

## Cyanocarboxylation of Activated Olefins

By **Donald A. White**, Corporate Research Department, Monsanto Company, St. Louis, Missouri 63166, U.S.A.

Tetraethylammonium cyanide gives a 1 : 1 adduct with carbon dioxide which can be used for the simultaneous addition of cyanide ion and a carboxy-group to the double bond of an activated olefin. The limitations of this synthesis, due to the reversibility of some of the steps involved in certain cases, are discussed.

CYANIDE ion, especially in the form of its tetra-alkylammonium salts, is a very strong nucleophile. Its nucleophilic addition to polarized double bonds is well known and plays an important role in the catalysis of activated olefin dimerization and oligomerization by tetra-alkylammonium cyanides.<sup>1</sup> It is now reported that these catalytic reactions are completely suppressed

by the presence of carbon dioxide, and that other, stoichiometric reactions take place.

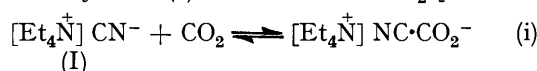
### RESULTS AND DISCUSSION

*Reaction of Tetraethylammonium Cyanide with Carbon Dioxide.*—Gas volumetric measurements show that tetraethylammonium cyanide (I) in acetonitrile or dimethylformamide solution takes up about 1 mol. equiv. of carbon dioxide, after allowance for solvent absorption. In analogy with the reaction of the cyanide (I) with carbon disulphide ( $\text{NC}\cdot\text{CS}_2^-$  formed)<sup>2</sup> it is assumed that

<sup>1</sup> D. A. White and M. M. Baizer, *J.C.S. Perkin I*, 1973, 2230.

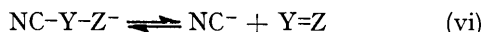
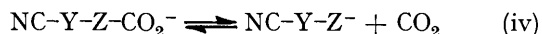
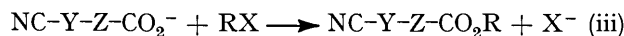
<sup>2</sup> H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Amer. Chem. Soc.*, 1962, **84**, 4756.

the cyanofornate ion is formed [equation (i)].\* Whereas the cyanodithioformate ion reacts with methyl iodide to give the corresponding methyl ester, reactions of solutions of the cyanide (I) saturated with CO<sub>2</sub> [henceforth



referred to as carboxylated (I)] with alkyl halides leads to liberation of carbon dioxide and formation of the alkyl cyanide. This can be understood if the carboxylation is reversible. A small amount of the highly nucleophilic cyanide ion present, but not detected by the volumetric measurements reported here, could react to form the alkyl cyanide. The ensuing displacement of the equilibrium would explain the results observed. The cyanofornate ion should be a relatively poor nucleophile in comparison with cyanide ion.

*Reactions of Carboxylated (I) with Unsaturated Compounds.*—In analogy to the reaction of carboxylated (I) with alkyl halides, preferential reaction of cyanide ion present in the equilibrium mixture with unsaturated electrophiles (Y=Z) can occur. The resulting cyanide adduct (NC-Y-Z<sup>-</sup>) can react with carbon dioxide liberated to form a cyanocarboxylated adduct [reaction (ii)]. Subsequent treatment with alkyl halides (usually methyl iodide)

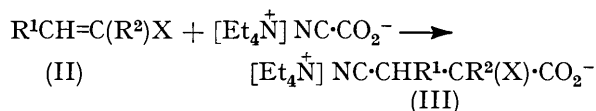


has afforded three types of product. First, cyano-esters may be formed [reaction (iii)]. Secondly, if the carboxylation (iv) is reversible, cyanoalkylated products are observed [reaction (v)]. Thirdly, if both carboxylation (iv) and cyanide addition (vi) are reversible, nitriles result [reaction (vii)]. Examples of all three types have been observed, as will be evident from the following examples.

