Tetra-alkylammonium Cyanides as Nucleophilic and Basic Reagents

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The title compounds catalyse the dimerization and polymerization of activated olefins, the Michael reaction, and other base-catalysed reactions. The mechanism of these reactions is discussed in relation to that of the similar tertiary-phosphine-catalysed reactions. Nucleophilic behaviour is inferred in the dimerization and polymerization reactions, and basic behaviour in olefin isomerization. Under comparable conditions the title compounds are more powerful nucleophiles (towards alkyl halides) than sodium cyanide.

TETRA-ALKYLAMMONIUM cyanides offer a convenient source of cyanide ion, which is very soluble in organic solvents, e.g., molar solutions of the tetrabutylammonium salt may be obtained in tetrahydrofuran. A general synthetic method for these compounds has been recently reported.[1],† The present work, which was prompted by the unexpected behaviour of some cobalt cyanide complexes as basic or nucleophilic catalysts,‡ explores the behaviour of these compounds towards activated olefins.

RESULTS AND DISCUSSION

Pentacyanocobalt(II) *Catalysis of the Dimerization of Activated Olefins.*—The preparation of tris(tetraethylammonium) pentacyanocobaltate(II) (I) and tris(tetraethylammonium) pentacyano(superoxo)cobaltate(III) (II) has been reported recently.[2] During their characterization they were treated with cyclohexa-1,4-diene; no reaction was observed with (I), but with (II), 1 mol of

$$(Et_4N)_3[Co(CN)_5] \qquad (Et_4N)_3[Co(CN)_5O_2]$$
$$(I) \qquad\qquad (II)$$
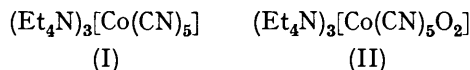
benzene was produced for every 2 mol of complex, suggesting the reaction (1). The hydroperoxide complex anion has been previously obtained as the lithium and
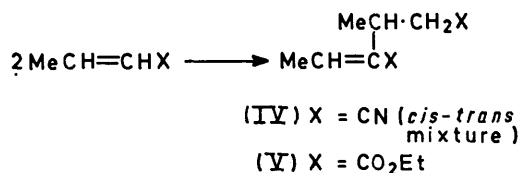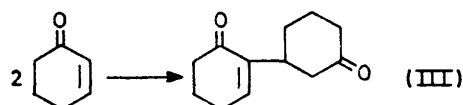
$$C_6H_8 + 2[Co(CN)_5OO\cdot]^{3-} \longrightarrow$$
$$C_6H_6 + 2[Co(CN)_5OOH]^{3-} \quad (1)$$
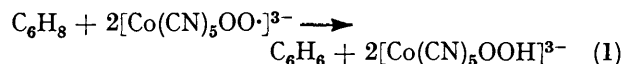
potassium salts by Pregaglia and his co-workers.[3] Since a similar dehydrogenation of cyclohexanone to cyclohexenone and, subsequently, to phenol has been achieved[4] with palladium(II) compounds, compound (II) was treated with both the saturated and the unsaturated ketones. No reaction was observed with the former, but cyclohexenone was dimerized to (III). In contrast to the reaction with cyclohexadiene, this reaction was catalytic (up to 40 mol of monomer dimerized per mol of complex) and complex (I) also showed similar reactivity. The dimer (III) has been obtained by treatment of cyclohexenone with sodium hydroxide.[5] Similarly, crotononitrile and ethyl crotonate afforded

(IV) and (V), which have been previously obtained by using an alkoxide[6] or a potassium–benzylpotassium catalyst.[7] Behaviour of compounds (I) and (II) as bases or nucleophiles is unexpected since the former usually behaves as a radical[8] and in reaction (1) the latter

$$2 MeCH=CHX \longrightarrow MeCH=\overset{\overset{\displaystyle MeCH\cdot CH_2X}{|}}{C}X$$

(IV) X = CN (*cis–trans* mixture)
(V) X = CO₂Et

appeared to show similar behaviour. These reactions were characterized by an induction period (sometimes as long as 2 h) during which no dimerization occurred. This was followed by a very vigorous reaction giving the dimer. It is possible that the added complex is not the catalytically active species but that the latter is produced during the induction period by interaction of added complex and substrate. (The induction period was not removed by prolonged contact of complex and solvent prior to addition of the substrate.)

Tetra-alkylammonium Cyanide-catalysed Reactions of Activated Olefins.—That the active species in the cobalt complex catalysed formation of compounds (III)—(V) from their monomers is tetraethylammonium cyanide is confirmed by the observation that the free cyanide catalyses their formation, but without the induction period noted when the complexes are used.

Although crotononitrile is dimerized by tetraethylammonium cyanide, acrylonitrile is converted into a solid polymer (VI). The reactions of these two nitriles have been further investigated with a view to determining their mechanisms. The crotononitrile dimer (IV) is clearly formed by addition of a carbanion derived from

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† The compounds [R₄N]CN may also be obtained by reaction of NaCN and [R₄N]Cl in dimethylformamide (M. M. Baizer, unpublished observations).

‡ The term ' base catalysis ' is generally used to cover reactions in which the catalyst behaves as a base (*i.e.* abstracts a proton) and also some in which it behaves as a nucleophile (*e.g.* the benzoin condensation). Although these are both examples of basic behaviour in the Lewis sense, they are two different types of reaction mechanism and subsequently in this paper they are distinguished as ' basic catalysis ' and ' nucleophilic catalysis.'

