

preliminary Communication.¹⁷ However, it strongly depressed the m.p. of authentic XVII prepared by the method of Leven, *et al.*,⁴⁶ and was found to contain nitrogen. The product of m.p. 59° did not depress the m.p. of authentic XIX, m.p. 57–59°, prepared by the Fischer indole synthesis.⁴⁷ Also, it formed a picrate, m.p. 137–138°, and a styphnate, m.p. 142–144°; the reported melting points of the picrate and styphnate of XIX are 139° and 147°, respectively.⁴⁸ The product is thus 2-methylindole (XIX).¹⁷

In other runs, XIX was obtained in 10% yield from treatment of XV with potassium amide (3 equivalents) in liquid ammonia (without ether being present). No XIX was obtained by treatment of XV with potassium amide in dry ether (without ammonia) or with lithium diethylamide in ether. In no case was any XVII or any 2-methylbenzofuran (another conceivable product) isolated.

Other Experiments. Action of Potassium Amide on *o*-Chlorophenylthiourea.—The standard ring closure procedure was employed, with 10.0 g. of *o*-chlorophenylthiourea and 8.4 g. of potassium metal being used. A white precipitate appeared three minutes after the potassium amide solution was added to the thiourea in ammonia, and soon turned yellow. When ammonium nitrate was added after 1 hour, the precipitate dissolved. Ether was added, the ammonia was evaporated, water was added, and the resulting suspension was filtered. The solid collected would neither melt nor burn. After evaporation of the ether layer, only a trace of pleasant smelling substance remained. The water layer was treated with decolorizing charcoal; upon neutralization of the resulting solution a precipitate formed and hydrogen sulfide was evident by odor. The precipitate when dried was a brown powder; 4.2 g. Recrystallization from ethanol and then from benzene-pe-

troleum ether gave 3.47 g. of white crystals, m.p. 105–106°. Elemental analysis was positive for chlorine and nitrogen but negative for sulfur. The infrared spectrum showed strong absorption peaks at 3340, 3190 and 2250 cm.⁻¹ but no absorption between 1615 and 2100 cm.⁻¹. The bands observed are typical of N—H, aromatic C—H and C≡N, respectively. The substance is believed to be *o*-chlorophenylcyanamide,³⁴ m.p. 104–105°.

Action of Potassium Amide on Thiobenz-(2-bromo-3-methyl)-anilide (VI).—The potassium amide from 5.1 g. (0.13 mole) of potassium metal was allowed to act for 1 hour upon 10.0 g. (0.033 mole) of VI by the standard ring closure procedure. The crude reaction product was treated with ether and aqueous alkali. The aqueous layer was acidified and extracted with ether. Recrystallization from cyclohexane of the residue from evaporation of the ether furnished yellow crystals of VI, weight 6.91 g., m.p. 73–75° not depressed on admixture with the original VI. Efforts to isolate other pure substances from the product mixture were fruitless. A fraction expected to contain basic compounds was chromatographed on alumina and several fractions of indefinite melting point around 40° were obtained. These fractions were combined in benzene and dry hydrogen chloride was introduced; 0.65 g. of a precipitate melting about 130–140° separated. The basic material recovered from this hydrochloride was impure, and no crystalline sublimate was obtained.

Action of Sodium Ethoxide in Ethanol on Ia.—Sodium metal (4.6 g.) was "dissolved" in 100 cc. of absolute ethanol, and 14.6 g. of Ia was added. The mixture was refluxed 5 hours, during which the color was constantly pale yellow. The mixture was then poured into water which was acidified with sulfuric acid. From the heavy yellow precipitate which formed, 14.13 g. of Ia, m.p. 83–85° not depressed on admixture with the original Ia, and 0.16 g. of pale yellow crystals of m.p. 60–65° (presumably impure Ia) were obtained by standard procedures. From the acidic solution, 0.09 g. of white crystals m.p. 110° not depressed on admixture with authentic IV, was isolated by standard methods. The latter depressed the melting point of Ia.

(46) N. Leven, B. H. Graham and H. G. Kolloff, *J. Org. Chem.*, **9**, 380 (1945).

(47) H. M. Klissman, D. W. Farnsworth and B. Witkop, *J. Am. Chem. Soc.*, **74**, 3948 (1952).

