell, *J. Am. Chem. Soc.*, **78**, 6072 (1956).

[11] S. V. Lebedev, *J. Russ. Phys. Chem. Soc.*, **43**, 820, 1735 (1911).

[12] J. D. Roberts and C. M. Sharts, "Cyclobutane Derivatives from Thermal Cycloaddition Reactions," *Org. Reactions*, **12**, 23–25 (1962).

[13] J. C. Traynard, *Bull. soc. chim. France*, 19 (1962); *Compt. rend.* **250**, 1504 (1960). The conditions we used are similar to those reported for addition of hydrogen chloride to vinylacetylene [W. H. Carothers, G. J. Berchet, and A. M. Collins, *J. Am. Chem. Soc.*, **54**, 4066 (1932)].



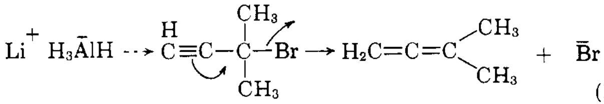
$$CH_3{=}\overset{CH_3}{C}C{\equiv}CH \longrightarrow BrCH_2\overset{CH_3}{C}{=}C{=}CH_2 \rightleftharpoons H_2C{=}C(CH_3){-}C(Br){=}CH_2$$

VII XIII XIV

XIII and XIV. Our addition was carried out in the presence of cuprous bromide which would rearrange IV to V. IV was absent from our product on the basis of infrared spectra, but small amounts of V would have escaped detection. Extended shaking of our mixture with cuprous bromide did not alter its composition which suggests that XIII and XIV might have been in equilibrium. Models indicate that the double bonds in XIV cannot be in the same plane because the bromine interferes with methyl or methylene; thus XIV may not be much more stable than XIII. The spectrum indicated that XIV was not present among the rearrangement products of V.

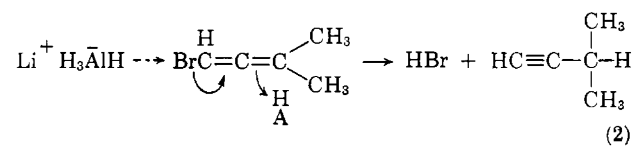
Dehalogenation of haloallenes and propargyl halides has been studied earlier in this laboratory.[14] Dehalogenation of 3-bromo-3-methyl-1-butyne (IV) with lithium aluminum hydride in diethylcarbitol gave a 98% yield of a mixture of hydrocarbons which was shown to be 99% 3-methyl-1,2-butadiene and 1% 3-methyl-1-butene (obtained after hydrolysis of the reaction mixture). A trace of a 1-alkyne, presumably 3-methyl-1-butyne, was also detected. A similar dehalogenation of 1-bromo-3-methyl-1,2-butadiene (V) gave a hydrocarbon mixture in 70% yield of which 61%, obtained before hydrolysis of the reaction mixture, was 3-methyl-1-butyne. After hydrolysis a mixture of isopentane (36%) and 3-methyl-1-butene (3%) was isolated. Conjugated diene VI gave a 70% yield of hydrocarbon products under similar conditions. An infrared spectrum and vapor phase chromatogram of the product showed it to be over 95% isoprene. The remaining constituents appeared to be 2-methyl-2-butene (~4%) and 2-methyl-1-butene (1%).

It was suggested earlier[14] that the dehalogenation of 3-chloro-3-methyl-1-butyne occurred by an S$_N$2′ process involving hydride ion or AlH_4^- attack on the terminal acetylenic carbon with shift of the bonds to an allenic system and displacement of the halogen. This mechanism seems probable for IV (equation 1).



$$Li^+\ H_3\bar{A}lH \dashrightarrow \overset{H}{C}{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}Br \longrightarrow H_2C{=}C{=}C(CH_3)_2 + \bar{B}r \quad (1)$$

A similar process could account for formation of 3-methyl-1-butyne from 1-bromo-3-methyl-1,2-butadiene but this requires a displacement reaction on a tertiary carbon which is doubly bonded, a somewhat less likely process. A more reasonable mechanism involves nucleophilic attack on halogen with a shift of bonds and possibly concerted donation of a proton at the γ-carbon (equation 2).

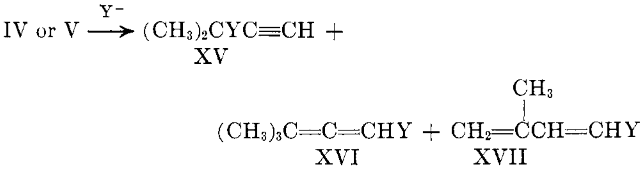


$$Li^+\ H_3\bar{A}lH \dashrightarrow Br\overset{H}{C}{=}C{=}C(CH_3)_2 \longrightarrow HBr + HC{\equiv}C{-}\underset{CH_3}{\overset{CH_3}{C}}{-}H \quad (2)$$

A

The mechanism of the process leading to hydrogenation of the carbon–carbon bonds will be discussed later.[14]

Preliminary experiments were carried out on other displacement reactions of IV and V. At low conversions IV with sodium iodide in acetone gives mainly XVIa with smaller amounts of XVa; at fairly high conversion the conjugated diene XVIIa is the main product. Thus rearrangement of XVI to XVII is much more rapid with iodide than with bromide and no attempt was made to isolate XVIa. Nearly pure



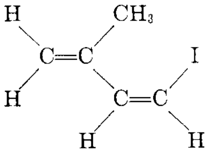
$$\text{IV or V} \xrightarrow{Y^-} (CH_3)_2CYC{\equiv}CH + (CH_3)_2C{=}C{=}CHY + CH_2{=}\overset{CH_3}{C}CH{=}CHY$$

XV XVI XVII

XVa, XVIa, XVIIa (Y = I)
XVb, XVIb, XVIIb (Y = SC_6H_5)

XVIIa was isolated but the study was not carried to completion because an explosion occurred toward the end of the distillation. XVIIa polymerized rapidly even in the refrigerator. The explosiveness and general instability of the iodides in this series were reported by Favorskaya,[5] who found that the reaction of carbinol III with hydroiodic acid gave a mixture of XVIa and XVIIa.

