order. The ease of second rearrangement (IIb → III) is $X = O \sim NH > CH_2$ and third rearrangements (III → IV) follow the order $X = O > NH > CH_2$. Carbonylation proceeds by a rate-limiting first rearrangement after which two more rearrangements can occur readily. The first rearrangement for (I, $X = CH_2$) occurs very readily and protonation or alkylation of $[R_3BCCH]^-$ is probably rate determining in the alkynylborate processes. The cyanoborate process could proceed via several possible rate-determining steps and is probably more dependent on reaction conditions than carbonylation or alkynylborate processes.

Acknowledgment. This work was supported by grants from the Science Research Council and the Royal Society. Dr. P. Mallinson (University of London, Computer Centre) and the late P. E. Corles (Swansea) carried out the transfer of the ULCC version of the GAUSSIAN 70 program from London (ULCC) to Manchester (UMRCC). The MNDO and 6-31G* calculations were performed at the Universität Erlangen-Nürnberg, using facilities generously provided by Professor P. v. R. Schleyer. Helpful discussions with J. Collins, K. Krogh-Jespersen and P. v. R. Schleyer (Erlangen), and A. Pelter and K. Smith (Swansea) are gratefully acknowledged.

Appendix

During the course of this work heats of formation of small boron-containing molecules were calculated (Table VI). A few large discrepancies between the various methods are observed, partly because the 6-31G* results require a vibrational correction.[6a,6c] Clearly absolute values are more difficult to calculate than the energy differences (rotations and isomerizations) discussed above.

Registry No. I (R = H; X = O), 13205-44-2; I (R = H; X = NH), 60048-47-7; I (R = H; X = CH_2), 51220-37-2; II (R = H; X = O), 32375-83-0; II (R = H; X = NH), 5844-50-8; III (R = H; X = O), 79723-20-9; III (R = H; X = NH), 71720-68-8; III (R = H; X = CH_2), 39517-80-1; IV (R = H; X = O), 79723-21-0; IV (R = H; X = NH), 79723-22-1; IV (R = H; X = CH_2), 79723-23-2; HOBO, 13460-50-9; BH_3CNCH_3, 79723-24-3; BH_2BH_2, 18099-45-1; BH_2NH_2, 14720-35-5; BH_2OH, 35825-58-2; BH_2CHCH_2, 5856-70-2; BH_3, 13283-31-3; CH_3BH_2, 12538-96-4; CH_2BH, 56125-75-8; NHBH, 15119-97-8; OBH, 20611-59-0; $(CH_3)_3B$, 593-90-8; B_2H_6, 19287-45-7.

Hydrogen Bonded Complexes. 3. Some Anomalous Acid Salts of Dibasic Acids[1]

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A large number of salts of dibasic acids, H_2Y, with amines and quaternary ammonium hydroxides are reported. These include the normal neutral salt (R_2Y), the normal acid salt (RHY), and two series of anomalous salts (RH_3Y_2 and $R_2H_4Y_3$), in all of which R^+ represents the cation formed from the neutralizing base. Infrared spectroscopy has been used to draw some inferences about the structures of the anomalous salts.

Our continuing interest in conducting systems for electrolytic capacitors has occasioned the preparation of many substituted ammonium and quaternary ammonium salts of dibasic acids. The dibasic acids form two series of normal salts, the neutral or disalts (R_2Y) and the acid or monosalts (RHY), in both of which H_2Y represents the dibasic acid and R^+ the cation formed from the neutralizing base. In addition, the dibasic acids form two types of anomalous salts, RH_3Y_2 and $R_2H_4Y_3$, but only with selected neutralizing cations. The neutral salts are readily preparable when both dissociation constants of the acid are of sufficient magnitude (e.g., as with fumaric acid). The structures of the salts that result present no problems and are of little interest.