(48) L. Marion and C. W. Oldfield, *Can. J. Research*, **25B**, 1 (1947).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF IOWA, IOWA CITY, IOWA]

Polymerization of Non-conjugated Diynes by Complex Metal Catalysts^{1,2}

By J. K. STILLE AND D. A. FREY

RECEIVED OCTOBER 25, 1960

The polymerization of 1,6-heptadiyne by Ziegler type catalysts leads to soluble, highly colored polymers of 10,000–20,000 molecular weight, which contain alternating double and single bonds along the backbone of the polymer chain and a cyclic recurring unit as the main structural features. Polymerization of 1,7-octadiyne and 1,8-nonadiyne under the same conditions, however, affords mostly crosslinked polymers.

Recently, it has been established that non-conjugated diolefinic monomers can polymerize to yield linear, high molecular weight polymers.³ An alternating intramolecular–intermolecular propagation mechanism has been postulated to account for the absence of crosslinking and the cyclic recurring units. The monomers 1,6-heptadiene, biallyl and bimethallyl have been shown to form

cyclic recurring units by this mechanism when initiated by an aluminum triisobutyl–titanium tetrachloride catalyst.⁴ An X-ray investigation of polybiallyl has shown it contains the methylenecyclopentane recurring units.⁵ Polymerization of the higher members in the α -diolefin series gives greater amounts of non-cyclic crosslinked polymers.⁶

Since acetylene and various substituted monoacetylenes have recently been polymerized by complex metal catalysts to olefinic polymers,⁷

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(2) Presented in part at the April, 1959, Meeting of the American Chemical Society, Boston, Mass.

(3) (a) G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, **79**, 3128 (1957); (b) G. B. Butler, A. Crawshaw and W. L. Miller, *ibid.*, **80**, 3615 (1958); (c) A. Crawshaw and G. B. Butler, *ibid.*, **80**, 5464 (1958); (d) M. D. Barnett, A. Crawshaw and G. B. Butler, *ibid.*, **81**, 5946 (1959); (e) M. D. Barnett and G. B. Butler, *J. Org. Chem.*, **25**, 309 (1960); (f) K. D. Berlin and G. B. Butler, *J. Am. Chem. Soc.*, **82**, 2712 (1960); (g) C. S. Marvel and R. D. Vest, *ibid.*, **79**, 5771 (1957); (h) **81**, 984 (1958); (i) J. F. Jones, *J. Polymer Sci.*, **33**, 7 (1958); (j) **33**, 15 (1958); (k) N. D. Field, *J. Org. Chem.*, **25**, 1006 (1960).

(4) C. S. Marvel and J. K. Stille, *J. Am. Chem. Soc.*, **80**, 1740 (1958).

(5) H. S. Makowski and B. K. C. Shim, Preprints of papers presented at the Polymer Section of the Cleveland Meeting, April, 1960, p. 101.

(6) C. S. Marvel and W. E. Garrison, Jr., *J. Am. Chem. Soc.*, **81**, 4737 (1959).

(7) (a) G. Natta, G. Mazzanti and P. Pino, *Angew. Chem.*, **69**, 685 (1957); (b) S. P. A. Montecatini, Belgian Patent 546,151 (1956); Italian Patent 530,753 (1955); (c) Belgian Patent 558,728 (1957); Italian Patent 985,125 (1956); (d) G. Natta, G. Mazzanti, G. Pregaglia and M. Peraldo, *Gazz. chim. ital.*, **89**, 465 (1959).

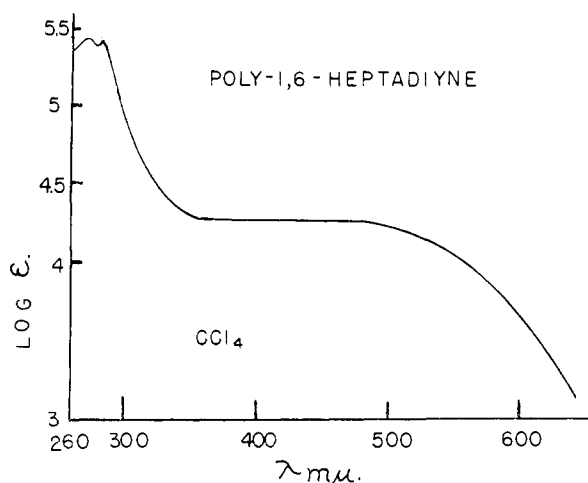


Fig. 1.—The ultraviolet spectrum of poly-1,6-heptadiyne.

the polymerizations of α,ω -diacetylenes were investigated in an attempt to manufacture a polymer which would contain alternating double and single bonds along the backbone of the polymer chain and a cyclic recurring unit.

The diacetylene 1,6-heptadiyne (I) was first chosen for polymerization since this monomer could be expected to give the most facile polymerization reaction by an internal head-to-tail propagation which would lead to a six-membered carbocyclic recurring unit.⁶ This methylene cyclohexene unit should then be easily convertible by dehydrogenation to a polymer containing the benzenoid units along the chain.