An infrared spectrum of XVIIa indicated that it contained a little XVIa. This spectrum was very similar to that of *trans* V which suggests that XVIIa is mainly *trans*. Although the large size of iodine would be expected to prevent the planar "chair" conformation XVIII for *cis* XVIIa, it is difficult to account for the different steric course of XVI → XVII when Y is iodine. Possibly *cis–trans* isomerization occurs more readily in this system or is catalyzed by impurities that are present.



XVIII

Reaction of IV with sodium thiophenoxide gave a high yield of organic sulfide consisting mainly of XVIb with perhaps 10% of XVb. Almost pure XVIb was isolated but slow distillation through an efficient column gave a less pure product probably partly rearranged to XVIIb on the basis of infrared spectra.

A similar reaction of V gave XVb and high boiling, viscous material. An infrared spectrum failed to show any XVIb although a little XVIIb may have been present.

IV reacted completely with excess diethylamine in benzene (room temperature, 24 hours) but the infrared spectrum of the product showed no absorption characteristic of either acetylenes or secondary amines; allene absorption at 1953 cm.$^{-1}$ was very weak. Strong peaks at 1753 and 1620 cm.$^{-1}$ suggested that the prod-

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[14] T. L. Jacobs, E. G. Teach, and D. Weiss, *J. Am. Chem. Soc.*, **77**, 6254 (1955). A detailed study of the dehalogenation of 3-chloro-3-methyl-1-butyne and 1-chloro-3-methyl-1,2-butadiene with lithium aluminum hydride has been completed and will be reported soon (R. D. Wilcox, Ph.D. thesis, UCLA, 1962).

uct contained a carbonyl and olefinic linkage. Possibly an allenic amine was formed and hydrolyzed during the washing procedure.

Mechanisms of displacement reactions in the propargyl–allenyl system represented by IV and V appear to be complex on the basis of the work reported by Shiner, *et al.*,[2] as well as the experiments described above. Although the latter offer very little evidence on the problem, they do suggest that different nucleophiles differ greatly in their behavior with this system. Thiphenoxide ion appears especially attractive for further study and is being investigated along with other nucleophilic reagents.

Experimental

Infrared spectra were obtained on a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. A 0.03-mm. cell was used with neat liquids unless otherwise indicated. Ultraviolet spectra were obtained on a Cary Model 14 spectrophotometer.

3-Bromo-3-methyl-1-butyne (IV).—A mixture of 420 g. (5.0 moles) of 2-methyl-3-butyn-2-ol (III)[15] and 50 g. (0.63 mole) of pyridine was stirred in a 1-l., three-necked, round-bottom flask cooled in ice while 512 g. (1.89 moles) of phosphorus tribromide was added during 5 hr. The mixture was stirred for an additional 4 hr. at 0° and 20 hr. at room temperature. The volatile products were distilled from the flask under reduced pressure with mild warming, the final conditions approximating 75° and 25 mm. The distillate (343 g.) was washed twice with 500-ml. portions of sodium bicarbonate solution and dried over anhydrous magnesium sulfate. The product was distilled under reduced pressure through an 18-in. column packed with glass helices to yield 25 g. (8%) of 2-methyl-1-buten-3-yne, b.p. 33°, $n^{25}{}_D$ 1.4118, and 184 g. (25%) of 3-bromo-3-methyl-1-butyne, b.p. 42.2° (106 mm.), $n^{25}{}_D$ 1.4583, $d^{25}{}_4$ 1.268.

Anal. Calcd. for C_5H_7Br: C, 40.85; H, 4.80. Found: C, 40.63; H, 4.79.

Infrared spectrum: 640 (s), 708 (w), doublet (769, 785) (s), 945 (m), 1013 (w), 1108 (s), 1167 (s), 1228 (s), 1290 (m, broad), 1370 (s), 1388 (s), triplet (1437, 1448, 1462) (s), 2122 (w), triplet (2822, 2910, 2965) (s), 3280 (s) cm.$^{-1}$. This spectrum is very similar to that of 3-chloro-3-methyl-1-butyne from 1500 to 3500 cm.$^{-1}$.

The reaction mixture from which volatile products had been removed by distillation was poured into 1400 ml. of crushed ice and water. The heavy organic layer was separated, washed with saturated bicarbonate solution, and dried over magnesium sulfate. It was combined with the pot residue from the distillation of 3-bromo-3-methyl-1-butyne and distilled under vacuum through the same column to yield 90 g. (12%) of *trans*-1-bromo-3-methyl-1,3-butadiene (VI), b.p. 42° (40 mm.), $n^{25}{}_D$ 1.5133, $d^{25}{}_4$ 1.319.

Anal. Calcd. for C_5H_7Br: C, 40.85; H, 4.80. Found: C, 40.94; H, 5.08.

Ultraviolet spectrum in 95% ethanol: λ_{max} 230 mμ (ϵ 17,600); 236 (18,600); shoulder, 243 (14,400).