[1] J. Solodar, Synth. Inorg. Metal-org. Chem., 1971, 1, 141.
[2] D. A. White, M. M. Baizer, and A. J. Solodar, Inorg. Chem., 1972, 11, 2160.
[3] G. Pregaglia, D. Morelli, F. Conti, G. Gregorio, and R. Ugo, Discuss. Faraday Soc., 1968, 46, 110.
[4] R. J. Theissen, J. Org. Chem., 1971, 36, 752.
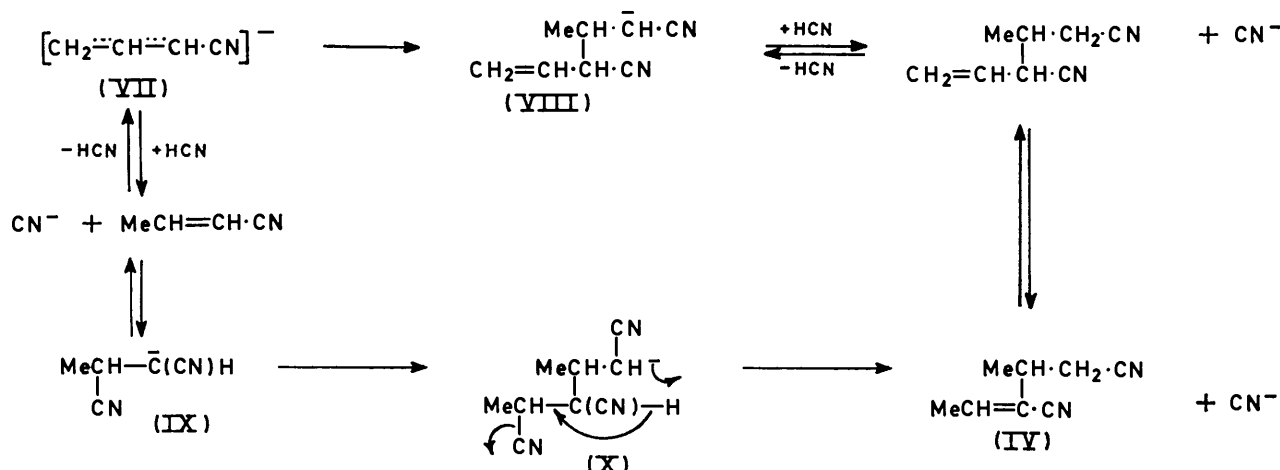[5] N. J. Leonard and W. J. Musliner, J. Org. Chem., 1966, 31, 639.
[6] Ger.P. 927,384 (Chem. Abs., 1956, 50, 8711).
[7] J. Shabtai and H. Pines, J. Org. Chem., 1956, 30, 3854.
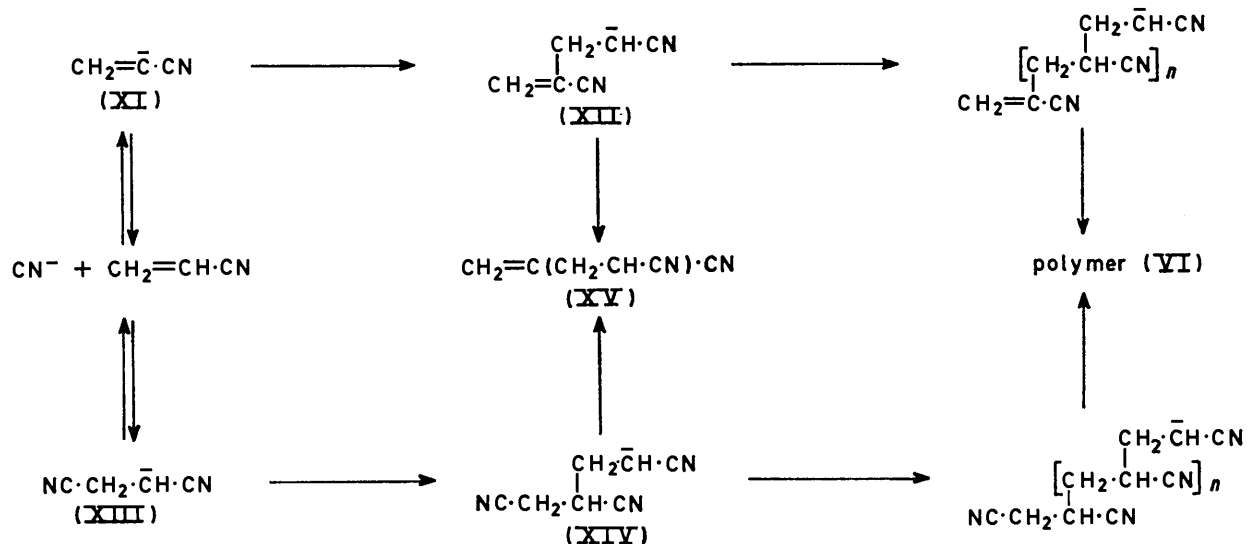[8] E.g. P. B. Chock and J. Halpern, J. Amer. Chem. Soc., 1969, 91, 582.

