

## Allylic Addition of Olefins to Activated Acetylenes

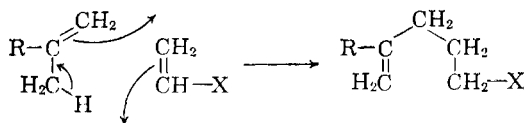
J. C. SAUER AND G. N. SAUSEN

Contribution No. 768, Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

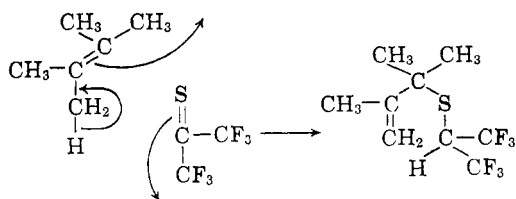
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The addition of the allylic hydrogen atom of olefins to activated acetylenes takes place readily by heating to 145–250° under autogeneous pressures. The products, isolated in yields up to 80%, are 2,5-dienes and are probably formed through pseudo six-membered ring intermediates.

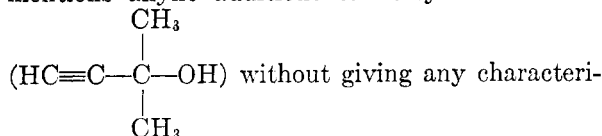
The addition of the allylic hydrogen atom of an olefin to a negatively substituted olefin has been reported.<sup>1</sup> A special case in which a thio ketone functions as the activated olefin has been recently



described,<sup>2a</sup> and cases in which the carbonyl groups of perfluorocyclobutanone<sup>2b</sup> and hexafluoroacetone<sup>2c</sup> function as the "olefin" to give the corresponding carbinols by allylic addition have been reported. The allylic interaction of an olefin with



an activated acetylene has not been reported, although Arnett has reported the special case of allylic addition to a benzyne,<sup>3</sup> and a German patent mentions allylic additions to acetylenic alcohols



without giving any characteri-

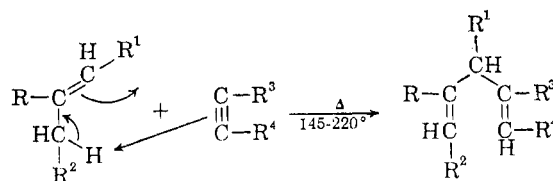
zation of the products beyond boiling points.<sup>4</sup> We have found that the addition of allylic hydrogen takes place readily with negatively substituted acetylenes. For example, isobutylene and hexafluoro-2-butyne react at 145° under autogeneous pressure to give in 80% yield 1,1,1-trifluoro-3-trifluoromethyl-5-methyl-2,5-hexadiene (R = CH<sub>3</sub>, R<sup>1</sup> and R<sup>2</sup> = H, R<sup>3</sup> and R<sup>4</sup> = CF<sub>3</sub>).

(1) C. J. Albisetti, N. G. Fisher, M. J. Hogsed, and R. M. Joyce, *J. Am. Chem. Soc.*, **78**, 2637 (1956).

(2)(a) W. J. Middleton, E. G. Howard, and W. H. Sharkey, *J. Am. Chem. Soc.*, **83**, 2589 (1961); (b) D. C. England and R. V. Lindsey, Jr., Abstracts of the 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961, p. 13-M; (c) H. R. Davis, *ibid.*, p. 25-M.

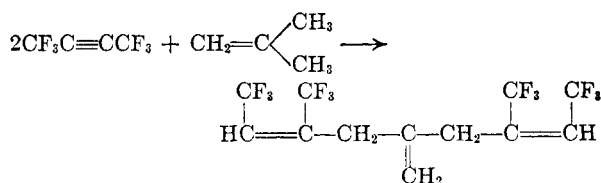
(3) E. M. Arnett, *J. Org. Chem.*, **25**, 324 (1960).