Infrared spectrum: 685 (w), 753 (s), 790 (s), 892 (s), 940 (s), 1021 (w), 1092 (w), 1203 (s), 1283 (m), 1310 (m), 1383 (s), doublet (1442, 1452) (s), 1478 (w), 1579 (s), 1620 (s), 1670 (w), 1724 (w), 1785 (w), group (2900–2950) (m), 3065 (m).

Addition of 93 g. (1.1 moles) of III to 100 g. (0.37 mole) of phosphorus tribromide at 0° with stirring during 2 hr., slow heating to 65°, maintenance of this temperature for 1 hr. and distillation of the volatile product gave 31% of crude IV. The pot residue was poured onto ice, separated, washed with bicarbonate solution, and dried over anhydrous magnesium sulfate to give 30 g. of crude product. Distillation through a small, glass spiral column gave material, b.p. 90° (25 mm.), $n^{26}{}_D$ 1.5442. The infrared spectrum of this distillate had a strong band at 1636 cm.$^{-1}$ suggesting an olefin. Moulin[6] reported b.p. 70–71° (8 mm.), $d^{17}{}_4$ 1.779, $n^{18}{}_D$ 1.5481, for the dibromide from reaction of hydrobromic acid with III.

IV was also prepared with thionyl bromide. A magnetically stirred solution of thionyl bromide (212 g., 1.02 moles) in 500 ml. of dry pentane in a 1-l., three-necked, round-bottom flask was refluxed at −25° by suitable reduction of the pressure (condenser cooled with circulating methanol at −80°) while 84.1 g. (1.0 mole) of 2-methyl-3-butyn-2-ol was added dropwise during 45 min. The reaction mixture was maintained at −10° for 1.5 hr., allowed to warm slowly to normal reflux temperature (∼37°) by increase of pressure and maintained there for 2 hr. Solvent was distilled through a Vigreux column (hood) and when most of the pentane was gone vigorous evolution of sulfur dioxide began. Heating was continued until bubbling ceased. The pot residue was cooled, washed twice with saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and distilled at room temperature under reduced pressure to give 57 g. (39%) of quite pure IV (no allene absorption in the infrared) boiling below room temperature at 25 mm. A fraction, b.p. 60° (1 mm.), was also obtained; redistillation gave a pale yellow liquid, $n^{25}{}_D$ 1.5840.

Anal. Calcd. for $C_5H_7Br_3$: C, 19.57; H, 2.30; Br, 78.13. Found: C, 19.73; H, 2.30; Br, 78.11.

The infrared spectrum of this tribromide showed a medium peak at 1615 cm.$^{-1}$ and a strong peak at 1576 cm.$^{-1}$ in the olefin region. When this compound was allowed to stand overnight with zinc bromide and then vacuum distilled the peak at 1615 cm.$^{-1}$ had increased in intensity and that at 1576 cm.$^{-1}$ had decreased. The tribromide was probably a mixture of $(CH_3)_2CBr{=}CHBr$ and $(CH_3)_2C{=}CBrCHBr_2$.

A slightly lower yield of IV was obtained from thionyl bromide and III in the presence of pyridine.

Rearrangement of IV.—Cuprous bromide was the most effective catalyst found for rearrangement of IV to V. At room temperature 69% rearrangement occurred in 19 hr. of shaking with 1% of the salt, and 95% after 60 hr. The extent of rearrangement was the same with 10% catalyst. Lithium bromide was less effective; shaking for 24 hr. caused 6% rearrangement. Rearrangement was relatively complete when IV was stirred with 48% hydrobromic acid for 28 hr. or with saturated aqueous sodium bromide for 46 hr. but 1 *M* perchloric acid produced no rearrangement. The rearrangement is reversible; pure V gave 2% IV when shaken for 15 days with cuprous bromide.

1-Bromo-3-methyl-1,2-butadiene (V). Method 1.—IV was stirred for 60 hr. at room temperature with 10% by weight of finely powdered cuprous bromide. The infrared of the resulting mixture indicated a composition of 5% IV. Catalyst was removed by filtration and product distilled at low temperature and pressure into a Dry Ice trap. The colorless distillate was distilled through a Sargent column (1 m. long, 7-mm. i.d.) at 0.25 mm. to give excellent recovery of V, b.p. −19° (0.25 mm.), 34° (18 mm.), $n^{25}{}_D$ 1.5164, $d^{25}{}_4$ 1.317.

Anal. Calcd. for C_5H_7Br: C, 40.85; H, 4.80. Found: C, 40.77; H, 5.20.

Ultraviolet absorption in 95% ethanol: single broad peak, λ_{max} 221 mμ (ϵ 7000).

Infrared: 631 (s), doublet (722, 747) (s), 963 (w), 1010 (s), 1063 (w), 1161 (s), 1195 (m), 1383 (w), 1349 (s), 1364 (s), 1450 (broad, s), 1956 (s), 2682 (w), and a group of C—H stretching peaks at 2835, 2880, 2960, and 3030.

Distillation of V at pressures above 20 mm. where the boiling point is above 35° cause appreciable rearrangement to VI as indicated by infrared peaks at 1579 and 1615 cm.$^{-1}$. Our best samples of V did not show these peaks although traces of VI may have been present. VI probably boils no more than 7° below V at 18 mm. or below so separation by distillation is very difficult.

Method 2.—V can be synthesized from III in better yield with hydrobromic acid but it then contains a little VI. When small amounts of VI were not detrimental, V prepared as follows was used.

A mixture of 470 g. (5.6 moles) of III, 1000 ml. of 48% tech. hydrobromic acid, 200 g. of ammonium bromide and 70 g. of cuprous chloride was shaken for 4.5 hr. in a large bottle. The organic layer was separated, washed twice with sodium bicarbonate solution, once with saturated sodium bisulfite solution, and dried over anhydrous calcium chloride. Distillation at low pressure gave 500 g. (61%) of crude product which was redistilled through an 18-in. column packed with glass helices to yield almost pure V, b.p. 34° (18 mm.), $n^{25}{}_D$ 1.5163; infrared showed a trace of VI.