one monomer to a second molecule of monomer. Since cyanide ion may behave as a base or a nucleophile, the carbanion may be derived by proton abstraction from (Scheme 1, upper route) or nucleophilic addition to (Scheme 1, lower route) the monomer. That polymerization occurs with acrylonitrile is not surprising since this

dimerization of crotononitrile proceed *via* nucleophilic catalysis. The evidence is as follows. First, in the reaction with crotononitrile considerable amounts of trimers are formed but very little higher boiling oligomers. A clean break at the trimer stage may be explained by the possibility of cyanide elimination from the trimer

$$[CH_2\!\!=\!\!CH\!\!=\!\!CH\cdot CN]^- \quad (VII)$$

$$\xrightarrow{} \quad \begin{array}{c} MeCH\cdot \bar{C}H\cdot CN \\ | \\ CH_2\!\!=\!\!CH\cdot CH\cdot CN \end{array} \quad (VIII) \quad \underset{-HCN}{\overset{+HCN}{\rightleftharpoons}} \quad \begin{array}{c} MeCH\cdot CH_2\cdot CN \\ | \\ CH_2\!\!=\!\!CH\cdot CH\cdot CN \end{array} \quad + \ CN^-$$

$$(VII) \quad \updownarrow \ {}^{-HCN}_{+HCN}$$

$$CN^- + MeCH\!\!=\!\!CH\cdot CN$$

$$\updownarrow$$

$$\begin{array}{c} MeCH\!\!-\!\!\bar{C}(CN)H \\ | \\ CN \end{array} \quad (IX) \xrightarrow{} \begin{array}{c} MeCH\cdot CH \\ | \\ MeCH\!\!=\!\!C(CN)\!\!-\!\!H \\ | \\ CN \end{array} \quad (X) \xrightarrow{} \begin{array}{c} MeCH\cdot CH_2\cdot CN \\ | \\ MeCH\!\!=\!\!C\cdot CN \end{array} \quad + \ CN^-$$

$$(IV)$$

SCHEME 1   Possible crotononitrile dimerization mechanisms

$$\begin{array}{c} CH_2\!\!=\!\!\bar{C}\cdot CN \end{array} \quad (XI) \xrightarrow{} \begin{array}{c} CH_2\cdot\bar{C}H\cdot CN \\ | \\ CH_2\!\!=\!\!C\cdot CN \end{array} \quad (XII) \xrightarrow{} \begin{array}{c} CH_2\cdot\bar{C}H\cdot CN \\ | \\ [CH_2\cdot CH\cdot CN]_n \\ | \\ CH_2\!\!=\!\!C\cdot CN \end{array}$$

$$\updownarrow$$

$$CN^- + CH_2\!\!=\!\!CH\cdot CN \qquad CH_2\!\!=\!\!C(CH_2\cdot CH\cdot CN)\cdot CN \quad (XV) \qquad polymer \ (VI)$$

$$\updownarrow \qquad\qquad\qquad \uparrow \qquad\qquad\qquad \uparrow$$

$$\begin{array}{c} NC\cdot CH_2\cdot\bar{C}H\cdot CN \end{array} \quad (XIII) \xrightarrow{} \begin{array}{c} CH_2\bar{C}H\cdot CN \\ | \\ NC\cdot CH_2\cdot CH\cdot CN \end{array} \quad (XIV) \xrightarrow{} \begin{array}{c} CH_2\cdot\bar{C}H\cdot CN \\ | \\ [CH_2\cdot CH\cdot CN]_n \\ | \\ NC\cdot CH_2\cdot CH\cdot CN \end{array}$$

SCHEME 2   Possible acrylonitrile polymerization mechanisms

olefin is much more susceptible to Michael-type addition of carbanions [*e.g.* (XI) or (XIII)], and again two possible mechanisms (Scheme 2) need to be considered. Although (XI) is probably a high energy species and makes basic catalysis an unlikely route for acrylonitrile polymerization, this species has been postulated as an intermediate in other systesm.[9-12]

In the present case, the results (Table 1) indicate that oligomerization of acrylonitrile and possibly also the

carbanion (XVI) *via* a six-membered cyclic transition state.

Secondly, the reactions of both nitriles are little affected by changing the solvent from acetonitrile to t-butyl alcohol. This is difficult to rationalize on the basis of a mechanism dependent on proton removal and addition. It is also unexpected if the catalyst behaves as a nucleophile since, with a tertiary phosphine catalyst, elevated temperatures are required to dimerize acrylonitrile in

[9] T. Saegusa, Y. Ito, H. Kinoshita, and S. Tomita, *Bull. Chem. Soc. Japan*, 1970, **43**, 877.
[10] T. Saegusa, Y. Ito, S. Tomita, and H. Kinoshita, *J. Org. Chem.*, 1970, **35**, 670.
[11] A. Zilkha and Y. Avny, *J. Polymer Sci. (A)*, 1963, **1**, 549.
[12] M. A. Frankel, A. Ottolenghi, M. Albeck, and A. Zilkha, *J. Chem. Soc.*, 1959, 3858.

t-butyl alcohol,[13] whereas in decalin, polymerization occurs at room temperature.[14] (The tertiary phosphine is a nucleophilic catalyst.[15])

Thirdly, olefinic end groups are not evident in the n.m.r. spectrum of (VI) as would be expected for basic catalysis. In the case of nucleophilic catalysis, cyanide elimination from oligomers higher than the trimer should be difficult. Thus, other termination mechanisms, such as transfer of charge to nitrogen as in (XVII),[16] may compete with cyanide elimination. Although the nature of the termination step, in the present case, has not been determined, the incorporation of cyanide ion into the

add to another acrylonitrile molecule, giving (XIV) and eventually polymer, as is observed in the present case. This result does not discount the possibility that cyanide behaves as a base towards crotononitrile but as a nucleophile towards acrylonitrile, with the latter being a more ready reaction. However, the mixed reaction shows clearly that polymerization of acrylonitrile takes place by nucleophilic catalysis (Scheme 2, lower route).