(4) M. Seefelder and J. Speck, German Patent 1,082,257, May 25, 1960.



Similar reactions took place with yields of 15–60% in the addition of isobutylene to dimethyl acetylenedicarboxylate, methyl propiolate, or 1,1,1-trifluoropropyne, and of 2-butene to hexafluoro-2-butyne. With such unsymmetrical acetylenes as 1,1,1-trifluoropropyne (R<sup>3</sup> = H and R<sup>4</sup> = CF<sub>3</sub>), two isomers are possible, and both are formed.

As expected for olefins having more than one allylic hydrogen, diadducts are also formed. Thus, the conversion to diadduct in the reaction of hexafluoro-2-butyne with isobutylene increases from a trace to 14% as the reaction temperature is increased from 145° to 240°. The structure of the principal diadduct is that indicated below:



### Experimental<sup>5</sup>

**1,1,1-Trifluoro-3-trifluoromethyl-5-methyl-2,5-hexadiene.**—A Pyrex Carius tube, 2 × 60 cm., was charged with 20 g. (0.12 mole) of hexafluoro-2-butyne,<sup>6</sup> 15 g. (0.27 mole) of isobutylene, and 5 ml. of acetone. The tube was cooled to -196°, evacuated, and sealed. It was subsequently heated at 145° for 8 hr. The colorless, liquid product amounted to 30.7 g. Distillation of the product through a 12-in. micro spinning-band still gave 21.2 g. (79% yield) of colorless product, b.p. 111–112°, n<sub>D</sub><sup>20</sup> 1.3488.

(5) Boiling points are uncorrected. Fluorine n.m.r. spectra were obtained from a Varian Associates high-resolution n.m.r. spectrometer and associated electromagnet operating at 56.4 Mc./sec. and approximately 14,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the F<sup>19</sup> resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane. Negative frequency displacements are for resonances occurring at lower field than the reference. Proton resonance spectra were obtained from a Varian Associates A-60 spectrometer. Spectra were calibrated on the τ scale with tetramethylsilane as an external reference, unless otherwise stated.

(6) C. I. Gochenour, U. S. Patent 2,546,997, April 3, 1951.

*Anal.* Calcd. for  $C_8H_8F_6$ : C, 44.04; H, 3.70; F, 52.26; M.W., 218. Found: C, 44.61; H, 3.89; F, 51.85; M.W., 214.

The infrared spectrum showed bands at 5.9 and 6.05  $\mu$  ( $C=C$ ), 7.2  $\mu$  ( $CH_2$  deformation), 7.54  $\mu$ , 7.77  $\mu$ , and 7.88  $\mu$  ( $C-F$ ), and 11.05  $\mu$  ( $CH_2=C$ ). The ultraviolet spectrum showed the absence of conjugated unsaturation, and a band at 1.63  $\mu$  in the near infrared region confirmed the presence of a terminal methylene group. Fluorine n.m.r. showed the presence of two  $CF_3$  groups, a quadruplet centered at  $-145$  c.p.s. and a quintuplet centered at  $-420$  c.p.s. The hydrogen resonance showed  $CH_3$  (8.32  $\tau$ ), two  $CH_2$  peaks (7.08  $\tau$  and 5.15  $\tau$ , split) and  $CH$  centered at 4.22  $\tau$  and split.

Ozonization of a sample of the diene in methylene chloride solution at  $-75^\circ$  gave a low yield of formaldehyde, isolated as its dimedone derivative, m.p. 187–192°. The melting point of the derivative was not depressed on admixture with an authentic sample of the dimedone derivative of formaldehyde.

