creasing the effective size of the cation by specific solvation inhibits the tendency .to form micelles. In a spherical *inverse* micelle of this type, it is obvious that the cations must be small relative to the anions to permit them to be encapsulated in a lipophilic anionic shell. It is interesting that, of many benzene-soluble electrolytes studied by Kraus,[13] only those with a large lipophilic ion and a relatively small counterion showed a particular tendency to agglomerate to form aggregates of high association number.

Finally, the results of the present work provide a clear answer to the problem posed in the introductory paragraph. There is no quantitative correlation between the alkylation rate and the disperisty of the sodium enolate. Sedimentation studies were conducted at salt concentrations equal to or higher than the rate measurements.[1,2] Yet at additive concentrations providing 100% monomer at these salt concentrations no rate maxima are observed.[14] Indeed, no significant discontinuities in log–log plots of rate *vs.* solvent composition are observable for the three additives studied in the present work. From these observations it can be concluded that the solvated monomeric ion pair that is in equilibrium with the micellar system is a kinetically insignificant species compared to some others that must be present in these solvent systems.

Registry No.—Sodio diethyl *n*-butylmalonate, 22600-93-7.

[13] C. A. Kraus, *J. Chem. Educ.*, **35**, 330 (1958); *J. Phys. Chem.*, **60**, 129 (1956).

[14] See Figure 1 of ref 2, or Figure 1 of ref 3.

Specific Solvent Effects. VII. Ion-Pair Processes in the Alkylation of Alkali Enolates

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The observed lack of a common-ion rate depression for the alkylation of sodio diethyl *n*-butylmalonate in DMF shows that at the substrate concentrations used ($\sim 10^{-1}$ *M*) this reaction is an ion-pair process. Proton magnetic resonance studies have been added to previous uv studies to confirm the strong tendency of malonate ions to form tight ion pairs with alkali cations, even in DMF. The kinetic and sedimentation properties of this system in binary solvent mixtures can be reconciled by postulating that, in THF, DME, and DMF (and their mixtures with benzene or cyclohexane), the reactive species is an ion pair more highly solvated than the one shown to be in equilibrium with the micellar system (*cf.* preceding paper). However, the kinetic behavior in the presence of the powerful alkali cation solvator, dicyclohexyl-18-crown-6 polyether, indicates that, in this case, the monosolvated ion pair is the reactive species.

In the preceding study[1] it was found that, in certain mixtures of benzene with three aprotic solvents (S = THF, DME, or DMF), sodio diethyl *n*-butylmalonate (A^-Na^+) consists of at least three species in equilibrium.

$$\underset{\substack{n\,\sim\,50\\ \mathbf{1}}}{(A^-Na^+)_n} \rightleftharpoons \underset{\mathbf{2}}{nA^-Na^+} \overset{nS}{\rightleftharpoons} \underset{\mathbf{3}}{nA^-Na^+\cdot S}$$

In benzene the micelle **1** is the predominant form. In the pure solvent, S, the solvated ion pair **3** and presumably other monomeric forms derived from it are the only detectable species. Results also indicated that specific *cation* solvation by the additive accounts for the equilibrium shift from **1** to **3**. Because of the absence of a quantitative correlation between the increase in concentration of **3** and the previously measured[2] acceleration in the rate of alkylation of A^-Na^+ under identical conditions of solvent variation, the relative kinetic insignificance of **3** was a necessary conclusion. Therefore, other species derivable from **3** must be the reactive forms accounting for the observed rate acceleration. Only two general possibilities remain: more effectively solvated (and more reactive) ion pairs,[3] and "free" anions (A^-).

Previous work[6] demonstrated the lack of a correlation between dielectric constant (and dipole moment) of the additive and its effect on the alkylation rate. Although this would tend to exclude the "free" anion, A^-, as a kinetically important species, a more direct experimental test of this conclusion is included in the present work: a probe of the effect of added salts (both Na^+ and Li^+) on the rate of alkylation of A^-Na^+ in DMF. Because these experiments were conducted at fairly high salt concentrations, their validity was tested using identical conditions in the alkylation of sodio-3-phenyl-2-benzofuranone. Ultraviolet spectral studies[7] have shown that the capacity of this enolate to form ion pairs in dilute DMF solutions is distinctly inferior to that of enolates structurally similar to malonate.