The catalyst systems, aluminum triisobutyl or aluminum triethyl in combination with titanium tetrachloride, titanium trichloride, or titanium tetraethoxide were investigated (Table I). Of

TABLE I
POLYMERIZATION OF 1,6-HEPTADIYNE

AlR ₃	TiX _n	AlR ₃ / TiX _n	Conver- sion, %	Color	
Al(<i>i</i> -Bu) ₃	TiCl ₄	3:1	80-90	Red	
		2:1	62	Red	
		1:1	0	..	
Al(Et) ₃	TiCl ₃	3:1	10	Red	
		2:1	8	Red	
	Ti(OEt) ₄	25:1	30-45	Black ^a	
		TiCl ₄	2:1	8	Red
			1:1	6	Red
			2:1	6	Red
	Ti(OEt) ₄	25:1	12	Black ^a	

^a Insoluble polymer; polymerization temperatures ranged from 24 to -20°.

these, the aluminum triisobutyl-titanium tetrachloride catalyst gave the best conversion. Aluminum triisobutyl-titanium tetraethoxide, a soluble catalyst system, produced a large amount of crosslinked polymer in addition to the soluble material. The polymerization reaction in the case of the aluminum triisobutyl-titanium tetrachloride catalyst was extremely exothermic. The polymers obtained from these catalyst systems were dark red or black, which indicates a high order of conjugation in the polymer.

The polymer obtained from the aluminum triisobutyl-titanium tetrachloride system had an intrinsic viscosity of 0.06. Fractionated polymer, $\eta_i = 0.058$, showed \bar{M}_n (osmotic pressure) = 13,500. The ultraviolet spectrum of this sample shows absorption in the visible region as well as maxima near 270 m μ . On prolonged standing in solution, exposure to air or on heating, most of the absorption in the visible region was lost, and the polymer acquired a pale yellow color. This seems to indicate an oxidation involving the double bonds and an interruption of long segments of conjugation along the molecule. The maxima at 270 m μ are as yet unexplained, although these could be due to contributions from the individual methylene-cyclohexene units.

The infrared spectrum of the polymer showed neither the acetylenic hydrogen stretching nor the carbon triple bond carbon stretching present in the monomer. Instead, the carbon-carbon double bond stretching frequency at 1605 cm.⁻¹ indicates a highly conjugated unsaturation.

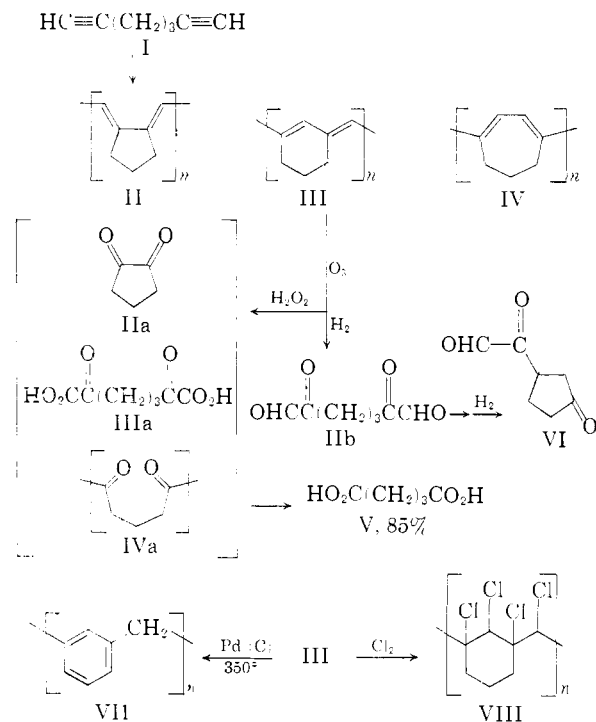
Dehydrogenation of poly-1,6-heptadiyne at 350° with a palladium catalyst gave a soluble polymer VII whose infrared spectrum could be interpreted to explain a *m*-xylene recurring unit. The ultraviolet spectrum of the dehydrogenated polymer showed a maximum at 273 m μ and little absorption in the visible region. Although molecular weight values were not determined for the dehydrogenated polymer, it did not appear to suffer any great loss in molecular weight during dehydrogenation.

A quantitative hydrogenation of poly-1,6-heptadiyne was not successful since the rate of addition of hydrogen was too low for accurate measurement. Treatment of the polymer with chlorine, however, produced a white polymer (VIII) which showed no unsaturation in the infrared characteristic of carbon-carbon double bonds and contained 91% of theoretical amount of chlorine calculated on the basis of the addition of two moles of chlorine for each recurring unit.