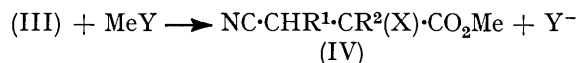
(a) *Monoactivated olefins.* The reactions of the activated olefins (II) with carboxylated (I) were followed by n.m.r. spectroscopy (benzonitrile as solvent). The salts (III) formed were identified by their n.m.r. spectra (Table 1). The reactions are slow, taking *ca.* 4–8 h for (IIb) and (IIe). The smooth reaction of (IIc) with stoichiometric quantities of carboxylated (I) contrasts with the vigorous oligomerization induced by traces of (I) alone.<sup>1</sup> The intermediate carbanion (NC·CH<sub>2</sub>·ĊH·CN) is evidently trapped efficiently by carbon dioxide. Quaternary ammonium carboxylates react rapidly with alkyl halides to form esters.<sup>3</sup> As expected, treatment of solutions of

\* Evidence for this structure has not been obtained. It represents the extreme in charge transfer from CN<sup>-</sup> to CO<sub>2</sub>, and it is desirable to determine whether the reactions described in this paper can be explained in terms of this formulation. The hypothesis of reversible formation of the cyanofornate ion does this, but a complex in which charge transfer was less complete would also suffice.

the salts (IIIa–c and e), prepared in acetonitrile (to facilitate isolation of the products), with methyl iodide afforded the corresponding esters (IVa–c and e) in good



- a; R<sup>1</sup> = H, R<sup>2</sup> = H, X = CO<sub>2</sub>Me  
 b; R<sup>1</sup> = H, R<sup>2</sup> = Me, X = CO<sub>2</sub>Me  
 c; R<sup>1</sup> = Me, R<sup>2</sup> = H, X = CO<sub>2</sub>Me  
 d; R<sup>1</sup> = H, R<sup>2</sup> = H, X = CN  
 e; R<sup>1</sup> = H, R<sup>2</sup> = Me, X = CN



yield. However, (IIIId) gave a mixture of the expected product [*i.e.* (IVd)] and (IVe). In this case treatment

TABLE 1

<sup>1</sup>H N.m.r. spectra of the ions NC·CHR<sup>1</sup>·CR<sup>2</sup>(X)·CO<sub>2</sub><sup>-</sup> as tetraethylammonium salts

Compd.	δ Values (J in Hz) <sup>a,b</sup>			
	H	R <sup>1</sup>	R <sup>2</sup>	X
(IIIa)	<i>ca.</i> 3.1 (m)	<i>ca.</i> 3.2 (m)	<i>ca.</i> 3.7 (m) <sup>c</sup>	3.78 (s)
(IIIb)	3.18 (d, J 16)	3.30 (d, J 16)	1.82 (s)	3.72 (s)
(IIIc)	<i>ca.</i> 3.15 (m)	1.45 (d, J 7)	<i>ca.</i> 3.7 (m) <sup>c</sup>	3.73 (s)
(IIIId)	3.26 (d, J 6)	3.26 (d, J 6)	3.91 (t, J 6)	
(IIIe)	3.12 (d, J 17)	3.30 (d, J 17)	1.80 (s)	

<sup>a</sup> Measured in benzonitrile solution at 100 MHz; internal Me<sub>4</sub>Si reference. <sup>b</sup> All spectra showed bands due to Et<sub>4</sub>N<sup>+</sup> at δ *ca.* 3.4 (q, J 7 Hz) and *ca.* 1.3 (t × t, J<sub>H,H</sub> 7, J<sub>H,N</sub> 1.5). <sup>c</sup> Partially obscured by CO<sub>2</sub>Me resonance.

with dimethyl sulphate gave pure (IVd) in high yield and diethyl sulphate the corresponding ethyl ester (V).



Because of these satisfactory results, the anomalous reaction of (IIIId) with methyl iodide was not pursued further. The results on the overall conversion of the activated olefins (II) into the esters (IV) and (V) are summarized in Table 2.

The esters (IV) and (V) were identified *via* their n.m.r. spectra (Table 3) and by comparison with authentic samples made *via* literature procedures [(IVa and d) and (V)] or alternative syntheses [(IVb, c, and e); see Experimental section].

(b) *Diactivated olefins.* Unlike monoactivated olefins, 1,1-diactivated olefins give a stable carbanion on reaction with cyanide ion. Thus, addition of (I) to dimethyl isobutylidenemalonate (VI) in benzonitrile gave the stable salt (VII), identified by its n.m.r. spectrum (Table 4) which showed equivalent methyl ester resonances as expected for the planar carbanion. Treatment of the solution with carbon dioxide had no substantial effect on the n.m.r. spectrum, except for some broadening. Addition of methyl iodide to solutions of

<sup>3</sup> J. H. Wagenknecht, M. M. Baizer, and J. L. Chruma, *Synth. Comm.*, 1972, **2**, 215.

