TABLE IV

CONSTANTS FOR THE METHYLMERCAPTO, METHYLSULFONYL AND ACETYL GROUPS

Reaction	m-CH_3S	p-CH_3S	m-CH_3SO_2	p-CH_3SO_2	m-CH_3CO	p-CH_3CO
Apparent ionization constants of benzoic acids, 50% ethanol, 25°	+0.14	−0.01	+0.65	+0.72	+0.35	+0.43
Alkaline hydrolysis of ethyl benzoates, 56% acetone, 25°[a]	+ .10[b]	− .07[b]	+ .65	+ .76		
Ionization of phenols, water, 25°	+ .16	+ .16	+ .70	+ .98	+ .32	+ .87
Acidity constants of anilinium ions, water 25°	+ .19	+ .06	+ .69	+1.13		
Hydrolysis of arylsulfuric acids, water 78.6°[c]					+ .31[c]	+ .87[c]

[a] C. C. Price and J. J. Hajduk, private communication. [b] Measured at 0°, a previous value of −0.047 was recorded for p-CH_3S, see ref. 4, p. 188. [c] Ref. 4, p. 188.

from sigma constants indicates, therefore, that the CH_3SO_2 group should be classified electronically with resonating groups such as CH_3CO, CN, etc., rather than with the $(CH_3)_3N^+$ group.

Recently Koch and Moffitt[13] have reviewed the evidence for conjugative effects of the $-SO_2-$ group, and have suggested that the existing rather contradictory data can be made consistent by assuming that only a weak conjugation is possible in a sulfone only one of whose carbon atoms is part of an unsaturated or conjugated system, but that a strong conjugation is possible in systems where both carbons are unsaturated such as the thiophene 1-dioxides. An analysis using the molecular orbital theory was found to be consistent with this hypothesis. The spectroscopic evidence for conjugation in alkyl aryl sulfones[14] was rationalized by assuming that conjugation of groups with CH_3SO_2 may be important in excited states or transition states but not in ground levels. The present data indicate that conjugative effects may be appreciable in sulfones only one of whose carbons is unsaturated even in the ground state.[15]

The fact that m-CH_3S increases the acidity of benzoic acid whereas p-CH_3S decreases the acidity, can be interpreted as being due to an acid-weakening resonance for the para group,[16] p-$CH_3\overset{\frown}{S}—C_6H_4—C(OH)=\overset{\frown}{O}$. This effect is similar to that observed for p-CH_3O, but smaller in magnitude.[17] It seemed possible *a priori* that p-CH_3S might exert a resonance effect comparable to that of p-CH_3SO_2 in conjunction with O^- and NH_2 groups, *i.e.*, $CH_3\bar{S}=C_6H_4=\overset{+}{N}H_2$. In line with this the sigma constants of p-CH_3S determined for phenols and anilinium ions are somewhat more positive than those for benzoic acids. Similar effects are noted, however, with p-CH_3O, and a better interpretation is probably that the more positive sigma value reflects a resonance effect which is present in the p-CH_3O and p-CH_3S benzoic acids, but absent in the corresponding phenols and anilines.

(13) H. P. Koch and W. E. Moffitt, *Trans. Faraday Soc.*, **47**, 7 (1951); see also ref. 2.

(14) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949); *ibid.*, **72**, 1292 (1950); H. P. Koch, *J. Chem. Soc.*, 408 (1949).

(15) Note, however, that the sulfonyl group does not appear to be able to conjugate with an odd electron (C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950); C. G. Overberger, D. E. Baldwin and H. P. Gregor, *ibid.*, **72**, 4864 (1950)).

(16) C. K. Ingold, *J. Chem. Soc.*, 1124 (1933), first used this explanation for the m- and p-CH_3O benzoic acids.

(17) The order of resonance effects $CH_3O > CH_3S$ is in line with the similar order observed for the halogens, F > Cl, Br > I. Other evidence pointing to a lesser resonance effect of -S- than -O- is found in the lack of shortening of the C-S bond in CH_3COSH (W. Gordy, *J. Chem. Phys.*, **14**, 560 (1946)).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Stereospecificity of Hydrogen Migration in the Pinacol Rearrangement

BY KURT MISLOW AND MAURICE SIEGEL[1]

The synthesis and resolution of 2-methylbenzilic acid are described. Reduction of the optically active acid to 1-phenyl-1-*o*-tolylglycol, followed by acid-catalyzed rearrangement to optically active phenyl-*o*-tolylacetaldehyde, substantiates that hydrogen migration in the rearrangement is stereospecific.

