dropwise with agitation and under argon atmosphere to a solution of DNBF in xylene (5 g, 250 cm<sup>3</sup>) which was previously warmed to 80 °C on an oil bath. After the addition, the solution was heated to about 110 °C for 1 h, then maintained at 100 °C for a further 5 h. and cooled. The solvent was removed under reduced pressure, yielding a dark residue which was purified by column (40 cm long, 5 cm diameter) chromatography, using Florisil as the adsorbent and benzene-hexane mixtures as the eluent. Employment first a 75:25 (v/v) hexane-benzene mixture allowed the unreacted DNBF to be eluted. Then, the benzene content of the elution mixture was increased progressively from 25% to 50% to 75%. Concentration of the corresponding filtrates yields orange crystals of DNBZ (3.06 g, 65.8%). The melting point was obtained after recrystallization from carbon tetrachloride, mp 133 °C (lit.<sup>13,14</sup> 129-132 °C). Note that heating the xylene solutions at reflux results in a decrease in the yields of DNBZ.

The other materials were reagent grade and were used without further purification.

Rate and pH Measurements. Stopped-flow determinations were performed on a Durrum stopped-flow spectrophotometer the cell compartment of which was maintained at  $\pm 0.5$  °C. All kinetic runs were carried out under pseudo-first-order conditions with a substrate concentration of about  $3 \times 10^{-5}$  M. Rate constants are accurate to  $\pm 3\%$  with the exception of some  $k^{A^-}$  and  $k^{AH}$  rate constants which may be to  $\pm 10\%$  in some cases.

The pH of the buffer solutions was measured on a Radiometer Model pH meter according to standard methods.<sup>16</sup> The pH values are relative to the standard state in pure methanol.<sup>16,17</sup>

Registry No. 3a, 91948-44-6; 3b, 91948-45-7; 4, 61487-11-4; DNBZ, 70264-71-0; DNBF, 5128-28-9; MDNBZ, 22714-04-1.

Supplementary Material Available: Observed first-order rate constants  $k_{obsd}$  for the formation and/or decomposition of the adducts 3a, 3b, and 4 in methanol (Table S1), the pH dependence of  $k_{\rm f}$  (s<sup>-1</sup>) and  $k_{\rm d}$  (s<sup>-1</sup>) for the formation and decomposition of the adduct **3b** in methanol at t = 20 °C, I = 0.02 M (Figure S1), and the Brønsted plots for the formation and decomposition of the adduct 3a in methanol at t = 20 °C and I =0.02 M (Figure S2) (3 pages). Ordering information is given on any current masthead page.

## The Effect of Lewis Acid and Solvent on Concerted 1,2-Acyl Migration

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Lewis acid catalyzed 1.2-benzoyl migration in (E)- and (Z)-1.3-diphenyl-2-buten-1-one oxides (dypnone oxides) is a concerted process that occurs with inversion of configuration at the migration terminus when nonpolar solvents are employed. In methanol solvent acid-catalyzed epoxide ring opening occurs with net retention of configuration affording a mixture of diastereomers of 1,3-diphenyl-2-hydroxy-3-methoxy-1-butanone and with no detectable acyl migration. A mechanism is postulated for carbonyl migration that involves reverse polarization of the carbonyl  $\pi$ -bond. The concerted 1,2-acyl migration is suggested to involve neighboring group participation at carbonyl carbon in the rate limiting step.

The unusual migratory propensity of the carbonyl group was first established by House in a series of mechanistic papers.<sup>2</sup> Carbonyl migration, catalyzed by boron trifluoride, has been reported with epoxy ketones,<sup>2</sup> esters,<sup>3</sup> and thiol esters.<sup>4</sup> This intramolecular migration<sup>2c</sup> has also been used in several synthetic applications.<sup>5</sup> Our efforts have been directed toward establishing the concerted nature of this reaction. We have shown that 1,2-carbethoxy migration in ethyl (E)-3-methyl-3-phenylglycidate occurred with inversion of configuration and without loss of optical purity.<sup>6a</sup> We have also excluded a carbenium ion intermediate in the rearrangement of (E)- and (Z)-1,3-di-

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phenyl-2-buten-1-one oxides (dypnone oxides, 1 and 2).6b The silver ion catalyzed carbonyl migration with chiral chlorohydrins 3 and 4 also proceeded with complete in-

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Table I. Lewis Acid Catalyzed Rearrangement of Dypnone Oxides in Methylene Chloride

		conditions		yields,ª %					
substrate	Lewis acid (equiv)	temp, °C	time, h	5	7	6	3	4	
1	$Mg(ClO_4)_2$ (0.1)	35	2.5	83	3	0			
2	$Mg(ClO_4)_2$ (0.1)	35	2.5	79	0	15			
2	$Mg(ClO_4)_2$ (2.5)	35	2.5		$18^{c}$	66°			
2	$Mg(ClO_4)_2 (2.5)^b$	35	0.25	14	0	86°			
1	$LiClO_4$ (3.0)	35	48	100	0	0			
1	SE $30^{\overline{d}}$	183	0.25	91	0	9			
1	$CF_{3}CO_{2}H(2.0)^{e}$	25	0.25	$5^{f}$	$12^{f}$				
i	$ClSO_{3}H$ (0.12)	0	0.5	92	0	0			
1	$HClO_{4}$ (0.5)	0	0.5	94	0	0			
2	$ZnCl_{2}(2.0)$	35	17	81	0	0			
1	$ZnCl_{2}(2.0)$	35	1	62	0	0			
1	$AlCl_{2}(0.3)$	25	0.5	99	0	0	0	0	
2	$AlCl_{3}(0.3)$	25	0.5	86	0	0	0	0	
1	$CuCl_{2}$ (1.0)	35	17	89 <sup>h</sup>	0	0	0 <sup>g</sup>	0s	
2	$\operatorname{CuCl}_{2}(1.0)$	35	17	69 <sup>h</sup>	0	0	0	0	
1	$CuCl_{2}$ (1.0)	25	24	$24^{h}$	0	0	0	0	
2	$CuCl_{2}(0.1)$	35	17	$70^{h}$	0	0	0	0	
1	CuCl (3.0)	35	56	$25^{c,h}$	0	Ō	$15^{c,h}$	0	
1	$MgCl_{2}$ (3.0)	35	56	35	0	Ó	54	0	
1	$BCl_{3}(0.1)$	-78	9.25	17	0	Ō	62	10	
1	$BCl_{3}(0.1)^{i}$	-78	0.25	10	0	0	45	45	
1	$BCl_3(0.1)$	25	0.25	0	0	40	0	0	