To show that this difference in ion pairing ability extends to the more concentrated solutions used in the rate studies, the effect of dilution on the nmr spectra of the lithium and sodium salts of both diethyl malonate and 3-phenyl-2-benzofuranone were compared in the present work. Also, to support the validity of this method, alkali salts of two phenolate ions, differing widely in ion pairing capacity, were compared.

Finally, to examine further the question of more effectively solvated ion pairs as the kinetically important species in the sodiomalonate alkylation, four more

[1] Part VI: G. H. Barlow and H. E. Zaugg, *J. Org. Chem.*, **37**, 2246 (1972).

[2] H. E. Zaugg, *J. Amer. Chem. Soc.*, **83**, 837 (1961).

[3] The concept of multiple ion pairs has become firmly grounded in the chemical literature relating to the behavior both of carbonium ions[4] and of carbanions.[5]

[4] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 167–171.

[5] T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307, 318 (1966); M. Szwarc, *Science*, **170** (3953), 23 (1970).

[6] H. E. Zaugg, *J. Amer. Chem. Soc.*, **82**, 2903 (1960).

[7] H. E. Zaugg and A. D. Schaefer, *ibid.*, **87**, 1857 (1965).

binary solvent systems were studied using the rate of the standard alkylation as a probe. Of special interest was the behavior of the powerful sodium ion solvator, dicyclohexyl-18-crown-6 ether.[8]

Experimental Section

Materials.—Benzene,[2] *n*-butyl bromide,[2] cyclohexane,[7] diethyl *n*-butylamalonate,[2] and dimethylformamide[7] were of the purity previously specified. Reagent grade 1,2-dimethoxyethane (DME) was stored in a column (3 × 45 cm) of basic alumina (activity grade I) and drawn off just before use. Sodium hydride was in the form of a 50–60% dispersion in mineral oil, and lithium hydride was in the powdered, nondispersed form. 3-Phenyl-2-benzofuranone[9] was recrystallized to a constant melting point (114–116°) from 2-butanone. Dicyclohexyl-18-crown-6 ether was prepared and purified by the method of Pedersen[8] and was used as a mixture of geometric isomers. The following commercially available compounds were purified by distillation or recrystallization: *p*-cresol, bp 56° (1 mm); *p*-nitrophenol, mp 114–114.5° (sublimed); and diethyl malonate, $n^{25}\text{D}$ 1.4134, 99,7% (vpc). Sodium *p*-nitrophenoxide was prepared by a method reported previously.[7]

Lithio Diethyl Malonate.—To a stirred, cooled solution of lithium ethoxide (from 0.72 g, 0.09 mol of LiH) in 100 ml of absolute ethanol, diethyl malonate (16 g, 0.1 mol) was added dropwise. After warming to room temperature, the solution was filtered from a small amount of insoluble material and concentrated to dryness under reduced pressure (water pump). The residual, white solid was slurried in dry ether, collected at the filter, and washed with dry ether. Drying at 80° under reduced pressure gave the pure salt.

Anal. Calcd for $C_7H_{11}LiO_4$: C, 50.61; H, 6.68. Found: C, 50.37; H, 6.72.