Even though a head-to-tail internal propagation would be expected, there are three possible cyclic recurring units (II-IV) which can be written to account for a soluble non-acetylenic polymer with alternating double and single bonds along the backbone of the chain. Ozonolysis of the polymer in methylene chloride was accomplished by the adsorption of the ozone in an oxygen stream on silica at -78° and subsequent elution of the ozone by a nitrogen current.³ Oxidative decomposition of the ozonide gave an 85% yield of glutaric acid (V) (in addition to a small amount of polymeric material), which could arise from any of the structures II-IV, by an oxidative decarboxylation of IIIa or peroxide oxidation of the 1,2-diketones IIa and IVa. Reductive decomposition gave evidence to support structure III for the polymer. One phenylhydrazine derivative of the reduced ozonide had a com-

(8) (a) G. A. Cook, A. D. Kiffer, C. V. Klumpp, A. H. Malik and L. A. Spence, papers presented at the International Ozone Conference, Chicago, Ill., Nov. 28-30, 1956; *Adv. in Chem. Ser.*, **21**, 44 (1958); (b) C. E. Thord, "Bibliography of Ozone Technology," Vol. I, Armour Research Foundation of Illinois Institute of Technology, Chicago, Ill., 1954.

position which corresponded to a derivative of VI. None of the known 2,4-dinitrophenylhydrazine derivatives of cyclopentane-1,2-dione or glyoxal could be isolated. Thus the structure III must be assigned for at least a portion of the polymer chain. Samples of poly-1,6-heptadiyne were tested for possible use as organic semiconductors.⁹ The data indicated a resistivity of 10^{10} – 10^{13} ohm-cm. This high resistance is probably due to the instability of the polymer to many reagents and air, since a few reactions at various points along the chain would break the conjugated system.



The monomers 1,7-octadiyne and 1,8-nonadiyne gave 84 and 92% conversion to polymer, respectively, with the aluminum triisobutyl-titanium tetrachloride catalyst. In contrast to poly-1,6-heptadiyne, neither polymer is highly colored nor shows any absorption in the visible region. Of the total conversion to polymer, 49% of the poly-1,7-octadiyne (η 0.063) is soluble while only 22% of the poly-1,8-nonadiyne (η 0.067) is soluble in a continuous extraction with refluxing xylene.

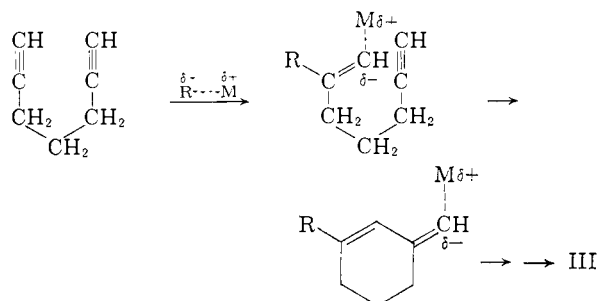
The soluble portion of poly-1,7-octadiyne shows only the highly conjugated carbon-carbon double bond absorption maximum in the infrared region at 1605 cm^{-1} and no maxima characteristic of the acetylenic moiety. The soluble portion of the poly-1,8-nonadiyne shows maxima at 3295 and 2120 cm^{-1} , characteristic of the acetylene group as well as a maximum at 1605 cm^{-1} for the conjugated carbon-carbon double bond.

Since it has been generally observed that active hydrogens on an olefinic monomer destroy Ziegler-type catalysts,¹⁰ it is unusual that 1-acetylenes are polymerized by the same catalysts as 1-olefins. However, an intramolecular-intermolecular propa-

(9) We are grateful to E. I. du Pont de Nemours and Co. and the Diamond Ordnance Fuze Laboratoires for these measurements.

(10) J. K. Stille, *Chem. Rev.*, **58**, 541 (1958).

gation reaction must take place to account for these observations.



The two higher members 1,7-octadiyne and 1,8-nonadiyne can form only seven- and eight-membered rings, respectively through a head-to-tail propagation. In the polymerization of these monomers, the acetylenic ends prefer to polymerize independently of one another which gives rise to predominantly crosslinked polymers. The soluble portion of poly-1,7-octadiyne undoubtedly contains some rings in the chain backbone and possibly a few long chain branches resulting from the independent polymerization of the two ends of any given monomer. The branching is apparently extensive enough to disrupt the long segments of a conjugated system which would give it some color, but not extensive enough to cause the polymer to gel.

