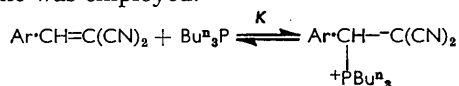


**263.** *Nucleophilic Attacks on Carbon-Carbon Double Bonds. Part IX.<sup>1</sup> The Primary (Equilibrium) Step. The Reaction of Tri-n-butylphosphine with Arylmethylenemalononitriles in Methanol.*

By ZVI RAPPOPORT and SIDY GERTLER.

The thermodynamic parameters for the formation of the adducts  $\text{Ar}\cdot\text{CH}(\text{P}^+\text{Bu}^n_3)\text{-C}(\text{CN})_2$  from tri-n-butylphosphine and seven arylmethylenemalononitriles in methanol have been measured:  $\Delta H = -13.4$  to  $-21.4$  kcal. mole<sup>-1</sup>;  $\Delta S = -27.4$  to  $-50$  e.u.; the equilibrium constants varied strongly, from  $17.4 \times 10^3$  to  $37$  l. mole<sup>-1</sup>, and decreased when the dielectric constant of the medium was lowered. The infrared spectra are consistent with a zwitterionic structure. The results are discussed in relation to the first step of nucleophilic reactions on carbon-carbon double bonds.

In nucleophilic reactions on carbon-carbon double bonds the initially formed carbanion or zwitterion may enter a variety of different pathways, resulting in addition, substitution, etc.<sup>2</sup> For several reactions which were studied kinetically the overall rate constant is composed from the equilibrium constant for the first nucleophilic step multiplied by the rate constant for the step following it.<sup>3-5</sup> Hence, a knowledge of the value of the equilibrium constant and the corresponding thermodynamic parameters is important for an understanding of nucleophilic attacks on carbon-carbon double bonds. A suitable model reaction to obtain the required data is that of trialkylphosphines with arylmethylenemalononitriles, in which stable zwitterionic adducts are formed.<sup>6,7</sup> The similarity of the spectra of the adducts to those of the arylmethylenemalononitriles suggests dissociation equilibria of the adducts and their components in solution. In the present study tri-n-butylphosphine was employed.



### RESULTS

A spectrophotometric method was used in the measurements. Preliminary experiments, beginning from the adducts side, had shown that the decomposition of the adducts is very rapid in all the solvents studied, and constant values of optical density at the  $\lambda_{\text{max}}$  of the arylmethylenemalononitriles were obtained after the minimum time required for the dissolution of the compounds. At room temperature, the adduct of 4-methylbenzylidenemalononitriles, at  $3.35 \times 10^{-5}$  mole l.<sup>-1</sup> concentration, is completely dissociated in methanol, benzene, or dioxan, and the benzylidenemalononitrile adduct is completely dissociated at  $3 \times 10^{-5}$  mole l.<sup>-1</sup> concentration in dioxan. In these concentrations even the much more stable 4-nitrobenzylidenemalononitrile adduct (see below) is dissociated to a large extent in acetic acid or methanol, and the average of eight experiments showed it to be approximately 90% dissociated in dioxan; increases in the concentration of this compound, to 3.96, 7.92, and  $11.5 \times 10^{-4}$  mole l.<sup>-1</sup>, gave 32, 20, and 3% decomposition, respectively. Although these experiments are not directly comparable, as the temperatures were not the same, they show that the dissociation of the adducts is an equilibrium process. The spectra of the reaction mixtures was always similar to that of the arylmethylenemalononitriles and no shift in the  $\lambda_{\text{max}}$  was found as observed previously

<sup>1</sup> Part VIII, Rappoport and Horowitz, preceding paper.

<sup>2</sup> Patai and Rappoport, *J.*, 1962, 377.

<sup>3</sup> Rappoport, Degani, and Patai, *J.*, 1963, 4513.

<sup>4</sup> Rappoport, Greenzaid, and Horowitz, *J.*, 1964, 1334.

<sup>5</sup> Crowell and Francis, jun., *J. Amer. Chem. Soc.*, 1961, **83**, 591.

<sup>6</sup> Horner and Klüpfel, *Annalen*, 1955, **591**, 69.

<sup>7</sup> Ford and Wilson, *J. Org. Chem.*, 1961, **26**, 1433.

with the 4-nitrobenzylidenemalononitrile-triethylphosphine adduct.<sup>6</sup> The adducts show practically no absorption at the  $\lambda_{\max}$  of the arylmethylenemalononitriles. Addition of tri-*n*-butylphosphine to solutions of arylmethylenemalononitriles caused the absorption of the solution to decrease with increasing tri-*n*-butylphosphine concentration. Here again, the final values were obtained immediately, and the rate of the reaction from either direction could not be studied.