Kinetics.—All tabulated second-order rate constants were determined under pseudo-first-order conditions using a refinement of the method previously described.[2,10] Stock solutions of the sodio derivative in the appropriate solvent (cyclohexane, benzene, DME, or DMF) were prepared by magnetically stirring, in a nitrogen atmosphere, the acid (diethyl *n*-butylmalonate or 3-phenyl-2-benzofuranone) with an excess of sodium hydride in a cylindrical reaction vessel (45–50-ml capacity) made to fit the cups (3 cm diameter × 10 cm deep) of a standard centrifuge. The supernatant solution was decanted from the centrifuged excess hydride, in an atmosphere of nitrogen, through glass wool into a 50-ml conical storage vessel using the apparatus and procedure previously described for the handling and storage of a Grignard reagent[11] (note especially Figure 4 of ref 11). Stock solution was transferred from the conical storage vessel to the reaction vessel using a Hamilton gas-tight syringe fitted with a 23-gauge needle. The reaction vessel was a simple flat-bottomed cylinder (*ca.* 15-ml capacity) with a single opening (5–6-mm i.d.) at the top suitable for closure with a rubber septum (sleeve stopple). The only critical dimension was a less than 2-in. distance from the top of the septum to the bottom of the vessel. All reactions were carried out so that the combined volumes of reactants and diluents totaled 10 ml. At appropriate time intervals, 1-ml aliquots were removed using a Hamilton gas-tight syringe equipped with a 2-in. 23-gauge needle. These aliquots were quenched in an excess of standard hydrochloric acid and back-titrated with standard sodium hydroxide solution. The concentration of the original stock solution was similarly measured using three 2-ml aliquots. Nearly all reactions were carried well past 50% of completion and many of the faster ones to the 75–90% range. The data for each run were subjected to statistical analysis for determination of the slope and standard deviation from linearity of the plot of log *c vs.* time, where *c* = concentration of sodio derivative.

To test the reproducibility of results by the new procedure, the rates of alkylation (n-C_4H_9Br) at 25° of sodio-*n*-butylmalonic ester at two concentrations of dimethoxyethane (DME) in benzene were determined and compared with corresponding rates determined by the old procedure. In 1.44 *M* DME three separate runs gave 10^5k_2 (M^{-1} sec^{-1}) = 4.51, 4.59, and 5.02, compared to 4.73–4.74 by the old procedure (see Figure 1 of ref 2). In 1.92 *M* DME three runs gave 10^5k_2 = 6.81, 7.07, and 7.18 compared to 6.34 by the old method.

Also, to check the bimolecularity of the rate law, four determinations (at 25°) were carried out under second-order conditions (equimolar concentrations of the two reactants) in 1.905 to 1.928 *M* concentrations of DME. Although reproducibility was poorer, the range of k_2's (5.33–6.68 × 10^{-5}) so measured encompassed the range (6.31–6.39 × 10^{-5}) obtained under pseudo-first-order conditions (ref 2, Figure 1).

Nmr Measurements.—Proton magnetic resonance spectra were obtained using a Varian Model A-60 spectrometer. The temperature of all measurements was 33 ± 2°. Tetramethylsilane in solution was the reference standard.

DMF solutions of the salts were prepared by treating solutions of the organic acids of appropriate concentration with excess amounts of sodium or lithium hydride using a glove-box procedure previously described.[7] After completion of the reaction, the clear (filtered or supernatant) solution was transferred by pipette to an nmr tube, stoppered with an air-tight closure, and transferred immediately from the glove-box to the spectrometer. As independent checks on the method, it was found that solutions prepared by dissolving pure solid sodium *p*-nitrophenoxide and solid lithio diethyl malonate in DMF gave spectra identical with those obtained using comparable solutions prepared by the foregoing procedure.

Results

Kinetics.—The effects of added salts on the alkylation rates in DMF of the two sodio derivatives are given in Table I. These data reveal the absence of a significant common-ion effect on the alkylation of the sodio malonate (A) in this solvent. A marked cation effect, however, is evidenced by the 7–8-fold decrease in rate observed in the presence of 0.1 *M* lithium perchlorate.

TABLE I

SALT EFFECTS ON THE RATES OF ALKYLATION AT 25° IN DMF OF DIETHYL SODIO-*n*-BUTYLMALONATE (A) AND OF SODIO-3-PHENYL-2-BENZOFURANONE (B) WITH *n*-BUTYL BROMIDE

A			B		
Salt	Concn, *M*	10^5k_2, M^{-1} sec^{-1}	Salt	Concn, *M*	10^5k_2, M^{-1} sec^{-1}
None	0	323 ± 6	None	0	33.4 ± 0.4
		345 ± 7			34.6 ± 1.1
		339 ± 5[a]	$NaClO_4$	0.103	24.9 ± 0.3
$NaClO_4$	0.101	338 ± 3			25.4 ± 0.4
		332 ± 3			25.7 ± 0.2
$LiClO_4$	0.100	35.0 ± 0.8			
	0.101	46.2 ± 0.5	$LiClO_4$	0.103	19.6 ± 0.3
					21.2 ± 1.2

[a] From ref 2.