<sup>a</sup> Unless otherwise indicated all yields were determined by GLC. <sup>b</sup> cis-2 was added to a refluxing solution of Mg (ClO<sub>4</sub>)<sub>2</sub>. <sup>c</sup> Isolated yield. <sup>d</sup> Rearrangement performed during GLC. <sup>e</sup>Benzene was used as solvent. <sup>f</sup>A trifluoroacetate adduct was the suspected major product. <sup>g</sup> Some chlorohydrins were present, but no yield determinations were made. <sup>h</sup> The remaining product was unreacted starting material. <sup>i</sup>Rapid addition of BCl<sub>3</sub>.

version of configuration at the migration teminus even though the ground-state conformer necessary for this stereochemical pathway must involve the least stable of three possible conformers.<sup>6c</sup> Our stereochemical studies are outlined in Scheme I. These highly concerted carbonyl rearrangements were carried out in nonpolar solvents and we suggested that neighboring group participation (NGP) by the *carbonyl carbon* was involved in the rate-limiting step. The developing positive charge at the migration terminus may be stabilized in the transition state through a *reverse polarization of the carbonyl*  $\pi$ -bond in much the same fashion that a homoallylic cation collapses to a cyclopropylcarbinyl cation. We now provide additional evidence in support of this unique type of stabilization.

## **Results and Discussion**

Effect of the Lewis Acid on Carbonyl Migration. We selected dypnone oxides 1 and 2 for this mechanistic study since their stereochemistry<sup>7a</sup> and that of the products of their rearrangement<sup>7b</sup> have been established. There are three basic pathways available to dypnone oxide upon treatment with a Lewis acid catalyst. The  $\alpha,\beta$ -epoxy ketone can either experience carbonyl migration (path a), hydrogen migration (path b), or possibly form a halohydrin intermediate (path c, Scheme II).

The most common Lewis acid employed for the rearrangement of  $\alpha,\beta$ -epoxy carbonyl compounds has been boron trifluoride. In order to test the role of the Lewis acid in these transformations, and to gain more insight into the mechanism of acyl migration, *cis*- and *trans*-dypnone oxides were treated with a variety of Lewis acids. The results are summarized in Table I. In all cases where the Lewis acid was a metal salt, the reaction mixture was heterogeneous and required prolonged reaction times. Traces of water apparently do not prevent rearrangement since many Lewis acids that successfully initiated rearrangement were in their hydrated forms. For most entries in Table I the yields and product distributions were in-



dependent of the order of addition of the reagents. Similar reactivities were observed for both isomers of epoxy ketone 1 and 2.

One major exception to these generalities occurred when magnesium perchlorate was employed. Large concentrations of magnesium perchlorate in refluxing methylene chloride with cis-dypnone oxide (2) effected hydride migration, giving significant amounts of 1,3-diphenyl-1,2butanedione (6). This  $\alpha$ -diketone was also a minor product from the trans isomer. The perchlorate anion was not the cause of this anomaly, because lithium perchlorate<sup>8</sup> induced acyl migration in *trans*-1 to give the aldehyde 5, with no trace of diketone 6. There are many examples of hydride migration in the rearrangement of  $\alpha,\beta$ -epoxy carbonyl compounds,<sup>3b,8</sup> although this is the first observation of this reaction pathway with dypnone oxides.<sup>2a</sup> When the magnesium perchlorate was present in only catalytic amounts, acyl migration again predominated over hydrogen migration, keeping with the established migratory preferences of acyl > alkyl > hydrogen.<sup>2e,3b</sup> These results indicate that magnesium ion in large concentrations impedes acyl migration, possibly by complexation with the

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Table II. Lewis Acid Induced Rearrangement of Chlorohydrins 3 and 4

		conditions			product yields," %					
compou	ind Lewis acid (equiv)	solvent	temp, °C,	time, h	5	7	6	3	4	
3	$AgO_2CCF_3$ (1.5)	Et <sub>2</sub> O	25	0.5	72	0	0	0		
4	$AgO_2CCF_3$ (1.5)	$Et_2O$	25	0.5	99	0	0		0	
3	$AgBF_4$ (2.0)	$Et_2O$	25	0.5	70	0	0	0		
3	$AgNO_3$ (5.0)	$Et_2O$	35	2	$28^{c}$	20°			ь	
3	$CuCl_{2}$ (1.0)	$H_2CCl_2$	35	17	98	0	0	0		
4	$CuCl_{2}(1.0)$	$H_2CCl_2$	35	17	86	0	0		0	
3	$\operatorname{ZnCl}_{2}(1.0)$	$H_2CCl_2$	25	17	98	0	0	0		
3	$ZnCl_2$ (1.0)	$H_2CCl_2$	35	17	88	0	0	0		
3	BF <sub>3</sub> (0.1)	$H_2CCl_2$	25	1	0	0	0	94		

<sup>a</sup> Unless otherwise indicated, all yields were determined by GLC. <sup>b</sup> Some organic nitrate may have been formed. <sup>c</sup> Isolated yield.



intramolecular 1,2 hydride shift; no loss of deuterium

carbonyl oxygen, permitting hydrogen migration to occur. This unusual effect of magnesium ion was not observed for copper or zinc, although boron trichloride produced the diketone 6 as the only product from reaction with trans-1 at room temperature.

Deuterium labeled *cis*-dypnone oxide was rearranged with 4.0 equiv of magnesium perchlorate in the presence of 4.0 equiv of methanol in refluxing methylene chloride (Scheme III) in order to prove that the diketone 6 is formed by an intramolecular 1,2-hydride shift and not by an elimination-addition mechanism. NMR evidence suggested that the diketone 6 was formed with no detectable loss of deuterium, signifying that an elimination-addition of hydrogen is not operating.

Because the presence of excess magnesium ion could conceivably alter the reaction pathway, optically pure (+)-(2S,3R)-trans-dypnone oxide was rearranged to test the mechanism of acyl migration operating under these conditions. When reaction conditions where both hydride and acyl migration are observed were employed, the product of acyl rearrangement, (-)-(S)-5, was 99% optically pure ( $[\alpha]^{25}_{D}$  -411.0°). In a series of experiments the ratio of  $Mg(ClO_4)_2$  to (+)-1 was varied from 4.5 to 0.1 and the optical purity of (-)-5 was always found to be >99%. Thus, excess magnesium ion does not appear to affect the stereospecificity of carbonyl migration in 1.

