30% over-all yield was obtained, and considerably longer reaction times were involved.

Experimental Section

Complete exclusion of moisture from apparatus and reagents is required for the best results. Dimethyl sulfoxide is dried by shaking with calcium chloride, filtration onto calcium hydride, and distillation of the filtered, dried solvent under vacuum. The usual precautions must be observed when handling cyanide.

Identity of materials with authentic samples was confirmed by comparison of the infrared and/or proton magnetic resonance spectra in addition to the usual physical constants (*i.e.*, boiling point or melting point, refractive index).

Some variation in technique is possible and examples are given of typical reactions.

Valeronitrile.—To a mixture of 9 ml of 1-butanol and 15 ml of carbon tetrachloride was added in one portion 22.5 g of triphenylphosphine. The mixture was heated on a steam bath until vigorous refluxing occurred. After several minutes a portion of 100 ml of dimethyl sulfoxide was added, the temperature of the solution was raised almost to 100°, and 5 g of sodium cyanide was added. After some time the reaction was allowed to cool, and the nitrile was isolated by diluting the mixture with dilute, aqueous sodium sulfate, extraction with chloroform, drying the washed chloroform layer, and fractionation. Valeronitrile was obtained as a colorless liquid, bp 135–138°, $n^{20}\text{D}$ 1.3967 (85% yield).

2-Methyloctanonitrile.—A mixture of 14 ml of 2-octanol, 15 ml of CCl_4, and 20 g of triphenylphosphine was heated on a steam bath under reflux for several minutes, 80 ml of dimethyl sulfoxide was then added, and the solution was distilled until a temperature of approximately 90° was obtained. The solution was then heated under reflux with portionwise addition of 4.7 g of sodium cyanide. Heating and stirring were continued for an additional 2 hr under reflux. The cooled solution was poured onto an ice plus aqueous ferrous sulfate solution, the combined mixture was extracted with chloroform (three 100-ml portions), and the dried extracts were fractionated under vacuum. 2-Methyloctanonitrile was obtained, bp 85–90° (water pump), $n^{20.5}\text{D}$ 1.4201 (70% yield). By similar methods 1-hexanol, 1-pentanol, 1-decanol, and 1-heptanol may be converted to the nitrile.

Production of chloroform in the reaction was confirmed as follows. A mixture of 10 ml of 1-pentanol, 25 ml of carbon tetrachloride, and 26 g of triphenylphosphine was heated under reflux. The mixture was then roughly fractionated and material of bp 58–68° was compared with solvent chloroform by gas-liquid partition chromatography and proton magnetic resonance. The material was mainly chloroform contaminated with some carbon tetrachloride and 1-chloropentane.

Production of triphenylphosphine oxide was confirmed by recrystallization of the reaction residues after removal of volatile material. The white, crystalline material, mp 148–150°, was identical in infrared spectrum and behavior on thin layer chromatography with that of authentic triphenylphosphine oxide, the melting point of which it did not depress.

Methyl 2,3,4-Tri-O-acetyl-6-deoxy-α-D-glucohepturononitrile.—A solution of 9.6 g of methyl 2,3,4-tri-O-acetyl-α-D-glucoside in 50 ml of carbon tetrachloride was heated under reflux with 7.9 g triphenylphosphine for 15 min and 100 ml of dimethyl sulfoxide was then added; solvent was removed on the steam bath until approximately 45 ml of distillate had collected, and a 2.5-g portion of sodium cyanide was then added. Heating was continued on the steam bath for 1.5 hr. The mixture was then poured onto ice (approximately 800 g) and set aside to reach room temperature. The solid was separated, washed several times with cold water, and then dissolved in boiling methanol and filtered while hot. The solvent was removed *in vacuo* and the residue was recrystallized from a little warm methanol. The product (4.5 g) was dissolved in chloroform and petroleum ether was added until a faint turbidity still persisted on heating the solution. On cooling, white crystals, mp 132–133°, $[\alpha]^{18}\text{D}$ +147° (*c* 0.7, $CHCl_3$), were obtained. These liberated ammonia with hot aqueous sodium hydroxide and showed no hydroxyl band in the infrared. Bands at 2215 and 1745 cm^{-1} indicated nitrile and acetyl to be present.