The acid salts are the most readily available and most easily prepared. Some interest is attached to the structures of these salts because of the structure of the hydrogen maleate anion, in potassium hydrogen maleate for example. For this anion there is evidence from infrared spectroscopy,[2] from a two-dimensional neutron-diffraction study,[3] and from a three-dimensional structure analysis with X-rays[4] to indicate that the two carboxyl groups of the monoionized anion are crystallographically equivalent and linked by a "very short" and probably symmetrical hydrogen bond. Similar, symmetrical hydrogen bonds also occur in some acid salts, RHX_2, of monobasic acids, HX.[5]

Of present interest are the anomalous acid salts of dibasic acids.[5] In almost every case we have obtained the anomalous salt in a serendipitous manner while trying to prepare a normal salt. Moreover, we have encountered two types of anomalous salts, one with two dibasic acid molecules per cation and the other with three dibasic acids per two cations. It is our present purpose to record the properties of the salts that we have prepared and to discuss such structural considerations as are permitted by infrared spectroscopy.

Results and Discussion

As already noted the neutral disalts of dibasic acids are of minimal interest. The few that were prepared and analyzed to verify the stoichiometry are given in Table I.

The acid monosalts of dibasic acids are useful as solutes in organic electrolyte systems, and we have had occasion to prepare a large number of them. In fact, our first encounters of anomalous, acid salts of dibasic acids resulted from attempts to prepare the normal monosalts. In Table

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(1) For the previous paper in this series, see J. E. Barry, N. E. Cipollini, M. Finkelstein, and S. D. Ross, *Tetrahedron*, **37**, 1669 (1981).

(2) H. M. E. Cardwell, J. D. Dunitz, and L. E. Orgel, *J. Chem. Soc.*, 3740 (1953).

(3) S. W. Peterson and H. A. Levy, *J. Chem. Phys.*, **29**, 948 (1958).

(4) S. F. Darlow and W. Cochran, *Acta Crystallogr.*, 14, 1250 (1961).

(5) For an excellent review article on acid salts of both monocarboxylic acids and dicarboxylic acids and a discussion of the anomalous acid salts, see J. C. Speakman, *Struct. Bonding (Berlin)* 12, 141 (1972).

0022-3263/82/1947-0064$01.25/0

Table I. Disalts of Dibasic Acids, R_2Y

				analysis, %					
				calcd			found		
acid	cation	crystallizn solv	mp, °C	C	H	N	C	H	N
fumaric	diethylammonium	methanol-ether	140-145 dec			10.68			10.40
fumaric	*tert*-butylammonium	methanol	211-214 dec	54.94	10.03	10.68	55.00	10.03	10.65
fumaric	*n*-butylammonium	methanol	156-163			10.68			10.53
adipic	*tert*-butylammonium	methanol-ether	175-185			9.58			9.46

Table II. Monosalts of Dibasic Acids, RHY

				analysis, %							
				calcd				found			
acid	cation	crystallizn solv	mp, °C	C	H	N	NE[a]	C	H	N	NE[a]
adipic	piperidinium	methanol-ether	132-134	57.12	9.15	6.06	231	57.40	9.29	6.64	233
adipic	diethylammonium	methanol-ether	110-112			6.39				6.33	
adipic	methylammonium	methanol-ether	120-122			7.90				7.73	
adipic	dimethylammonium	methanol-ether	72-78			7.32				7.08	
adipic	diisopropylammonium	2-propanol-hexane	98-101			5.66				5.54	
adipic	*N*-ethylpiperidinium	dimethylformamide-Propasol P-ether	75-78				259				259
phthalic	tetramethylammonium	methanol-ether	143-147				239				239
phthalic	triethylammonium	ethanol-ether	100-102			5.24				5.18	
phthalic	*tert*-butylammonium	acetone-ether	166-170			5.85	240			5.77	240
phthalic	diisopropylammonium	2-propanol	153-155			5.24	267			5.18	267
fumaric	piperidinium	methanol-ether	148-152				201				202
fumaric	*n*-butylammonium	methanol	157-160			7.40	189			7.33	189
fumaric	tetraethylammonium	2-propanol	245-249 dec	58.75	9.45	5.71	245	58.65	9.50	5.62	245
fumaric	tri-*n*-propylammonium	methanol-ether	121-123			5.40	259			5.33	257
maleic	piperidinium	2-propanol-hexane	99-101				201				202
maleic	tetramethylammonium	2-propanol-ether	188-191	50.78	7.99	7.40	189	50.71	8.11	7.23	190
maleic	*tert*-butylammonium	acetone	99-101 dec				189				195

[a] NE = neutralization equivalent.