The soluble portion of poly-1,8-nonadiyne may have the same sort of structure, but a considerable portion of the monomer has polymerized through only one acetylene bond leaving acetylenic tails hanging from the polymer backbone.

Experimental

The acetylenic monomers¹¹ were dried over calcium chloride and freshly distilled in a nitrogen atmosphere before each polymerization. The infrared spectra¹² of the monomers showed 3270 cm^{-1} ($\equiv\text{C}-\text{H}$ str.) and 2115 cm^{-1} ($\text{C}\equiv\text{C}$ str.). The aluminum triisobutyl (Hercules Powder Co.) and the aluminum triethyl (Ethyl Corporation) were not further purified. Prior to each run, 10% solutions of those aluminum alkyls in heptane were prepared for ease in handling. The titanium tetrachloride and titanium tetroxide¹³ were also handled as freshly prepared 10% solutions, while the titanium trichloride was weighed in a nitrogen-filled dry-box.

Polymerization of the Diacetylenes.—The catalysts were prepared in a dry-box under a nitrogen atmosphere by adding measured amounts of the 10% solutions of aluminum alkyl and titanium salts to 15 ml. of dry heptane in a reaction flask. In the case of titanium trichloride, a weighed amount of the solid was added directly to the flask. In each case, 2.5×10^{-4} mole of titanium salt was employed, and the amount of aluminum alkyl varied to acquire the desired catalyst ratio. The reaction flask was removed from the dry-box and fitted with a micro-buret and an outlet tube. The outlet tube, under a positive nitrogen pressure, was connected to a mercury bubbler and the flask was cooled in an ice-bath. The monomer, 10 g., was added dropwise through the buret. In the case of catalysts prepared with titanium tetrachloride salts (3:1 and 2:1 molar ratios aluminum alkyl to titanium tetrachloride), a strongly exothermic reaction took place on the addition of the first portion of the monomer. Where smaller amounts of

(11) A. L. Henne and K. W. Greenlee, *J. Am. Chem. Soc.*, **67**, 484 (1945).

(12) The infrared spectra of the monomers and polymers were run as films, carbon disulfide solutions and carbon tetrachloride solutions on a Perkin-Elmer model 21 infrared spectrophotometer.

(13) F. Bischoff and H. Adkins, *J. Am. Chem. Soc.*, **46**, 256 (1924).

monomer were polymerized the amount of solvent and catalyst was cut down proportionally. In the polymerization of 1,7-octadiyne and 1,8-nonadiyne, only the 3:1 aluminum triisobutyl-titanium tetrachloride catalyst was employed.

All reactions were kept at 0° for 5 hours after which time the mixture was allowed to warm to room temperature for an additional 20 hours. The samples were decomposed with absolute methanol, and the polymer samples were reprecipitated by dissolving the polymer in the minimum amount of benzene and adding the benzene solution to methanol. The samples were dried under reduced pressure at room temperature for 48 hours and stored under a nitrogen atmosphere. In the case of the polymers obtained from an aluminum alkyl-titanium ethoxide catalyst, after the initial precipitation the samples were subjected to continuous extraction with benzene. About 5% of these polymer samples were soluble.

Poly-1,6-heptadiyne (III).—Studies on the structure of poly-1,6-heptadiyne were made on a sample prepared with the aluminum triisobutyl-titanium tetrachloride catalyst (3:1 molar ratio, Table I). The results reported here have been obtained from a sample which had been partially fractionated as follows: The sample was extracted with heptane at room temperature, about 10% of which was soluble. The residue was twice reprecipitated from benzene with methanol, $\eta_i = 0.058$. *Anal.* Calcd. for $(C_7H_8)_n$: C, 91.25; H, 8.75. Found: C, 90.26; H, 8.80. The viscosities (Ostwald-type viscometer) of a number of samples obtained from this catalyst ranged from 0.05 to 0.07 (0.25 g./100 ml. of benzene).

The infrared spectrum (film) did not show bands characteristic of 1,6-heptadiyne. Instead, a band was observed at 1605 cm^{-1} . The ultraviolet spectrum showed a broad absorption from 350 to 550 $m\mu$, $\log \epsilon$ 4.25 and maxima at 270 and 280 $m\mu$, $\log \epsilon$ 5.43. The extinction coefficients were calculated on the basis of a molecular weight of 13,500 or 147 monomer units/polymer molecule.

Molecular Weight Determination on Poly-1,6-heptadiyne.—The molecular weight of the fractionated sample described above was determined in benzene with Zimm-Myerson osmometer.¹⁴ Du Pont No. 600 cellophane, treated as described by Flory,¹⁵ was used as the membrane, \bar{M}_n 13,500.