Anal. Calcd for $C_{14}H_{19}NO_8$: C, 50.66; H, 5.67; N, 4.25. Found: C, 50.56; H, 5.78; N, 4.02.

Registry No.—Valeronitrile, 110-59-8; 7-butanol, 71-36-3; 2-methyloctanonitrile, 2570-96-9; 2-octanol, 123-96-6; 1-hexanol, 111-27-3; 1-pentanol, 71-41-0; 1-decanol, 112-30-1; 1-heptanol, 111-70-6; methyl 2,3,4-tri-O-acetyl-6-deoxy-α-D-glucohepturononitrile, 7432-71-5.

Allene Chemistry. VI.[1] Reaction of Sodium Thiolates with Allene

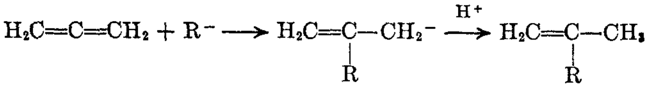
W. H. MUELLER AND K. GRIESBAUM

Central Basic Research Laboratory,
Esso Research and Engineering Company, Linden, New Jersey

Received September 9, 1966

Considerable advances have been made during the past decade in the understanding of electrophilic and of free-radical addition reactions to allene.[2] In contrast, very little is known to date about the course of anionic additions to allene and to allenic systems in general.

In analogy with the well-documented facile addition of nucleophiles to acetylenes[3] and in line with the preferred formation of the least substituted carbanion intermediates in such reactions one might anticipate a preferential attack at the central sp carbon atom of allene to yield a vinylic monoadduct.



$$H_2C=C=CH_2 + R^- \longrightarrow H_2C=\underset{\overset{|}{R}}{C}-CH_2^- \xrightarrow{H^+} H_2C=\underset{\overset{|}{R}}{C}-CH_3$$

Such a preferred reaction course was indeed reported for the addition of ethanol to allene in the presence of potassium hydroxide.[4] The Ziegler-type polymerization of allene, on the other hand, which was also formulated as an anionic reaction was reported to follow precisely the opposite reaction path *via* a preferred terminal attack on allene.[5]

$$H_2C=C=CH_2 + R^- \longrightarrow R-CH_2-\bar{C}=CH_2 \xrightarrow{H_2C=C=CH_2} \longrightarrow \underset{\text{polymer}}{\longrightarrow}$$

In the light of this apparent discrepancy we have undertaken a brief investigation of this reaction, using the strongly nucleophilic thiolate ions[6] as adding species. The freshly prepared sodium thiolates were in each case treated with a 100% molar excess of allene in methanol as a solvent at elevated temperatures (Table I) in pressure tubes. After arbitrary periods of reaction times the unreacted gases were withdrawn and analyzed, and the remaining liquid products were worked up as described in the Experimental Section.

It was a common feature of all of these reactions that the corresponding 2-propenyl sulfides (I) were formed in very high selectivities (~90%), along with

---

(1) For the previous report in this series, see K. Griesbaum, *Angew. Chem.*, **78**, 953 (1966); *Angew. Chem. Intern. Ed. Engl.*, **5**, 933 (1966).

(2) For leading references, see footnote 1.

(3) (a) W. E. Truce in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press Inc., New York, N. Y., 1961, pp 112–120; (b) W. E. Truce, H. C. Klein, and R. B. Kruse, *J. Am. Chem. Soc.*, **83**, 4636 (1961).

(4) A. Faworsky, *J. Prakt. Chem.*, [2] **44**, 208 (1891).

(5) W. P. Baker, Jr., *J. Polymer Sci.*, **A1**, 655 (1963).

(6) For a summary, see footnote 3 in ref 3a.