TABLE 2

## 1,2-Cyanocarboxylation of activated olefins (II)

Substrate	Time <sup>a</sup> (h)	Alkylating agent	Product	Yield (%)	B.p. (°C) [mmHg]
(IIa)	2	MeI	(IVa)	77	87—88 [0.1]
(IIb)	20	MeI	(IVb)	82	65—66 [0.02]
(IIc)	20	MeI	(IVc)	68	86—87 [0.05]
(IId)	2	Me <sub>2</sub> SO <sub>4</sub>	(IVd)	78	78—79 [0.03]
(IId)	2	Et <sub>2</sub> SO <sub>4</sub>	(V)	75	85—86 [0.03]
(IIe)	20	MeI	(IVe)	85	78—79 [0.03]

<sup>a</sup> Time allowed for the formation of the intermediate salt (III).

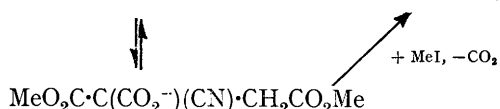
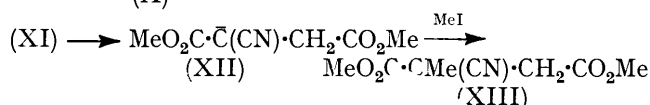
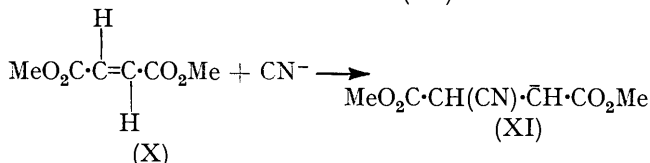
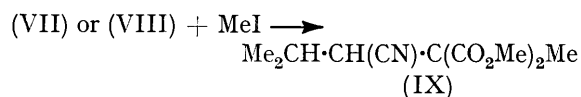
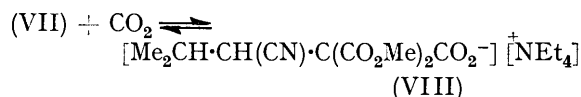
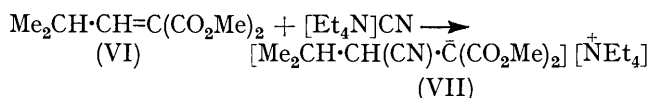
TABLE 3

<sup>1</sup>H N.m.r. spectra of compounds (IV) and (V)

Compd.	δ Values (J in Hz) <sup>a</sup>				
	H	R <sup>1</sup>	R <sup>2</sup>	X	CO <sub>2</sub> R
(IVa)	2.90 (d, J 7)	2.90 (d, J 7)	3.72 (t, J 7)	3.80 (s)	3.80 (s)
(IVb)	2.92 (s)	2.92 (s)	1.62 (s)	3.83 (s)	3.83 (s)
(IVc)	ca. 3.4 (m)	1.37 (d, J 7)	3.57 (d, J 7)	3.80 (s)	3.80 (s)
(IVd)	3.05 (d, J 7)	3.05 (d, J 7)	4.00 (t, J 7)		3.90 (s)
(IVe)	3.00 (s)	3.00 (s)	1.80 (s)		3.90 (s)
(V) <sup>b</sup>	3.03 (d, J 7)	3.03 (d, J 7)	3.98 (t, J 7)		1.35, 4.35 (t, J 7), (q, J 7)

<sup>a</sup> Measured in CDCl<sub>3</sub> solution at 60 MHz; internal Me<sub>4</sub>S reference. <sup>b</sup> R<sup>1</sup> = H, R<sup>2</sup> = H, X = CN.

(VII) gave the ester (IX). When the solutions had been treated with carbon dioxide or were prepared from carboxylated (I), carbon dioxide was re-evolved during the reaction with methyl iodide. Thus, although carbon



dioxide has little effect on the n.m.r. spectrum of (VII), it is, nevertheless, absorbed. This may be explained by a dynamic equilibrium, rapid on the n.m.r. time scale, between the carbanion (VII) and the carboxylate anion (VIII). Methyl iodide would react with the most nucleophilic species present (the carbanion) in the equilibrium mixture, and this reaction is of the cyanoalkylation type [(iv), (v)].