It is interesting to note that  $\alpha,\beta$ -epoxy carbonyl compounds have been reported to rearrange poorly with proton acids.<sup>2b,10,11</sup> Indeed, dypnone oxide, when treated with trifluoroacetic acid in benzene afforded a mixture of products. The crude reaction mixture displayed absorptions in the IR at 3380, 1790, and 1690 cm<sup>-1</sup>, suggesting that the trifluoroacetic acid may have added to the epoxide to give a trifluoroacetate. However, nonnucleophilic acids, such as perchloric and chlorosulfonic acids, in methylene chloride at 0 °C rearranged trans-dypnone oxide 1 cleanly to the aldehyde 5 in 92% yield. Thus, nonnucleophilic protic acids and very mild Lewis acids such as  $Mg(ClO_4)_2$ readily induce carbonyl migration. Both dypnone oxides, when the carbonyl is strongly complexed by magnesium ion, exhibited competing hydride migration. We attribute this to a polarization of the carbonyl  $\pi$ -bond toward oxygen





product, formed with complete retention of configuration,<sup>11</sup> when boron trifluoride was the Lewis acid. Under all conditions where the epoxide 9 rearranged to 11 the fluorohydrin 10 did likewise.<sup>2d</sup> Similar examples were reported with boron trifluoride and epoxy ketones in ether.<sup>12,2c</sup> Since we have shown that chlorohydrins 3 and



<sup>a</sup>  $M^+X^- = F_2BF$ ,  $Cl_2BCl$ ,  $CuCl_2$ ,  $ZnCl_2$ ,  $MgCl_2$ ,  $Mg(ClO_4)_2$ , etc.

which reduces the capability of this  $\pi$ -bond to participate in NGP at carbon<sup>6c</sup> in the rate-limiting step.

We next chose to examine reaction conditions where a halohydrin intermediate may be on the overall pathway for acyl migration. Because cupric chloride and zinc chloride rearrange both dypnone oxides 1 and 2 and chlorohydrins 3 and 4 equally well (Table II), the possibility arises that a chlorohydrin (path c) may be an intermediate under these reaction conditions. If an intermediate like 8 (Scheme IV) were formed from dypnone oxide with complete retention of configuration, and underwent subsequent acyl rearrangement with complete inversion of configuration, the resulting stereochemistry of the aldehyde 5 would be indistinguishable from that obtained by a one-step concerted reaction (with inversion) directly from the epoxy ketone 1. This concept is not unprecedented because fluorohydrin 10 was a proposed intermediate in the conversion of the ketone 9 to the aldehyde<sup>2h,2d,11</sup> 11 (eq 1). Fluorohydrin 10 was the major

<sup>(10)</sup> Wasserman, H. H.; Aubrey, N. E. J. Am. Chem. Soc. 1956, 78, 1726(11) House, H. O. J. Org. Chem. 1956, 21, 1306.

4 rearrange with complete inversion of configuration, a general intermediate like 8 could account for the stereochemical results obtained from the rearrangement of the dypnone oxides without the steric strain assumed to attend a highly concerted reaction with NGP at carbonyl carbon in a geometrically constrained epoxy ketone. Despite the attractiveness of a chlorohydrin intermediate during rearrangements with chloride containing Lewis acids, the results from Tables I and II provide strong evidence against the necessary intermediacy of a species like 8. Several key experiments are outlined below.

Treatment of trans-dypnone oxide (1) with aluminum trichloride (AlCl<sub>3</sub>) afforded 5, the product of acyl migration, as the only product. When the chlorohydrin 3 was treated under identical conditions, however, no reaction occurred. Even under forcing conditions, greater than 90% of unreacted 3 was recovered. With cuprous chloride (CuCl), trans-dypnone oxide reacted slowly to give, after 56 h at 35 °C, 25% acyl rearrangement product 5 and 15% of the chlorohydrin 3, formed with retention of configuration. This chlorohydrin was resubjected to the reaction conditions, and no reaction was observed. Clearly, with cuprous chloride, chlorohydrin formation occurs simultaneously with acyl migration, but the chlorohydrin cannot be an intermediate leading to the aldehyde 5.

Even more convincing evidence against the necessity of a chlorohydrin intermediate is found in the rearrangement of *trans*-dypnone oxide with boron trichloride. The epoxy ketone 1, at -78 °C, affords the aldehyde 5 in only 17% yield, while 72% of the product is a mixture of chlorohydrins 3 and 4 in a ratio of 6:1. For any intermediate resembling 8 to be compatible with the stereospecificities observed in the formation of 5, it must be formed with complete retention of configuration (Scheme IV). To test this point, (-)-(2R.3S)-trans-dypnone oxide (46% optical purity) was rearranged with BCl<sub>3</sub> to (+)-(R)-5,  $[\alpha]^{25}$ <sub>D</sub> 186.7°, corresponding to an optical purity of 45%. Acyl migration, using  $BCl_3$  as the Lewis acid, occurred with 98% stereospecificity. Finally, in a separate experiment, chlorohydrin 3 was shown to be totally inert to the action of BCl<sub>3</sub> at -78 °C.

While silver trifluoroacetate and silver tetrafluoroborate induced acyl migration in high yield, silver nitrate and silver fluoride under similar conditions gave no reaction. We attribute this result to the very low solubility of the latter salts in nonpolar solvents such as ethyl ether. It is noteworthy that no epoxide formation was observed when silver carbonate and silver oxide were reacted with the chlorohydrin 3. These results contrast those obtained by Kagan<sup>3d</sup> for the corresponding glycidic esters, where epoxide formation was the major reaction pathway using these particular basic silver salts.

The results in Tables I and II demonstrate that even though the chlorohydrins 3 and 4 rearrange as easily as the dypnone oxides in certain cases, they are not required intermediates. Furthermore, concerted acyl migration directly from the epoxy ketones is possible in at least the three cases described above. Thermal rearrangement of (+)-1 has also been shown to involve concerted acyl migration.<sup>13</sup>

Effect of Solvent Polarity on Carbonyl Migration. In all of the rearrangements discussed thus far, the solvents employed were ether, benzene, or methylene chloride. Acyl migration has been generally observed to proceed best in

nonpolar solvents, although some exceptions are known.<sup>14</sup> Our results on the rearrangement of dypnone oxides 1 and 2, and chlorohydrins 3 and 4, exclude even a short lived carbenium ion from being a possible intermediate. We attributed this to NGP by the carbonyl group. However, since NGP is attended by the strain energy associated with formation of a three-membered ring, one should not necessarily anticipate NGP by a carbonyl group (or even a phenyl group) in a highly polar solvent that can provide adequate stabilization to a tertiary carbenium ion. We, therefore, decided to study the acyl migration process in a polar solvent like methanol and also in methylene chloride with variable amounts of added methanol. These experiments should provide an additional test for our contention that NGP by the carbonyl moiety is actually essential to the process of 1.2-carbonyl migration to an adjacent positive center.

As discussed earlier (Table I), catalytic chlorosulfonic  $(CISO_3H)$  and perchloric  $(HCIO_4)$  acids in methylene chloride rearranged the dypnone oxides in high yield to the aldehyde 5. We felt that for a meaningful comparison of rearrangements in polar and nonpolar solvents a proton would be the most suitable catalyst since the chemical integrity of Lewis acids (BF<sub>3</sub>, BCl<sub>3</sub>, etc.) in methanol is not known. Certainly the environment of the proton would differ from polar to nonpolar medium, but the nature of the protonated epoxide leading to rearranged products should be similar in the two solvents.