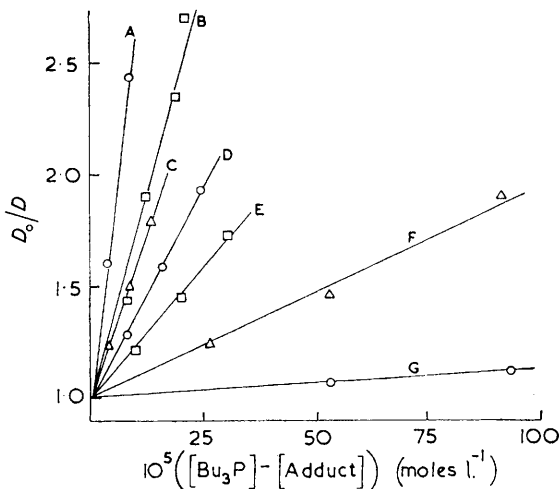
The equilibrium constants for the adduct formations defined by eqn. (1) were measured

$$K = [\text{Adduct}]/([\text{ArMN}]_0 - [\text{Adduct}])(\text{Bu}^n_3[\text{P}]_0 - [\text{Adduct}]) \quad (1)$$

for seven arylmethylenemalononitriles in dry methanol at three temperatures, and calculated as follows:  $[\text{ArMN}]_0$  and  $[\text{ArMN}]$  are the concentrations of the arylmethylenemalononitrile before and after the addition of tri-*n*-butylphosphine. Hence,  $[\text{ArMN}]_0\epsilon = D_0$  and  $[\text{ArMN}]\epsilon = D$ , where  $D_0$  and  $D$  are the respective optical densities, and  $\epsilon$  is the molar extinction coefficient of the arylmethylenemalononitrile. Since the absorption of

Dependence of  $D_0/D$  on the concentration of free tri-*n*-butylphosphine in the reaction with arylmethylenemalononitriles in methanol at 34°.

Substituents in aryl group: A, 4-NO<sub>2</sub>; B, 3-NO<sub>2</sub>; C, 2-Cl; D, 4-Cl; E, unsubst.; F, 4-Me; G, 4-OMe.



the adducts is negligible at the wavelength of the measurements, eqn. (2) is obtained from eqn. (1). From eqn. (2) a plot of  $D_0/D$  against the concentration of the free tri-*n*-butylphosphine must give a straight line with a slope equal to the equilibrium constant.

$$(D_0 - D)/D = (D_0/D) - 1 = K([\text{Bu}^n_3\text{P}] - [\text{Adduct}]) \quad (2)$$

Reasonably straight lines (Figure) were obtained with all the compounds studied, although upward curvatures were sometimes obtained with the most reactive compounds at high phosphine concentrations. This method was used for the calculation of the equilibrium constants in Table 1. Equilibrium constants for the 4-chlorobenzylidenemalononitrile adduct calculated directly from eqn. (1) are given in

TABLE 1.

Equilibrium constants (l. mole<sup>-1</sup>) for the formation of adducts of tri-*n*-butylphosphine with arylmethylenemalononitriles in methanol.

Temp.	Substituent in aryl group						
	4-NO <sub>2</sub>	3-NO <sub>2</sub>	2-Cl	4-Cl	H	4-Me	4-OMe
26°	—	—	13,000	7000	—	—	—
34	17,400	7000	5750	3700	2360	960	190
44	6600	2940	2480	1600	1160	450	115
54	2020	1060	1180	—	500	240	37*

\* Based on a total decrease of only 2—5% in the absorption.

Table 2. The agreement between the two methods of calculation is shown by the  $K$  values 7000, 3700, and 1600 at 26, 34, and 44°, respectively, as obtained by the least squares calculation from the graphs, compared to 7200, 3630, and 1590 obtained from the average values calculated by eqn. (1). The slight increase in the equilibrium constants of Table 2 with the increase in the phosphine concentration may have some significance,

TABLE 2.

Equilibrium constants for the 4-chlorobenzylidenemalononitrile (4-CIBMN)–tri- $n$ -butylphosphine ( $\text{Bu}_3^{\text{n}}\text{P}$ ) adduct in methanol, from the absorption data at 315  $\mu$ .

	At 26°					At 34°				
	$10^6[4\text{-CIBMN}]^*$	27.69	18.66	13.89	10.59	8.246	26.72	20.82	16.80	13.85
$10^6[\text{Bu}_3^{\text{n}}\text{P}]^\dagger$	0	70.50	145.16	221.34	298.48	0	80.70	163.30	246.9	
$10^6[\text{Adduct}]^\ddagger$	—	8.97	13.80	17.10	19.44	—	5.90	9.92	12.87	
$10^3 D^\S$	638	430	320	244	190	652	508	410	338	
$K$ (l. mole <sup>-1</sup> ) <sup>¶</sup>	—	6800	6850	7300	7900	Av. 7200.	—	3520	3600	3760 Av. 3630.

		At 44°				
$10^6[4\text{-CIBMN}]^*$		27.15	24.44	21.78	19.67	17.84
$10^6[\text{Bu}_3^{\text{n}}\text{P}]^\dagger$		0	76.77	153.59	230.96	308.61
$10^6[\text{Adduct}]^\ddagger$		—	2.71	5.37	7.48	9.31
$10^3 D^\S$		632	569	507	458	415
$K$ (l. mole <sup>-1</sup> ) <sup>¶</sup>		—	1450	1600	1640	1680 Av. 1590.