Surprisingly, cyanoalkylation was also observed in the case of a 1,2-diacetivated olefin, dimethyl fumarate (X). Treatment of solutions of (X) in acetonitrile with either (I) or carboxylated (I) followed by methyl iodide afforded the same product (with evolution of CO<sub>2</sub> in the latter case), identified by its n.m.r. spectrum as compound (XIII). Presumably, the initially formed carbanion (XI) rearranges to the more stable (XII). This carbanion may be reversibly carboxylated [*cf.* (VII)], and again reaction of methyl iodide with the most nucleophilic species (the carbanion) in the equilibrium mixture leads to displacement of the equilibrium, carbon dioxide evolution and C-methylation. The fact that the carbanion

TABLE 4

<sup>1</sup>H N.m.r. of compounds (VI), (VII), and (IX)

Compd.	Solvent	δ Values (J in Hz) <sup>a</sup>			
		Me <sub>2</sub> CH	CH	CO <sub>2</sub> Me	Other
(VI)	CDCl <sub>3</sub>	1.07 (d, J 7), 2.65 (m)	6.77 (d, J 10.5)	3.72 (s), 3.80 (s)	
(VI)	PhCN	0.43 (d, J 7), 2.13 (m)	6.20 (d, J 10.5)	3.13 (s), 3.23 (s)	
(VII) <sup>b</sup>	PhCN	0.35 (d, J 7), 1.88 (m)	3.43 (d, J 10)	3.06 (s)	2.76 (q, J 7), <sup>c</sup> 0.72 (t × t) <sup>c,d</sup>
(IX)	CDCl <sub>3</sub>	1.08 (d, J 7), 1.9 (m)	3.36 (d, J 4)	3.78 (s)	1.61 (s) <sup>e</sup>

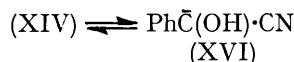
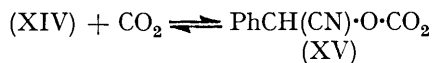
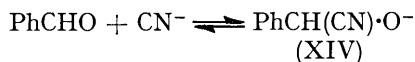
<sup>a</sup> Measured at 60 MHz; reference internal (with CDCl<sub>3</sub>) or external (with PhCN) Me<sub>4</sub>Si. <sup>b</sup> Tetraethylammonium salt. <sup>c</sup> Spectrum of tetraethylammonium ion. <sup>d</sup> J<sub>H,H</sub> 7, J<sub>H,N</sub> 1.5 Hz. <sup>e</sup> CMe.

(XI) has time to arrange indicates that, when carboxylated (I) adds to activated olefins, the cyanide addition and carboxylation are sequential rather than concerted, a possibility that might be considered because of the efficient trapping of the carbanion observed when acrylonitrile (IId) is the substrate. The rearrangement of the carbanion (XI) is similar to that of the intermediate carbanion in the Michael reaction of ethyl cyanoacetate and ethyl acrylate.<sup>4</sup> N.m.r. spectral observations with (X) as substrate were not very informative. The spectra were consistent with the structure (XII), but the methylene resonance was obscured by the methylene resonance of the cation. Again, the presence or absence of carbon dioxide had little effect on the n.m.r. spectrum.

(c) *Benzaldehyde*. Addition of benzaldehyde to a solution of carboxylated (I) in dimethyl sulphoxide produced a species characterized by singlet n.m.r. signals at δ 7.45 and 5.87 with a 5 : 1 area ratio. Subsequent

<sup>4</sup> E. D. Bergman, D. Ginsburg, and R. Pappo, *Org. Reactions*, 1959, **10**, 179 (esp. pp. 185—186 and references therein).

addition of methyl iodide led to reformation of benzaldehyde, evolution of carbon dioxide, and formation of acetonitrile. In the absence of carbon dioxide, addition of (I) followed by methyl iodide led to benzoin formation.\* The carbon dioxide evidently traps one of the benzoin



intermediates [(XIV) or (XVI)<sup>5</sup>] very efficiently. The similarity of the observed spectrum to that of mandelonitrile [singlets at  $\delta$  7.37 and 5.42 in  $\text{CDCl}_3$  for  $\text{C}_6\text{H}_5$  and  $\text{C}_6\text{H}_5\text{CH}$ , respectively]<sup>6</sup> together with the non-removal of the higher field resonance by  $\text{D}_2\text{O}$  [expected for carboxylation of the carbanion (XVI)] suggests the structure (XV). Whatever the structure of this intermediate, the equilibria leading to its formation are completely reversed on addition of methyl iodide, and this is a case in which both cyanide ion addition (iv) and carboxylation (vi) are reversible.