The stereospecificity of the pinacol–pinacolone rearrangement seems well established[2]; in many instances the rearrangement of optically active glycols or aminoalcohols has yielded optically active ketones, the migrating group in those cases being phenyl or benzyl.[3] Of particular interest is the work done on the optically active tolylhydrobenzoins. It was shown[4] that the rearrangement of the *o*- and *m*-tolyl isomers, but not of the *p*-isomer, led to the corresponding optically active tolyldesoxybenzoins, results which were taken as evidence for the stereospecific 1,2-shift of hydrogen. The interpretation of these data was, however, made with some reservations: the product of the more critical rearrangement, α-phenyl-α-*o*-tolylacetophenone, was never definitely identified, and

(1) The major portion of this material was abstracted from the thesis submitted by Maurice Siegel to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Master of Science, 1951.

(2) E. R. Alexander and D. C. Dittmer, THIS JOURNAL, **73**, 1665 (1951), and references given therein.

(3) R. Roger and A. McKenzie, *Ber.*, **62**, 272 (1929); A. McKenzie and W. S. Dennler, *ibid.*, **60**, 220 (1927); A. McKenzie, R. Roger and G. O. Wills, *J. Chem. Soc.*, 779 (1926); H. J. Bernstein and F. C. Whitmore, THIS JOURNAL, **61**, 1324 (1939); S. Kanao, *J. Pharm. Soc. Japan*, **64**, 137 (1944) [*C. A.*, **45**, 5136 (1951)].

(4) A. McKenzie, R. Roger and W. B. McKay, *J. Chem. Soc.*, 2597 (1932); R. Roger and W. B. McKay, *ibid.*, 332 (1933).

the same product could also arise through the migration of the *o*-tolyl group, although in dilute sulfuric acid solution there is only a small likelihood for this alternative.[5]

The present work was undertaken in order to clarify these questions by a study of the rearrangement of a closely related glycol. 2-Methylbenzilic acid was prepared through the base catalyzed rearrangement of 2-methylbenzil, and was resolved by the repeated crystallization of the cinchonine salt from ethanol. (+)-2-Methylbenzilic acid was reduced with lithium aluminum hydride to (+)-1-phenyl-1-*o*-tolylglycol which was then rearranged in dilute sulfuric acid. Only three possible products of such a rearrangement are conceivable. If either of the hydrogens is the migrating entity, the product will be phenyl-*o*-tolylacetaldehyde, which is capable of optical activity; if, on the other hand, the phenyl or the *o*-tolyl group should migrate, the product would be benzyl *o*-tolyl ketone or α-*o*-tolylacetophenone, respectively. The latter alternative, besides resulting in loss of asymmetry, is less likely *a priori* for it would be expected that the electrophilic center required for migration would be stabilized to a far lesser degree on a carbon bearing two hydrogens than on a carbon bearing two aryl groups. The observed result, rearrangement to (+)-phenyl-*o*-tolylacetaldehyde, bears out the foregoing arguments.

It is therefore established that asymmetry is retained when hydrogen migrates in a pinacol rearrangement.

The reported case appears also to serve as the first instance of a pinacol shift resulting in an optically active aldehyde. The rotation of the aldehyde obtained from the rearrangement was $[\alpha]_D$ + 1.36° (no solvent); since the starting glycol was 63% active (based on the rotation of the starting acid) this rotation does not represent a maximum. Nevertheless it appears low if one is to judge by the rotation of the closely related α-phenyl-α-*o*-tolylacetophenone,[4] and it is likely that appreciable racemization occurred during the rearrangement. The surprising result is rather that the racemization of the aldehyde was not complete under the conditions of the rearrangement. A plausible explanation might be based on the peculiar steric effect of the *o*-tolyl group, already observed in the rearrangements studied by Roger and McKay.[4]

Experimental[6]

2-Methylbenzilic Acid.—A hot solution of 2.8 g. of 2-methylbenzil[7] in 15 ml. of ethanol was made saturated by the judicious addition of water, care being exercised that the solution did not become turbid. The addition of 3 g. of potassium hydroxide to this solution produced a deep violet color. After it was refluxed for one hour, the solution was brought to *p*H *ca.* 8 with dilute hydrochloric acid. The dark brown precipitate was filtered and the filtrate was made strongly acid. The resulting brown oil was shaken thoroughly with a 5% sodium carbonate solution. The solution was decanted from the remaining viscous oil and acidified; the light tan oil thus formed solidified on standing in the refrigerator overnight. Recrystallization from ether–ligroin afforded chunky prisms, m.p. 113.5–114.5°, in yields varying from 50 to 68%.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.39; H, 5.82; neut. equiv., 242.3. Found: C, 74.31; H, 6.08; neut. equiv., 240.8.