In contrast, a significant common-ion rate depression is observable for sodio-3-phenyl-2-benzofuranone (B) in DMF. A cation effect is detectable as well for B, but not to the extent observed for A.[12] It should be noted that B, like A, alkylates exclusively at carbon. Hence, no ambident alkylations are involved here.

Four binary solvent effects on the rates of alkylation of sodio *n*-butylmalonate were studied in the present work. They are summarized in Table II and plotted

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(8) C. J. Pedersen, *J. Amer. Chem. Soc.*, **89**, 2495, 7017 (1967); **92**, 386 (1970).

(9) A. Bistrzycki and J. Flatau, *Ber.*, **28**, 989 (1895).

(10) H. E. Zaugg, B. W. Horrom, and S. Borgwardt, *J. Amer. Chem. Soc.*, **82**, 2895 (1960).

(11) H. E. Zaugg and W. M. Lauer, *Anal. Chem.*, **20**, 1022 (1948).

(12) Similar salt effects were studied in DME solution. Marked cation (Li^+) effects were observed for both A and B, but no significant common-ion rate depression was detectable for either salt. Although DME clearly does not prevent cation exchange, its relatively low dielectric constant presents the possibility that, unlike the situation in DMF (*cf.* Table IB), the absence of a common-ion rate depression for B is caused by insufficient dissociation of $NaClO_4$.

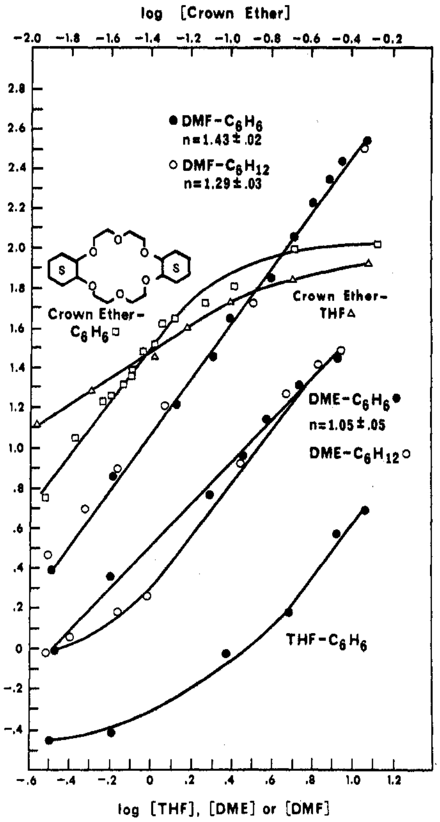

Figure 1.—Log–log plots of rates of alkylation at 25° of diethyl sodio-*n*-butylmalonate with *n*-butyl bromide in seven solvent systems. (Except for the crown ether solutions, the right ends of the lines represent molarities of neat additives diluted only by the reactants.)