(d) *General comments.* The introduction of both a nitrile and carboxy-group into a molecule in a single reaction as exemplified in section (a) may be of some synthetic interest. The main purpose of the reports in sections (b) and (c) is to illustrate some of the pitfalls in the application of this reaction caused by the reversibility of some of the steps involved.

#### EXPERIMENTAL

Tetraethylammonium cyanide, prepared by the method of Solodar,<sup>7</sup> was stored and handled in a nitrogen-flushed dry-box. The activated olefins and benzaldehyde were distilled before use. The solvents used were dried over molecular sieves. Dialkyl sulphates were washed with aqueous sodium carbonate followed by water, dried over calcium sulphate, distilled, and dried and stored over molecular sieves. If the hygroscopic tetraethylammonium cyanide is not handled in a dry atmosphere or the reagents or solvents are not dry, HCN addition products (*i.e.* succinonitrile from acrylonitrile) generally contaminate the products. The n.m.r. spectra of the salts (III) were recorded at 100 MHz with a Varian HA-100 machine; the other spectra were obtained at 60 MHz with a Varian T-60 machine.

*Authentic Samples.*—Dimethyl cyanomethylmalonate (IVa)<sup>8</sup> and methyl and ethyl 2,3-dicyanopropionate [(IVd) and (V)<sup>9</sup>] were prepared by literature methods.

(a) *Methyl 2,3-dicyano-2-methylpropionate* (IVe). Methyl 2-cyanopropionate was prepared by the reaction of commercial ethyl 2-bromopropionate with sodium cyanide in meth-

\* An intermediate anionic species having a complex aromatic region n.m.r. spectrum was observed in this case. The same spectrum was generated by treating benzoin with (I). This species may be  $\text{PhCH}(\text{OH})\cdot\text{C}(\text{O}^-)(\text{CN})\text{Ph}$  [ $\longleftrightarrow$   $\text{Ph}(\text{CHO}^-)\cdot\text{C}(\text{OH})(\text{CN})\text{Ph}$ ] or  $\text{PhCH}(\text{O}^-)\cdot\text{COPh}$ , but the non-aromatic proton signals could not be located and no assignment could be made.

<sup>5</sup> J. P. Kuebrich, R. L. Schowen, M-s Wang, and M. E. Lupes, *J. Amer. Chem. Soc.*, 1971, **73**, 1214.

<sup>6</sup> C. J. Pouchert and J. R. Campbell, 'The Aldrich Library of NMR Spectra,' vol. III, Aldrich Chemical Co., 1974.

anol (*cf.* preparation of the ethyl ester<sup>10</sup>). A mixture of methyl 2-cyanopropionate (11.3 g, 0.1 mol), chloroacetonitrile (7.55 g, 0.1 mol), potassium carbonate (13.8 g, 0.1 mol), and dimethylformamide (50 ml) was stirred for 24 h, then filtered, and the residue was washed with dimethylformamide. The combined filtrate and washings were evaporated to dryness and the residue was distilled to give the product (IVe) (11.8 g, 78%), b.p. 103–105° at 0.1 mmHg (Found: C, 55.5; H, 5.3; N, 18.7.  $\text{C}_7\text{H}_8\text{N}_2\text{O}_2$  requires C, 55.3; H, 5.3; N, 18.4%).

Similarly prepared were *dimethyl cyanomethyl(methyl)malonate* (IVb) (Found: C, 51.5; H, 6.2; N, 7.6.  $\text{C}_8\text{H}_{11}\text{NO}_4$  requires C, 51.9; H, 6.0; N, 7.6%) from chloroacetonitrile and dimethyl methylmalonate and *dimethyl 2-cyano-2-methylsuccinate* (XIII) (Found: C, 51.9; H, 5.9; N, 7.8.  $\text{C}_8\text{H}_{11}\text{NO}_4$  requires C, 51.9; H, 6.0; N, 7.6%) from ethyl bromoacetate and methyl 2-cyanopropionate.