**1,1,1,9,9,9-Hexafluoro-3,7-bis(trifluoromethyl)-5-methylene-2,7-nonadiene.**—In a stainless steel shaker tube was charged 50 g. (0.3 mole) of hexafluoro-2-butyne and 10 g. (0.2 mole) of isobutylene. The tube was closed and heated under autogenous pressure at  $240^\circ$  for 1.7 hr. After removal of the unreacted starting materials by evaporation, distillation of the residual liquid gave 12 g. of the 1:1 adduct, b.p. 60–63° (140 mm.) and 8 g. (14% conversion) of the diadduct, b.p. 94–96° (25 mm.),  $n_D^{25}$  1.3590.

*Anal.* Calcd. for  $C_{12}H_8F_{12}$ : C, 38.0; H, 2.1; F, 59.9; M.W., 380;  $H_2NO_2$ , 0.0156. Found: C, 38.5; H, 2.3; F, 59.5; M.W., 370;  $H_2NO_2$ , 0.0128, 0.0136.

A band at 1.62  $\mu$  with approximate intensity of 0.32 l./mole cm. in the near infrared spectrum indicated one terminal methylene group per molecule.<sup>7</sup> The infrared spectrum showed bands at 3.23, 3.29  $\mu$  (unsaturated  $CH$ ), 3.35, 3.41, 3.49  $\mu$  (saturated  $CH$ ), 5.92, 6.02  $\mu$  ( $C=C$ ), and 7.75, 8.72  $\mu$  ( $C-F$ ). The ultraviolet spectrum showed the absence of conjugated unsaturation, except possibly in trace amounts.

A n.m.r. study of proton and fluorine resonance suggested the presence of an isomeric mixture. Attempted purification by gas chromatography on a 12 ft.  $\times$  3/4 in. column of 30% Dow-Corning Silicone (703) on "Chromosorb" at  $100^\circ$  gave a purer grade product, although it is believed that *cis-trans* isomers were still present. Proton resonance showed a quadruplet centered at 4  $\tau$  for the proton

split by  $-CF_3$  ( $=CH$ ). The  $-CH_2-$  protons were a singlet at 6.81  $\tau$ . A single peak for the  $CH_2=C$  protons at 4.75  $\tau$  was associated with a smaller peak at 4.60  $\tau$ ; integration of the peaks demonstrated that these two peaks for the  $CH_2=C$  protons were required to give a 1:1:2 proportion. Fluorine n.m.r. showed two peaks for the  $CF_3$  groups. One was a quadruplet for the  $CF_3/CF_3$  splitting at  $-179$  c.p.s. The other was a quintuplet at  $-415$  c.p.s. (a quadruplet split into doublets by hydrogen).

**1,1,1-Trifluoro-3-trifluoromethyl-4-methyl-2,5-hexadiene.**—An 80-ml. shaker tube was charged with 20 g. (0.12 mole) of hexafluoro-2-butyne, 10 g. (0.18 mole) of 2-butene, and 10 ml. of acetone and heated with shaking at  $250^\circ$  for 8 hr. Distillation of the crude product through a 12-in. micro spinning-band still gave two principal fractions: (1) 8.5 g., b.p. 109–111°,  $n_D^{25}$  1.3498, and (2) 2.1 g., b.p. 195–205,  $n_D^{25}$  1.3645. Fraction 1, a colorless liquid, corresponds to a 32% yield of the 1:1 addition product.

*Anal.* Calcd. for  $C_8H_8F_6$ : C, 44.04; H, 3.70; F, 52.26. Found: C, 44.01; H, 4.53; F, 52.21.

The ultraviolet spectrum showed the absence of conjugated unsaturation. An absorption peak at 1.63  $\mu$  in the near infrared region characteristic of a terminal methylene group was present. The infrared absorption spectrum showed bands at 3.24  $\mu$  (unsaturated  $CH$ ), 3.34, 3.39, 3.46  $\mu$  (saturated  $CH$ ), 5.96  $\mu$  ( $C=C-CF_3$ ), 6.11  $\mu$  ( $C=C$ ), with

strong  $CF$  absorption in the 8  $\mu$  region and bands at 10.04  $\mu$  and 10.78  $\mu$  which arise from the terminal methylene group. The fluorine n.m.r. bands for the  $CF_3$  groups were located at  $-236$  c.p.s. (quadruplet) and  $-440$  c.p.s. (quintuplet). Hydrogen resonance was present at 8.74  $\tau$  ( $CH_3$ ; doublet), with a  $CH_2$  peak at 6.78  $\tau$  (split) and overlapping  $CH$  absorption from 5.1–4.0  $\tau$ .