TABLE II

RATES OF ALKYLATION AT 25° OF DIETHYL SODIO-*n*-BUTYLMALONATE WITH *n*-BUTYL BROMIDE IN FOUR BINARY SOLVENT SYSTEMS

Concn, M	$10^5 k_2$, M^{-1} sec^{-1}	Concn, M	$10^5 k_2$, M^{-1} sec^{-1}
A. Dicyclohexyl-18-crown-6 Ether in Benzene		B. DME in Cyclohexane	
0.0116	5.72 ± 0.17	0.301	0.93 ± 0.02
0.0164	11.2 ± 0.8	0.388	1.15 ± 0.01
0.0228	17.0 ± 0.8	0.684	1.48 ± 0.02
0.0249	18.3 ± 1.3	0.954	1.84 ± 0.02
0.0290	21.1 ± 1.1	2.820	9.11 ± 0.22
0.0305	23.0 ± 1.2	4.720	18.7 ± 0.6
0.0313	23.3 ± 2.0	6.710	25.5 ± 0.1
0.0358	30.6 ± 1.2	C. DMF in Cyclohexane	
0.0406	32.7 ± 0.8	0.308	2.91 ± 0.06
0.0447	42.1 ± 1.7	0.464	4.97 ± 0.09
0.0509	43.2 ± 0.5	0.681	7.69 ± 0.13
0.0741	51.3 ± 1.2	1.194	15.96 ± 0.55
0.1015	63.6 ± 0.5	3.293	53.1 ± 0.6
0.202	95.4 ± 1.6	D. Dicyclohexyl-18-crown-6 Ether in THF	
0.527	138.1 ± 2.4		
		0.01	13.5 ± 0.5
		0.02	19.7 ± 0.4
		0.03	24.5 ± 0.3
		0.04	29.7 ± 0.5
		0.06	41.1 ± 0.6
		0.10	55.3 ± 0.5
		0.20	69.2 ± 0.9
		0.50	84.7 ± 1.2

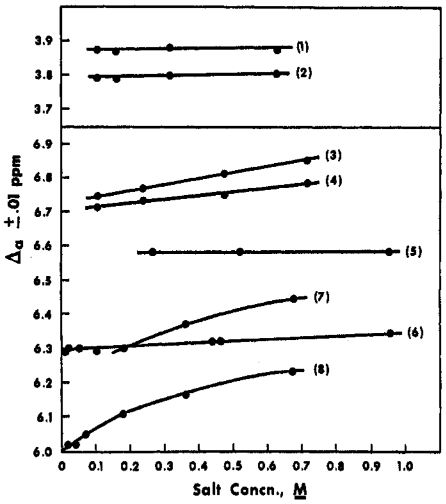

Figure 2.—Effect of concentration on the chemical shifts (Δ*a*) in DMF of protons in the anions of alkali salts: α-H of lithio (1) and sodio (2) diethyl malonate; most intensea romatic resonance peak of lithio- (3) and sodio- (4) 3-phenyl-2-benzofuranone (not a true chemical shift); ortho H of lithium (5) and sodium (6) *p*-cresolate; ortho H of lithium (7) and sodium (8) *p*-nitrophenolate.

in Figure 1 along with three others from previous work.[2] Of interest is the observation that the kinetic order of participation (*n*)[13] of DMF is roughly the same in both benzene and cyclohexane mixtures, and is virtually constant (*i.e.*, gives a linear log–log plot) over the whole range of solvent compositions studied. Although DME exhibits a constant unit participation order over the whole range of mixtures with benzene, in cyclohexane there is a slight deviation from this line.

Especially noteworthy is the high activity exhibited by the crown ether. In benzene solutions only 0.036 *M* in crown ether the alkylation rate is already equal to that observed in neat (8.70 *M*) DME. Significantly, however, this high activity does not increase indefinitely. Although the participation order of the crown ether at low concentrations (0.01–0.05 *M*) is constant and roughly equal to that of DMF (1.3–1.4), it begins to decline at 0.05 *M* and approaches zero at 0.5 *M* concentration (*i.e.*, no further rate increase with increased concentration of additive). A similar approach to a slightly lower rate maximum is also characteristic of the crown ether in THF.[14] Initial participation orders in this system are necessarily lower than in crown ether–benzene because the base rate in the latter (*i.e.*, in neat benzene) is much lower than in the former (*i.e.*, in neat THF).[15]

Nmr Measurements.—Figure 2 shows the effect of concentration change on the chemical shifts of selected protons in four pairs of alkali salts (Li^+ and Na^+) including two enolates (1–4) and two phenolates (5–8). In the range of concentrations studied (0.01–1.0 *M*), the presence of ion pairs in all four systems

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(13) Given by the slope of the log–log plots in Figure 1.

(14) Because rate measurements at higher concentrations of crown ether in benzene were much less reproducible than in THF, the difference between the two rate maxima may not be significant. The maximum observed in THF is the more reliable one.