The acrylonitrile polymer (VI) is a yellow solid soluble in polar organic solvents, such as acetonitrile, dimethylformamide, and dimethyl sulphoxide. Its n.m.r. spectrum (in [^{2}H$_3$]acetonitrile) shows two broad overlapping

TABLE 1

Reactions of crotononitrile and acrylonitrile catalysed by tetraethylammonium cyanide

Reaction no.	Substrate (mmol)	Solvent (ml)	[Et$_4$N]CN [a] (mmol)	Time (h)	Product (yield) [b]
1	MeCH=CH·CN (100)	MeCN (10)	0·1	0·5	(IV) (54) + trimers [c]
2	MeCH=CH·CN (100)	Bu^{t}OH (10)	0·2	0·5	(IV) (52) + trimers [c]
3	CH$_2$=CH·CN (100)	MeCN (15)	0·1	8 [d]	(VI) (trace) [e]
4	CH$_2$=CH·CN (100)	MeCN (15)	1·0	8 [d]	(VI) (37) [f]
5	CH$_2$=CH·CN (100)	Bu^{t}OH (15)	2·0	8 [d]	{ (VI) (15) {(XV) (ca. 0·5)
6	{MeCH=CH·CN (100) {CH$_2$=CH·CN (100)	MeCN (15)	1·0	8 [d]	(VI) (30)

[a] Added as 1·0M-solution in MeCN. [b] Yield expressed as number of mmol to which the product corresponds. [c] Yield of trimers in reactions 1 and 2 were comparable (g.l.c.). [d] Reaction appeared to be complete within 30 min. [e] Unchanged CH$_2$=CH·CN was >95 mmol (n.m.r.). Pouring the reaction mixture into MeOH (100 ml) gave an opaque solution but no solid removable by filtration. [f] Unchanged CH$_2$=CH·CN was ca. 60 mmol (n.m.r.).

polymer is reflected in the lower conversions (compare reactions 1 and 3 in Table 1) obtained with acrylonitrile.

(XVI)

(XVII)

(XVIII)
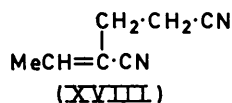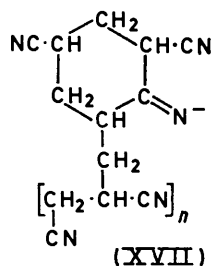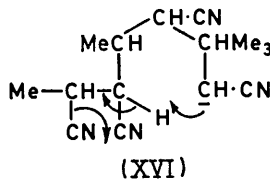
Fourthly, the reaction of a mixture of the two nitriles with tetraethylammonium cyanide also gives the polymer (VI), crotononitrile remaining unchanged. If the catalyst behaved as a base, crotononitrile would be preferentially attacked, giving (VII), which would preferentially attack acrylonitrile, giving the mixed coupled product (XVIII). This is the observed product with a benzyltrimethylammonium hydroxide [17] or a copper(I)–isocyanide [9,10] catalyst. On the other hand, if the catalyst behaves as a nucleophile, acrylonitrile will be preferentially attacked, giving (XIII), which will preferentially

bands at δ ca. 2·2 and 2·6. It is evident from the colour and the presence of oxygen (Table 2) that the isolated material is not a simple linear polymer. The oxygen appears to be present in hydroxy-groups or water (i.r.) and may be incorporated during the isolation of the polymer.

It is of interest to compare these reactions of acrylo- and crotono-nitriles with those catalysed by tributylphosphine. The phosphine is a very weak base (pK 6·00 in EtOH–H$_2$O) [18] and is, therefore, unlikely to abstract a proton even from crotononitrile. In the case

TABLE 2

Analytical data for acrylonitrile polymers

Reaction no. [a]	C (%)	H (%)	N(%)	O (%)	M [b]
4	66·1	6·0	25·3		1350
	66·1	6·1	25·3		
5	66·2	5·9	25·7	2·45	1450
	66·0	6·0	25·6	2·5	
6	66·0	6·1	25·3	2·55	1370
	66·1	6·0	25·2	2·55	
(Mean)	66·1	6·0	25·4	2·5	1387

[a] See Table 1. [b] Measured by gel permeation chromatography.

of acrylonitrile polymerization it acts as a nucleophile.[14,15] In dilute tetrahydrofuran (THF) solution acrylonitrile gives the dimer (XV) as the major product (Table 3). Again, as with cyanide ion as the catalyst, reaction of a

[13] J. D. McClure, Fr.P. 1,411,003 (Chem. Abs., 1966, 64, 1972).
[14] L. Horner, W. Jurgeleit, and K. Klupfel, Annalen, 1955, 591, 108.
[15] M. M. Baizer and J. D. Anderson, J. Org. Chem., 1965, 30, 1357.

[16] M. Szwarc, 'Carbanions, Living Polymers, and Electron Transfer Processes,' Interscience, New York, 1968, p. 656.
[17] H. A. Bruson and T. W. Reiner, J. Amer. Chem. Soc., 1943, 65, 18.
[18] K. Issleib and H. Bruchlos, Z. anorg. Chem., 1962, 316, 1.

mixture of the two nitriles gives the same product, the crotononitrile remaining unchanged. Thus, the behaviour of tetraethylammonium cyanide is similar to
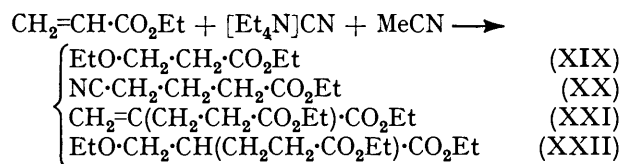
TABLE 3

Tributylphosphine-catalysed reactions *

Substrate (mmol)	Solvent THF (ml)	Major products (mmol of monomer converted)
MeCH=CH·CN (40)	25	(IV) (7·8)
CH₂=CH·CN (40)	25	{ (XV) (9·2) (VI) (6·0)
MeCH=CH·CN (20)	25	(XV) (7·8)
CH₂=CH·CN (20)		(VI) (trace)

* Carried out at room temperature by addition of the olefin (olefin mixture) in the solvent shown to the phosphine (1·0 mmol). After 16 h, the products were estimated by g.l.c. (dimers) or filtration and weighing (oligomers).