When trans-dypnone oxide (1) was treated with chlorosulfonic acid in methanol solvent at 0 °C for 30 min. a mixture of diastereomers of 1,3-diphenyl-2-hydroxy-3methoxy-1-butanone (12 and 13) was formed as the only products in 82% isolated yield (Scheme V). The ratio of these  $C_3$  epimers was determined by NMR analysis to be 76:24, and this ratio was not altered by purification of the mixture. Thus, in methylene chloride, the dypnone oxides rearrange exclusively to the aldehyde 5 via acyl migration, while in methanol the  $C_{\beta}$ -O bond in the epoxide is cleaved, giving only the methanol adducts 12 and 13. There was no simple way to determine which of these two adducts predominated on the basis of spectral data. Therefore, the methanolysis products of chiral trans-dypnone oxide were degraded to compounds of known absolute configuration (Scheme V). This enabled us to establish that methanolysis proceeded with net retention of configuration at C<sub>3</sub> as shown in 12.

When (-)-(2R,3S)-1 (44.9% optical purity) was used, the O-methyl adducts 12 and 13 were obtained from methanolic chlorosulfonic acid, in a ratio of 3:1, as determined by NMR analysis. This mixture was oxidized with periodic acid and converted with chromium trioxide to the predominately (+)-(S)-2-methoxy-2-phenylpropionic acid (15) whose absolute configuration has been determined.<sup>15a</sup> The optical purity of 15 was 26.9% on the basis of specific rotation ( $[\alpha]^{25}_{D}$  26°) reported for the resolved acid.<sup>15b</sup> The (+)-(S)-acid 15 was then converted to the corresponding (+)-(S)-methyl ester 16 to facilitate the NMR analysis.<sup>16</sup> The optical purity of 16 (and 15) was determined by NMR analysis<sup>16</sup> to be 21.8%. These results indicate that the methanolysis of *trans*-1 gives, stereoselectively, 75% of 12

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<sup>(15) (</sup>a) Cram, D. J.; Kopecky, K. R. J. Am. Chem. Soc. 1959, 81, 2748.
(b) Angiolini, L.; Bizarri, C.; Tramontin, M. Tetrahedron 1969, 25, 4211.
(16) The shift reagent employed was "Eu-Opt" (Ventron, Beverly, MA 01915)



with retention of configuration at  $C^3$  and 25% of 13 formed by the addition of methanol with inversion of configuration at  $C_3$ . Having determined the stereochemistry of 12 and 13, NMR analysis was used to determine the ratios of these diastereomers in all subsequent reactions.

Treatment of the cis diastereomer 2 with chlorosulfonic acid in methanol gave the methoxy adducts 12 and 13 in 81% yield. The ratio of the product formed with retention, to the product of inversion 12, was 90:10 (eq 2). Again,



no trace of any acyl rearrangement product was observed under these reaction conditions. Identical results were obtained with perchloric acid in methanol, but longer reaction times were required. The ratios of 12 and 13 from the dypnone oxides were also found to be invariant to changes in the reaction temperature in the range -15 °C to 26 °C.

Since the reaction pathway differed so drastically upon changing from methylene chloride to methanol solvent, we decided to treat *trans*-dypnone oxide (1) in methylene chloride containing various amounts of methanol with chlorosulfonic acid or perchloric acid at 0 °C for 30 min. With either proton source and 2 equiv of methanol, the amount of acyl migration observed from 1 was reduced to 45-46%. The remaining products were formed from

cleavage of the oxirane to afford, with perchloric acid, the methanol adduct 12 in 54% yield. With chlorosulfonic acid, the cleavage of the oxirane gave not only the methanol adduct 12 but also the chlorohydrin 3 was formed, both with complete retention of configuration. The formation of the chlorohydrin was established by acetylation of the reaction product mixture and the isolation of 3chloro-1,3-diphenyl-2-acetoxybutan-1-one (17) in high yield. Undoubtedly, the chlorohydrin 3 was formed from the hydrogen chloride, arising from the partial methanolysis of the chlorosulfonic acid under the conditions employed. As the number of equivalents of methanol was systematically increased, the yield of rearranged aldehyde 5 continued to decrease until at 12 equiv of methanol, only 18% of the reaction proceeded by acyl migration. In all cases, the cleavage of the oxirane yielded products with 100% retention of configuration at the  $\beta$ -carbon.

These results indicate that methanol, even in small amounts, permits epoxide opening to become as favorable as acyl migration, to the extent that in methanol solvent no trace of any acyl rearrangement is observed. In order to establish that acyl migration under these conditions does occur by a concerted mechanism, we treated (-)-(2R,3S)-trans-dypnone oxide (44.8% optical purity) in methylene chloride with 3.0 equiv of methanol and 0 us formed in 35% yield with a specific rotation of  $[\alpha]^{25}_{\rm D}$ 192.4°, corresponding to 46.1% optical purity. Thus, in the presence of methanol acyl migration also occurs (within experimental error) with 100% stereospecificity as observed in pure methylene chloride.

An extremely rapid reaction occurred when chlorohydrins 3 and 4 were mixed with silver trifluoroacetate in methanol. Analysis of the products showed only a mixture of the methanol adducts 12 and 13, with no trace of acyl rearrangement. The ratio of 12 to 13 was 75:25 from the chlorohydrin 3, while the epimeric chlorohydrin 4 gave 12 and 13 in a ratio that varied from 50:50 to 24:76 depending on the method of addition of the reagents. In the absence of silver ion, the chlorohydrins show no reaction with methanol after 1 h. In no case did either the dypnone oxides or the chlorohydrins give any methanolic adducts with net inversion of configuration.

We believe that the results obtained from trans-dypnone oxide and the chlorohydrins 3 and 4 in methanol adequately describe the fate of these compounds, when carbenium ion intermediates are involved. Certainly, the carbenium ion character of the  $\beta$ -carbon in methanolic solvent must be considerably greater than when methylene chloride was utilized.<sup>17</sup> It appears that with a solvent capable of dispersing the positive charge at the  $\beta$ -carbon, that acyl rearrangement, with epoxy ketones and chlorohydrins, is not a favorable reaction pathway. This could be the result of solvation of the acyl group by the polar solvent, decreasing the migratory aptitude of the acyl group. Earlier, we saw the same phenomena when high concentrations of magnesium ion made hydride migration in 1 the predominant pathway. We conclude that in a highly polar solvent like methanol the carbenium ion stability of the  $\beta$ -carbon and the attendant solvation of the carbonyl moiety prevent acyl migration that requires NGP at carbonyl carbon.