These three preparations are based on the previously reported use of potassium carbonate in dimethylformamide as a convenient system for the alkylation of malonic esters.<sup>11</sup>

(b) *Dimethyl (1-cyanoethyl)malonate* (IVc). Commercial diethyl ethylidene malonate (3.72 g, 20 mmol) was added to a 0.1M-solution of sodium cyanide in dimethylformamide (250 ml). The yellow solution was evaporated and the residue treated with acetic acid (2 ml) (CAUTION: excess of  $\text{CN}^-$  converted into HCN). Water (100 ml) was added. The oil which separated was extracted with ether. The extract was washed with aqueous sodium carbonate followed by water, dried ( $\text{CaSO}_4$ ), filtered, and evaporated to give diethyl (1-cyanoethyl)malonate. This was converted into the dimethyl ester by refluxing in methanol (200 ml) containing sodium methoxide (0.27 g, 5 mmol) for 4 h. Acidification with acetic acid (0.05 ml) followed by addition of water and extraction with ether afforded *dimethyl (1-cyanoethyl)malonate* (IVc) (2.4 g, 65%), b.p. 102–103° at 0.15 mmHg (Found: C, 51.4; H, 6.3; N, 7.7.  $\text{C}_8\text{H}_{11}\text{NO}_4$  requires C, 51.9; H, 6.0; N, 7.6%).

*Gas Volumetric Measurements.*—The absorption of carbon dioxide by solutions of tetraethylammonium cyanide was measured with a conventional gas handling/vacuum line. Absorption by stirred degassed dimethylformamide (10 ml) was slow and the value (23 ml at 25 °C and 756 mmHg) after 1 h was taken as a blank. Absorption by tetraethylammonium cyanide (0.31 g, 2.0 mmol) in dimethylformamide (10 ml) was initially rapid and after 1 h amounted to 75 ml at 25 °C and 756 mmHg. The difference corresponds to 1.0<sub>5</sub> mol per mol of tetraethylammonium cyanide. A similar measurement in acetonitrile gave a value of 0.94 mol per mol of the cyanide.

On treatment of the carboxylated solutions with 1-bromododecane, carbon dioxide was evolved and tridecanonitrile was formed (identified by g.l.c. comparison with an authentic sample).

*Reactions of Activated Olefins.*—These reactions are exemplified by that of methacrylonitrile (IIe).

(a) *N.m.r. Spectra.* Tetraethylammonium cyanide (1.56 g, 10 mmol) was suspended in benzonitrile (10 ml) and carbon dioxide was bubbled through for 40 min. To the clear

<sup>7</sup> J. Solodar, *Synth. Inorg. Metal-org. Chem.*, 1971, **1**, 141.

<sup>8</sup> C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, 1960, **82**, 6132.

<sup>9</sup> G. Casini, O. Cicchetti, and M. Ferappi, *Ann. Chim. (Italy)*, 1961, **51**, 366 (*Chem. Abs.*, 1961, **55**, 27,051).

<sup>10</sup> M. Atkinson and A. M. Horsington, *J. Chem. Soc. (C)*, 1969, 2186.

<sup>11</sup> A. K. Sen and S. Sarma, *J. Indian Chem. Soc.*, 1967, **44**, 644.

solution obtained was added methacrylonitrile (0.67 g, 10 mmol). The solution was examined by n.m.r., which showed a slow conversion into tetraethylammonium 2,3-dicyano-2-methylpropionate (IIe) (*ca.* 40% after 1 h, *ca.* 90% after 4 h, 100% after 8 h). The conversion was easily estimated by measuring the relative areas of the methyl resonances of the starting material and the product. Similarly, methyl methacrylate (IIb) showed *ca.* 50% conversion into (IIb) in 1 h and was completely converted in 4 h. With the other olefins complete conversion into the salt, judged by disappearance of the olefinic resonances, was observed within 1 h [(IIa and d)] or 4 h [(IIc)].

(b) *Methyl 2,3-dicyano-2-methylpropionate* (IVe). Carbon dioxide was bubbled through a suspension of tetraethylammonium cyanide (15.6 g, 0.1 mol) in acetonitrile (100 ml) for 1 h. Methacrylonitrile (6.7 g, 0.1 mol) was added and the flask was stoppered and set aside for 20 h. The mixture was then cooled to 5 °C and methyl iodide (15.6 g, 0.11 mol) was added. The flask was allowed to warm up to room temperature (*ca.* 1 h). The tetraethylammonium iodide which had crystallized was filtered off and washed with acetonitrile. The combined filtrate and washings were evaporated to dryness. The residue was stirred with ether (*ca.* 200 ml) and further tetraethylammonium iodide was filtered off. The residue was washed with ether and the combined filtrate and washings were evaporated and distilled. The fraction with b.p. 78–79° at 0.03 mmHg was collected as a water-white liquid, identified as methyl 2,3-dicyano-2-methylpropionate (IVe) (12.9 g, 85%) [Found: C, 55.0, 55.4; H, 5.4, 5.5; N, 18.4, 18.7%; *M*, 151, 152 (by molecular weight chromatography). Calc. for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: C, 55.3; H, 5.3; N, 18.4%; *M*, 152]. The n.m.r. spectrum of the product (Table 3) was identical with that of an authentic sample (see above).