Rearrangement and Dimerization of V.—Samples of V containing, respectively, 4% by weight of di-*t*-butyl peroxide, 6%

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[15] We wish to thank the Air Reduction Chemical Co. for a generous supply of this carbinol.

of *t*-butyl catechol, and no added material were kept at 60° for 43 hr. The second and third samples then had essentially identical absorption in the infrared; they were mainly unchanged V containing small amounts of dimer (absorption at 1652 cm.$^{-1}$) but almost no conjugated diene VI (absorption at 1615 and 1579 cm.$^{-1}$). The first sample contained essentially no V, about the same amount of dimer as the other samples, and large amounts of VI. Similar samples containing, respectively, 2% of benzoyl peroxide and no added catalyst were heated at 75° for 3.5 days. The sample containing the peroxide was completely converted to dimer and VI (medium absorption at 1652 cm.$^{-1}$, strong bands at 1615 and 1579 cm.$^{-1}$). The uncatalyzed sample contained some unchanged V; absorption at 1652 cm.$^{-1}$ indicated about 1.7 times the amount of dimer present in the catalyzed sample, while lower absorption at 1615 and 1579 cm.$^{-1}$ showed that less VI had been formed. Two neat samples sealed under vacuum in Pyrex and quartz, respectively, were irradiated with ultraviolet light (2537 Å) at 0° for 91 hr. The sample in the quartz tube then showed 2% more absorption at 1615 and 1579 cm.$^{-1}$ and 6% more at 893 cm.$^{-1}$ ($=CH_2$ out-of-plane deformation) than the other; transmission in the olefin region was still above 90% in both.

Unfiltered radiation from a quartz mercury vapor lamp also proved to be very poor in effecting the rearrangement.

For product isolation 300 g. of V prepared by method 2 and 0.5 g. of benzoyl peroxide were heated at 80° for 46 hr.; infrared then indicated that V was absent. The material was kept at −20° for 22 hr. to allow the dimer to crystallize (55 g. obtained). The supernatant liquid was decanted and vacuum transferred to yield 156 g. (52%) of a mixture of the *cis* and *trans* forms of VI, n^{25}_D 1.5097. These were cleanly separated by v.p.c. at 100° with a 2-m. didecyl phthalate column (40–60-mesh firebrick as support) followed in series by a 2-m. di-2-ethylhexyl sebacate column. Peak areas indicated equal amounts of the geometric isomers. The *cis* isomer left the column first, n^{25}_D 1.5042, d^{25}_4 1.29.

Anal. Calcd. for C_5H_7Br: C, 40.85; H, 4.80. Found: C, 40.66; H, 5.02.

Ultraviolet spectrum in 95% ethanol very similar to that of the *trans* isomer but less intense: λ_{max} 232 mμ (ϵ 11,200); λ_{max} 238 mμ (ϵ 11,500); shoulder, 246 (ϵ 8900).

Infrared spectrum: 670 (s), 752 (s), 812 (m), 882 (w), 893 (s), doublet 961 and 970 (w), 1018 (m), 1132 (w), 1240 (m), 1299 (s), 1330 (s), 1378 (s), 1442 (shoulder, s), 1454 (s), 1581 (m), 1615 (s), 1670 (w), 1790 (w), 2900 (m), 2940 (s), 3060 (m) cm.$^{-1}$.

The residue from the distillation of VI gave more crystalline dimer when allowed to stand at −20° (total crystalline dimer, 84 g., 28%). Recrystallization from 95% ethanol gave only yellow crystals, but acetone and water gave white material, m.p. 90.5–92°.

Anal. Calcd. for $C_{10}H_{14}Br_2$: C, 40.85; H, 4.80; mol. wt., 294. Found: C, 40.78; H, 4.72; mol. wt. (cryoscopic in benzene), 285.

Ultraviolet spectrum in 95% ethanol: λ_{max} 221 mμ (ϵ 13,400); λ_{max} 285 mμ (ϵ 8300).

Infrared spectrum (10% solution in carbon tetrachloride): 663 (s), 879 (w), 922 (w), 1000 (w), 1085 (w), 1137 (s), 1177 (m), 1202 (m), 1255 (m), 1368 (s), 1443 (s), 1652 (s), 2693 (w), 2812 (m), 2870 (s), 2940 (m) cm.$^{-1}$.

The dark residue (60 g., 20%) which remained after all of diene VI and dimer IX had been removed was distilled at the full vacuum of an oil pump to give 46 g. of a yellow liquid, b.p. 60–90°. Only a trace of crystalline material was obtained after this liquid had stood at −20° for a week. Redistillation through a short Vigreux column gave no sharp-boiling fractions; the material came over from 64 to 90° at 0.3 mm.

Anal. Calcd. for $C_{10}H_{14}Br_2$: C, 40.85; H, 4.80; Br, 54.35. Found: C, 40.72; H, 4.73; Br, 54.00.

Ultraviolet spectrum in 95% methanol: rising absorption from 315 mμ to the limit of the instrument at 213 mμ; some semblance of a peak around 264 mμ (ϵ ~10,000).

Infrared spectrum: strong peaks at 897, 1138, 1170, 1190, 1205, 1277, 1364, 1441, 1450, 2900, and 2930 cm.$^{-1}$; medium peaks at 760, 775, 1104, 1220, 1290, 1600, 1659, and 2840 cm.$^{-1}$. This spectrum indicates that the liquid is different from IX, although some IX may be present in the mixture.