While this conclusion seems reasonable in methanol solvent, the intermediate leading to the formation of the methanol adduct 12 in methylene chloride solvent is more obscure. The most striking feature of these reactions, with

<sup>(17)</sup> Nenitzescu, C. D. In "Carbonium Ions"; Olah, G., Schleyer, P. v. R., Eds.; Interscience: New York, 1968; Vol. 1, p 1.

1-12 equiv of methanol, is that the methanol added to *trans*-dypnone oxide (1) with 100% retention of configuration. Even the hydrochloric acid, present when chlorosulfonic acid was used, gave only the chlorohydrin 3 (retention). In constrast, 100% of the acyl migration that occurred under these circumstances took place with inversion of configuration at the  $\beta$ -carbon. Obviously, the mechanism of acyl migration has not changed under these reaction conditions. Furthermore, the sudden decrease in acyl migration cannot be due to a change in the polarity of the solvent, because even 12 equiv of methanol constituted only 2% of the solvent mixture.

We feel that our results from the rearrangement of trans-1 with acid and added methanol in methylene chloride reflect the very delicate balance between two different reaction pathways of comparable activation energy. Path a represents a completely concerted acyl migration consistent with all the results already presented. In path c oxirane cleavage at the  $\beta$ -carbon occurs, and the developing empty p orbital at  $C_3$  is captured by the nucleophile X or X<sup>-</sup>. In nonpolar solvents (ether, methylene chloride), where a means of charge dispersal and NGP are important, acyl migration occurs. In some cases where geometric constraints impede facile NGP by the carbonyl moiety, a halohydrin intervenes to afford rearranged product. We emphasize that 8 is not a necessary intermediate on the pathway to 5. In polar solvents like methanol where the cleavage of the  $C_{\beta}$ -O bond does not require nucleophilic assistance (NGP) for acyl migration, we observe solvent capture (12 or 13) as the primary kinetic product.

The oxirane cleavage in *trans*-1 occurs with retention of configuration in nonpolar solvents. When the Lewis acid contains a nucleophilic anion (BCl<sub>3</sub>, MgCl<sub>2</sub>, CuCl, HCl), the results are reminiscent of those obtained in cyclopropane ring cleavage. It has been demonstrated that cyclopropanes will open with retention when the nucleophile is anionic.<sup>18</sup> An edge-protonated cyclopropane ion pair has been proposed as an intermediate in these reactions. It is interesting to speculate that a comparable intermediate for oxirane ring opening with retention is possible.

In summary, we have established that acyl migration in  $\alpha,\beta$ -epoxy ketones and chlorohydrins is 100% concerted, occurring with complete inversion of configuration at the migration terminus. Acyl migration involves a delicate balance between a concerted rearrangement and oxirane cleavage at the  $\beta$ -carbon where polar solvents shift this balance to favor the intermediacy of carbenium ion intermediates. Thus, one should only anticipate carbonyl migration under those conditions that favor NGP by the migrating carbonyl moiety. The overall concepts involved are quite analogous to those involved in the homoallyl cation rearrangement to a cyclopropylcarbinyl cation<sup>19</sup> where concerted rearrangement has also been noted to proceed with inversion at the migration terminus.<sup>20</sup> We suggest that the Walsh orbitals of the cyclopropyl ring

provides a stabilizing influence on the transition state and that a cycloproyloxenium  $ion^{21}$  resembling 18 lies on the reaction surface for a concerted acyl migration.



## **Experimental Section**

NMR spectral measurements are reported in  $\delta$  units from Me<sub>4</sub>Si or in hertz by generating an external signal with a Hewlett Packard Model 200 DB oscillator using Me<sub>4</sub>Si as a standard. All yield determinations by GLC were performed by using a 2-ft 20% SE-30 column, with either pentadecane or hexadecane as the internal standard.

**Rearrangement with Magnesium Perchlorate**  $(Mg(ClO_4)_2, 2.5 Equiv)$ . To 200 mg (0.84 mmol) of *trans*-dypnone oxide in 25 mL of methylene chloride was added 470 mg (2.5 equiv) of magnesium perchlorate under anhydrous conditions. The mixture was refluxed for 2.5 h and extracted with water. The methylene chloride was dried (MgSO<sub>4</sub>) and concentrated to give 217 mg of a yellow oil. Analysis by GLC demonstrated the presence of 1,3-diphenyl-1,2-butanedione (6, 29%) and the aldehyde 5 (34%). The ratio of these products was confirmed by NMR analysis.

cis-Dypnone oxide under similar conditions afforded a mixture of the  $\alpha$ -diketone 6 and the aldehyde 5, which were purified by preparative TLC using benzene-hexane (1:1) to yield 66% of 6 and 18% of  $\alpha$ -methyldesoxybenzoin (7), which resulted from the decomposition of 5. The spectral properties of both materials were identical with those of authentic samples.

(+)-(2S,3R)-trans-Dypnone Oxide with 2.5 and 4.5 Equiv of Magnesium Perchlorate. Using the procedure described for racemic material, we treated (+)-(2S,3R)-trans-1 (100% optically pure)<sup>16</sup> with 4.5 equiv of magnesium perchlorate. The resulting (-)-(S)-aldehyde 5 was purified by preparative GLC and had a specific rotation of  $[\alpha]^{25}_{D}$ -411.8° (c 1.1, HCCl<sub>3</sub>). GLC analysis on a small aliquot of the crude sample demonstrated that the yield of 5 was 84%. Comparable results were obtained when trans-1 was treated with 2.5 equiv of magnesium perchlorate. The (-)-(S)-aldehyde 5 (94%),  $[\alpha]^{25}_{D}$ -410.3° (c 0.4, HCCl<sub>3</sub>), was 99% optically pure.

Using an inverse addition, we added 150 mg (0.630 mmol) of cis-dypnone-2-d oxide (2a, 70.4% D) to 25 mL of refluxing methylene chloride containing 48  $\mu$ L of methanol (4.0 equiv) and 0.702 g of magnesium perchlorate (4.0 equiv). Integration of the methine quartet at 276 Hz relative to the methyl resonances at 95 Hz and 88 Hz (CHCH<sub>3</sub>) and 91.5 Hz (CDCH<sub>3</sub>) indicated that 70.3% deuterium remained. The yields of  $\alpha$ -diketone 6 and 1,2-diphenyl-2-methyl-1,3-propanedione (5) were determined to be 83% and 17%, respectively, by GLC analysis. All attempts at purification of the  $\alpha$ -diketone 6 resulted in the partial loss of deuterium.