that of tributylphosphine, and different from that of basic catalysts such as benzyltrimethylammonium hydroxide.[17]

As noted above, ethyl crotonate gives the dimer (V) on treatment with tetraethylammonium cyanide in acetonitrile. With ethyl acrylate the product mixture is more complex. The compounds (XIX)—(XXII) result if the

$$CH_2=CH \cdot CO_2Et + [Et_4N]CN + MeCN \longrightarrow$$

EtO·CH₂·CH₂·CO₂Et	(XIX)
NC·CH₂·CH₂·CH₂·CO₂Et	(XX)
CH₂=C(CH₂·CH₂·CO₂Et)·CO₂Et	(XXI)
EtO·CH₂·CH(CH₂CH₂·CO₂Et)·CO₂Et	(XXII)

ester is treated with tetraethylammonium cyanide without external cooling. If the temperature is kept below 5°, only (XIX) and (XXII) result. The formation of these two products indicates that displacement of ethoxide ion from the starting material occurs, followed by its addition to the activated double bond. The other product(s) formed in the displacement reaction have not been detected (they may be very reactive species, such as CH₂=CH·CO·CN or CN·CH₂CH=C=O). The formation of (XX) involves Michael addition of acetonitrile to the olefin. Although tetraethylammonium cyanide does catalyse the Michael reaction (see below), it has not been possible to obtain acetonitrile adducts with compounds other than esters. Thus, it is possible that ethoxide ion is the catalyst for this particular reaction. The protons required for formation of (XIX) and (XII) appear to come from Hofmann degradation of the cation, since triethylamine is also detectable in the reaction mixture. Owing to the consumption of cyanide in the formation of these compounds, the yields of the dimer (XXI) are very low.

In several cases it has been shown that tetrapropyl- and tetrabutyl-ammonium cyanides are equally effective in the reactions described above.

[19] E. D. Bergman, D. Ginsburg, and R. Pappo, *Org. Reactions*, 1959, **10**, 179.
[20] D. A. White and M. M. Baizer, submitted to *Tetrahedron Letters*.
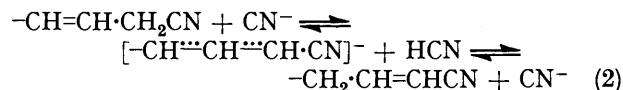[21] J. Solodar, *Tetrahedron Letters*, 1971, 287.

Other Reactions catalysed by Tetra-alkylammonium Cyanides.—Addition of carbanions to activated double bonds is a key step in the reactions discussed above and in the Michael addition of carbon acids to activated olefins,[19] a reaction which is also catalysed by tetra-alkylammonium cyanides. Some examples are the formation of the adducts (XXIII) (from cyclohexenone and nitromethane) and (XXIV) (from ethyl acrylate and

(XXIII)   (XXIV)
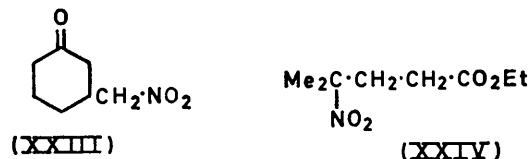
2-nitropropane). Alcohols may also be added to activated olefins, *e.g.* the adducts (XIX) and (XXII) are obtained by reaction of ethanol with ethyl acrylate or diethyl 2-methyleneglutarate.

Again, cyanide ion may behave as a base or a nucleophile, the former corresponding to the usual Michael reaction mechanism[19] and the latter to that observed with tertiary phosphine catalysts.[20] In view of the higher basicity of cyanide ion (compared to that of a tertiary phosphine) and the alkalinity of its aqueous solutions, the normal mechanism would seem most likely in the present case.

Basic catalysis is observed in reactions with but-3-enonitrile and 1,4-dicyanobut-2-ene. Isomerization to

$$-CH=CH \cdot CH_2CN + CN^- \rightleftharpoons$$
$$[-CH \cdots CH \cdots CH \cdot CN]^- + HCN \rightleftharpoons$$
$$-CH_2 \cdot CH=CHCN + CN^- \quad (2)$$

the conjugated isomer occurs in both cases (2). With the former, the crotononitrile formed is converted into dimer (IV) and trimer but, unlike the reaction with crotononitrile itself, an induction period is observed. This may be associated with the isomerization process, a vigorous reaction ensuing when sufficient conjugated isomer has accumulated. In a similar reaction of the latter, the conversion into dimer was lower and the conjugated isomer was isolated on distillation.

Aqueous solutions of tetra-alkylammonium cyanides catalyse the benzoin condensation.[21] This reaction may also be carried out in an organic solvent, such as acetonitrile, whereby yields comparable with those obtained with sodium cyanide in aqueous ethanol[22] result. The present reaction allows a tenfold increase in the benzoin/cyanide ratio and proceeds at room temperature, as opposed to the reflux temperature of 50% aqueous ethanol.[22] Sodium cyanide in dimethylformamide also catalyses the benzoin condensation, but full details have not yet been published.[23,24]

[22] R. Adams and C. S. Marvel, *Org. Synth.*, Coll. Vol. I, 1932, p. 88.
[23] J. L. Kuebrich and R. L. Schowen, unpublished work quoted in ref. 24.
[24] J. L. Kuebrich, R. L. Schowen, M.-S. Wang, and M. E. Lupes, *J. Amer. Chem. Soc.*, 1971, **93**, 1214.

Stoicheiometric Reactions with Alkyl Halides.—Tetra-ethylammonium cyanide reacts almost instantaneously with primary alkyl iodides, rapidly with the bromides, and slowly with the chlorides to give nitriles. The reaction with methyl iodide has been used in many cases to destroy the cyanide after completion of catalysed reactions, as noted in the Experimental section.