Table III. Anomalous Acid Salts with Two Dibasic Acid Molecules per Cation, RH_3Y_2

				analysis, %							
				calcd				found			
acid	cation	crystallizn solv	mp, °C	C	H	N	NE[a]	C	H	N	NE[a]
fumaric	tetramethylammonium	methanol-ether	199 dec	47.21	6.27	4.59	102	47.16	6.31	4.54	103
maleic	tetramethylammonium	2-propanol	104-106	47.21	6.27	4.59	102	47.48	6.35	4.61	101
phthalic	tetramethylammonium	2-propanol-ether	149-152	59.25	5.72	3.46	135	59.26	5.98	3.77	135
phthalic	tetraethylammonium	2-propanol-ether	104-107	62.46	6.77	3.03	154	62.90	7.04	3.16	155
glutaric	tri-*n*-propylammonium	acetonitrile-ether	65-67			3.44	136			3.37	136

[a] Neutralization equivalent.

Table IV. Anomalous Acid Salts with Three Dibasic Acid Molecules per Every Two Cations, $R_2H_4Y_3$

				analysis, %							
				calcd				found			
acid	cation	crystallizn solv	mp, °C	C	H	N	NE[a]	C	H	N	NE[a]
fumaric	*tert*-butylammonium	methanol	191-193 dec	48.58	6.93	5.66	124	48.49	6.98	5.71	125
fumaric	tetraethylammonium	methanol-ether	151-154	55.43	8.31	4.62	152	55.45	8.28	4.68	155
adipic	tri-*n*-propylammonium	acetonitrile-ether	50-51	59.64	10.01	3.86	181	59.80	9.99	3.91	182
succinic	*N*-ethylpiperidinium	2-propanol-ether	62-63	53.78	8.33	4.82	145	53.97	8.41	4.82	148

[a] Neutralization equivalent.

II we have listed the monosalts that we have prepared from four of the acids, adipic, fumaric, maleic and phthalic, that have also given anomalous acid salts. The list includes only those that we had occasion to make. Many more are possible, and it should be apparent that these normal acid salts are what are to be anticipated as products from reaction of dibasic acids with amines or quaternary ammonium hydroxides.

This abundance of normal acid salts attaches even greater interest to the occasional occurrence of anomalous acid salts. Two types of anomalous salts have been observed. Those listed in Table III involve two dibasic acid molecules per cation. The complex salt has two dibasic acid molecules joined together, probably by hydrogen bonds, and only one of the four available carboxyl groups is neutralized by the base. It may be represented by RH_3Y_2, where H_2Y is the dibasic acid and R^+ is the cation. Some anomalous acid salts of dibasic acids having this stoichiometry have been reported previouly. These include a potassium acid succinate (KH_3Y_2, where H_2Y is succinic acid)[6] a potassium acid glutarate (KH_3Y_2, where H_2Y is glutaric acid),[7] and acid oxalates ($MH_3Y_2{\cdot}2H_2O$, where H_2Y is oxalic acid and M is K, Rb, Tl or NH_4).[8]

The second type of anomalous acid salt has a more complex stoichiometry. The examples that we have encountered are shown in Table IV. These salts result from the reaction of 3 mol of the dibasic acid with 2 mol of the amine or quaternary ammonium hydroxide. The salts contain four unneutralized carboxyl groups and may be represented as $R_2H_4Y_3$, where R^+ is the cation and H_2Y is the dibasic acid. Salts showing this stoichiometry are rare, although at least one, $Na_2H_4Y_3$, where H_2Y is cyclobutane-*trans*-1,3-dicarboxylic acid, has been reported.[9] These anomalous salts occurred most frequently when the reacting base was a quaternary ammonium hydroxide, but the result in any particular case was unpredictable. With fumaric acid and tetramethylammonium hydroxide we were unable to prepare the normal acid salt, RHY. On reacting fumaric acid with tetramethylammonium hydroxide in acid to base ratios of 1:1, 3:2, or 2:1, the only product that we obtained was the anomalous acid salt, RH_3Y_2. In contrast, when maleic acid was reacted with 1 equiv of tetramethylammonium hydroxide we obtained the normal monosalt, RHY, in 92% yield. However, when maleic acid was reacted with 0.5 equiv of tetramethylammonium hydroxide the product was the anomalous salt, RH_3Y_2. When fumaric acid was treated with tetraethylammonium hydroxide with acid to base in a molar ratio of either 2:1 or 3:1, the product obtained after crystallization from methanol–ether was the anomalous acid salt, $R_2H_4Y_3$, mp 151–154 °C. This salt could be crystallized repeatedly from methanol–ether without changing its composition. However, when crystallized from 2-propanol the salt was converted to the normal monosalt, RHY, mp 245–249 °C dec.