**Rearrangement with Boron Trichloride (BCl<sub>3</sub>).** To 150 mg (0.630 mmol) of *trans*-dypnone oxide (1) in 10 mL of methylene chloride at -78 °C was added over 5 min 1.0 mL of a methylene chloride solution saturated with boron trichloride gas. This solution was prepared by bubbling boron trichloride gas through 15 mL of methylene chloride for 15 min, under an argon atmosphere. After 15 min at -78 °C, the mixture was poured directly into a solution of 10% hydrochloric acid. The methylene chloride solution was dried (MgSO<sub>4</sub>) and concentrated to yield a yellow oil. Analysis by GLC demonstrated the presence of the

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<sup>York, 1972; Vol. 3, p 1295.
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(c) Winstein, S.; Adams, R. Ibid. 1948, 70, 838.</sup> 

<sup>(21) (</sup>a) Bach, R. D.; Domagala, J. M. Tetrahedron Lett. 1976, 4025.
(b) Bach, R. D.; Klix, R. C. Ibid., in press.

In benzene, ether, and carbon tetrachloride, no volatile materials were obtained at any temperature.

When the first procedure was applied to (-)-(2R,3S)-transdypnone oxide (1, 46.2% optical purity<sup>16</sup>), (+)-(R)-5 was formed in low yield. After two purifications by preparative GLC the specific rotation was  $[\alpha]^{25}_{D}$  186.7° (c 0.5, HCCl<sub>3</sub>). The actual isolated yield was 2%.

**Rearrangement with Chlorosulfonic Acid (HSO**<sub>3</sub>Cl). To 150 mg (0.630 mmol) of *trans*-dypnone oxide (1) in 10 mL of methylene chloride at 0 °C was added 21  $\mu$ L (0.5 equiv) of chlorosulfonic acid in 1 mL of methylene chloride over 1 min. After 5 min no starting material could be observed by TLC. The mixture was stirred for 30 min, diluted with methylene chloride, and extracted with water. The organic layer was dried (MgSO<sub>4</sub>) and concentrated to give 151 mg of a colorless oil, whose spectral properties were identical with those of the aldehyde 5. The yield of 5 was determined by GLC analysis to be 85%.

The same procedure gave 5 (92%) when 0.12 equiv of chlorosulfonic acid was employed at 0 °C.

**Rearrangement with Perchloric Acid (HClO<sub>4</sub>).** Using the above procedure, we rearranged 150 mg (0.630 mmol) of *trans*-dypnone oxide (1) at 0 °C with 0.5 equiv of 70% perchloric acid. The only product was the aldehyde **5** (94%) as determined by GLC.

Rearrangement of Dypnone Oxide with Proton Acids in the Presence of Methanol. trans-Dypnone Oxide in Methanol with Chlorosulfonic Acid. To 700 mg (2.94 mmol) of trans-dypnone oxide in 45 mL of methanol at 0 °C was added 0.5 mL of chlorosulfonic acid (2.5 equiv). After the mixture stirred for 30 min, it was diluted with methylene chloride and extracted with water. The methylene chloride was dried  $(MgSO_4)$  and concentrated to a thick, colorless oil, which was purified by preparative TLC using hexane-ethyl acetate (9:1), affording 435 mg (54%) of a mixture of diastereomers of 1,3-diphenyl-2hydroxy-3-methoxy-1-butanone (12 and 13). This mixture crystallized on standing, or by trituration with pentane, to give a white powdery solid: mp 62-68 °C; NMR (DCCl<sub>3</sub>) & 8.1-7.3 (m, 10 H, Ar), 5.25 (d, J = 9 Hz,  $\alpha$ -CH<sub>2</sub>OH), J = 9 Hz,  $\beta$ -CHOH), 3.92 (d, J = 9 Hz,  $\beta$ -CHOH), 3.58 (d, J = 9 Hz,  $\alpha$ -CH<sub>2</sub>OH), 3.12 (s,  $\alpha$ -CH<sub>3</sub>O), 3.00 (s,  $\beta$ -CH<sub>3</sub>O), 1.82 (s,  $\alpha$ -CH<sub>3</sub>), 1.60 (s,  $\beta$ -CH<sub>3</sub>-); IR (Nujol) 3480, 1670 cm<sup>-1</sup>

Anal. Calcd for  $C_{17}H_{18}O_3$ : C, 75.53; H, 6.71. Found: C, 75.74; H, 6.56.

Integration of the methyl singlets indicated that the ratio of 3 to 4 was 76:24 in both the crude and purified mixtures. When the amount of chlorosulfonic acid was decreased to 0.5 equiv, the yield of the methanol adducts 12 and 13 was 89%, and the ratio was 76:24.

cis-Dypnone Oxide with Chlorosulfonic Acid in Methanol. Using conditions similar to those described for *trans*-dypnone oxide, we treated 150 mg (0.630 mmol) of finely ground *cis*-dypnone oxide (2) in 10 mL of methanol, at 0 °C with 0.1 mL (2.5 equiv) of chlorosulfonic acid. The mixture stirred for 30 min. The methanol adducts 12 and 13 were obtained in 81% yield as a crystalline white solid: mp 75–77 °C. Analysis by NMR revealed that the ratio of 12 to 13 was 10:90 in both the crude and purified forms.

(-)-(2R,3S)-trans-Dypnone Oxide in Methanol with Chlorosulfonic Acid. Using conditions similar to those described above for racemic material, we treated 628 mg (2.60 mmol) of (-)-(2R,3S)-trans-dypnone oxide,  $[\alpha]^{25}_D$ -71.27° (c 1.1, HCCl<sub>3</sub>), whose optical purity was 44.9% by NMR,<sup>16</sup> with 150 µL (0.87 equiv) of chlorosulfonic acid in methanol at 0 °C for 30 min. The crude product was 730 mg of an oil composed of a mixture of the methanol adducts 12 and 13 in a ratio of 74.8:25.2 as determined by NMR analysis. This material was oxidized by periodic acid without purification.

trans-Dypnone Oxide in Methanol with Perchloric Acid. Using the conditions described for chlorosulfonic acid, treatment of 150 mg (0.630 mmol) of trans-dypnone oxide in 10 mL of methanol with 28  $\mu$ L (0.5 equiv) of 70% perchloric acid at 0 °C for 3.5 h, afforded 129 mg (76%) of 12 and 13 in a ratio of 73:27 as determined by NMR analysis.

trans-Dypnone Oxide with Perchloric Acid and Methanol in Methylene Chloride. The following procedure is general and in subsequent experiments only the number of equivalents of methanol was changed.

To 150 mg (0.630 mmol) of trans-dypnone oxide in 10 mL of methylene chloride and 49  $\mu$ L of methanol (2.0 equiv) at 0 °C was added 28  $\mu$ L of 70% perchloric acid in 2 mL of methylene chloride in 30 s. After the mixture had stirred for 30 min, it was extracted with water. The methylene chloride was dried (MgSO<sub>4</sub>) and concentrated. The crude mixture was then analyzed by NMR to determine the ratios of 1,2-diphenyl-2-methyl-1,3-propanedione (5) to the epimeric 1,3-diphenyl-2-hydroxy-3-methoxy-1-butanones (12 and 13) by integration of the aldehyde resonance of 5 relative to the methine or methoxy resonances of 12 and 13. In this experiment the ratio of 5 to 12 was 53:47, with no trace of 13 detectable by NMR analysis.