Resolution of 2-Methylbenzilic Acid.—Attempts were made to resolve the acid by the fractional crystallization of one of its alkaloidal salts. Of the several alkaloidal salts which were employed for this purpose, among them those of morphine, strychnine and brucine, the cinchonine salt was found to be the most suitable.

To a solution of 60.0 g. (0.247 mole) of 2-methylbenzilic acid in 350 ml. of hot 95% ethanol was added 73.0 g. (0.247 mole) of cinchonine. On cooling, the solution deposited 68 g. of salt,[8] $[\alpha]^{26}D$ +106° (*c* 0.63, methanol).

Seven recrystallizations from 95% ethanol gave 13.3 g. of salt, $[\alpha]^{26}D$ +117° (*c* 1.47, methanol), whose rotation remained unchanged upon further recrystallization. This salt was hydrolyzed with dilute sulfuric acid and the desired acid extracted with ether. Evaporation of the ether yielded 5.0 g. of a residue, m.p. 93–98°. Seven recrystallizations, from ligroin–ether, in which the more soluble tail fractions proved to concentrate the optically active component, yielded needle rosettes of constant m.p. 93–95°, and constant rotation $[\alpha]^{26}D$ +11.4° (*c* 6.87, ethanol).

1-Phenyl-1-*o*-tolylglycol.—A solution of 11.2 g. of 2-methylbenzilic acid in 100 ml. of absolute ether was added dropwise to a well stirred solution of 2.1 g. of lithium aluminum hydride in 150 ml. of absolute ether. The addition required 30 minutes and refluxing was continued by external heating for one hour. The reaction mixture was worked up to yield 11.2 g. of a mixture, m.p. 70–88°, of the desired glycol and of unreacted acid. An ethereal solution of the product was shaken with dilute ammonia, from which 2.1 g. of unreacted acid could later be recovered, and the ether layer was evaporated. The remaining 7.8 g. (76%) of solid, after four recrystallizations from ether–ligroin, melted at 71–72°.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.92; H, 7.07. Found: C, 78.92; H, 7.23.

When this reaction was repeated on optically impure 2-methylbenzilic acid, $[\alpha]^{26}D$ +7.2° (*c* 4.58, ethanol), the resulting glycol, m.p. 61–69°, had a rotation of $[\alpha]^{26}D$ +5.7° (*c* 4.94, ethanol).

Phenyl-*o*-tolylacetaldehyde.—A suspension of 5.2 g. of 1-phenyl-1-*o*-tolylglycol in 15 ml. of water, to which had been added three drops of sulfuric acid, was refluxed two hours with constant agitation. Extraction with ether and distillation of the extracts afforded 2.2 g. (46%) of a viscous liquid, b.p. 121–122° (1 mm.), $n^{25}D$ 1.5901, d^{25}_4 1.103; M_D calcd., 64.28; found, 64.34.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.70; H, 6.71. Found: C, 85.68; H, 6.33.

The compound gave a positive Tollens test and formed a 2,4-dinitrophenylhydrazone, yellow crystals from ethyl acetate, m.p. 181–182° dec.

By this method the rearrangement of 1-phenyl-1-*o*-tolylglycol, $[\alpha]^{26}D$ +5.7 (ethanol), gave the desired aldehyde, $[\alpha]^{26}D$ +1.36° (no solvent). A racemization study proved to be impracticable since the addition of ethanolic potassium hydroxide to an ethanolic solution of the optically active aldehyde caused the development of a yellow-brown color which rendered polarimeter readings irreproducible.

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(5) The products of the rearrangement in *dilute* sulfuric acid are diphenyl-*o*-tolylacetaldehyde and α-phenyl-α-*o*-tolylacetophenone, which would indicate that loss of oxygen occurred primarily at the carbon bearing the *o*-tolyl group; in *concentrated* sulfuric acid, diphenylmethyl *o*-tolyl ketone and α-phenyl-α-*o*-tolylacetophenone are obtained, indicating a preferential loss of oxygen at the carbon bearing the hydrogen.

(6) Microanalyses by W. C. Woodland and W. Manser.

(7) A. McKenzie and A. L. Kelman, *J. Chem. Soc.*, 412 (1934).

(8) The salt, in varying degrees of purity, did not melt sharply but decomposed near 200°. The temperature of the decomposition depended on the rate at which the temperature was raised.