Phthalic acid, reacted with tetramethylammonium hydroxide or tetraethylammonium hydroxide in a molar acid to base ratio of 2:1, gave only the anomalous salt, RH_3Y_2, where R^+ is the tetramethylammonium or the tetraethylammonium cation. Recrystallization of the tetramethylammonium salt from either 2-propanol–ether or acetone–ether did not result in any change in its composition. Similarly, the tetraethylammonium salt was unaltered by recrystallization from 2-propanol–ether or acetonitrile. But by reacting phthalic acid with 1 equiv of tetramethylammonium hydroxide and crystallizing the product from methanol–ether it was possible to obtain the normal salt, RHY.

Three of the five anomalous acid salts, RH_3Y_2, shown in Table III have the tetramethylammonium ion as the cation. This suggested that the size and shape of this ion may have some special significance, i.e., that perhaps it fits most readily into the crystal structures of the resultant salts. To explore this possibility we studied the reaction of *tert*-butylamine with three of the acids, fumaric, maleic and phthalic, that gave anomalous salts with tetramethylammonium hydroxide. It was our hope that the *tert*-butylammonium ion would prove to be reasonably isosteric with the tetramethylammonium ion. As with everything else that we have done in this field, the results defied our expectations. Maleic and phthalic acids gave only the normal acid salt, RHY. Fumaric acid did provide an anomalous acid salt, but it was the product shown in Table IV with the composition $R_2H_4Y_3$ and a melting point of 191–193 °C dec. This product was obtained with acid to amine in the ratio of 1:1 or 3:2. With the ratio at 1:2 the product was di-*tert*-butylammonium fumarate (R_2Y), mp 211–214 °C.

Another possibility to explain the prevalence of quaternary ammonium cations in the anomalous salts of Table III is the fact that they cannot function as hydrogen donors in hydrogen bonding. This may create greater opportunities for hydrogen bonding between COO^-–COOH or COOH–COOH in these salts. We have not succeeded in devising an experimental test for this notion, but a quaternary ammonium cation is not a necessary condition, since one salt in Table III has a tri-*n*-propylammonium ion as a cation.

The detailed structures of these anomalous salts represent a fascinating problem, complicated by the fact that only measurements made in the solid state are valid. A complete crystal structure determination would fully define the structure, and useful information might result from NMR studies in the solid state. Unfortunately neither of these experimental techniques is available to us. Some qualitative structural information is available from infrared spectroscopy. To simplify interpretation of the results, we have focused on the salts of those acids which have the two carboxy groups coplanar and either cis or trans to one another, e.g., maleic acid, fumaric acid, and phthalic acid. A further simplification was achieved by stressing those salts in which the cation is a quaternary ammonium ion. This simplifies the spectra by eliminating the confusing hydrogen bonding interactions involving the N–H of the substituted ammonium cations.