Dehydrogenation of Poly-1,6-heptadiyne.—To a solution of 0.44 g. of poly-1,6-heptadiyne in benzene was added 0.11 g. of 10% palladium-on-charcoal. The benzene was removed under reduced pressure, depositing the polymer on the catalyst. This mixture was heated to 350° under a nitrogen atmosphere for 4 hours, after which time the mixture was allowed to cool and the polymer was extracted continuously with benzene. The benzene solution of the dehydrogenated polymer was subjected to freeze drying to give 0.35 g. (80%) of polymer. The infrared spectrum of the dehydrogenated polymer VII showed maxima at 1580–1610, 1455, 860–800 and 790 cm^{-1} ; ultraviolet spectrum, λ_{max} 273 $m\mu$, ϵ 6.5 $\times 10^5$. The polymer did not appear to suffer any great loss in molecular weight during dehydrogenation.

On heating a sample of poly-1,6-heptadiyne, absorption in the visible region was lost, but λ_{max} 270 $m\mu$ was retained. Similar results were observed when benzene or carbon tetrachloride solutions of the polymer were allowed to remain at room temperature for several days.

Chlorination of Poly-1,6-heptadiyne.—Dry chlorine was bubbled through a solution of 2.7 g. of poly-1,6-heptadiyne in 120 ml. of carbon tetrachloride at 0° for 66 hours. The polymer solution lost its deep red color after 1 hour, and faded to a light yellow. The solvent was removed under reduced pressure and the polymer was reprecipitated twice by the addition of its benzene solution to methanol. The white polymer VIII was subjected to freeze drying from a benzene solution to yield 3.5 g. (51.2% based on the addition of two moles of chlorine to each recurring unit). The infrared spectra showed no unsaturation but only C–Cl stretching in the 750–800 cm^{-1} region. *Anal.* for $C_7H_8Cl_2$: C, 35.92; H, 3.44. Found: C, 41.52; H, 3.60. On the

basis of the carbon analysis, the polymer had absorbed 91% of the theoretical amount of chlorine.

Ozonolysis of Poly-1,6-heptadiyne.—Polymer solutions for ozonolysis were prepared by dissolving 5–10 g. of poly-1,6-heptadiyne in 100 ml. of methylene chloride. To this solution at –5° was added approximately 10–20 ml. of methanol. Ozonized oxygen (5–6% O_3) was passed through a silica column at –78°. The adsorption of ozone on the silica column was followed by the intense blue color which developed. After the column had been filled, it was swept for 5 minutes at –78° with dry nitrogen to remove traces of adsorbed oxygen. The column was then connected to the flask containing the polymer solution and the ozone was swept off the column by nitrogen by gradually raising the column out of the cooling bath. In oxidative decomposition, ten times the equivalent amount of ozone was passed through the solution while an equivalent amount was passed for reductive decompositions.

Oxidative Decomposition of the Ozonide.—A sample of the ozonized mixture corresponding to 4.5 g. of polymer was decomposed by an equal volume of a 5% sodium hydroxide–3% hydrogen peroxide solution. The methylene chloride was removed under reduced pressure and the remaining aqueous solution was acidified and subjected to continuous extraction with ether. The ether extract was dried and the ether was removed under reduced pressure leaving a white solid residue which was recrystallized from benzene to give 5.5 g. (84%) of acid V, m.p. 96–97.5°. A mixed melting point with glutaric acid was not depressed.

No oxalic acid could be obtained either from the residue left on evaporation of the extracted aqueous layer or from the small amount of white solid residue which was insoluble in benzene.

Reductive Decomposition of the Ozonide.—A sample of an ozonized mixture from 4.5 g. of polymer was decomposed by an equal volume of aqueous saturated sulfur dioxide solution. The excess sulfur dioxide and methylene chloride were removed under reduced pressure and the aqueous solution was continuously extracted with ether. The ether extract was dried and the ether was removed under reduced pressure at 0°. The clear, slightly yellow liquid residue was dried at 0° (0.01 mm.) for 4 hours; 5.3 g. (70%). The infrared spectrum of this residue showed bands at 2650 (C–H str., aldehyde), 1725 (C=O str., aldehyde), 1710 (C=O str., ketone) and 1440 and 1370 cm^{-1} (aliphatic aldehydes).