Generally, alkali metal cyanides are very sparingly soluble in aprotic organic solvents, but a 0·1M-solution of the sodium salt may be obtained in dimethylformamide. A comparison of the rates of bromide ion displacement from 1-bromododecane in this solution and in a similar solution of the tetraethylammonium salt is shown (Table 4). For 95% conversion, a reaction time

TABLE 4

Comparative data [a] on displacement of Br^- from n-$C_{12}H_{25}Br$ by [Et_4N]CN and by NaCN

NaCN	Time (min.)	2	10	15	20	25	30	40	50	60
	Extent of reaction (%) [b]		71	85	90	92	95	97	98·5	99·5	100
[Et_4N]CN	Time (min.)	1	6·5	9·5	16					
	Extent of reaction (%) [b]	93·5	97·5	99	100					

[a] For details, see text. [b] Times for 95% reaction, estimated graphically, are 25 (NaCN) and 2·5 min ([Et_4N]CN).

of 25 min is observed for sodium cyanide, compared to 2·5 min for tetraethylammonium cyanide. The higher nucleophilicity of the latter may be attributed to the weaker ion-pairing expected when close approach of cyanide ion to the positively charged centre is hindered by four alkyl groups.

EXPERIMENTAL

Except as noted, experiments were carried out in a nitrogen filled dry-box. Spectroscopic grade acetonitrile and reagent grade dimethylformamide were dried over molecular sieves. Commercially available acrylonitrile, crotononitrile, ethyl acrylate, cyclohexenone, tributylphosphine, n-dodecyl bromide, and benzaldehyde were fractionally distilled. Nitromethane, 2-nitropropane, but-3-enonitrile and 1,4-dicyanobut-2-ene were used as supplied. All solvents and reagents were deoxygenated and stored in the dry-box. Tetra-alkylammonium cyanides were prepared by the method of Solodar.[1]

Proton n.m.r. spectra were recorded at 60 MHz on a Varian T-60 machine, and chemical shifts are reported in p.p.m. downfield from internal tetramethylsilane.

The analytical data for compounds marked with an asterisk are given in Table 5.

Note on the Use of the Dry-box.—Tetra-alkylammonium cyanides are hygroscopic and in the present work they were stored, handled, and weighed out in the dry-box. If weighing out in air is attempted, the water which is invariably picked up may protonate carbanionic intermediates in the catalytic reactions. As well as leading to additional products [*e.g.* MeCH(CN)·CH₂·CO₂Et from ethyl crotonate], the cyanide catalyst may be removed from the solution with resulting low catalytic efficiencies (yields per mol [R_4N]CN).

Reaction of Complex (II) *with Cyclohexa-1,4-diene.*—The complex was prepared *in situ* by exposing a solution of tris-

(tetraethylammonium)pentacyanocobaltate(II) (I) (580 mg, 1·0 mmol) in acetonitrile (1 ml) to air. After returning it to the dry-box, the diene (50 mg, 0·75 mmol) was added. The solution was left at room temperature overnight. N.m.r. then showed that it had become diamagnetic. Peaks, due to unchanged cyclohexadiene (δ *ca.* 5·7.) and benzene (δ *ca.* 7·3), were observed with relative areas 1 : 3.

TABLE 5

Analytical data

| | | Found | | | | Calc. | | | |
Compound	Formula	C (%)	H (%)	N (%)	M	C (%)	H (%)	N (%)	M
(III)	$C_{12}H_{16}O_2$	74·7 74·5	8·3 8·5		192 [a]	75·0	8·4		192
(IV)	$C_8H_{10}N_2$	71·9 71·9	7·2 7·3	20·8 20·9	134 [a]	71·6	7·5	20·9	134
(V)	$C_{12}H_{20}O_4$	62·4 62·4	8·7 9·0		228 [a]	63·2	8·8		228
(XIX)	$C_7H_{14}O_3$	57·2 57·2	9·5 9·7		146 [a,b]	57·5	9·7		146
(XXII)	$C_{12}H_{22}O_5$	58·0 58·0	9·1 9·1		247 [b]	58·5	9·0		246
(XXIII)	$C_7H_{11}NO_3$	53·6 53·7	7·0 7·0	8·9 8·9	156 [b]	53·5	7·1	8·9	157
(XXIV)	$C_8H_{15}NO_4$	50·9 50·9	8·0 7·9	7·4 7·3	190 [b]	50·8	8·0	7·4	189
n-$C_{12}H_{25}CN$	$C_{13}H_{25}N$	79·2 79·4	12·5 12·4	7·0 7·0	197 [b]	80·0	12·8	7·2	195
Crotono-nitrile trimers	$C_{12}H_{15}N_3$	71·3 70·8	7·7 7·4	21·1 21·1	194 [c]	71·6	7·5	20·9	201

[a] By mass spectroscopy. [b] By molecular weight chromatography. [c] By osmometry in $CHCl_3$.

This is consistent with reaction of 2 mol of complex with 1 mol of the diene, producing 1 mol of benzene. No reaction was observed with unoxygenated complex (I) itself, even after several days.