**1,1,1-Trifluoro-5-methyl-2,5-hexadiene (and Isomers).**—An 80-ml. shaker tube was charged with 12 g. (0.13 mole) of trifluoropropyne,<sup>8</sup> 10 g. (0.18 mole) of isobutylene and 10 ml. of acetone and heated with shaking at  $225^\circ$  for 7 hr. A total yield of 17.2 g. of liquid product was obtained. Distillation of the crude product through a 12 in.-micro spinning-band still gave 2.82 g. of distillate, b.p. 93–95°,  $n_D^{25}$  1.3665. This represents a 15% yield of the 1:1 adduct.

*Anal.* Calcd. for  $C_7H_8F_3$ : C, 56.00; H, 6.04; F, 37.96. Found: C, 56.24; H, 6.31; F, 38.42.

The infrared absorption spectrum showed a doublet at 5.95 and 6.05  $\mu$  ( $C=C$ ), strong  $CF$  absorption in the 8  $\mu$  region and a band at 11.1  $\mu$  (terminal methylene group) as well as  $CH$  stretching bands for saturated and unsaturated  $CH$  groups. The ultraviolet absorption spectrum showed the absence of conjugated unsaturation, and the presence of a band at 1.63  $\mu$  in the near infrared region confirmed the terminal methylene group.

A n.m.r. study of the adduct suggested the presence of a mixture of the two 1:1 adducts, namely 1,1,1-trifluoro-5-methyl-2,5-hexadiene and 2-trifluoromethyl-4-methyl-1,4-pentadiene with the possible presence of geometric isomers also. The fluorine resonance showed  $CF_3$  resonance at  $-105$  c.p.s. split into at least a quintuplet. Hydrogen resonance showed major peaks at 8.78  $\tau$  ( $CH_3$ ), 8.00  $\tau$ , (badly split), doublets centered at 7.70  $\tau$ , 6.72  $\tau$ , and 5.75  $\tau$ , and minor resonance "smeared" from 5.20–3.90  $\tau$ . A mixture of products was also suggested by the large forerun obtained from the distillation, 2.31 g., b.p. 85–93°,  $n_D^{25}$  1.3644. Addition of this forerun to the fraction boiling at 93–95° (see above) gives a 27% yield of 1:1 adduct. Attempted purification of the product by gas chromatography on a Silicone "200" on "Chromosorb" column at  $85^\circ$  gave two principal cuts. A n.m.r. study of the cuts suggested that purification was not achieved, and the presence of an isomeric mixture was indicated.

**Methyl 3-Methoxycarbonyl-5-methyl-2,5-hexadienoate.**—Into a 400-ml. stainless steel shaker tube was charged 100 ml. of benzene, 28.4 g. (0.2 mole) of dimethyl acetylenedicarboxylate, and 12.2 g. (0.22 mole) of isobutylene. The tube was closed and heated at  $135^\circ$  under autogenous pressure for 10 hr. After cooling to room temperature, the reaction mixture was discharged from the tube and distilled. There was recovered 11 g. of unchanged dimethyl acetylenedicarboxylate, and the adduct then distilled at 78–80° (2 mm.),  $n_D^{25}$  1.4617, 10 g. (41% yield).

*Anal.* Calcd. for  $C_{10}H_{14}O_4$ : C, 60.8; H, 7.1. Found: C, 60.8; H, 7.3.