We begin with the spectra of the normal acid salts of maleic acid, since the spectrum of potassium hydrogen maleate, which has been fully described and interpreted,[2] provides a convenient point of reference. As a mull in Fluorolube this potassium salt shows no free O–H absorption above 3000 cm^{-1} and no absorption between 3000 and 2400 cm^{-1} that might be attributed to hydrogen bonded OH. In the carbonyl region it shows a single absorption at 1575 cm^{-1}. This band is characteristic of the carboxylate ion, and there is no evidence of any significant absorption due to the carboxyl group. These spectral characteristics have been attributed to an anion in which the two carboxylate groups are equivalent and linked by a short, symmetrical hydrogen bond, and this interpretation has been supported by independent evidence.[3,4]

The infrared spectrum of tetramethylammonium hydrogen maleate is very similar. It shows a small absorption band at ~3000 cm^{-1} (C–H stretch) and a small shift in the carbonyl absorption at 1585 cm^{-1}. Other characteristics are unaltered, and we conclude that the anion structure is essentially the same as in the potassium salt.

In contrast to the foregoing, the spectrum for *tert*-butylammonium hydrogen maleate is highly complex. It shows absorption at 3300–3400 cm^{-1} attributable to free OH or NH, a series of absorptions from 2500 to 3000 cm^{-1} due to hydrogen bonded OH or NH, and a series of carbonyl absorptions from 1550 to 1725 cm^{-1}. In the spectrum of monotetramethylammonium hydrogen phthalate there is no absorption between 3100 and 4000 cm^{-1} due to free OH. Broad absorption bands, with several submaxima, from 2200 to 3000 cm^{-1} and possibly the broad band from 1850 to 2000 cm^{-1} are indicative of hydrogen bonded OH. In addition there are two carbonyl absorptions at 1695 (COOH) and 1565 cm^{-1} (COO^-). The evidence supports a hydrogen bonded structure but not one with the strong,

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[6] H. Marshall and A. T. Cameron, *Proc. Chem. Soc.*, **23**, 214 (1907); *J. Chem. Soc.*, 1519 (1907); *Chem. Abstr.* **2**, 534 (1908).

[7] A. L. Macdonald and J. C. Speakman, *J. Chem. Soc., Perkin Trans. 2* 942 (1972).

[8] D. J. Haas, *Acta Crystallogr.*, 17, 1511 (1964); M. Currie, J. C. Speakman, and N. A. Curry, *J. Chem. Soc. A*, 1862 (1967).

[9] E. Adman and T. N. Margulis, *J. Amer. Chem. Soc.*, **90**, 4517 (1968.

Table V. Infrared Spectra of Anomalous Acid Salts

acid	cation	stoichiometry	carbonyl abs, cm^{-1} COOH	carbonyl abs, cm^{-1} COO
phthalic	tetramethylammonium	RH$_3$Y$_2$	1715	1640
maleic	tetramethylammonium	RH$_3$Y$_2$	1720	1625
fumaric	tetramethylammonium	RH$_3$Y$_2$	1740	1640
fumaric	tetraethylammonium	R$_2$H$_4$Y$_3$	1700	1590

symmetrical hydrogen bond observed in the maleate.

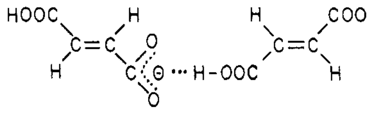
We have limited our study of the infrared spectra of the anomalous acid salts to the quaternary ammonium salts, in particular the three tetramethylammonium salts (RH$_3$Y$_2$) of Table III and the tetraethylammonium salt (R$_2$H$_4$Y$_3$) of Table IV. We first note that the anomalous salt spectra are not compatible with a superposition of the spectra of the free acid and the normal acid salt. Thus for the anomalous tetramethylammonium phthalate, RH$_3$Y$_2$, the carboxyl absorption occurs at 1715 cm^{-1}, compared to 1685 cm^{-1} for phthalic acid and 1695 cm^{-1} for tetramethylammonium hydrogen phthalate, and the carboxylate absorption occurs at 1640 cm^{-1} compared to 1565 cm^{-1} for the normal acid salt.

The remarkable aspect of the spectra of these anomalous acid salts is that they are all so very similar. This is regardless of whether the stoichiometry corresponds to RH$_3$Y$_2$ or to R$_2$H$_4$Y$_3$ and regardless of whether the carboxyl groups in the starting acid are cis and capable of intramolecular interaction as in maleic acid or trans, where interactions must be intermolecular, as in fumaric acid. The infrared spectra of all four salts show broad, multiband absorption from 1800 to 2800 cm^{-1} due to hydrogen-bonded OH and no absorption due to free OH. The carbonyl absorptions for both COOH and COO$^-$ are shown in Table V, where it is to be recognized that there is a remote but finite possibility of confusing absorption due to COO$^-$ and C=C.