Dehydrohalogenation of VI.—To a solution of 30 g. of potassium hydroxide in 100 ml. of 95% ethanol was added 45 g. (0.31 mole) of VI (mixture of *cis* and *trans*) during 10 min. The mixture was refluxed for 2 hr. and the low boiling product distilled through a Vigreux column (b.p. 31–32°). The distillate was washed with water and dried over anhydrous magnesium sulfate to give 8.3 g. (41%) of 2-methyl-1-buten-3-yne, n^{25}_D 1.4129, identified by infrared. The distillation residue was diluted with 300 ml. of water and extracted twice with 50-ml. portions of methylene chloride. The combined extract was washed thrice with 200-ml. portions of water, dried over anhydrous magnesium sulfate, and stripped of solvent under vacuum; the residue (15 g.) was *trans* VI free from the *cis* isomer within the limits of detection by infrared; this represents 66% recovery based on *trans* VI present in the starting material.

Carboxylation of VI and Reduction of the Product.—Ethyllithium was prepared from 15 g. (2.2 moles) of lithium ribbon and 118 g. (1.1 moles) of ethyl bromide in 600 ml. of anhydrous ether. This solution was transferred to a 2-l. beaker in a hood and 73 g. (0.5 mole) of VI (mixture of *cis* and *trans*) in 100 ml. of ether was added slowly with stirring. The exchange reaction was very exothermic and much ether was lost. Three minutes after all of the VI was added the mixture was poured through glass wool into excess Dry Ice in a dewar flask and allowed to stand overnight. Precipitated lithium salt was dissolved by addition of 500 ml. of water and the ether layer was separated. The aqueous solution was washed twice with 150-ml. portions of ether, acidified with 100 ml. of concentrated hydrochloric acid, and extracted twice with 125-ml. portions of ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate, filtered, and placed in a 500-ml. Parr bomb with 0.5 g. of 10% palladium on carbon. The solution was shaken for 23 hr. under a pressure of hydrogen which decreased from 44 to 26 p.s.i. The catalyst was removed by filtration, the ether removed at reduced pressure, and the residual acid distilled through a small glass helix column to yield 18.7 g. (23%) of 4-methylpentanoic acid, b.p. 200°, n^{25}_D 1.419. An infrared spectrum of this acid was identical to that of known 4-methylpentanoic acid (Eastman Kodak, White Label, n^{25}_D 1.4124). A phenylhydrazide, m.p. 146.8–147.2°, and anilide, m.p. 113.4–114.5°, were prepared; mixtures with known samples showed no melting point depression.

The n.m.r. spectrum[16] **of IX** consists of a small single peak attributable to the ring hydrogens and at higher field a large doublet arising from the twelve hydrogens of the methyl groups. One might expect the six hydrogens on the methyls that are oriented toward each other to show different shielding from the six hydrogens of the methyls that point away. Dreiding models indicate that the hydrogen nuclei are only 0.3 Å. apart at closest approach and that the farthest these nuclei can be separated if normal angles are maintained is about 1.2 Å. Since the van der Waals radius of hydrogen is 1.2 Å.[17] some interference must occur. The small peak is separated from the closer of the two large peaks by 121 c.p.s. and the two large peaks are separated by 7 c.p.s. The simplicity of the spectrum rules out most alternative structures.

Reactivity of Bromines in IX.—A mixture of 2.0 g. of IX and 25 ml. of acetone saturated with sodium iodide was refluxed for 4 hr. Iodine was formed and 1.2 g. (85%) of sodium bromide was isolated.

IX in 2% alcoholic silver nitrate gave an immediate precipitate of silver bromide. The solution was refluxed for 15 min. and 1.96 moles of silver bromide recovered for each mole of IX.

Ozonization of IX.—A solution of 10 g. (0.034 mole) of dimer IX in 100 ml. of chloroform was treated at −25° with ozonized oxygen during 5 hr. (~0.11 mole of ozone). Solvent was removed from the clear ozonide solution under vacuum (safety precautions necessary) and the viscous ozonide stirred with 30 ml. of ice-water for 2 hr. When the mixture was heated on the steam cone for 1 hr., it turned dark and carbon dioxide was evolved. The mixture was steam distilled until 50 ml. of distillate was collected. This distillate was extracted with four 10-ml. portions of methylene chloride; the extracts were combined and washed with 10 ml. of saturated potassium carbonate solution, dried over anhydrous magnesium sulfate, and distilled through a small glass helix column to yield a 4-ml. fraction, b.p. 41.5–49.0°, containing acetone. A 2,4-dinitrophenylhydra-

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(16) We wish to thank Prof. J. D. Roberts of the California Institute of Technology for determining the n.m.r. spectrum of this compound for us before a spectrometer was available at UCLA. This spectrum was obtained on a 40-Mc. instrument in 1956 and has not been repeated since 60-Mc. instruments became available.

(17) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, New York, N. Y., 1960, p. 260.

zone, m.p. 125.4–126.4° cor., was prepared; no melting point depression when mixed with authentic acetone 2,4-dinitrophenylhydrazone.

During the steam distillation crystals of acetone peroxide collected in the condenser: these were recovered and recrystallized from pentane to give white crystals, m.p. 130.6–131.2° cor. A peroxide of nearly the same m.p. (132–133°) has been obtained from ozonization in chloroform of other unsaturated compound expected to yield acetone (*e.g.*, ref. 18) and also directly from acetone.[19] Attempts to isolate other identifiable products from the ozonide failed.