(15) It is noteworthy that two diazapolyoxamacrobicyclic compounds[16] (one diamine and one diamide), kindly supplied by Professor J. M. Lehn, produced marked accelerations in the alkylation nearly equal to the effect of crown ether. The powerful alkali cation solvating properties of these polydentate ligands also has been amply demonstrated.[17]

(16) J. M. Lehn, J. P. Sauvage, and B. Dietrich, *Tetrahedron Lett.*, 2885, 2889 (1969); *J. Amer. Chem. Soc.*, **92**, 2916 (1970).

(17) J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **9**, 175 (1970); B. Metz, D. Moras, and R. Weiss, *Chem. Commun.*, 217 (1970).

is clearly shown by the uniformly greater deshielding effect of Li^+ on the selected protons.

The influence of concentration change, however, is quite different for the two pairs of enolate salts. A barely significant effect is evident for the two mlaonate salts (1, 2),[18] but for the benzofuranone salts (3, 4) dilution results in a diminution of the cationic deshielding effect, which is more marked for the lithium than for the sodium salt. This convergent tendency of lines 3 and 4 suggests that, at sufficiently low concentrations, the cation effect should disappear. Previous uv-spectral examination of DMF solutions of 3 and 4 has shown that at concentrations of the order of 10^{-4} M the cation effect has indeed vanished.[7]

The insensitivity of the electronic transition energy of malonate anions to changes in environmental charge prevented experimental examination of ion pairing in this system at low concentrations.[7] However, in the closely related β-diketone system (*e.g.*, 2-4-pentanedione) the presence of ion pairs could be seen[7] even at 10^{-4} M concentrations in DMF.[19]

Similar contrasting behavior is revealed in the two phenolate systems (5–8). Both salts of *p*-cresol (5, 6) exhibit the insensitivity to dilution characteristic of tight ion pairs, while salts of the stronger acid, *p*-nitrophenol (7, 8), show a greater tendency to dissociate.[20]

Consistent with these observations are the previous findings[7] that at $\sim 10^{-4}$ M concentrations in DMF, ion pairs of 5 and 6 are still clearly visible (uv), but are no longer detectable for 7 and 8.

Discussion

The absence of a common-ion rate depression for the alkylation of sodio diethyl *n*-butylmalonate in DMF shows that this reaction is essentially an ion-pair process. The strong tendency of malonate ions to form tight ion pairs even in DMF, as indicated by the nmr experiments, is thus corroborated by this kinetic behavior. This is not to imply that whatever "free" anions are present in DMF[19] are unreactive. At the concentrations of sodiomalonate used in the present study (purposely rather high to approximate preparative conditions), the concentration of "free" anions is clearly so low compared to that of reactive ion pairs that the latter furnish the only *detectable* kinetic pathway. Furthermore, because all other solvent systems used in this work represent media of lower dielectric constant than DMF, it is safe to conclude that all of the sodiomalonate alkylations studied represent nearly pure ion-pair processes.

What, then, is the nature of the reactive ion pairs? The sedimentation studies[1] have already ruled out the initially solvated ion pair **3**, at least for the three additives THF, DME, and DMF. However, the kinetic observations for these additives (Table II and Figure 1) are explainable simply in terms of more highly solvated ion pairs **4** as the reactive species.[21] It is reasonable to expect that the more donor sites that are accommodated by the cation, the more its charge will tend to become neutralized with a consequent increase in the nucleophilicity of the associated anion.

$$\underset{\mathbf{3}}{A^-Na^+\cdot S} \overset{S}{\rightleftharpoons} \underset{\mathbf{4}}{A^-Na^+\cdot S_2}$$

Thus, the formation of **4**, like **3**, involves specific solvation of the cation. In accord with this view is the observation that the rate accelerations produced by either DMF or DME are only slightly affected by a change from benzene to cyclohexane. Also, the order of effectiveness of the three additives, DMF > DME > THF, is the same as that for their efficiency in specifically solvating alkali cations. Indeed, relative to the other two, the monodentate ether, THF, is such a poor specific cation solvator that high concentrations are required to produce appreciable amounts of **4**, thus accounting for the upward curvature of its log-log plot (Figure 1). However, even the best of the three additives (DMF) is still not active enough to shift the equilibrium, **3** ⇄ **4**, completely to the right, since no rate maximum is observed even in neat additive.