Dimerization of Cyclohexenone by Complex (II).—A solution of the complex, obtained by exposure of complex (I) (580 mg 1·0 mmol) in acetonitrile (2 ml) to air, was treated with cyclohex-2-enone (1·92 g, 20·0 mmol). After *ca.* 10 min, a very vigorous reaction ensued leading to boiling of the solution. After 30 min when the reaction had subsided, n.m.r. showed the mixture to be still paramagnetic and that almost all the ketone had been consumed (*cf.* cyclohexadiene reaction above). Evaporation and distillation afforded 2-(3-oxocyclohexyl)cyclohex-2-enone (III) * as a viscous liquid (1·16 g, 59%), b.p. 125—130° at 0·3 mmHg. Its n.m.r. spectrum (CDCl₃) showed a triplet for the olefinic proton at δ 6·77, the remaining resonances lying between δ 1·1 and 3·2 (rel. area 15). Both this and its i.r. spectrum (ν_{CO} 1725 and 1690 cm⁻¹) were identical with those of an authentic sample.[5]

Cyclohex-2-enone was converted into (III) in similar yield by treatment with unoxygenated complex (I).

Dimerization of Crotononitrile by Complex (I).—A solution of the complex (145 mg, 0·25 mmol) in acetonitrile (0·5 ml) was added to crotononitrile (6·7 g, 100 mmol). The light-green solution remained unchanged for *ca.* 2 h, after which a very exothermic reaction occurred. Evaporation and distillation afforded (i) *trans* (+ small amount of *cis*)-2-ethylidene-3-methylglutaronitrile (IV) * as a liquid (3·35 g, 50%), b.p. 72—74° at 0·4 mmHg and (ii) a mixture of trimers as a viscous yellow liquid (2·25 g, 33%), b.p. 150—165° at 0·2 mmHg.* In its n.m.r. spectrum (CCl₄) the dimer

(IV) showed a quartet olefinic resonance at δ 6·40, the remaining resonances lying between δ 1·0 and 3·2 in which doublet methyl resonances at δ 1·27 (J 6 Hz) and 2·00 (J 7 Hz) could be distinguished.

From ethyl crotonate, diethyl 2-ethylidene-3-methyl-glutarate (V) * was similarly obtained as a liquid (30%), b.p. 74—75° at 0·2 mmHg, δ (CCl_4) 6·70 (1H, q, J 7 Hz, =CH–), 4·05 (4H, 1 q, 2 × OCH_2CH_3), 3·22 (1H, m, CH), 2·53 (2H, 2 d, –CH_2–, J 6—8 Hz), 1·83 (3H, d, J 7 Hz, =CHMe), and ca. 1·1 (9H, complex, 3 × Me).

Dimerization of Crotonitrile by Tetraethylammonium Cyanide.—The reactions 1 and 2 (Table 1) were carried out by addition of tetraethylammonium cyanide, as a 1·0M-solution in acetonitrile, to the substrate in the solvent shown. A vigorous, exothermic reaction began immediately. When this had subsided (ca. 30 min), g.l.c. showed the formation of dimer (IV) and trimers in yields comparable with those obtained with the complex (I) or (II) as the catalyst. After destruction of tetraethylammonium cyanide by addition of a few drops of methyl iodide, the dimer was isolated by distillation.

Polymerization of Acrylonitrile by Tetraethylammonium Cyanide.—The reactions 3—6 (Table 1) were carried out in a manner similar to the crotononitrile dimerizations. The product was isolated by precipitation with methanol (100 ml), except for reaction 5 in which the polymer precipitated spontaneously. The polymers were removed by filtration and washed with methanol. After brief drying, they were dissolved in acetonitrile and reprecipitated with methanol. After filtration and methanol washing, they were dried *in vacuo* at room temperature.

Reactions with Tributylphosphine.—The reactions (Table 3) were carried out as indicated. In the solvent used (THF) the polymer (VI) precipitated. It was removed by filtration, washed well with THF, and dried *in vacuo* at room temperature.

Reactions of Unsaturated Esters with Tetraethylammonium Cyanide.—A 1·0M-solution of the cyanide (2·5 ml, 2·5 mmol) in acetonitrile was added to ethyl crotonate (5·7 g, 50 mmol). The solution became orange and heat was evolved. After 4 h, g.l.c. showed the formation of the dimer and other minor higher boiling products. After addition of a few drops of methyl iodide ([Et_4N]I precipitated), the mixture was distilled to give the dimer (3·81 g, 67%), b.p. 84—85° at 0·3 mmHg.

A solution of the cyanide (1·56 g, 10 mmol) in acetonitrile (10 ml) was added to ethyl acrylate (20 g, 200 mmol) over 10 min. The mixture became hot. After it had cooled (1 h) unchanged ethyl acrylate (ca. 18 g) was evaporated off and the residue was distilled *in vacuo* (b.p. 90—120° at 0·3 mmHg). The distillate contained four major products identified as compounds (XIX)—(XXII) on the basis of the following evidence: (i) their g.l.c. retention times were identical with those of authentic samples [(XIX) and (XXII) prepared as below, (XX) [25] and (XXI) [26] prepared by literature methods]; (ii) their molecular weights (by molecular weight chromatography) were, respectively, 146, 141, 193, and 249 (calc. 146, 141, 200, and 249); (iii) mass spectroscopy of the g.l.c. eluate showed parent ions for (XX) (m/e 141) and (XXI) (m/e 200) and for the ethers the highest peaks observed [m/e 117 (XIX), 217 (XXII)] corresponded to the [$M - C_2H_5$]$^+$ ion; (iv) in the n.m.r. spectrum of the mixture, (XX) was evident from the quintet (δ 1·65) of its γ-methylene protons, (XXI) from its olefinic resonances (δ 5·37 and 5·87), and (XIX) and (XXII)

from the resonances (δ ca. 3·6) due to the methylene protons adjacent to the ether oxygen atoms.

In a similar experiment in which the cyanide solution (10 mmol) was added slowly (ca. 90 min) to ethyl acrylate (200 mmol) and the temperature of the mixture was kept below 5°, only the ethers (XIX) and (XXII) were formed in appreciable quantities. Distillation gave (XIX) {0·51 g, 30% (based on [Et_4N]CN)}, b.p. 85—90° at 20 mmHg and (XXII) (0·35 g, 14%) b.p. 85—95° at 0·25 mmHg.