\* Concn. (moles l.<sup>-1</sup>) of the "free" 4-chlorobenzylidenemalononitrile, *i.e.*, the difference between the concentration introduced (the first value at each temperature) and the adduct concentration.

† Concn. (moles l.<sup>-1</sup>) of the "free" tri- $n$ -butylphosphine, *i.e.*, the difference between the concentration of the added  $\cdot\text{Bu}_3^{\text{n}}\text{P}$  and the adduct concentration. ‡ Calc. from the eqn.  $\{(D_0 - D)/D_0\} \times [4\text{-CIBMN}]$ .

§ Optical density. ¶ Calc. from eqn. (1).

but since the error in individual equilibrium constants is rather large (an error of 3% in the optical density corresponds to 10% error in  $K$ ), this may be a result of experimental error. Further, slow cleavage of arylmethylenemalononitriles to the corresponding aldehyde and malononitrile<sup>8</sup> by traces of water takes place in methanol (*e.g.*, 41% cleavage was found after 71 hours in the case of 4-nitrobenzylidenemalononitrile). With the increase in the phosphine concentration, hydroxide ions are formed as a result of the equilibrium  $\text{PBU}_3 + \text{H}_2\text{O} \rightleftharpoons \text{PBU}_3\text{H}^+ + \text{OH}^-$ , and, as these are much more effective nucleophiles, the cleavage reaction becomes more important.<sup>8,9</sup> Another complicating factor is the loss of tributylphosphine in the reaction mixture by oxidation, resulting in lower  $K$  values. Indeed, an aged batch of phosphine, even though stored under nitrogen, gave smaller equilibrium constants, but the relative order of reactivities was the same as in Table 1. As the adducts decompose even on standing, and calculation of the equilibrium constants requires the independent determination of  $\epsilon$ , measurements from the adduct side were not performed. In the one case studied, the equilibrium constant for the decomposition of  $4.98 \times 10^{-4}$  mole l.<sup>-1</sup> of the 3-nitro-adduct at 54° was 1020, compared to 1060 from the arylmethylenemalononitrile side.

Electron-attracting substituents increase the equilibrium constants, and electron-donating ones decrease them (Table 1). This was shown previously by the inability to obtain the 4-methoxy-, the 4-hydroxy-, and the 2,4-dimethoxy-adducts.<sup>6,7</sup> In our case also the 4-methoxy adduct was not isolated. The *o*-chlorophenyl group is more stabilising than the *p*-chlorophenyl group. In plots of  $\log K$  against the  $\sigma$ -values of Jaffé<sup>10</sup> the scatter of the points was much higher than usual (owing to the error in the  $K$  values). The point for the 4-methoxy-substituent is much lower than predicted from the graph and the value for this substituent was not used in the calculation of  $\rho$ . The  $\rho$  values at the three temperatures are positive, being 1.27, 1.12, and 0.85, at 34, 44, and 54°, respectively.

*Thermodynamic Parameters.*—The thermodynamic parameters for the formation of the adducts, as calculated from the values in Table 1, are given in Table 3. The accuracy

<sup>6</sup> Patai and Rappoport, *J.*, 1962, 383.

<sup>9</sup> Patai and Rappoport, *J.*, 1962, 392.

<sup>10</sup> Jaffé, *Chem. Rev.*, 1953, 53, 191.

of these values is not high as the equilibrium constants from which they are derived have relatively large errors. This is shown by comparing them (Table 3) with the values obtained from another (aged) batch of tri-*n*-butylphosphine (see below). With the exception of the 4-nitro-derivative, the  $\Delta H$  values are practically constant within the limit of their accuracy, being approximately  $-14$  to  $-16$  kcal. mole<sup>-1</sup>. The values of the entropy of formation are high and negative ( $-27.4$  to  $-38$  e.u.) and again the 4-nitro-derivative has a much lower value.

*Effect of the Solvent.*—Addition of *t*-butyl alcohol (dielectric constant 10.9 at 30°)<sup>11</sup> to the methanol (dielectric constant 32.6 at 25°)<sup>11</sup> decreased substantially the equilibrium

TABLE 3.

Thermodynamic parameters for the formation of adducts of tri-*n*-butylphosphine with arylmethylenemalononitriles in methanol.

Subst. in aryl group:	4-NO <sub>2</sub>	3-NO <sub>2</sub>	2-Cl	4-Cl	H	4-Me	4-MeO
$-\Delta H^*$ (kcal. mole <sup>-1</sup> )	21.4	16.9	15.7	13.4	14.9	15.5	15.2
	(19.5) §	(14.8) §			(16.9) §	(15.2) §	
$-\Delta F$ (307°) (kcal. mole <sup>-1</sup> ) †	5.9	5.2	5.2	5.0	4.7	4.2	3.8
$-\Delta S$ (307°) (e.u.) ‡	50.5	38	34	27.4	33	37	38

\* Estimated  $\pm 2.5$  kcal. mole<sup>-1</sup>. † Estimated  $\pm 0.5$  kcal. mole<sup>-1</sup>. ‡ Estimated  $\pm 0.5$  e.u. § Calc. by using the equilibrium constants obtained from the use of the aged tri-*n*-butylphosphine solution.

constant of the 4-nitro-adduct; the decrease is approximately 50-fold from pure methanol to pure *t*-butyl alcohol. A linear relation exists between the logarithms of the equilibrium constants and the % volume of *t*-butyl alcohol in the solvent. Comparison of the observed with the calculated values for log  $K$  is shown in Table 4; the differences are at most 2%.