The polydentate donor, crown ether, however, presents a different picture. Its powerful cation solvating ability is clearly reflected in its extraordinary capacity to accelerate the alkylation even at concentrations equivalent to that of substrate. Most significant, however, is its attainment of a rate maximum in both benzene and THF.[22] Combined with its high specific activity, this observation suggests that this multidentate ligand possesses enough donor sites in one molecule to provide maximum solvation (*i.e.*, a further increase in crown ether concentration results in no increase in cation solvation).[23] In other words, the monosolvated ion pair **3** is the reactive species in the crown ether catalyzed reactions.[24]

Finally, it is tempting to suggest that the two ion pairs **3** and **4** may be, respectively, solvated contact ion pair and solvent-separated ion pair. However, recent spectral studies of alkali-metal salts of 1,3-diphenylbutene-1 have provided evidence for the existence, in weak solvating agents, of two distinct contact ion pairs in different solvation states.[25] Thus, **3** and **4** both could be contact ion pairs, with **4** having a larger interionic distance, but not large enough to accommodate a solvent molecule between the ions.

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(18) The unsubstituted diethyl malonate rather than the *n*-butyl derivative was chosen for this study so that the remaining α hydrogen in the corresponding salt, being directly attached to the delocalized system, would be most sensitive to changes in electron density near the anion. Thus, for example, the cation effect on the α H in going from 1 to 2 is −0.08 ppm. The same effect on the $-OCH_2-$ group is −0.05 ppm, and on the C methyls only −0.02 ppm.

(19) Free ions are, of course, present in DMF solutions of sodiomalonates. At 25°, the molar conductance of diethyl sodio-*n*-butylmalonate (0.01 M in DMF) is 5.36. That of sodio-3-phenyl-2-benzofuranone, however, is higher by nearly one order ($\Lambda_{0.1\,M}^{25°} = 51.7$). In DME the conductance of both salts is still detectable, but in benzene neither salt conducts.

(20) Compare R. L. Buckson and S. G. Smith, *J. Phys. Chem.*, **68**, 1875 (1964).

(21) There is no experimental evidence to suggest that **3** is a discrete monosolvate and **4** is a pure disolvate. Digits are used merely to simplify the discussion.

(22) A. M. Grotens, J. Smid, and E. de Boer, *Chem. Commun.*, 759 (1971), using nmr line width studies of ^{23}Na, have found that crown ethers readily replace THF in the cationic solvation shell of $Na^+B^-(C_6H_5)_4$ in THF solution.

(23) Although the larger alkali cations are able to accommodate more than one molecule of crown ether, Pederson[8] found that crystalline complexes of sodium salts generally consist of a 1:1 ratio of polyether to salt.

(24) This means that, for crown ether, there should be a quantitative correlation between the rate acceleration and sedimentation behavior.[1] Unfortunately, attempted determination of the micelle–monomer ratio (*i.e.*, **1**:**3**) in benzene–crown ether mixtures gave results that were too poorly reproducible to be useful.

(25) J. W. Burley and R. N. Young, *J. Chem. Soc. B*, 1018 (1971).

Registry No.—Lithio diethyl malonate, 34727-00-9; diethyl sodio-*n*-butylmalonate, 22600-93-7; sodio-3-phenyl-2-benzofuranone, 34727-02-1; *n*-butyl bromide, 109-65-9; sodio diethyl malonate, 18424-75-4; lithio-3-phenyl-2-benzofuranone, 34727-03-2; lithium *p*-cresolate, 1121-69-3; sodium *p*-cresolate, 1121-70-6; lithium *p*-nitrophenolate, 1124-32-9; sodium *p*-nitrophenolate, 824-78-2.

Specific Solvent Effects. VIII. The Solvation of Sodiomalonate Ion Pairs by the Tertiary Amide Group

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The rate of alkylation of sodio *n*-butylmalonate with *n*-butyl bromide has been used to probe the mechanism of ion-pair solvation by the tertiary amide function. Changes in catalytic effect produced by varying the distance between two amide groups in the same molecule have been measured. Mutual assistance of the two groups is observed for separations of 4 and 5 carbon atoms (adipamide and pimelamide), but smaller separations (*i.e.*, glutaramide, succinamide, and oxamide) result in mutual hindrance of ion-pair solvation. These findings are consistent with the view that the tertiary amide function solvates the sodium ion by a π-donor mechanism and that, when two such groups are a proper distance apart, intramolecular disolvation of the cation can occur by such a mechanism.