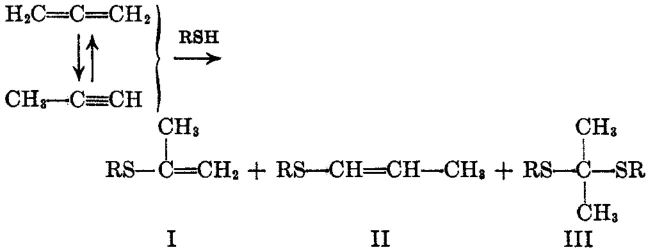
TABLE I

SODIUM THIOLATE-ALLENE OR -METHYLACETYLENE ADDUCTS AND SOME PHYSICAL-ANALYTICAL DATA OF THE PRODUCTS

Mercaptan	Substrate	Conditions: Temp, C°	Conditions: Time, hr	Conversion, %	% adduct selectivity[a]: $CH_2{=}C(SR)CH_3$	% adduct selectivity[a]: RSCH=CHCH$_3$	% adduct selectivity[a]: Diadducts	Summary formula	Bp uncor, °C (mm)	Major adduct, $CH_2{=}C(SR)CH_3$, Elemental compn, %: Calcd C	Calcd H	Calcd S	Found C	Found H	Found S
C_6H_5SH	$CH_2{=}C{=}CH_2$	85	144	52	88	10	1 $C_6H_5S(CH_2)_3SC_6H_5$[b,c]	$C_9H_{10}S$	97–98 (20)	72.00	6.66	21.33	71.64	6.69	20.95
CH_3SH	$CH_2{=}C{=}CH_2$	65	144	20	98	1	1 $(CH_3S)_2C(CH_3)_2$	C_4H_8S	91 (atm)	54.54	9.09	36.36	54.75	8.80	35.83
C_2H_5SH	$CH_2{=}C{=}CH_2$	85	192	35	90	3	6 $(C_2H_5S)_2C(CH_3)_2$[b]	$C_5H_{10}S$	113–14 (atm)	58.82	9.80	31.37	58.87	9.78	31.30
C_2H_5SH	$CH_3C{\equiv}CH$	85	192	38	90	3	4 $(C_2H_5S)_2C(CH_3)_2$[b]	$C_5H_{10}S$	113–14 (atm)						

[a] From combined glpc and semiquantitative nmr analysis. [b] Small amounts of other isomeric diadducts remain unidentified. [c] The symmetrical 1,3 diadduct, 1,3-bis(phenylthio)propane, which was observed during the addition of sodium phenyl thiolate to allene was probably the result of a concurrently occurring free-radical addition of not completely removed phenyl mercaptan to allene. For the course of such free, radical additions, see K. Griesbaum, A. A. Oswald, E. R. Quiram, and W. Naegele, *J. Org. Chem.*, **28**, 1952 (1963); T. L. Jacobs and G. E. Illingworth, Jr., *ibid.*, **28**, 2692 (1963).

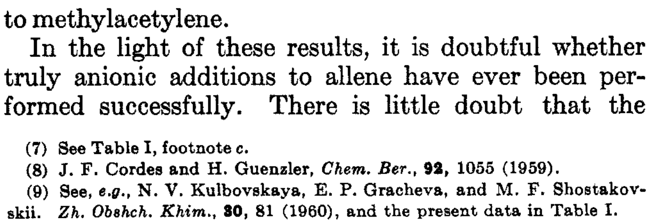
minor amounts of the isomeric 1-propenyl sulfides (II) and small amounts of diaddition products (III).[7] In each case, the unreacted gas consisted of an equilibrium mixture[8] of allene (15%) and methylacetylene (85%). This, coupled with the fact that the same adduct- and allene–methylacetylene distributions were obtained starting from methylacetylene[9] did *a priori* not allow any conclusion with regard to the preferred reaction path, since the major products (I) could be equally well derived from a center addition to allene or to methylacetylene.



I II III

Efforts to answer this question by the addition of thiolate ions to tetramethylallene, which cannot be isomerized into an acetylene, did not lead to any detectable addition products; instead the tetramethylallene was largely recovered. Although this is not a compelling proof, the complete lack of reaction in this case may well indicate that the above-described additions occurred predominantly or completely to methylacetylene rather than to allene.