The infrared spectrum showed bands at 3.27  $\mu$  (unsaturated  $CH$ ), 6.05  $\mu$  for  $C:C$  double bond, 5.77  $\mu$  for ester  $>C=O$ , 3.4 and 3.52  $\mu$  for saturated  $CH$ , 7.30  $\mu$  for  $CH_3-C$ , and 11.12  $\mu$  for  $CH_2=C$ . The proton resonance<sup>9</sup> indicates five different protons in the expected ratio of

1:2:6:2:3, peaks occurring at 3.95  $\tau$  ( $=CH$ ), 5.03  $\tau$  ( $=CH_2$ ), 6.19  $\tau$  (ester- $CH_3$ ), 6.83  $\tau$  ( $-CH_2-$ ), and 8.24  $\tau$  ( $=C-CH_3$ ) respectively. Additional structure proof consisted in hydrogenation to the isobutylsuccinic ester which was hydrolyzed to isobutylsuccinic acid, m.p. 102–103° (on recrystallization from water). The melting points for isobutylsuccinic acid recorded in the literature range from 102–109°.<sup>10</sup>

(8) Trifluoropropyne was prepared by fluorination of propiolic acid with sulfur tetrafluoride according to the method of W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

(9) The spectrum in this case was calibrated against toluene external.

(10) R. Fittig, *Ann.*, **304**, 271 (1899).

(7) R. F. Goddu and D. A. Delker, *Anal. Chem.*, **32**, 140 (1960).

*Anal.* Calcd. for  $C_{10}H_{18}O_4$ : neut. equiv., 87. Found: neut. equiv., 83.

**Methyl 5-Methyl-2,5-hexadienoate.**—A mixture of methyl propiolate (30 g., 0.36 mole) and isobutylene (28 g., 0.50 mole) was heated in a stainless steel shaker tube at 220° for 4 hr. From the viscous reaction mixture there was obtained 2.7 g. of product distilling at 30–94° (2 mm.), almost all of which distilled under 40°. Redistillation gave a major fraction,  $n_D^{25}$  1.4541, which has the probable structure

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}=\text{CH}-\text{COOCH}_3 \\ | \qquad \qquad \qquad | \\ \text{CH}_3 \qquad \qquad \qquad \text{COOCH}_3 \end{array}$$

The minor fraction was not investigated but probably was the isomeric

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_2=\text{C}-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2 \\ | \qquad \qquad \qquad | \\ \text{CH}_3 \qquad \qquad \qquad \text{COOCH}_3 \end{array}$$

*Anal.* Calcd. for  $C_8H_{12}O_2$ : C, 68.7; H, 8.6. Found: C, 69.5; H, 9.1.

The combined infrared, near infrared, and proton resonance spectra are in agreement with the structure having one terminal methylene group. Thus a band at 1.63  $\mu$  in the near infrared at approximate intensity 0.341./mole cm. indicates one terminal methylene group per molecule. The infrared spectrum shows bands at 3.24  $\mu$  (unsaturated CH), 3.36, 3.39, 3.43, 3.51  $\mu$  (saturated CH), 5.78  $\mu$  (carbonyl), 6.03  $\mu$  (C=C), 11.20  $\mu$  ( $\text{CH}_2=\text{C}<$ ), and 7.26  $\mu$  ( $\rightarrow \text{C}-\text{CH}_3$ ). The ultraviolet spectrum shows the absence of conjugated unsaturation.

