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.

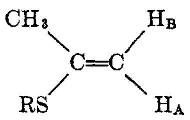
For the analysis of adducts from phenyl thiolate an F & M Model 500 linear programmed-temperature gas chromatograph with a 3-ft, 0.25-in. o.d. column was used. The column packing consisted of 3% Dowfax 9N40 (an ethylene oxide–*p*-nonylphenol polyether of a 40:1 molar ratio) on 60–80 mesh Gas Chrom P.

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.

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[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

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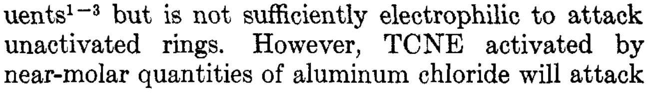
Tetracyanoethylene (TCNE) attacks aromatic systems highly activated by electron-donating substituents[1-3] but is not sufficiently electrophilic to attack unactivated rings. However, TCNE activated by near-molar quantities of aluminum chloride will attack benzene, toluene, fluorobenzene, and naphthalene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



$$ArX + (NC)_2C{=}C(CN)_2 \xrightarrow{AlCl_3} X\text{-}C_6H_4\text{-}C(CN){=}C(CN)_2$$

$$X = H, F, CH_3$$

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[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.

TABLE I

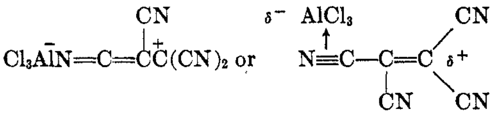
PREPARATION AND PROPERTIES OF TRICYANOVINYL AROMATICS

Ar of $ArC{=}C(CN)_2$ CN	Yield, %	Mp, °C	Recrystn solvent	Formula	Anal., %							
					Carbon		Hydrogen		Nitrogen		Other	
					Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
C_6H_5	35	98.3–99.2[a]	Benzene	$C_{11}H_5N_3$	73.8	73.4	2.81	3.01	...	...		
p-$CH_3C_6H_4$	23[b]	115 5–117	Ether	$C_{12}H_7N_3$	74.6	75.0 74.8	3.66	3.95 3.86	21.8	21.2		
p-FC_6H_4	17[c]	122–123	Benzene–cyclohexane	$C_{11}H_4N_3F$	67.1	67.2	2.05	2.20	21.3	21.0	F, 9.6	F, 9.7
β-$C_{10}H_7$	20[d]	174–178	Acetone–ethanol	$C_{15}H_7N_3$	78.6	78.5	3.08	3.21	18.4	18.5		

[a] Lit.[2] mp 96–97°. [b] *para* substitution shown by 830-cm^{-1} band in infrared (no strong band in 810–750-cm^{-1} region) and proton nmr in d_6-acetone: (CH_3) 2.5 ppm, aromatic typical A_2B_2 centered at -7.75 ppm relative to tetramethylsilane, $\delta = 0.4$ ppm and $J = 6$ cps. [c] *para* substitution proved by spectral comparison to authentic *p*-fluoro(tricyanovinyl)benzene prepared by literature procedure (ref 2 and 3) of condensing *p*-fluorobenzaldehyde with malononitrile followed by addition of HCN and oxidation. [d] *o*-Dichlorobenzene used as solvent. Reaction run on 8.8 g of naphthalene, 6.0 g of TCNE, and 6 g of $AlCl_3$ in 200 ml of solvent.

by comparison with authentic 1-fluoro-4-(tricyanovinyl)benzene prepared from *p*-fluorobenzaldehyde by a literature procedure.[2] Attack in the β position of naphthalene was indicated by spectral analysis and proved by hydrolysis of the tricyanovinyl derivative[2] to 2-naphthoic acid.[4] In each case, the orientation of substitution is toward minimum steric interactions, suggesting that steric effects are important in the rate-controlling step of substitution. No products could be isolated from reaction of TCNE with durene, probably because steric interference is too great. Chlorobenzene also did not react, but its aromatic ring is more strongly deactivated than that of fluorobenzene.[5]

The interaction of TCNE with aluminum chloride to form a more electrophilic species such as



$Cl_3\bar{A}lN{=}C{=}C(CN)\overset{+}{C}(CN)_2$

could explain the enhanced activity of TCNE in attack on a π system, but this species is not electrophilic enough to attack chlorobenzene. When the TCNE solution in benzene is added to aluminum chloride in benzene, the reaction mixture turns from yellow (normal for TCNE–benzene π complex) to red, suggesting formation of a π complex of aluminum chloride–TCNE with benzene. Qualitatively, most of the aluminium chloride remains undissolved, and much of the TCNE can be recovered from the mixture before heating by filtering off the insoluble aluminum chloride and evaporating the red solution. Aluminum chloride is required in molar amounts because it (or some other aluminum salt from reaction with HCN) complexes strongly with the product. Thus the product had to be isolated by chromatography over alumina, and, although tricyanovinylbenzene sublimes quickly at 90° (0.1 mm), only a trace of it was recovered on attempted sublimation of the crude reaction mixture at 150° (0.1 mm). In a control experiment, pure tricyanovinylbenzene was shown to behave similarly when complexed with alumina. Spectral analysis (infrared, ultraviolet, and nmr) on a crude reaction mixture verified that tricyanovinylbenzene was formed in the reaction and not by some rearrangement catalyzed by the alumina in the chromatographic column. Boron trifluoride (anhydrous or as etherate) is not effective as a catalyst. The detailed mechanism proposed for attack of TCNE on N,N-dimethylaniline[3] could accommodate our observations on these catalyzed tricyanovinylations.

Experimental Section

Tricyanovinylation of Benzene.—A mixture of 6.4 g (0.050 mole) of TCNE and 6.6 g (0.050 mole) of $AlCl_3$ in 100 ml of benzene was refluxed for 1 hr. The reaction mixture, which turned from initially deep red to brown, was chromatographed on 200 g of acid-washed alumina in a 90-mm-diameter column using approximately 1.5 l. of 80% ether–20% benzene as eluent. (The chromatography conditions are critical since the product is destroyed by long contact with alumina.) The crude tricyanovinylbenzene, mp 94–95°, was obtained in a yield of 3.2 g (35%) and, after recrystallization from acetonitrile or benzene and sublimation, was identical with an authentic sample prepared previously in this laboratory.[2] A small yield of TCNE was recovered in some reactions.

When 6.4 g (0.050 mole) of TCNE was refluxed with 0.38 g (0.003 mole) of $AlCl_3$ in benzene, 61% of the TCNE was recovered (from chromatography), and only 0.24 g (2.7%) of tricyanovinylbenzene was isolated.

The results for all tricyanovinylations are given in Table I along with analytical data and physical properties on the new tricyanovinylaryl compounds.

Registry No.—$C_{11}H_5N_3$, 4364-80-1; $C_{12}H_7N_3$, 7634-91-5; $C_{11}H_4N_3F$, 7634-92-6; $C_{15}H_7N_3$, 7634-93-7.

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(4) (a) The naphthoic acid from hydrolysis, mp 182–184° (lit.[4b] melting points of naphthoic acids: 1 isomer 161°; 2 isomer 184°), had an infrared spectrum identical with that of authentic 2-naphthoic acid. (b) I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, 1953, p 559.

(5) L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963).

Nucleosides of Thioguanine and Other 2-Amino-6-substituted Purines from 2-Acetamido-5-chloropurine[1]

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The synthesis of 9-substituted nucleosides of guanine, thioguanine, and other 2-amino-6-substituted purines generally has not been accomplished by the direct condensation of guanine or a blocked derivative with a

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