The only products that could be compatible with a terminal attack on allene are the 1-propenyl sulfides (II), obtained in low selectivities and possibly formed by a base-catalyzed isomerization[10,11] of the terminal addition products (IV). The formation of the adducts (II) may, however, be equally well explained by a free-radical addition of the corresponding thiols to methylacetylene which may occur inadvertently at the elevated reaction temperatures. In fact, the higher selectivity for II in the case of the addition of phenyl mercaptan (Table I), which is known to possess an enhanced reactivity over that of alkyl mercaptans in free-radical reactions, may well be indicative of this reaction course. At any rate, the over-all low occurrence of the adducts (II) shows conclusively that terminal addition to allene is either less favorable than center addition to allene or less favorable than addition to methylacetylene.



In the light of these results, it is doubtful whether truly anionic additions to allene have ever been performed successfully. There is little doubt that the

---

(7) See Table I, footnote c.

(8) J. F. Cordes and H. Guenzler, *Chem. Ber.*, **92**, 1055 (1959).

(9) See, *e.g.*, N. V. Kulbovskaya, E. P. Gracheva, and M. F. Shostakovskii. *Zh. Obshch. Khim.*, **30**, 81 (1960), and the present data in Table I.

(10) D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952).

(11) C. C. Price and W. H. Snyder, *J. Org. Chem.*, **27**, 4639 (1962).

previously reported anionic addition of ethanol,[4] which was also accompanied by an allene–methylacetylene equilibration, may have also occurred on methylacetylene, in contrast to the conclusions of the early workers. On the other hand, the classification of the reported Ziegler polymerization of allene[5] as an anionic type reaction becomes questionable if one considers that allene has also been polymerized in a 1,2 manner by transition metal π complexes,[12,13] while no high molecular weight polyallene could be obtained by the usual methods of anionic polymerization.[5]

Experimental Section

Materials.—The allene used was +99% pure. It contained traces of propane and *ca.* 0.5% propene. Methylacetylene was *ca.* 99.5% pure, containing 0.5% butane. The thiols used for the preparation of the sodium thiolates were CP chemicals.

Methods of Analysis.—The adducts from methyl and ethyl mercaptide have been analyzed by capillary gas chromatography. A Perkin-Elmer Model 226 linear programmed-temperature gas chromatograph with a 200-ft, 0.02-in. i.d. Golay column coated with a mixture of 50% phenylsilicone and 50% nitrilesilicone was used. Temperatures of the injection block and detector were 270 and 190°, respectively. The temperature of the column was first held for 10 min at 50°; afterwards, it was programmed at a rate of 10°/min up to 160° and there maintained at that temperature isothermally until the end of the analysis.

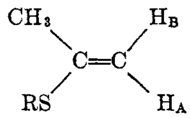
For the analysis of adducts from phenyl thiolate an F & M Model 500 linear programmed-temperature gas chromatograph with a 3-ft, 0.25-in. o.d. column was used. The column packing consisted of 3% Dowfax 9N40 (an ethylene oxide–*p*-nonylphenol polyether of a 40:1 molar ratio) on 60–80 mesh Gas Chrom P.

Operating conditions were as follows: detector, 250°; injector, 170°; column heating rate, 5.6°/min; starting temperature, 50°; final temperature, 240°; sample size 0.5 µl.

Nmr spectra were recorded on a Varian Model A-60 proton resonance spectrometer (see Table II). The spectra were taken on 50% solutions in carbon tetrachloride as solvent. Chemical shifts were measured against tetramethylsilane as internal reference standard.

TABLE II

PARAMETERS OF NMR SPECTRA OF SOME 2-PROPENYL SULFIDES[a]



R		CH_3[b]	H_A[c]	H_B[b]
CH_3	2.16 s	1.94	4.52	4.92
CH_3CH_2 (a) (b)	(a) 1.25 t (b) 2.69 q [d]	1.92	4.52	4.95
C_6H_5	7.33 m	1.95	4.88	5.08

[a] The spectra were obtained from 50% solutions in CCl_4. Chemical shifts of structural units are in parts per million (ppm) downfield from TMS internal reference: s = singlet, t = triplet, q = quartet, m = multiplet. Assignments of structural units are based on comparison with those of the corresponding 2-halopropenes: K. Griesbaum, W. Naegele, and G. G. Wanless, *J. Am. Chem. Soc.*, **87**, 3151 (1965). [b] Appears as unresolved doublet, $J \approx 1$ cps. [c] Appears as unresolved multiplet owing to coupling with CH_3 and H_B. [d] $J = 7$ cps.