A second ozonization was carried out similarly. The chloroform solution of the ozonide was stirred overnight under aspirator pressure with 25 ml. of water; all solvent evaporated and a viscous, cloudy residue remained. To this was added 50 ml. of acetone and 25 ml. of water; the mixture was stirred for 2 hr. Then 10 ml. of 30% hydrogen peroxide and enough acetone to make a homogeneous solution were added and this stirred for 2.5 hr. The solution was treated with solid sodium bicarbonate until no more carbon dioxide was evolved and the resulting solution washed with methylene chloride, acidified with concentrated hydrochloric acid, and extracted with ether. The combined ether extract was dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure to yield 4.9 g. of a residue which did not crystallize. This residue was placed on a chromatographic column of 200 g. of 2:1 silica gel and Celite. Elution with 2:3 ether–pentane gave crystalline *dl*-dibromosuccinic acid. Recrystallization from ether–benzene gave a pure sample, m.p. 167–169° dec. (cor.). A mixture with authentic *dl*-dibromosuccinic acid prepared from maleic acid by addition of bromine[20] showed no melting point depression.

Anal. Calcd. for $C_4H_4O_4Br$: C, 17.40; H, 1.46; Br, 53.00. Found: C, 17.64; H, 1.60; Br, 58.18.

Reduction of IX.—Fifteen g. (0.051 mole) of IX in 100 ml. of ether was added during 20 min. to a refluxing solution of 4.0 g. (0.105 mole) of lithium aluminum hydride and 0.5 g. of *t*-butyl catechol in 100 ml. of ether. The mixture was refluxed for 16 hr., hydrolyzed with dilute hydrochloric acid (cooling), and the layers separated. The ethereal layer was washed with a solution of sodium bicarbonate and dried over anhydrous magnesium sulfate. Removal of the ether under reduced pressure gave a colorless mobile liquid which rapidly increased in viscosity and soon had the consistency of semihardened glue.

A second run was carried out and the ethereal solution hydrogenated at once over 1 g. of 10% palladium on carbon at 20 p.s.i. for 27 hr. The solution was filtered and the ether removed at reduced pressure. The residue was vacuum transferred to give 1.2 g. (17%) of 1,2-diisopropyl cyclobutane, b.p. (micro) 158°, n^{20}D 1.4265, d_4^{20} 0.7722.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.62; H, 14.31.

Lebedev[11] reported the following physical constants for this compound: b.p. 157–158.5° (760 mm.), n^{20}D 1.42787, d_4^{20} 0.7755.

Reduction of Other Dimeric Products.—To 10 g. (0.26 mole) of lithium aluminum hydride in 200 ml. of dry dioxane kept near room temperature by a water bath was added during 0.5 hr. 30.8 g. (0.105 mole) of the redistilled liquid dimer mixture in 50 ml. of dioxane. The bath was raised to 95° during 3 hr. and maintained at that temperature for 21 hr. The mixture was cooled to 0°, diluted with 250 ml. of pentane and hydrolyzed by dropwise addition of dilute hydrochloric acid. The pentane layer was separated, washed thrice with large volumes of sodium bicarbonate solution, and dried over anhydrous magnesium sulfate. Solvent was removed at reduced pressure and the residue which weighed 13.5 g. (94% yield) was distilled, b.p. 45–75° (24 mm.), to give 6.8 g. of clear liquid. This was hydrogenated at 20 p.s.i. in 150 ml. of pentane over 0.55 g. of 10% palladium on carbon for 18 hr. The solution was filtered and solvent removed at reduced pressure leaving 6.1 g. of liquid which was fractionally distilled through a small helix column to give a fraction, b.p. 143–146° (752 mm.), n^{20}D 1.4210, d_4^{20} 0.7582.

Anal. Calcd. for $C_{10}H_{20}$: C, 85.72; H, 14.28. Found: C, 85.71; H, 14.34.

Lebedev[11] gave the following for 1,1,2-trimethyl-3-isopropylcyclobutane: b.p. 145–146.5° (760 mm.), n^{20}D 1.42001, d_4^{20} 0.7598.

2-Bromo-3-methyl-1,3-butadiene, (XIV).—A mixture of 10 g. (0.15 mole) of 2-methyl-1-buten-3-yne (VII), 43 ml. of 48% hydrobromic acid, 4 g. of cuprous bromide, and 5 g. of ammonium bromide was shaken in a pressure bottle at room temperature for 14 hr. The organic product was extracted with methylene chloride, washed with sodium bicarbonate solution, dried over anhydrous magnesium sulfate, filtered, and the methylene chloride removed at 50 mm. The dark product (10 g.) was distilled through a 12-in. Vigreux column, b.p. 36° (38 mm.), n^{25}D 1.5027.

Anal. Calcd. for C_5H_7Br: C, 40.85; H, 4.80. Found: C, 41.07; H, 4.98.

Infrared spectrum: 630 (w), 723 (m), 747 (m), 808 (m), 880 (s), 900 (s), 940 (m), 1005 (m), 1094 (s), 1166 (m), 1196 (m), 1277 (m), 1371 (s), 1440 (s), 1450 (s), 1578 (s), 1613 (m), 1674 (m), 1772 (w), 1805 (w), 1954 (m), 2840 (m), 2915 (m), 2940 (m), 3065 (w) cm.$^{-1}$.

Reported[13] for XIV: b.p. 35.4° (40 mm.), n^{20}D 1.5030, d_4^{20} 1.330. Infrared: strong bands at 3100, 1610, and 1590 cm.$^{-1}$.

Reported[13] for XIII: b.p. 35–36° (21 mm.), n^{20}D 1.5213. Infrared: 1960 and 850 cm.$^{-1}$.