TABLE 4.

Equilibrium constants for the tri-*n*-butylphosphine-4-nitrobenzylidenemalononitrile adduct in methanol-*t*-butyl alcohol mixtures at 34°.

[Bu <sup>t</sup> OH] (% v/v)	0	30	50	70	100
$K$ (l. mole <sup>-1</sup> )	17,400	4450	1900	1170	337
log $K$	4.240	3.648	3.278	3.068	2.528
log $K$ (calc.) *	4.230	3.702	3.335	3.000	2.470

\* Calculated from the equation,  $\log K = 4.23 - 1.76 \times 10^{-2}[\text{Bu}^t\text{OH}]$ .

*Infrared Spectra.*—The infrared spectra of the adducts were taken in Nujol mulls, as rapidly as possible after the preparation of the mulls. The adducts are highly hygroscopic, slowly dissociating even in the solid state under nitrogen, and absorptions at  $2.86 \mu$  (O-H stretching) and in the range  $6-6.5 \mu$  were observed after a short time. The absorptions in the ranges of C=C and C=N stretching frequencies only are given in Table 5, and the

TABLE 5.

Characteristic infrared bands ( $\mu$ ) of arylmethylenemalononitriles (A) and their tri-*n*-butylphosphine adducts (B).\*

Subst. in Ar	(A)	(B)	Subst. in Ar	(A)	(B)
H	4.50, 6.30, 6.40	4.64, 4.77	2-Cl	4.53, 6.37	4.65, 4.78
4-Me	4.52, 6.35	4.65, 4.77	3-NO <sub>2</sub>	4.50, 6.30	4.61, 4.75
4-Cl	4.50, 6.34	4.65, 4.79	4-NO <sub>2</sub>	4.50, 6.29	4.62, 4.75, 6.29 †

\* Characteristic peaks for tri-*n*-butylphosphine are at 6.90, 7.14, 7.53, 7.74, 8.23, 8.77, 9.19, 10.01, 10.38, and 11.15  $\mu$ . † Observed even after crystallisation of the adduct from different solvents, and taking the spectra as rapidly as possible. However, the solid adduct smells faintly of tri-*n*-butylphosphine.

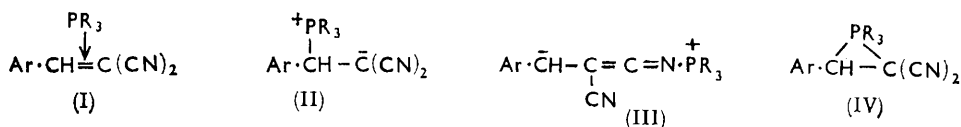
corresponding absorptions of the arylmethylenemalononitriles are given for comparison. The last values are slightly different from those found for the same compounds in potassium bromide discs.<sup>12</sup>

<sup>11</sup> "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., 41st edn., 1959-1960, pp. 2515, 2518.

<sup>12</sup> Zabicky, *J.*, 1961, 683.

## DISCUSSION

The adducts of trialkylphosphines with arylmethylenemalononitriles were described in the literature as zwitterions, but the evidence brought in favour of this structure is their protonation to  $\text{Ar}\cdot\text{CH}(\text{P}^+\text{R}_3)\cdot\text{CH}(\text{CN})_2 \text{X}^-$  (compounds which are obtained also directly by reaction of the arylmethylenemalononitriles with hydrogen halide and treatment of the product with the trialkylphosphine) and their analysis as 1 : 1 adducts. The dissociation of the adducts in solution renders the former evidence inconclusive, and other structures with the same analysis must be considered, especially as the adducts are formed and dissociated rapidly, a typical behaviour of  $\pi$ -complexes. Structures which have to be taken into account are: (a) a  $\pi$ -complex (I) with the tributylphosphine as donor and the activated double bond as acceptor; (b) a zwitterion (II) as suggested previously;<sup>6</sup> (c) a zwitterion with the structure (III), which is improbable *a priori* but which nevertheless should be considered by analogy with the suggested attack of triphenylphosphine at the 1-position of quinones,<sup>13</sup> another system capable of 1,4-reactions; (d) a three-membered ring (IV) with quinquevalent phosphorous.