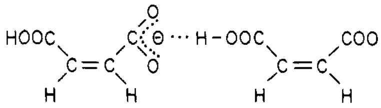
We recognize that the combination of definite stoichiometry and the infrared spectra does not permit detailed structural assignments for the anomalous acid salts. Nevertheless the similarities in the infrared spectra suggest some commonality of structure and permit some reasonable suggestions. We assume that: (1) the carboxyl hydrogen will hydrogen bond preferentially to the carboxylate anion rather than the neutral carboxyl group, and (2) the unit structures will be terminated in carboxyl groups, which, in the crystal structures, will undergo hydrogen bonding typical of carboxylic acids. The net effect is that the anions in the crystal are essentially polymeric, with the negative charges neutralized by appropriately located quaternary ammonium cations. For the fumarate and maleate anions of the RH$_3$Y$_2$ salts we suggest I and II, respectively, and for the fumarate anion of the R$_2$H$_4$Y$_3$ salt III and IV are possibilities.

Experimental Section

Preparative Procedures. The salts were usually prepared by adding the amine with cooling to the acid suspended or dissolved in a moderate volume of solvent, most commonly methanol or 2-propanol. When the mixture was cooled and ether or hexane added, the salts generally crystallized. When crystallization did not occur, the mixtures were taken to dryness under water pump pressure and the crude products were crystallized from a suitable solvent: methanol, 2-propanol, acetone, or these solvents in combination with ether or hexane. Where the neutralizing base was an aqueous solution of a quaternary ammonium hydroxide, it was added to acid in water or methanol. The mixture was taken to dryness, and the crude salt was recrystallized. The following detailed procedures are illustrative.



I



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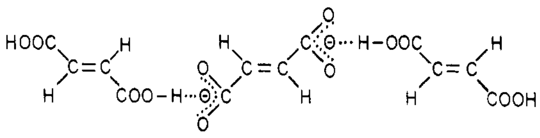

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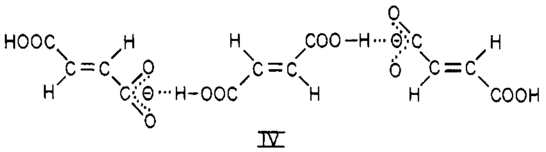

IV

Piperidinium Hydrogen Fumarate. Piperidine (8.5 g, 0.1 mol) in methanol (50 mL) was added with cooling to fumaric acid (11.6 g, 0.1 mol) also in methanol (50 mL). The mixture was warmed to dissolve all the solid and then again cooled. Ether (50 mL) was added. When the mixture was cooled further, the salt crystallized: yield 17.5 g (87%); mp 148–152 °C. Recrystallization from methanol–ether did not alter the melting point. The same product was obtained with 0.1 mol of amine added to 0.2 mol of acid, but the yield decreased to 64%.

Anomalous Tetramethylammonium Fumarate of Type RH$_3$Y$_2$. Tetramethylammonium hydroxide (46 mL of a 10% aqueous solution, 0.05 mol) was added to fumaric acid (11.6 g, 0.1 mol). The mixture was warmed, and enough methanol was added to bring all of the solid into solution. The solution was taken to dryness with the water pump, and the crude product was crystallized from methanol–ether: yield 11.2 g (72.3%); mp 191–199 °C dec. Recrystallization from methanol–ether raised the melting point to 199 °C dec. With the acid and quaternary ammonium hydroxide in a molar ratio of 3:2, the yield dropped to 68.7%, and with the molar ratio at 1:1 the yield was 44.5%.

Anomalous Tetraethylammonium Phthalate of Type RH$_3$Y$_2$. Tetraethylammonium hydroxide (73.6 g of a 10% aqueous solution, 0.05 mol) was added to phthalic acid (16.6 g, 0.1 mol). The solution was taken to dryness with the water pump. The crude product was crystallized from 2-propanol–ether: yield 22.3 g (93%); mp 106–107 °C. The melting point was unchanged by recrystallization from either 2-propanol–ether or acetonitrile.