The crude products of this experiment and a duplicate run (1.26 mm total) were purified by preparative TLC using hexane-ethyl acetate (9:1). The 1,2-diphenyl-2-methyl-1,3-propanedione (5), which slowly deformylates on silica gel, was removed from the preparative plates with deformylated material, and the mixture was refluxed in ethanol (25 mL) and sodium acetate (excess), giving 120 mg (46%) of  $\alpha$ -methyldesoxybenzoin (7). The 1,3-diphenyl-2-hydroxy-3-methoxy-1-butanone (12), 160 mg (47%), with the above  $\alpha$ -methyldesoxybenzoin accounted for 93% of the theoretical material.

(-)-(2R,3S)-trans-Dypnone Oxide with Perchloric Acid in Methanol and Methylene Chloride. Using the procedure described for racemic material, we treated 300 mg (1.26 mmol) of (-)-(2R,3S)-trans-dypnone oxide (1) with 56  $\mu$ L of perchloric acid (0.5 equiv) and 147  $\mu$ L (3.0 equiv) of methanol. After aqueous extraction and drying (MgSO<sub>4</sub>), the methylene chloride was removed in vacuo and the crude (+)-(R)-5 was separated from 12 by preparative GLC (SE-30, 170 °C). The purified (+)-(R)-5,  $[\alpha]^{25}_{D}$  +192.4° (c 1.1, HCCl<sub>3</sub>) was identical spectroscopically with racemic material. Analysis of the crude reaction mixture by NMR revealed that the ratio of 5 to 12 was 35:65.

2-Acetoxy-3-chloro-1,3-diphenyl-1-butanone (17). To 150 mg (0.546 mmol) of  $\alpha$ -chlorohydrin 3 was added 6 mL of acetyl chloride. The mixture was refluxed for 4 h and poured over ice and methylene chloride. The mixture was extracted below 20 °C with 6 M sodium hydroxide until all the acetic acid was neutralized. The methylene chloride was dried (MgSO<sub>4</sub>) and concentrated. Purification by preparative TLC using hexane-ethyl acetate (9:1) yielded 159 mg (92%) of 2-acetoxy-3-chloro-1,3-diphenyl-1-butanone (17): NMR (DCCl<sub>3</sub>)  $\delta$  7.7-7.0 (m, 10 H, Ar), 3.8 (s, 1 H, CH-OAc), 2.16 (s, 6 H, CH<sub>3</sub> and -O<sub>2</sub>CCH<sub>3</sub>); IR (neat) 3060, 1745, 1690, 1235 cm<sup>-1</sup>; MS (70 eV), m/e (relative intensity) 316 (1), 281 (1), 238 (4), 222 (17), 176 (20), 134 (81), 105 (100), 77 (51), 43 (45).

Anal. Calcd for  $C_{18}H_{17}O_3Cl$ : C, 68.23;H, 5.42. Found: C, 68.24;H, 5.42.

Identification of 3-Chloro-1,3-diphenyl-2-hydroxy-1-butanone (3) from trans-Dypnone Oxide and Chlorosulfonic Acid in Methanol and Methylene Chloride. From 400 mg (1.68 mmol) of trans-dypnone oxide in methylene chloride with 8.0 equiv of methanol and 1.0 equiv of chlorosulfonic acid, under the general conditions described above, 350 mg of a mixture of 12 and 3 was obtained after preparative TLC. Analysis by NMR indicated that these products were present in a ratio of 1:1. The entire mixture was refluxed in acetyl chloride for 2 h as described for the preparative TLC on the mixture of acetates using hexane-ethyl acetate (9:1) afforded 180 mg (45% by weight) of 17 identical in all respects with authentic material.

Degradation of 1,3-Diphenyl-2-hydroxy-3-methoxy-1-butanones. 2-Methoxy-2-phenylpropanal (14). To 200 mg (0.741 mmol) of a mixture of the epimeric 1,3-diphenyl-2-hydroxy-3methoxy-1-butanones (12 and 13) in 5 mL of acetic acid and 7 mL of diethyl ether at 0 °C was added 158 mg of periodic acid ( $H_5IO_6$ , 1.1 equiv). The mixture was stirred at 0 °C for 5 h and was then poured into an ice-methylene chloride bath. The acetic acid was neutralized by 12 M sodium hydroxide. The methylene chloride was dried (MgSO<sub>4</sub>) and concentrated to give, as a clear yellowish oil, 123 mg (100%) of 2-methoxy-2-phenylpropanal (14): NMR (DDCl<sub>3</sub>)  $\delta$  9.50 (s, 1 H, CHO), 7.33 (s, 5 H, C<sub>6</sub>H<sub>5</sub>), 3.27 (s, 3 H, OCH<sub>3</sub>), 1.63 (s, 3 H, CH); IR (neat) 2820, 2690, 1735 cm<sup>-1</sup>. Further purification by preparative GLC (SE-30, 145 °C) did not alter the spectral properties reported above for unpurified material.

(S)-2-Methoxy-2-phenylpropanal (14). As with racemic material, 730 mg (2.7 mmol) of (2R,3S)- and (2R,3R)-1,3-diphenyl-2-hydroxy-3-methoxy-1-butanones (12 and 13) in a ratio of 74.8:25.2 gave, after 6 h at 0 °C with periodic acid, 424 mg (96%) of crude (S)-2-methoxy-2-phenylpropanal (14), which was used without purification in the chromium trioxide oxidation.

2-Methoxy-2-phenylpropionic Acid (15). To 200 mg (1.22 mmol) of 2-methoxy-2-phenylpropanal (14) in 15 mL of acetone at 0 °C was added 140 mg of concentrated sulfuric acid followed by 122 mg (1.3 equiv) of chromium trioxide. The mixture was stirred at 0 °C for 30 min and then diluted with methylene chloride and extracted twice with 10% sulfuric acid. The 2-methoxy-2-phenylpropionic acid (15) was then extracted twice with 50 mL of 1 M sodium hydroxide. The basic solution was acidified to pH 2 at 0 °C and extracted three times with 50 mL of methylene chloride. Drying (MgSO<sub>4</sub>) and concentration afforded 138 mg (63%) of dense colorless oil 15: NMR (DDCl<sub>4</sub>)  $\delta$  10.1 (br, 1 H, OH), 7.2–7.6 (m, 5 H, C, H), 3.30 (s, 3 H, OCH), 1.80 (s, 3 H, CH<sub>3</sub>); IR (neat) 1710 cm<sup>-1</sup>.