The most convincing evidence on the structure comes from the infrared spectra (Table 5). The C=C stretching frequencies of the arylmethylenemalononitriles in the 6.3—6.4  $\mu$  region (conjugated C=C) are absent from the spectra of the adducts, and there is no peak in the 6.0—6.8  $\mu$  region which can be attributed either to a C=C or to a C=N stretching frequency. This eliminates possibilities (a) and (c), since the C=C stretching frequency of a  $\pi$ -complex should be retained (possibly shifted) in the region 6.0—6.8  $\mu$ . In the region of the C=N vibration, the single peak of the conjugated nitrile group at 4.50—4.53  $\mu$ , found for all the arylmethylenemalononitriles, splits and shifts to higher wavelengths in the adducts. One of the two new peaks is located in the 4.61—4.65  $\mu$  region, while the second, stronger one is in the 4.75—4.78  $\mu$  region (Table 5). While unconjugated nitrile groups usually absorb at 4.40—4.45  $\mu$ <sup>14</sup> the conjugated ones absorb near 4.50  $\mu$ <sup>14</sup> and are usually single. Only cyanides like potassium cyanide and the ferri- and ferro-cyanides absorb at about 4.8  $\mu$ , because of their ionic nature.<sup>15</sup> Owing to the negative charge appearing on the C(CN)<sub>2</sub> group in the zwitterion (II) [possibility (b)], a shift to higher wavelengths may be expected. However, in formulation (d) the absorption due to the two cyano-groups on the three-membered ring may shift in the same direction. The differentiation between the two possibilities is based on the splitting of the nitrile peak. The occurrence of peaks at 4.54 and 4.65  $\mu$  was used to identify sodium pentacyanoethanide, as these absorptions were ascribed to a substituted malononitrile anion.<sup>16</sup> Moreover, the published infrared spectra of the known cyanocarbon acid carbanions shows that all of them (except the 1,1,2,3,3-pentacyanopropenide anion, for which C=N absorption occurs at 4.53  $\mu$ ) containing the malononitrile residue absorb in the region from 4.55  $\mu$  to higher wavelengths with splitting to two or three peaks.<sup>16,17</sup> Therefore, structure (II) is preferred on spectral grounds, although it must be noted that a shift to higher wavelengths of the cyanide absorption may be expected for  $\pi$ -complexes also, as shown for example by

<sup>13</sup> Schönberg and Michaelis, *Ber.*, 1936, **69**, 1080; Ramirez and Derschowitz, *J. Amer. Chem. Soc.*, 1956, **78**, 5614.

<sup>14</sup> Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1958, p. 263.

<sup>15</sup> Looney and Downing, *J. Amer. Chem. Soc.*, 1958, **80**, 2840.

<sup>16</sup> Webster, Mahler, and Benson, *J. Amer. Chem. Soc.*, 1962, **84**, 3678.

<sup>17</sup> Trofimenko, Little, and Mower, *J. Org. Chem.*, 1962, **27**, 433; Williams, *J. Amer. Chem. Soc.*, 1962, **84**, 3478; Hertler, Hartzler, Acker, and Benson, *J. Amer. Chem. Soc.*, 1962, **84**, 3387; Melby, Hertler, Mahler, Benson, and Mochel, *J. Amer. Chem. Soc.*, 1962, **84**, 3374.

the shift to higher wavelengths of the carbonyl frequency in molecular complexes of aldehydes with iodine, iodine monochloride, and iodine monobromide.<sup>18</sup>

Three additional arguments in favour of the zwitterionic structure are the solvent effect discussed below, the magnitude of the equilibrium constants, and the analogy with the structures suggested for other products obtained by reactions of substituted phosphines with electrophilic centres. The high values of the equilibrium constants are far above those for typical  $\pi$ -complexes even with a much more active acceptor like tetracyanoethylene,<sup>19</sup> although the arylmethylenemalononitriles are much weaker  $\pi$ -acids. Further, substituted phosphines are known to attack various electrophilic centres, including C=S, C=O, and C=N bonds, and in all the cases the adducts obtained are formulated as zwitterions.<sup>20</sup> Hence, the attack on an electrophilic C=C bond to give a zwitterion is an extension of these reactions. The solubility behaviour of the adducts points only to some ionic character. The 3-nitrobenzylidenemalononitrile adduct is insoluble in cold benzene, toluene, or ether, slightly soluble in dioxan, and soluble in methanol, ethanol, chloroform, and dimethylformamide. However, all the adducts are insoluble in water.

Regarding the rapid formation of the adducts, calculation of the rate constant for the attack on the  $\beta$ -carbon atom, on the assumption that the ratio of the attack by hydroxide ion on 4-methoxybenzylidenemalononitrile<sup>8</sup> and on methyl iodide<sup>21</sup> is similar to the same ratio in the attack by tributylphosphine,<sup>22</sup> gave a value of 1200 l. mole<sup>-1</sup> sec.<sup>-1</sup>, *i.e.*, the reaction is very rapid. The rapidity of the reverse reaction is probably a result of the neighbouring free electron-pair participation in the elimination process.