Anomalous Tetraethylammonium Fumarate of Type R$_2$H$_4$Y$_3$. Fumaric acid (17.4 g, 0.15 mol) was added to tetraethylammonium hydroxide (73.6 g of a 10% aqueous solution, 0.05 mol). Methanol was added, and the mixture was heated until all solid was in solution. The solution was taken to dryness with the water pump, and the crude product was crystallized from methanol–ether: yield 14.3 g (96%); mp 151–154 °C. This product can be recrystallized repeatedly from methanol–ether without altering the melting point. However, recrystallization from 2-propanol converts this salt quantitatively to the normal acid salt, tetraethylammonium hydrogen fumarate, mp 245–249 °C dec.

Analyses. The neutralization equivalents were determined by pH titration of aqueous solutions of the salts. Weighed samples of the salts were dissolved in 50 mL of water and titrated with standard 0.10 N sodium hydroxide. Endpoints were determined from plots of pH vs. the volume of added sodium hydroxide solution. The microanalyses for C, H, and N were by Galbraith Laboratories, Inc.

Infrared Spectra. The spectra were obtained as mulls in both Fluoroluble (perfluorohydrocarbon) and Nujol (mineral oil) by using a Perkin-Elmer Model 281B double beam infrared spectrophotometer. The spectra were scanned from 600–4000 cm^{-1}.

Fluorolube provides advantages as the mulling agent, since it is transparent in the region 1400–4000 cm^{-1}, where absorptions due to hydrogen bonding are observed.

Registry No. R_2Y (R = diethylammonium; Y = fumarate), 6270-48-0; R_2Y (R = *tert*-butylammonium; Y = fumarate), 79722-95-5; R_2Y (R = *n*-butylammonium; Y = fumarate), 79722-96-6; R_2Y (R = *tert*-butylammonium; Y = adipate), 79722-97-7; RHY (R = piperidinium; HY = adipate), 29867-86-5; RHY (R = diethylammonium; HY = adipate), 72357-28-9; RHY (R = methylammonium; HY = adipate), 79722-98-8; RHY (R = dimethylammonium; HY = adipate), 79722-99-9; RHY (R = diisopropylammonium; HY = adipate), 79723-00-5; RHY (R = *N*-ethylpiperidinium; HY = adipate), 79723-01-6; RHY (R = tetramethylammonium; HY = phthalate), 79723-02-7; RHY (R = triethylammonium; HY = phthalate), 79723-03-8; RHY (R = *tert*-butylammonium; HY = phthalate), 79723-04-9; RHY (R = diisopropylammonium, HY = phthalate), 79723-05-0; RHY (R = piperidinium; HY = fumarate), 79723-06-1; RHY (R = *n*-butylammonium; HY = fumarate), 79723-07-2; RHY (R = tetraethylammonium; HY = fumarate), 79723-08-3; RHY (R = tri-*n*-propylammonium; HY = fumarate), 79723-09-4; RHY (R = piperidinium; HY = maleate), 31754-76-4; RHY (R = tetramethylammonium; HY = maleate), 67037-15-4; RHY (R = *tert*-butylammonium; HY = maleate), 79723-10-7; RH_3Y_2 (R = tetramethylammonium; H_3Y_2 = fumarate), 79723-11-8; RH_3Y_2 (R = tetramethylammonium; H_3Y_2 = maleate), 79723-12-9; RH_3Y_2 (R = tetramethylammonium; H_3Y_2 = phthalate), 79723-13-0; RH_3Y_2 (R = tetraethylammonium; H_3Y_2 = phthalate), 79723-14-1; RH_3Y_2 (R = tri-*n*-propylammonium; H_3Y_2 = glutarate), 79723-15-2; $R_2H_4Y_3$ (R = *tert*-butylammonium; H_4Y_3 = fumarate), 79723-16-3; $R_2H_4Y_3$ (R = tetraethylammonium; H_4Y_3 = fumarate), 79723-17-4; $R_2H_4Y_3$ (R = tri-*n*-propylammonium; H_4Y_3 = adipate), 79723-18-5; $R_2H_4Y_3$ (R = *N*-ethylpiperidinium; H_4Y_3 = succinate), 79723-19-6.