In one ozonolysis run, the methylene chloride was removed under reduced pressure after the passage of ozone and the polymeric methoxy peroxide was dissolved in ethyl acetate and subjected to hydrogenolysis at 300 lb. with a palladium catalyst.¹⁶ The catalyst was removed by filtration and the ethyl acetate was removed from one portion of the mixture. The infrared spectrum of the residue showed bands at 3620 (O–H str.) 1615 (C=O str.) and 1042 cm^{-1} (C–O str.). To the remainder of the ethyl acetate solution was added 2,4-dinitrophenylhydrazine to produce an impure derivative which could not be suitably purified by recrystallization, but was possibly the 2,4-dinitrophenylhydrazone of 2,6-diketooheptane-1,7-diol. *Anal.* Calcd. for $C_{19}H_{20}N_4O_{10}$: C, 43.85; H, 3.87; N, 21.54. Found: C, 44.21; H, 3.54; N, 22.56.

The solvent from a 6.6-g. sample of polymer which was ozonized with 25% excess ozone was removed under reduced pressure and the polymeric methoxy peroxide was dissolved in 175 ml. of ethanol. To the solution was added the palladium-on-calcium carbonate catalyst and hydrogen was passed through the mixture at 1 atm. for 1 hour. The resulting solution was added to a 2,4-dinitrophenylhydrazine reagent containing 56.8 g. of 2,4-dinitrophenylhydrazine. The derivative, 11.1 g. (17.2% based on a tetraphenylhydrazine derivative of IIb), was chromatographed on an alumina column to yield two crystalline fractions. The fraction which corresponds to the derivative of two dinitrophenylhydrazone portions on VI had a melting point of 130–132°. *Anal.* Calcd. for $C_{19}H_{16}N_4O_8$: C, 45.60; H, 3.22; N, 22.40. Found: C, 45.33; H, 3.86; N, 23.20.

The 254–257° melting compound had the composition of one 2,4-dinitrophenylhydrazone to a 13-carbon fragment and showed carbonyl absorption in the infrared at 1710 cm^{-1} . *Anal.* Calcd. for $C_{19}H_{20}N_4O_6$: C, 57.00; H, 5.03; N, 13.99. Found: C, 57.08; H, 4.65; N, 13.87.

(14) B. H. Zimm and I. Myerson, *J. Am. Chem. Soc.*, **68**, 911 (1946).

(15) (a) P. J. Flory, *ibid.*, **65**, 372 (1943); (b) W. R. Krigbaum and P. J. Flory, *ibid.*, **75**, 1775 (1953).

(16) C. S. Marvel, P. E. Kiener and E. D. Vessel, *ibid.*, **81**, 4694 (1959).

A sample of ozonolysis product obtained in this manner by the reduction with hydrogen at 1 atm. gave only a small amount (1% yield) of non-crystalline derivative with *o*-phenylenediamine.

Poly-1,7-octadiyne and Poly-1,8-nonadiyne.—The polymerization of 9.3 g. of 1,7-octadiyne with the 3:1 aluminum triisobutyl-titanium tetrachloride catalyst afforded 7.78 g. (83.6%) of a light colored polymer which was 48.7% soluble in a continuous extraction with refluxing xylene. The soluble portion had an inherent viscosity of 0.063. The infrared spectrum of the soluble portion of this polymer showed an infrared absorption maximum at 1605 cm^{-1} and

no maxima characteristic of an acetylenic group. No absorption was shown in the visible region.

The polymerization of 10 g. of 1,8-nonadiyne with the same catalyst gave 9.2 g. (92%) of a light colored polymer which was 22% soluble in a continuous extraction with xylene. The soluble portion had an inherent viscosity of 0.067. The infrared spectrum of the soluble portion showed maxima at 3295 and 2120 cm^{-1} , characteristic of the acetylenic group as well as a maximum at 1605 cm^{-1} (C=C conj.). A quantitative comparison of the absorption for the acetylenic maxima of the polymer compared with the monomer showed that 25–30% of the monomer units had polymerized through only one of the acetylenic groups.

[CONTRIBUTION FROM THE RESEARCH CENTER, HERCULES POWDER CO., WILMINGTON, DEL.]

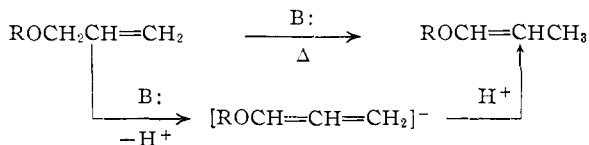
The Rearrangement of Allyl Ethers to Propenyl Ethers

By T. J. PROSSER

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Several mono- and polyfunctional allyl ethers have been rearranged to the corresponding propenyl ethers by treatment at 150–175° in the presence of a basic catalyst. The rearrangement reaction is stereospecific, yielding 95–100% *cis*-propenyl ether. A catalyst deactivation effect is observed with ultimate degree of rearrangement being a function of initial catalyst concentration but not of temperature. The rearrangement reaction affords a convenient preparative procedure for propenyl ethers.