Michael Reactions.—A mixture of cyclohex-2-enone (9·8 g, 100 mmol) and nitromethane (25 ml) was treated with 1·0M-tetrabutylammonium cyanide in THF (1·0 ml, 1·0 mmol). The mixture became yellow and heat was evolved. After 20 h, the mixture was treated with a few drops of methyl iodide and distilled to give 3-nitromethylcyclohexanone (XXIII) * as a pale yellow liquid (13·2 g, 84%), b.p. 115—116° at 0·2 mmHg. This material had i.r. and n.m.r. spectra identical with those of an authentic sample.[27] Its n.m.r. spectrum ($CDCl_3$) showed a doublet at δ 4·40 (J 6 Hz) and a complex signal at δ 1·1—2·9 (ring protons).

A mixture of ethyl acrylate (10·0 g, 100 mmol) and 2-nitropropane (25 ml) was treated with 1·0M-tetraethylammonium cyanide in acetonitrile. After 1 h, the mixture was distilled to give ethyl 4-methyl-4-nitrovalerate (XXIV)* (17·4 g, 92%), b.p. 80—81° at 0·2 mmHg, δ 1·22 (3H, OCH$_2Me$), 1·58 (6H, >CMe_2), 2·25 (4H, s, CH$_2$CH$_2$), and 4·07 (2H, ·OCH_2Me).

Similar Michael reactions have been carried out between acrylonitrile and 2-nitropropane, acetylacetone, nitromethane, or chloroform, and between ethyl acrylate and chloroform.

Ethoxylation Reactions.—A mixture of ethyl acrylate (10·0 g, 100 mmol) and ethanol (10 g) was treated with solid tetraethylammonium cyanide (0·78 g, 5 mmol). After the reaction had subsided, distillation afforded ethyl 3-ethoxypropionate (XIX) * (9·9 g, 68%), δ ($CDCl_3$) 1·25 and 4·13 (CO_2Et), 1·17 and 3·50 (EtO), 2·55 (CH_2CO_2Et), and 3·50 ($EtOCH_2$).

Similar treatment of diethyl 2-methyleneglutarate [26] afforded diethyl 2-(2-ethoxyethyl)glutarate (XXII) (25%), b.p. 94—96° at 0·25 mmHg,* δ ($CDCl_3$) 1·25, 4·13, and 4·16 (CO_2Et), 1·15 and 3·47 (EtO), 3·58 ($EtOCH_2$), and 1·6—2·9 ($EtOCOCH_2CH_2CH$), after removal of much unchanged starting material.

Similar reactions have been observed between acrylonitrile and alcohol or water.

Reactions involving Isomerization.—A solution of but-3-enonitrile (6·7 g, 100 mmol) in acetonitrile was treated with a 1·0M-solution (1·0 ml) of tetraethylammonium cyanide in acetonitrile. After ca. 10 min, a very vigorous exothermic reaction began and the solution turned orange. After 1 h, g.l.c. showed the presence of the dimer (IV) and trimers. Distillation gave the dimer as a liquid (3·28 g, 49%).

1,4-Dicyanobut-2-ene (21·2 g, 200 mmol) suspended in acetonitrile (80 ml) was treated with 1·0M-tetraethylammonium cyanide in the same solvent (0·4 ml, 0·4 mmol). On agitation the solid dissolved completely. The solution was left at room temperature for 18 h. G.l.c. showed the presence of two compounds having retention times similar to but not identical with that of the starting material, in addition to a much higher boiling product assumed to be the

[25] H. Lapin, V. Arsenijevic, and A. Horeau, *Bull. Soc. chim. France*, 1960, 1700.
[26] M. M. Rauhut and H. Currier, U.S.P. 3,074,999.
[27] A. McCoubrey, *J. Chem. Soc.*, 1951, 2931.

dimer. Distillation afforded a mixture of *cis*- and *trans*-1,4-dicyanobut-1-ene as a liquid (4·56 g, 22%), b.p. 74—82° at 0·15 mmHg, identified by comparison of its n.m.r. spectrum with that published.[28]

The Benzoin Condensation.—Tetrabutylammonium cyanide (1·0M) in tetrahydrofuran (1·0 ml, 1·0 mmol) was added to benzaldehyde (5·3 g, 50 mmol) in the same solvent (5 ml). The mixture was set aside for 16 h, after which a considerable quantity of white solid had precipitated. The mixture was stirred with methanol (20 ml) for a few minutes and filtered. The residue (4·9 g) was recrystallized from ethanol (30 ml) to give benzoin as needles (4·3 g, 81%), identical (i.r. and n.m.r. spectra and m.p.) with an authentic sample.[22]

Reactions of 1-*Bromododecane with Tetraethylammonium or Sodium Cyanide.*—The alkyl halide (1·50 g, 5·0 mmol) was added to a stirred 0·1M-solution of the cyanide in DMF (100 ml, 10 mmol) at 25 °C. The disappearance of the alkyl halide was followed by g.l.c. (10% SE-52 on Chromosorb W). The results are shown in Table 4. In the case of sodium cyanide, the product was isolated and identified as n-tridecanonitrile * (0·90 g, 92%), b.p. 82—83° at 0·15 mmHg. The same product was formed in similar yield in the tetraethylammonium cyanide reaction. These reactions were carried out in the air, the solutions having been made up in the dry-box and transferred to serum-capped bottles.

[28] A. Misono, Y. Uchida, M. Hidai, H. Shinohara, and Y. Watanabe, *Bull. Chem. Soc. Japan,* 1968, **41,** 396.