Stereoselective Control in the Alkylation and Annelation of Anions and Dianions Derived from 5-Norbornene-2,3-dicarboximides

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Lithiation of *endo*- (**1**) or *exo*-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]hex-8-ene (**2**) with 2 equiv of lithium diisopropylamide gives a common dilithiated species which methylates predominantly from the side of the one-carbon bridge. Lithiation of **1** and **2** with 1 equiv of i-Pr_2NLi gives different monolithiated species which methylate on opposite faces to give the products in which the cis stereochemistry of the ring function is retained. Sequential annelation of **1** and **2** with α,ω-dihalides involving formation of the monoanion, alkylation, formation of the alkylated monoanion, and intramolecular alkylation gives products in which the original stereochemistry of the product is retained. However, in the case of **2**, the isomer with opposite stereochemistry is also obtained, presumably because of the formation of the dianion. *endo*-10,10-Diethoxy-4-phenyl-4-azatricyclo[5.2.1.0^{2,6}]hex-8-ene (**14**) gives a dilithiated species which methylates predominantly from the two-carbon bridge face, presumably because of the steric protection afforded by the ethoxy groups. Annelation of this species with 1,3-dibromopropane gives the product derived from reaction on the two-carbon bridge face and annelation with 1,4-dichlorobut-2-ene also gives predominantly the product resulting from attack on that side.

Significant progress in the stereochemical control of organic reactions has been one of the major achievements in synthetic technology over the last three decades.[1] Such control depends on the adjustments of very small energy differences, usually no more than a few tens of kilojoules, and that such small differences in energy can be manipulated reflects both on the nature of organic reactions and the skill of organic chemists. We herein describe studies on the alkylation, including annelation, of anions and dianions derived from norbornene-2,3-dicarboximides which illustrates how ring strain and steric bulk can be employed to control the products obtained from these systems.

Methylation Studies

The *endo*- and *exo*-5-norbornene-2,3-dicarboximides (*endo*-**1**[2] and *exo*-**2**[3]) were prepared by known methods and each isomer was separately treated with 2 molar equiv of lithium diisopropylamide in THF below −100 °C.[4] After standing at this temperature for 30 min, the solutions were allowed to warm to the desired higher temperatures and were then treated with excess MeI. The reaction products were isolated, and the composition of the product mixtures is shown in Table I.

Table I

imide precursor	rctn temp,[a] °C	products (% yields)
1	-100	**4** (30), **5** (2), **1** (13), **6** (15)
	-70	**4** (50), **5** (8), **1** (10)
	-30	**4** (50), **5** (8)
2	-100	**4** (16), **5** (5), **2** (18), **7** (20)
	-70	**4** (20), **5** (10), **2** (15)
	-30	**4** (25), **5** (5)

[a] See Experimental Section for details of experimental conditions.

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(1) See Woodward, R. B. In "Perspectives in Organic Chemistry"; Todd, A. R., Ed.; Interscience: New York, 1956; p 155. Izumi, Y.; Tai, T. "Stereodifferentiating Reactions"; Academic Press: New York, 1977; Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. Stevens, R. F. *Ibid.* **1977**, *10*, 193. Meyers, A. I. *Ibid.* **1978**, *11*, 375. Hanessian, S. *Ibid.* **1979**, *12*, 159. Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476. Heathcock, C. H.; Pirrung, M. C.; Buse, C. T.; Hagen, J. P.; Young, S. D.; Sohn, J. E. *J. Am. Chem. Soc.* **1979**, *101*, 7077. Evans, D. A.; Nelson, J. V. *Ibid.* **1980**, *102*, 774.

(2) Wilder, P.; Culberson, C. F. *J. Am. Chem. Soc.* **1959**, *81*, 2021.

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(4) For our earlier studies on dilithiated vicinal dianions, see Bilyard, K. G.; Garratt, P. J. *Tetrahedron Lett.* **1981**, *22*, 1755 and references therein. Our studies on lithiated cyclic imides will be reported elsewhere.

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