The base-catalyzed rearrangement of an allyl ether to a propenyl ether apparently represents a further example of that group of reactions classified as true, three-carbon prototropic shifts.¹



The isomerization of certain allylic ethers has been mentioned briefly in the literature. Vinyl allyl ether is converted to vinyl propenyl ether by treatment with metallic sodium or alkoxide ion.² Partial rearrangement of 1-allyloxy-2-propanol is reported by refluxing with potassium hydroxide, and allyloxy end-group unsaturation in polypropylene glycol is isomerized to propenyloxy unsaturation at 100° under basic conditions.³ Also

(1) A true, three-carbon prototropic system is defined as one in which the nature of the activating groups is such that covalency changes beyond the limits of the three-carbon system itself are structurally excluded, *i.e.*, the negative charge on the allylic anion is located within the limits of the system itself (J. W. Baker, "Tautomerism," D. Van Nostrand Co., Inc., New York, N. Y., 1934, p. 80). That oxygen does not participate in resonance stabilization in the prototropic rearrangement of an allyl ether to a propenyl ether is suggested by the fact that allyl ethers do not rearrange under conditions which readily isomerize allyl sulfides to propenyl sulfides [(a) D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952); D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956)]. This difference is attributed to the ability of sulfur to expand its electron shell to a d-orbital and thus participate in resonance stabilization of the intermediate allylic carbanion. Other examples of three-carbon prototropy in the above sense are the base-catalyzed rearrangements of quaternary ammonium-substituted propylene [(b) C. K. Ingold and E. Rothstein, *J. Chem. Soc.*, 8 (1929); 1666 (1931)], the isomerization of olefinic hydrocarbons [(c) W. O. Haag and H. Pines, *J. Am. Chem. Soc.*, **82**, 387 (1960)], and the migration of double bonds in the Varrentrapp reaction [(d) R. G. Ackman, P. Linstead, B. J. Wakefield and B. C. L. Weedon, *Tetrahedron*, **8**, 221 (1960)].

(2) R. Paul, G. Roy, M. Fluchaire and G. Collardeau, *Bull. soc. chim. France*, 121 (1950); W. H. Watanabe and L. E. Conlon, *J. Am. Chem. Soc.*, **79**, 2828 (1957).

(3) D. M. Simons and J. J. Verbanc, *J. Polymer Sci.*, **44**, 303 (1960).

3-butoxy-2-methylpropene has been rearranged to 1-butoxy-2-methylpropene by treatment with potassium amide in liquid ammonia.⁴ A somewhat obscure example of the rearrangement is found in the conversion of bis-(1,3-diphenylallyl) ether to the corresponding dipropenyl ether by treatment with refluxing sodium ethoxide.⁵ Here, the isomerization could be ascribed entirely to the mobility of the 1,3-diphenylpropene systems.⁶

In the present work, a variety of mono- and polyfunctional allyl ethers have been rearranged to the corresponding propenyl ethers. Table I summarizes reaction conditions and results. In general, the reaction proceeds readily at 150–175° in the presence of 5% of a basic catalyst. Potassium *t*-butoxide was an effective catalyst in all cases, whereas sodium methoxide showed appreciable activity toward pentaerythritol tri- and tetraallyl ethers only. These differences probably are due to the fact that potassium *t*-butoxide is the more soluble catalyst and is a stronger base. The rearrangement of pentaerythritol ethers occurred also in the presence of sodium or potassium hydroxides.

Certain color changes are observed during the reaction. A yellow mixture was obtained upon addition of catalyst to the substrate. When the mixture was heated, the yellow color changed to orange or orange-red. The final product was usually light yellow. Such color changes are probably indicative of a process involving a carbanion intermediate^{4,7} as in eq. 1.

Rearrangements were followed qualitatively by inspection of the infrared spectra of reaction samples. The major spectral changes are the appearance of a sharp, very intense band at 5.98 μ , accompanied by strong, broad absorption at about

(4) A. J. Birch, *J. Chem. Soc.*, 1642 (1947).

(5) C. W. Shoppee, *ibid.*, 2567 (1928).

(6) C. K. Ingold and C. W. Shoppee, *ibid.*, 447 (1929).

(7) C. R. Hauser and S. W. Kantor, *J. Am. Chem. Soc.*, **73**, 1437 (1951).