It is interesting to know to what degree the present system can serve as a model for the first step of nucleophilic attacks on carbon–carbon double bonds. The choice of the arylmethylenemalononitriles as substrates seems to be a good one as this system and the related arylmethylenecyanoacetate system are known to participate in most types of nucleophilic attacks on double bonds, as addition, isomerisation, cleavage, etc.<sup>2</sup>

It was suggested that the equilibrium constant for the first step is low for the attack of water on a substituted  $\beta$ -nitrostyrene,<sup>5</sup> but a high equilibrium constant was found recently for the formation of the "living" trimer of  $\alpha$ -methylstyrene from the "living" dimer and  $\alpha$ -methylstyrene ( $K = 331$  l. mole<sup>-1</sup>),<sup>23</sup> while attack of alkylanilines on tetracyanoethylene gives a zwitterionic intermediate in an irreversible reaction.<sup>1,24</sup> Hence, as regards equilibrium constants, the present system can serve as a model for a number of other systems.

The most important results of the present work for the understanding of nucleophilic attacks on double bonds are the thermodynamic parameters (Table 3). In a number of such reactions studied recently,<sup>3,4</sup> the rate constant,  $k_{\text{exp}}$ , was equal to  $Kk_2$ , where  $k_2$  is a step following the equilibrium, and hence  $E_{\text{exp}} = \Delta H + E_2$ . As direct values of  $\Delta H$  were not available, they were estimated from the difference ( $E_1 - E_{-1}$ ). Average activation energies for the nucleophilic attack,  $E_1$ , were estimated from known values as 10–13 kcal. mole<sup>-1</sup> for various systems;<sup>3,4</sup> values somewhat lower than 30–37 kcal. mole<sup>-1</sup>, which is the activation energy  $E_{-1}$  for the *E1cB* elimination from carbanions,<sup>25</sup> were estimated for the elimination from zwitterions. Thus, the estimated  $\Delta H$  ( $= E_1 - E_{-1}$ ) is –15 to –20 kcal. mole<sup>-1</sup>, in good agreement with the results obtained (–13.4 to –21.4 kcal. mole<sup>-1</sup>) here from direct measurements in a single reaction system. This agreement is good evidence that these values can be used for other systems, but one may

<sup>18</sup> Augdahl and Klæboe, *Acta Chem. Scand.*, 1962, **16**, 1637, 1647, 1655.

<sup>19</sup> Merrifield and Phillips, *J. Amer. Chem. Soc.*, 1958, **80**, 2778.

<sup>20</sup> Horner and Hoffmann, *Angew. Chem.*, 1956, **68**, 473.

<sup>21</sup> Moelwyn-Hughes and Hurst, "Cinetica chimica," II° Corso estivo di chimica, Varenna, August 1957, p. 127.

<sup>22</sup> Henderson and Buckler, *J. Amer. Chem. Soc.*, 1960, **82**, 5794.

<sup>23</sup> Lee, Smid, and Szwarc, *J. Amer. Chem. Soc.*, 1963, **85**, 912.

<sup>24</sup> Rappoport, *J.*, 1963, 4498.

<sup>25</sup> Patai, Weinstein, and Rappoport, *J.*, 1962, 1741; Hine, Wiesboeck, and Ramsay, *J. Amer. Chem. Soc.*, 1961, **83**, 1222.

question whether the present system can serve as a model for reactions with smaller equilibrium constants and with short-lived carbanionic or zwitterionic intermediates. The justification for using these values is that the  $\Delta H$  values of Table 3 remain reasonably constant (except for the 4-nitro-derivative) when the equilibrium constants are decreased by a substantial factor. Extrapolation to systems with equilibrium constants not very far from those of the present work is therefore reasonable.

The formation of a zwitterion from two neutral molecules would lead to high negative entropy values ( $\Delta S = \Delta S_1 - \Delta S_{-1}$ ), as found experimentally. The use of these values with other systems is permissible as the decrease in entropy is associated more with the creation of charges than with their detailed nature. Indeed, it was suggested that the entropy associated with the initial equilibrium is the main contributing factor to the high negative activation entropy found recently in a nucleophilic isomerisation<sup>3</sup> or substitution.<sup>4</sup>

The high values of  $-\Delta H$  for the 4-nitro-adduct are outside the experimental error, and can result from an especially low value of  $E_1$ , as observed in the reaction of 4-nitro-benzylidenemalononitrile with water.<sup>8</sup> It was also suggested that for the 4-nitro-adduct the positive and the negative charges on the nitro-group can interact with those on the phosphorus atom and the  $\alpha$ -carbon atom.<sup>6</sup> Such an interpretation may account for the entropy value but not for the much smaller effects with the 3-nitro-adduct.