## Pyrolysis of Esters. XXII. Synthesis of Bisdiene from 2-Hydroxymethyl-1,3-butadiene<sup>1,2</sup>

WILLIAM J. BAILEY AND MATTHEW E. HERMES<sup>3</sup>

*University of Maryland, College Park, Maryland*

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A new synthesis of 2-hydroxymethyl-1,3-butadiene was developed starting from commercially available 2-amino-2-ethyl-1,3-propanediol and involving a pyrolysis of an amine oxide as well as the pyrolysis of an ester. When the hydroxymethylbutadiene was treated with vinyl acetate in the presence of a mercuric oxide–boron trifluoride etherate mixture, a 38% yield of bis(2-butadienylmethyl) acetal resulted. Treatment of the hydroxymethylbutadiene with hexamethylene diisocyanate gave a 76% yield of solid bis(2-butadienylmethyl) hexamethylenecarbamate, while treatment with *m*-xylylene diisocyanate gave a 91% yield of solid bis(2-butadienylmethyl) *m*-xylylenecarbamate.

In a research program designed to study polymeric Diels–Alder reactions, a series of bifunctional or bisdienes was required. One of the most interesting starting materials for the production of bisdienes appeared to be 2-hydroxymethyl-1,3-butadiene (I). In a previous paper in this series we reported two syntheses of hydroxymethylbutadiene—one a three-step synthesis starting with dimethyl itaconate and an alternative three-step synthesis starting from triethyl 1,1,2-ethanetricarboxylate. The key step in both these syntheses was the pyrolysis of an ester to produce the intermediate 2-acetoxymethyl-1,3-butadiene (II). Since the over-all yield in either of these two syntheses was not very high, a search for still a third route to hydroxymethylbutadiene was undertaken. Since 2-amino-2-ethyl-1,3-propanediol became commercially available, this polyfunctional compound appeared to be an excellent starting material for the synthesis of the required diene. Since it was shown previously that tertiary amides pyrolyze almost as easily as primary esters,<sup>4</sup> the 2-amino-2-ethyl-1,3-propanediol (III) was converted to the corresponding triacetate IV by treatment with acetic anhydride and sodium acetate. However, when the triacetate IV was pyrolyzed at 510°, a 59% yield of 4-acetoxy-

methyl-4-ethyl-2-methyloxazoline (V) was obtained. The oxazoline V was also prepared directly from the aminodiol III. To illustrate the nature of the reaction, 4-acetoxymethyl-2,4-dimethyloxazoline was prepared in a 58% yield from 2-amino-2-methyl-1,3-propanediol.

To avoid this ring closure, the nitrogen was methylated according to the procedure of Senkus<sup>5</sup> in an over-all yield of 87% by treatment with formaldehyde, followed by catalytic reduction. When the dimethylamino compound VI was treated with acetic anhydride, a 91% yield of the corresponding 2-(*N,N*-dimethylamino)-2-ethyl-1,3-propanediol (VII) was obtained. When the diacetate was treated with peracetic acid, the corresponding amine oxide resulted, but was not isolated. When this amine oxide was pyrolyzed according to the method of Cope, Bumgartner, and Schweizer,<sup>6</sup> a 53% yield of 2-acetoxymethyl-2-buten-1-yl acetate (VIII) was obtained.

Alternative procedures for preparation of the diacetate VIII were less satisfactory. When the dihydroxy compound VI was treated with hydrogen peroxide to produce the corresponding dihydroxyamine oxide, this gave a mixture of diols on pyrolysis. The mixture was not separated but was acetylated directly to give a 50% yield of a mixture of acetates consisting of 85 to 90% of 2-acetoxymethyl-2-buten-1-yl acetate (VIII) and 10

(1) Previous paper in this series, *J. Org. Chem.*, **27**, 1975 (1962).

(2) Presented before the Division of Polymer Chemistry at the 138th Meeting of the American Chemical Society, New York, New York, September, 1960.

(3) Office of Naval Research Fellow, 1956–1957; National Science Foundation Fellow, 1957–1959.

(4) W. J. Bailey and C. N. Bird, *J. Org. Chem.*, **23**, 996 (1958).

(5) M. Senkus, *J. Am. Chem. Soc.*, **67**, 1515 (1945).

(6) A. C. Cope, C. L. Bumgartner, and E. E. Schweizer, *ibid.*, **79**, 4729 (1957).