When the product was shaken an additional 12 hr. with cuprous bromide and a saturated solution of sodium bromide in 10% hydrobromic acid, an infrared spectrum of the product showed that the allene absorption at 1954 cm.$^{-1}$ was not diminished in intensity. A sample of the diene polymerized to a yellow gel after 4 days at −20°.

Lithium Aluminum Hydride Reductions of IV, V, and VI.—To a stirred mixture of 25 ml. of dry diethylcarbitol and 22 g. (0.56 mole) of lithium aluminum hydride cooled in ice was added 0.5 mole of the halide dropwise during 1 hr. The mixture was stirred an additional 2 hr. at 0° and overnight at room temperature. The pressure was then reduced to ~25 mm. and the flask warmed (finally to 85°) for 3 hr. with stirring, to permit distillation of the hydrocarbon product through the reflux condenser. The hydrocarbon distillate was collected in a Dry Ice trap, dried, and distilled through an efficient center-rod column to give the results reported. The lithium aluminum hydride reaction mixture was cooled to 0° and hydrolyzed with 100 ml. of water with stirring. After warming and brief refluxing the hydrocarbons produced were removed by distillation under reduced pressure, collected, and fractionated as before. The products were identified by means of boiling points, refractive indices, infrared spectra, and vapor phase chromatography.[14]

Reaction of IV with Sodium Iodide in Acetone.—A solution of 20.0 g. (0.136 mole) of IV and 40 g. (0.266 mole) of sodium iodide in 150 ml. of acetone was allowed to stand at room temperature for 68 hr. The sodium bromide recovered by filtration weighed 9.6 g. (64% reaction). Pentane (150 ml.) was added to the filtrate and the solution washed 4 times with large volumes of water. The pentane layer was dried over anhydrous magnesium sulfate and the solvent removed at reduced pressure to yield 18.5 g. (70% crude yield) of a yellow liquid. Infrared indicated some acetylenic (3277 cm.$^{-1}$) and allenic (1937 cm.$^{-1}$) material, but conjugated diene (1564 and 1614 cm.$^{-1}$) appeared to be the main component. The crude product was heated with 0.05 g. of cuprous bromide at 50° for 4 hr., the dark material vacuum transferred, and distilled through a small helix column, b.p. 49° (14 mm.), n^{25}D 1.5722. An explosion occurred near the end of the distillation.

Anal. Calcd. for C_5H_7I: C, 30.95; H, 3.61. Found: C, 31.34; H, 3.45.

Infrared spectrum: 675 (w), 702 (s), 779 (s), 888 (s), 943 (s), 1178 (s), 1240 (w), 1286 (m), 1303 (s), 1376 (s), 1436 (s), 1447 (s), 1564 (s), 1614 (s), 1674 (w), 1722 (s), 1785 (w), 2890 (m), 2920 (m), 2955 (s), and 3060 (m) cm.$^{-1}$.

A run half the above size left at room temperature for 24 hr. gave 3.5 g. of sodium bromide (34% yield) and 5 g. (38%) of crude iodide. The infrared of this iodide showed strong peaks at 1937 and 3227 cm.$^{-1}$ but essentially no absorption at 1564 cm.$^{-1}$.

Reaction of IV with Sodium Thiophenoxide.—To a cold solution of 0.195 mole of sodium methoxide from 4.5 g. of sodium in 150 ml. of methanol was added 20.0 g. (0.182 mole) of thiophenol. To this was added 10.0 g. (0.068 mole) of IV and the solution was allowed to stand for 24 hr. at room temperature. Benzene (100 ml.) was then added to the pale yellow solution and the mixture washed thrice with 10% sodium hydroxide solution and twice with water; it was then dried over anhydrous magnesium

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[18] I. M. Heilbron, W. M. Owens, and I. A. Simpson, *J. Chem. Soc.*, 873 (1929).

[19] A. Baeyer and V. Villiger, *Ber.*, **32**, 3625 (1899); **33**, 858 (1900); M. Pastureau, *Compt. rend.*, **140**, 1591 (1905).

[20] A. McKenzie, *J. Chem. Soc.*, 1196 (1912).

sulfate and the solvent removed at reduced pressure. The clear yellow residue (10.6 g., 88% crude yield) appeared to contain ~90% of 1-thiophenoxy-3-methyl-1,2-butadiene and ~10% of 3-thiophenoxy-3-methyl-1-butyne on the basis of infrared. Distillation through a small helix column gave fair recovery of material, b.p. 70° (0.4 mm.), n^{25}_D 1.5954, which was mainly allenic (perhaps 3% of the acetylenic isomer as contaminant). An attempt at further purification by careful fractional distillation through a more efficient column gave mainly nonvolatile, polymeric products. The distillate was partly rearranged as shown by new infrared peaks at 810, 845, 942, 1307, and 1613 cm.$^{-1}$.

Reaction of V with Sodium Thiophenoxide.—A solution of 0.27 mole of sodium thiophenoxide prepared from 6.8 g. of sodium, 150 ml. of methanol and 30 g. of thiophenol was treated with 15 g. (0.10 mole) of V and allowed to stand at room temperature for 16 days. The solution was worked up as above to yield 14.0 g. (87% yield, crude) of a pale yellow product. Infrared showed no allenic material, but a small peak at 2107 cm.$^{-1}$ and a strong one at 3242 cm.$^{-1}$ indicated an acetylenic compound. There was also a strong peak at 1578 cm.$^{-1}$ and a weak one at 1657 cm.$^{-1}$ which may indicate conjugated diene. Fractionation through a small helix column gave a moderate yield of product believed to be 3-methyl-3-thiophenoxy-1-butyne, b.p. 52° (0.4 mm.), n^{25}_D 1.5505, d^{20}_4 0.998.