*Substituent and Solvent Effects.*—Table 1 shows that the equilibrium constants are affected by a change in the substituent in the same manner, even in minor details (*e.g.*, the relative reactivity of the chlorophenyl isomers and the behaviour of the 4-methoxyphenyl substituent)<sup>8</sup> as the rate of the nucleophilic attack. Comparison of the positive  $\rho$  values with those for other nucleophilic attacks on double bonds shows them to be higher than that for the barbiturate anion- $\beta$ -nitrostyrene system ( $\rho = 0.74$ ),<sup>26</sup> but comparable to that in the methoxide ion-dibenzoyl ethylene system ( $\rho = 1.00$ )<sup>27</sup> and in the reactions of various nucleophiles with 1-arenesulphonyl-2-chloroethylenes ( $\rho = 1.21-1.85$ ),<sup>28</sup> and lower than that for the water-arylmethylenemalononitrile system in ethanol ( $\rho = 2.36$ ).<sup>8</sup> If the response of such reactions to substituent changes is similar to their response to effects of medium (*i.e.*, the more active systems have lower response to external changes<sup>8</sup>), then  $\rho$  has to decrease with the increase in the reactivity. Indeed, in the first system given above the double bond is strongly activated and the nucleophile is a reactive one, in the second and in the third systems the nucleophiles are still active but the double bond is less reactive, and in the last system, an activated system, is attacked by a weak nucleophile. On this basis,  $\rho$  for the equilibrium reaction is similar to that expected for the nucleophilic attack only, as tri-*n*-butylphosphine is a much stronger nucleophile than water. If the  $\rho$  value for the equilibrium is the difference between the values for the forward and the reverse reactions ( $\rho = \rho_1 - \rho_{-1}$ ), then  $\rho_{-1}$  has to be close to zero, either positive or negative. Unfortunately, information on the effect of substituents on such a type of *E1cB* reaction is absent. However a low value for  $\rho_{-1}$  is in accord with the solvent effect discussed below, as it shows that the equilibrium constants are governed much more by the nucleophilic attack than by the reverse reaction.

The lower response of the *E1cB* reaction to changes in medium, compared to that of the nucleophilic attack, is shown by the appreciable decrease of the equilibrium constant with the decrease in the dielectric constant. A high increase was found in the rate coefficients of some nucleophilic attacks of this type when the dielectric constant of the solvent was increased<sup>8,27</sup> (this is not the case where specific solvation of the nucleophile is important<sup>29</sup>), while for an *E1cB* elimination (although of a different charge type) a small

<sup>26</sup> Kamlet and Glover, *J. Amer. Chem. Soc.*, 1956, **78**, 4556.

<sup>27</sup> Crowell, Helsley, Lutz, and Scott, *J. Amer. Chem. Soc.*, 1963, **85**, 443.

<sup>28</sup> Maioli and Modena, *Gazzetta*, 1959, **89**, 854; Modena and Todesco, *ibid.*, 1959, **89**, 866; Modena, Todesco, and Tonti, *ibid.*, 1959, **89**, 878.

<sup>29</sup> Feit, Sinnreich, and Zilkha, *J. Org. Chem.*, 1963, **28**, 3245.

decrease was found.<sup>25</sup> The high solvent effect is an additional argument for the zwitterionic nature of the adduct, as this type of effect can only be found for a strongly polar adduct which is stabilised in a medium having high dielectric constant. The effect of solvent on the formation of a three-membered ring must be smaller. For  $\pi$ -complexes, various types of behaviour (increase, decrease, or initial increase followed by decrease) were found in solvent mixtures having a range of dielectric constants comparable to ours, but in all cases the magnitude of the change in the equilibrium constant was much smaller.<sup>30</sup> The only other case where the effect of solvent on the equilibrium constant, of the type discussed here, was predicted was in the tricyanovinylolation of dialkylanilines by tricyanovinyl chloride.<sup>4</sup> In this case,  $k_{\text{exp}} = Kk_2$ , where  $k_2$  is the rate constant for the elimination of the chloride ion, and the slight increase of the rates with the increase in the dielectric constant was ascribed to the increase of the equilibrium constant which somewhat overcompensates the decrease in the rate of the elimination process. This explanation is in accord with the present results.

Differences exist between the reactions of the adducts with hydrogen chloride, where protonation of the  $\alpha$ -carbon atom gives the phosphonium salts  $\text{Ar}\cdot\text{CH}(\text{P}^+\text{R}_3)\cdot\text{CH}(\text{CN})_2 \text{X}^-$ , and with methyl iodide where "cleavage" of the adducts to methyl-tri-*n*-butylphosphonium iodide and the original arylmethylenemalononitriles was observed.<sup>7</sup> This results from the dissociation equilibria, as the reaction with protons is reversible and hence the weaker acid should be formed. As the  $pK$  of tri-*n*-butylphosphine is 8.43<sup>31</sup> and that of the malononitrile is 11.2,<sup>32</sup> the results show that the  $\text{Ar}\cdot\text{CH}(\text{P}^+\text{R}_3)$ -substituent is not sufficiently electron-attracting to outweigh this difference in the  $pK$ 's. On the other hand, the reaction with methyl iodide is governed by a kinetic factor, as quaternisations of tributylphosphine are quantitative,<sup>22</sup> and the cleavage of carbon-carbon bonds is difficult. As no phosphonium salt of the type  $\text{Ar}\cdot\text{CH}(\text{P}^+\text{R}_3)\cdot\text{CMe}(\text{CN})_2 \text{X}^-$  was found, it seems that the nucleophilicity of the carbanionic carbon atom is much lower than that of the tri-*n*-butylphosphine. By extrapolation of the equilibrium constants to 0° it was calculated that, at 0.25–0.26 mole  $\text{l}^{-1}$  concentration of the 4-chloro- and 4-nitro-adducts (*i.e.*, under the conditions in which the cleavage was observed), the concentrations of the free tri-*n*-butylphosphine at equilibrium are 2 and  $0.4 \times 10^{-4}$  mole  $\text{l}^{-1}$ , respectively, *i.e.*, 0.8 and 0.16% of that of the adducts. Hence, the difference in the nucleophilicity of tributylphosphine is at least 3–4 orders of magnitude higher than that of the carbanionic  $\alpha$ -carbon atom. This is a clear demonstration of the decrease of nucleophilicity of a highly nucleophilic carbanionic carbon by a neighbouring positive charge, which results in higher stability of the adducts. The possibility of direct cleavage of the adducts by nucleophilic attack of the positive end of the adduct on methyl iodide is much less probable.