Compounds (IVa–d) and (V) were similarly prepared. The time allowed for the formation of the salt (III) was at least twice that observed to be required in benzonitrile (see above). The results are summarized in Table 2.

*Reactions of Deactivated Olefins.*—(a) *Reaction of dimethyl isobutylidenemalonate* (VI). The starting material was prepared by the method described<sup>12</sup> for the diethyl ester, and identified by its n.m.r. spectrum (in CDCl<sub>3</sub>; Table 4). Owing to a change in solvent and reference, its spectrum is shifted in benzonitrile solution (Table 4). A solution of tetraethylammonium cyanide (1.56 g, 10 mmol) and (VI) (1.86 g, 10 mmol) in benzonitrile shows a spectrum interpreted as indicating the structure

(VII). This spectrum was little changed by addition of carbon dioxide or by using carboxylated (I). Some broadening was the only change observed.

Treatment of a similar solution in acetonitrile with methyl iodide followed by the work-up procedure described above for (IVe) gave *dimethyl 1-cyano-2-methylpropyl(methyl)malonate* (IX) (82%), b.p. 74–75° at 0.02 mmHg (Found: C, 58.4, 58.5; H, 7.4, 7.6; N, 6.0, 6.2%. C<sub>11</sub>H<sub>17</sub>NO<sub>4</sub> requires C, 58.1; H, 7.5; N, 6.2%), identified by its n.m.r. spectrum (Table 4).

(b) *Reaction of diethyl fumarate* (X). The ester (2.88 g, 20 mmol) was added to a suspension of tetraethylammonium cyanide (3.12 g, 20 mmol) in acetonitrile (20 ml) and the mixture was stirred until the solid had dissolved. After 10 min, methyl iodide (3.12 g, 22 mmol) was added. The mixture was treated as described above for (IVe) to give *dimethyl 2-cyano-2-methylsuccinate* (XIII) (1.85 g, 50%), b.p. 83–84° at 0.1 mmHg (Found: C, 52.0, 52.3; H, 6.1, 6.1; N, 7.5, 7.4%. Calc. for C<sub>8</sub>H<sub>11</sub>NO<sub>4</sub>: C, 51.9; H, 6.0; N, 7.6%). Its n.m.r. spectrum (in CDCl<sub>3</sub>; internal Me<sub>4</sub>Si reference) showed bands at δ 1.67 (CMe), 2.92 and 2.97 (CH), and 3.70 and 3.83 (CO<sub>2</sub>Me). The material was identical with an authentic sample (see above.)

Similar results were obtained when carboxylated (I) was employed and carbon dioxide was evolved during the reaction with methyl iodide.

*Reaction of Benzaldehyde.*—Carbon dioxide was bubbled through a suspension of tetraethylammonium cyanide (1.56 g, 10 mmol) in dimethyl sulphoxide (10 ml). After *ca.* 30 min, the suspended salt had dissolved and benzaldehyde (1.06 g, 10 mmol) was added. The solution was examined by n.m.r. spectroscopy (after addition of Me<sub>4</sub>Si reference). In addition to peaks due to the solvent and the tetraethylammonium ion, singlets at δ 7.45 and 5.87 (5:1) were observed. The usual benzaldehyde resonances were absent. The n.m.r. sample was returned to the bulk of the solution with washing by dimethyl sulphoxide. The solution was cooled until the solvent began to crystallize (*ca.* 15 °C), and methyl iodide (1.56 g, 11 mmol) was added. The solution was set aside to warm up to room temperature for *ca.* 2 h. The crystallized tetraethylammonium iodide was filtered off and the filtrate was examined by n.m.r. spectroscopy, which showed the re-formation of benzaldehyde, with only traces of benzoin.

[6/228 Received, 3rd February, 1976]

<sup>12</sup> A. C. Cope, C. M. Hofman, C. Wyckoff, and E. Hardenbergh, *J. Amer. Chem. Soc.*, 1941, **63**, 3452.