(+)-(S)-2-Methoxy-2-phenylpropionic Acid (15). As with the racemic material, 424 mg of (S)-14 was converted to 418 mg (90%) of (+)-(S)-15,  $[\alpha]^{25}_{D}$  +6.28° (c 1.6, CH<sub>3</sub>OH). The acid 15 was purified further by column chromatography using hexaneethyl acetate-acetic acid 80:19:1, which raised the specific rotation to  $[\alpha]^{25}_{\rm D}$  +6.98° (c 1.1, CH<sub>3</sub>OH) [lit.<sup>15b</sup>  $[\alpha]^{25}_{\rm D}$  26.0 (CH<sub>3</sub>OH)]. (+)-(S)-Methyl 2-Methoxy-2-phenylpropionate (16). In a refluxing solution of sulfuric acid (50 mg) and methanol (30 mL), 300 mg (1.66 mmol) of (+)-(S)-15  $[\alpha]^{25}_{\rm D}$  +6.98°, was converted to the methyl ester (+)-(S)-16. The methanol was diluted with methylene chloride and extracted with 10% sodium hydroxide. The organic layer was dried (MgSO<sub>4</sub>) and concentrated, affording 306 mg (95%) of (+)-(S)-16:  $[\alpha]^{25}_{\rm D}$  +2.98° (c 1.0, CH<sub>3</sub>OH); NMR (DCDl<sub>3</sub>)  $\delta$  7.2-7.6 (m, 5 H, C<sub>6</sub>H<sub>5</sub>), 3.70 (s, 3 H, CO<sub>2</sub>CH<sub>3</sub>), 3.27 (s, 3 H, OCH<sub>3</sub>), 1.77 (s, 3 H, CH<sub>3</sub>); IR (neat) 2810, 1730, 1260 cm<sup>-1</sup>. Using a chiral shift reagent,<sup>16</sup> the CO<sub>2</sub>CH<sub>3</sub> singlet exhibited a doublet at 284 Hz and 272 Hz; integration indicated an optical purity of 22%.

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**Registry No.** (±)-1, 70774-47-9; (+)-1, 63257-41-0; (-)-1, 63257-42-1; (±)-2, 70774-48-0; (-)-2, 63257-44-3; (±)-2a, 91899-74-0; 3, 66364-97-4; 4, 70729-30-5; (±)-5, 70397-72-7; (+)-5, 66365-00-2; (-)-5, 66364-98-5; (±)-6, 91899-75-1; (±)-6-d, 91899-76-2; (±)-7, 67737-73-9; 12, 91899-77-3; (±)-12, 92007-86-8; 13, 91899-78-4; (±)-13, 92007-87-9; (±)-14, 92007-88-0; (R)-14, 91899-79-5; (S)-14, 66221-50-9; (±)-15, 92007-85-7; (R)-15, 24190-08-7; (S)-15, 24190-10-1; (R)-16, 24190-11-2; (S)-16, 26164-23-8; 17, 91899-80-8; Mg(ClO<sub>4</sub>)<sub>2</sub>, 10034-81-8; LiClO<sub>4</sub>, 7791-03-9; CF<sub>3</sub>CO<sub>2</sub>H, 76-05-1; CISO<sub>3</sub>H, 7790-94-5; HClO<sub>4</sub>, 7601-90-3; ZnCl<sub>2</sub>, 7646-85-7; AlCl<sub>3</sub>, 7446-70-0; CuCl<sub>2</sub>, 7447-39-4; BCl<sub>3</sub>, 10294-34-5; AgO<sub>2</sub>CCF<sub>3</sub>, 2966-50-9; AgBF<sub>4</sub>, 14104-20-2; AgNO<sub>3</sub>, 7761-88-8; BF<sub>3</sub>, 7637-07-2; HCl, 7647-01-0; HOAc, 64-19-7; AcCl, 75-36-5.

## Proximate Charge Effects. 6.<sup>1</sup> Anion-Cation-Zwitterion Triplets in Solution

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The reaction of *p*-nitrophenol with tetra-*n*-butylammonium taurinate in 95.3 mol % dioxane-water was found to give an anion-cation-zwitterion triplet which then dissociates to a zwitterion and to an ion pair. The equilibrium constants for the formation of this triplet,  $K_{\rm f}$ , and for dissociation,  $K_{\rm d}$ , were found to be  $K_{\rm f} = 3.57 \ {\rm L}^{1/2} \ {\rm mol}^{-1/2}$  and  $K_{\rm d} = 1.73 \times 10^{-7} \ {\rm mol} \ {\rm L}^{-1}$ .

Ion pairs, triplets, and higher aggregates of electrolytes in nonpolar solvents have been known for some time.<sup>2</sup> The driving force for their formation is principally the Coulomb force attraction of oppositely charged particles. Zwitterions (dipolar ions) have a net neutral charge, yet it appears plausible that electrostatic forces at their (oppositely) charged ends might, in nonpolar solvents, prove, in some cases, to be sufficient to cause self association into zwitterion pairs or association with ion pairs to form anion-cation-zwitterion triplets. We wish to report evidence for the existence of the latter entity with the zwitterion being taurine (<sup>+</sup>H<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>SO<sub>3</sub><sup>-</sup>) and the ion pair being tetra-*n*-butylammonium *p*-nitrophenoxide ([*n*-Bu]<sub>4</sub>N<sup>+</sup> *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>O<sup>-</sup>) in 95.3 mol % dioxane-water solvent. Anion-Cation-Zwitterion Triplet Formation and Dissociation. In connection with an investigation of the kinetics of the aminolysis of p-nitrophenyl esters by tetra-*n*-butylammonium taurinate, I, it became necessary to measure the equilibrium constant for the acid-base reaction between p-nitrophenol and I in 95.3 mol % dioxane-water solvent (eq 1).

$$p \cdot \text{NO}_2\text{C}_6\text{H}_4\text{OH} + \text{H}_2\text{NCH}_2\text{CH}_2\text{SO}_3^- + (n \cdot \text{Bu})_4\text{N}^+ \rightleftharpoons p \cdot \text{NO}_2\text{C}_6\text{H}_4\text{O}^- + (n \cdot \text{Bu})_4\text{N}^+ + {}^+\text{H}_3\text{NCH}_2\text{CH}_2\text{SO}_3^- (1)$$

Acid-base reactions of 2,4-dinitrophenol and amines in aqueous dioxane had been studied by Pearson & Vogelsong<sup>3</sup> and found to obey the equilibrium law

$$K = \frac{[\mathbf{B}\mathbf{H}^+\mathbf{A}^-]}{[\mathbf{A}][\mathbf{B}]} \tag{2}$$

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<sup>(3)</sup> Pearson, R. G.; Vogelsong, D. C. J. Am. Chem. Soc. 1958, 80, 1038.