## EXPERIMENTAL

*Materials.*—The arylmethylenemalononitriles were prepared by the method of Corson and Stoughton<sup>33</sup> and were crystallised to constant m. p. and spectrum. Tri-*n*-butylphosphine, b. p. 135°/27 mm. (lit.,<sup>34</sup> 136–137°/32.5 mm.), was prepared according to Davies and Jones<sup>35</sup> and was stored under nitrogen in the dark. The adducts were prepared by mixing equimolecular amounts of the two reactants in dioxan<sup>6</sup> and, after crystallisation from toluene, had the following m. p.s: 4-NO<sub>2</sub>, 116–118° (lit.,<sup>7</sup> 116–119°); 3-NO<sub>2</sub>, 145° (lit.,<sup>6</sup> 145°); 4-Cl, 123–125° (decomp.) (lit.,<sup>7</sup> 121–123°); unsubstituted, 124° (lit.,<sup>6</sup> 124°); 2-Cl, 127–129° (Found: C, 67.55; H, 8.2; Cl, 9.55; N, 6.95.  $\text{C}_{22}\text{H}_{32}\text{ClN}_2\text{P}$  requires C, 67.6; H, 8.25; Cl, 9.05; N, 7.15%) (yield 65%); 4-Me, 98–99° (decomp.) (Found: C, 74.6; H, 9.45; N, 7.95.  $\text{C}_{23}\text{H}_{33}\text{N}_2\text{P}$

<sup>30</sup> Ross and Labes, *J. Amer. Chem. Soc.*, 1955, **77**, 4916; Ross and Kuntz, *J. Amer. Chem. Soc.*, 1954, **76**, 300; Foster and Hammick, *J.*, 1954, 2685.

<sup>31</sup> Henderson and Steruli, *J. Amer. Chem. Soc.*, 1960, **82**, 5791.

<sup>32</sup> Pearson and Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

<sup>33</sup> Corson and Stoughton, *J. Amer. Chem. Soc.*, 1928, **50**, 2825.

<sup>34</sup> Mann and Purdie, *J.*, 1935, 549.

<sup>35</sup> Davies and Jones, *J.*, 1929, 33.



requires C, 74.55; H, 9.5; N, 7.55%) (yield 70%). Commercial absolute methanol was further dried according to Vogel.<sup>36</sup>

*Measurements.*—Stock solutions of tri-*n*-butylphosphine and the arylmethylenemalononitriles were prepared in methanol to which nitrogen was introduced before and after the preparation of the solutions. Dilutions to the required concentrations were also conducted in a nitrogen atmosphere. The solutions were transferred immediately to a silica absorption cell in a thermostat-controlled ( $\pm 0.1^\circ$ ) Beckman D.U. spectrophotometer; five readings or more of the optical density were taken during 10 min., and the average value was used for the calculations. The concentrations of the arylmethylenemalononitriles were  $1.3\text{--}3.7 \times 10^{-5}$  mole  $l^{-1}$ , and the tri-*n*-butylphosphine concentration was varied with various substrates in the region of  $6\text{--}200 \times 10^{-5}$  mole  $l^{-1}$ . The measurements were conducted at the  $\lambda_{\text{max}}$  of the arylmethylenemalononitriles.

*Side-reactions.*—The solutions of the adducts, especially if concentrated become yellow slowly as a result of side reactions. These reactions could be followed in chloroform, but in methanol they are slower than the establishment of constant optical density values at the  $\lambda_{\text{max}}$  of the arylmethylenemalononitrile. Hence, the side-reaction has no effect on the equilibrium constants and it was not studied further.

*Spectra.*—The relevant spectral data ( $\lambda_{\text{max}}$  in  $m\mu$ ;  $\epsilon$  in parentheses) for the measurements in methanol for the arylmethylenemalononitriles are: 4-NO<sub>2</sub> 306 (17,500), 3-NO<sub>2</sub> 290 (16,800), 2-Cl 298 (15,200), 4-Cl 315 (25,100), H 305 (22,700), 4-Me 320 (25,300), 4-OMe 346 (30,800).

Infrared spectra were measured in a Perkin-Elmer 137 spectrophotometer.

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DEPARTMENT OF ORGANIC CHEMISTRY,  
THE HEBREW UNIVERSITY, JERUSALEM, ISRAEL.

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<sup>36</sup> Vogel, "A Text-book of Practical Organic Chemistry," 3rd edn Longmans London, 1956, p. 169.

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