Anal. Calcd. for $C_{11}H_{12}S$: C, 74.94; H, 6.86; S, 18.19. Found: C, 74.72; H, 6.65; S, 18.31.

Infrared spectrum: 684 (s), 735 (s), 780 (m), 833 (w), 912 (w), 935 (w), 998 (w), 1010 (m), 1021 (m), 1064 (m), 1072 (m), 1086 (m), 1122 (s), 1171 (m), 1211 (s), 1260 (m), 1301 (m), 1325 (w), 1357 (m), 1378 (m), 1437 (s), 1471 (s), 1578 (m), 1657 (w), 1745 (w), 1794 (w), 1871 (w), 1946 (w), 2107 (w), 2812 (m), 2820 (s), 3017 (m), and 3242 (s) cm.$^{-1}$. The peaks at 2107 and 3242 cm.$^{-1}$ were much stronger in the redistilled product and the peaks at 1578 and 1657 cm.$^{-1}$ much weaker.

Reaction Rates by Distillation. X. The Condensation of Anilines with Benzoins

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The acid-catalyzed condensation of aniline with benzoin in benzene containing dimethylaniline as a "leveller" has been found to be first order with respect to each reactant and the catalyst. Electron releasing groups *para* to the carbonyl group of the benzoin tend to decrease the rate. In a group of eleven anilines the rate increased consistently as the electron releasing ability of the *meta* or *para* substituent increased. The points for the less basic anilines fell on one straight line of a $\rho-\sigma$ plot while those for the more basic anilines fell on a second straight line of decreased slope. Excellent yields of desylanilines were isolated in all cases. The results strongly favor reaction of the aniline with the carbonyl group rather than with the hydroxymethylene group of the benzoin. A mechanism analogous to that previously advanced for the condensation of aniline with benzaldehyde is evaluated.

The factors which determine the rate of reaction of anilines with benzoins have been studied by the distillation method previously employed for a variety of reactions which yield water as a by-product.[2]

$$\begin{array}{l}ArC{=}O\\ \quad|\\ Ar'CHOH\end{array} + PhNH_2 \longrightarrow \begin{array}{l}ArCHNHPh\\ \quad|\\ Ar'C{=}O\end{array} + H_2O$$

The standard conditions used are given at the top of Table I. When no dimethylaniline was employed (second experiment) the rate constants calculated at successive stages of reaction showed a distinct and consistent upward drift; this drift decreased to insignificance as the amount of dimethylaniline was increased (third and first experiments). The dimethylaniline "leveller" doubtlessly functions primarily to minimize changes in basicity of the reaction medium as the amount of unreacted aniline decreases.

TABLE I

REACTION OF ANILINE WITH BENZOIN

Standard conditions: 0.125 mole of aniline, 0.125 mole of benzoin, 0.0005 mole of PTS,[a] and 0.250 mole of dimethylaniline with benzene to give 500 ml.

Variable	$t_{50\%}$,[b] min.	$k \times 10^2$, l. mole^{-1} min.$^{-1}$
Standard conditions[c]	210	2.25 ± 0.02
No $C_6H_5N(CH_3)_2$	125	3.86 ± 0.21
Half std. amt. $C_6H_5N(CH_3)_2$[c]	148	3.12 ± 0.15
Half std. amt. PTS[a]	404	1.16 ± 0.01
Quarter std. amt. PTS[a]	780	0.61 ± 0.01
Double std. amt. $C_6H_5NH_2$	77	2.33 ± 0.03
Double std. amt. $C_6H_5COCHOHC_6H_5$	91	2.01 ± 0.02

[a] *p*-Toluenesulfonic acid monohydrate. [b] This is the time required for a 50% yield of water to collect. [c] For increased accuracy these experiments were double scale.

Comparison of the results for the last four experiments tabulated with those for the first experiment show that the reaction is first order with respect to the aniline, the benzoin, and the catalyst. First-order dependence on the aniline and benzoin is, of course, implicit in the fact that rate constants, calculated on the assumption of such dependence at successive stages of reaction showed no serious drift.

In Tables II and III are summarized the results for the condensation of eleven anilines with benzoin and five benzoins with aniline. The clear-cut nature of the reaction, a requirement for precise rate data, is emphasized by the high yields of products obtained and by the 98 to 102% yields of water collected in all cases; in most cases the yield of water was 99 to 101%. It would be difficult to improve on the facile distillation method as a preparative procedure. Since the reaction can be stopped as soon as complete, cyclization of the products to diarylindoles[3] is minimized.

A $\rho-\sigma$ plot for the experiments of Table II is given in Fig. 1. It is suggested that since the dimethylaniline leveller is less basic than the most basic anilines employed, incomplete levelling resulted for those anilines for which the line of decreased slope is drawn. In support of this view the percent average deviation for the three most basic anilines (first three experiments of Table II) was greater than for the other anilines and in these three cases the rate constants calculated at successive stages of reaction showed an upward drift analogous to that encountered in the absence of a

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[1] From a portion of the Ph.D. thesis of M. J. Kamlet, March, 1954.

[2] For the preceding paper in this series, see E. F. Pratt and M. J. Kamlet, *J. Org. Chem.*, **26**, 4029 (1961).

[3] P. L. Julian, E. W. Meyer, and H. C. Printy, "Heterocyclic Compounds," Vol. 3, R. C. Elderfield, ed., J. Wiley and Sons, Inc., New York, N. Y., 1952, pp. 22-35.