The distinctly superior catalytic action of 1,2-dimethoxyethane (DME) over tetrahydrofuran (THF) and certain geometrically constrained diethers (*e.g.*, 1,3-dioxolane and 1,4-dioxane) in accelerating the alkylation of sodio diethyl *n*-butylmalonate in benzene solution was interpreted[1] in terms of selective cation solvation resulting from the bidentate donor character of DME. This view was reinforced by the observation that the hexadentate donor, dicyclohexyl-18-crown-6 polyether, is vastly more effective than DME.[2] Also explained in terms of selective cation solvation was the marked acceleration caused by the addition of small amounts of N,N-disubstituted amides and certain *P*-, *S*-, and *N*-oxides.[1,3] Evidence indicated[3] that these substances act as π donors for the cation in the same way that the polyethers serve as n donors.

Work described in the preceding papers[2,4] strongly suggested that the alkylation of sodio diethyl *n*-butylmalonate in benzene–dimethylformamide (DMF) media is a process involving an ion-pair species containing a sodium ion that is at least disolvated. This, together with the observed increased effectiveness of the multidentate ethers, leads to the prediction that certain diamides structurally permitted to disolvate the cation by an intramolecular π-donor mechanism should accelerate the alkylation more effectively than either monamides or diamides unable to undergo bidentate π interaction with the cation. To check this prediction, the effect of a series of diamides on the alkylation rate is examined in the present work. The distance between the two amide functions is varied systematically, and rate comparisons are made with the monoamide, *N*,*N*-dimethylacetamide, serving as a standard.

Because these amides are more polar than the ethers studied previously,[1,2] the dielectric constants of several benzene–amide mixtures were measured to check any possible correlation of this bulk solvent effect with corresponding rate accelerations.

Experimental Section

Materials.—Hexamethylphosphoramide (Monsanto) was purified by distillation, bp 121° (19 mm), $n^{25}\text{D}$ 1.4570. The *N*,*N*,*N*^{1},*N*^{1}-tetramethyldiamides of the following acids were prepared according to published procedures: oxalic,[5] mp 78–80°; dimethylmalonic,[6] mp 79–80.5; succinic,[5] mp 83.5–84.5°; glutaric,[7] mp 45–47°; adipic,[5] mp 82–83°; pimelic,[5] bp 162–166° (0.7 mm), $n^{25}\text{D}$ 1.4828; phthalic,[8,9] mp 121–123°; isophthalic,[9] mp 135–136°. Specifications for the other reagents used in this work are listed in the preceding paper.

Kinetics.—Rate measurements were conducted as described in the preceding paper.[2] Log–log plots of additive concentration *vs.* rate were statistically analyzed to determine the slopes (*i.e.*, kinetic orders of participation) of the lines and their standard deviations from linearity.

Dielectric Measurements.—Dielectric constants were measured at 25° and at a frequency of 2 MHz, using a Model 3A dielectric constant meter of the Yellow Springs Instrument Co., Inc., Yellow Springs, Ohio. Benzene ($\epsilon_{25°}$ 2.3) was used as a standard.

Results

Figure 1 shows the log–log plots of the alkylation rate *vs.* amide group concentration in benzene for six homologous diamides determined in the present work, and for acetamide, which was previously measured.[10] For the diamides, amide group concentrations, [CON(CH_3)$_2$], are equal to twice the molar concentrations, and for acetamide the two factors are obviously equal. From the equation (Figure 1), the empirical kinetic order of additive participation, *n*, is given by the slope of the log–log plot. The numerical *n* values also are listed in Figure 1.

The seven amides of Figure 1 can be divided into three groups of participation orders: n = 0.8, 1.1, and 1.4. These results are consistent with previous measurements carried out in this concentration range.[1,10] It was found that, among a number of miscellaneous addi-

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