Preparation of Sodium Thiolates.—The respective mercaptan was slowly introduced into a methanolic solution of sodium methoxide. The reaction vessel was stirred and kept under a nitrogen atmosphere. An excess of the mercaptan (*ca.* 10%) was employed in order to assure complete conversion of the sodium methoxide. After completion of the addition the methanol and excess mercaptan was removed on a rotary evaporator at temperatures up to 100° (1 mm). The remaining white solid was then washed with dry ether, the solvent was evaporated, and the thus obtained sodium thiolate was used as such.

General Procedure for the Addition of Sodium Thiolate to Allene or Methylacetylene.—A methanolic solution of the sodium thiolate (*ca.* 25 g/100 ml of CH_3OH) was placed into a Pyrex tube, equipped with a magnetic stirring bar. After evacuation and cooling to Dry Ice temperature, allene or methylacetylene was condensed. The thiolate/unsaturate molar reactant ratio was 1:2. The sealed tube was then stirred and heated in a thermostated bath (for reaction conditions see Table I). In general the allene or methylacetylene was not completely soluble and, therefore, the existing two phases were frequently mixed by shaking the tube. After the reaction was completed the excess unsaturate was slowly vented and analyzed by glpc. The residual liquid had two phases. One was mainly composed of the addition products (phase I); the other contained unreacted thiolate and small amounts of adducts in methanol (phase II). After separation phase I was taken up in ether and washed with water, then with 5% aqueous $NaHSO_4$, 5% aqueous $NaHCO_3$, and again with water. Most of the methanol in phase II was removed by careful distillation over a column and the removed methanol analyzed by glpc. The products contained in the semisolid concentrate were then extracted with ether and the ether extracts washed as described for phase I. Both ethereal solutions from phase I and II were combined and dried over $MgSO_4$. Most of the ether was then removed by slow distillation over a column and the distillate was again analyzed for products. The residual crude product mixture was analyzed by glpc and nmr. The major monoadduct was obtained pure on fractional distillation and thus characterized (Table I and nmr data). The minor monoadduct and the diadducts have been identified by comparison of glpc retention times with those of authentic samples which have been previously synthesized and characterized in this laboratory.[14]

Registry No.—Allene, 463-49-0; phenyl-2-propenyl sulfide, 7594-43-6; methyl-2-propenyl sulfide, 7594-44-7; ethyl-2-propenyl sulfide, 7494-45-8.

---

[12] S. Otsuka, K. Mori, and F. Imaizumi, *J. Am. Chem. Soc.*, **87**, 3017 (1965).

[13] H. Tadokoro, Y. Takahashi, S. Otsuka, K. Mori, and F. Imaizumi, *Polymer Letters*, **3**, 697 (1965).

[14] See K. Griesbaum, A. A. Oswald, E. R. Quiram, and W. Naegele in footnote *c* of Table I.

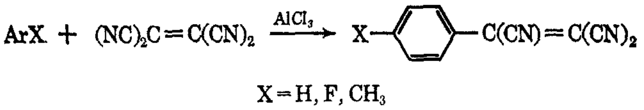
Cyanocarbon Chemistry. Tricyanovinylation

ROSETTA HENDERSON AND WILLIAM A. SHEPPARD

Contribution No. 1256 from Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received November 14, 1966

Tetracyanoethylene (TCNE) attacks aromatic systems highly activated by electron-donating substituents[1-3] but is not sufficiently electrophilic to attack unactivated rings. However, TCNE activated by near-molar quantities of aluminum chloride will attack



benzene, toluene, fluorobenzene, and naphthalene to give the corresponding tricyanovinyl aromatic compounds in 20 to 30% yield. The reaction with toluene and fluorobenzene resulted in *para* substitution, as determined by spectral analysis, and, in the fluoro case,

---

[1] B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *J. Am. Chem. Soc.*, **80**, 2806 (1958).

[2] G. N. Sausen, V. A. Engelhardt, and W. J. Middleton, *ibid.*, **80**, 2815 (1958).

[3] Z. Rappoport, *J. Chem. Soc.*, **1963**, 4498.