9.33, 9.48, 9.88, 10.28, 10.46, 10.65, 11.18 μ; $\delta_{\mathrm{TMS}}^{\mathrm{CCl_4}}$ 0.96 (C-10 CH_3), 0.79 ppm (C-4 CH_3 doublet, J = 6.5 Hz).

The distillate solidified upon refrigeration, and the analytical sample, mp 40.5-41.5°, was obtained after two sublimations.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.1; H, 12.0.

Registry No.—**6,** 16423-15-7; **7,** 16423-16-8; **8,** 16423-17-9; **9,** 16423-18-0; **10,** 16423-19-1; **12,** 16423-20-4; **13,** 16452-32-7.

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The Solvolysis of *p,p′*-Disubstituted Benzhydryl Halides

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The recent series of papers by Nishida on the additivity, or lack of additivity, in the alcoholysis of mono- and disubstituted benzhydryl halides[2] prompted us to report results of a similar, though less extensive study, which had similar objectives as its aim. Our data were obtained in aqueous acetone and therefore supplement the data of Nishida.

The problem of concern is whether two identical substituents in two different benzene rings act completely independently of each other in a reaction in which a carbonium ion is developed in the transition state, when both substituents are capable of interacting with the carbonium ion. Such a situation arises in the solvolysis of appropriately substituted benzhydryl halides. Although in most disubstituted chloro and methyl derivatives additivity occurs,[2,3] Nishida has demonstrated a characteristic deviation in the case of *p,p′*-dimethylbenzhydryl chloride, and it is this deviation from additivity which our data confirm for the acetone–water system. The problem has some added current interest because multiple methyl substitution has been utilized as a probe for the structure of carbonium ion transition states.[4]

Some of the required data have been in the literature for a long time. Ingold and coworkers, in the course of their study on mass law and salt effects, studied the solvolysis of *p*-methyl- and *p,p′*-dimethylbenzhydryl chloride in 80% aqueous acetone.[5] Their data show that one *p*-methyl group increases the reactivity by a factor of 29.6, but that *p,p′*-dimethylbenzhydryl chloride reacts only 567 times as fast as the parent compound, instead of 876 times, if additivity had strictly prevailed.

Our data are reported in Table I. Because of a slight difference in solvent composition (see Experimental Section) and the great sensitivity of the rates to water content,[6] our values for the rate constants differ slightly from those of Ingold, *et al.*, but the general pattern is the same. The solvolysis of *p,p′*-dimethylbenzhydryl chloride in aqueous acetone is not only very fast, but has a very strong mass law effect in the concentration range here used. The rate constants reported, ours, as well as the literature values, were obtained by extrapolation to 0% reaction, and our data for the dimethyl derivative are only approximate. However, in the alcoholysis (ethanolysis, 2-propanolysis) of the same compound, which is not beset by these difficulties, analogous results were obtained[2] which leaves no doubt as to the over-all validity of the results.

The *p,p′*-dimethyl compound does not react as fast as it should on the basis of additivity. This is also true of *p,p′*-di-*t*-butylbenzhydryl chloride, but with the less powerful electron-releasing effect of the *t*-butyl group, the difference between observed and calculated values is less than with methyl.

The situation is similar, although reversed in an absolute sense, when the substituents have an electron-attracting effect and therefore destabilize the carbonium ion. The chlorine atom in *p*-chlorobenzhydryl chloride lowers the rate of solvolysis, but the second chlorine hinders the reaction less than the first, and *p,p′*-dichlorobenzhydryl chloride does not solvolyze as slowly as calculated. This is true also of the bromine atom, but to a somewhat lesser extent. The deviations caused by the halogens are barely noticeable in the alcoholysis but the deviations become quite pronounced when more than two substituents are present.[2]

The results confirm that in this particular system characteristic deviations from additivity occur. Nishida has shown that this can formally be expressed by assigning two different ρ values to the reactions of mono- and disubstituted benzhydryl chlorides, or by modifying the Hammett equation by the inclusion of more parameters. But the physical meaning of the deviations must be that in a system such as the benzhydryl system, the second of two identical substituents does not affect the reaction to the same extent as the first, and that their effects appear to oppose each other. Consequently, both cannot interact with the developing carbonium ion as effectively as can one alone. The result which is noted in the rate studies is that the second substituent has less effect than the first, but, because of the complete symmetry of the system, the effect of both substituents must be diminished to the same extent.

This lack of additivity is not necessarily confined to transition states. It has also been noted in the dissociation of substituted triphenylmethyl halides in

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[1] Taken from the Ph.D. Thesis of M. Q. Malter, Bryn Mawr College, June, 1952.

[2] S. Nishida, *J. Org. Chem.*, **32**, 2692, 2695, 2697 (1967).

[3] Deviations from additivity in the solvolysis of benzhydryl chlorides have been observed and discussed by J. R. Fox and G. Kohnstam, *Proc. Chem. Soc.* (London), 115 (1964).

[4] P. D. Bartlett and G. D. Sargent, *J. Amer. Chem. Soc.*, **87**, 1297 (1965); P. von R. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966).

[5] E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 949 (1940); M. G. Church, E. D. Hughes, and C. K. Ingold, *ibid.*, 966 (1940); M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *ibid.*, 971 (1940); L. C. Bateman, E. D. Hughes, and C. K. Ingold, *ibid.*, 974 (1940); L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *ibid.*, 979 (1940).

[6] For instance, see V. J. Shiner, Jr., and C. J. Verbanic, *J. Amer. Chem. Soc.*, **79**, 369 (1957).

Table I

RATE DATA FOR THE SOLVOLYSIS OF SUBSTITUTED BENZHYDRYL CHLORIDES

Substituents	Solvent, % acetone	Temp, °C	$k_1 \times 10^5$, sec^{-1}	k/k_H	$(k/k_H)_{calcd}$	$(k/k_H)_{obsd}/(k/k_H)_{calcd}$
H	80	0	0.277			
p-CH_3	80	0	7.70	27.8[a]		
p,p′-di-CH_3	80	0	~162	~585	773	~0.76[b]
H	80	25	6.07			
p-Cl	80	25	1.93	0.318[c]		
p,p′-di-Cl	80	25	0.840	0.138	0.101	1.37
p-Br	80	25	1.66	0.273[c]		
p,p′-di-Br	80	25	0.555	0.0914	0.0745	1.23
H	90	25	0.507			
p-CH_3	90	25	11.2	22.1[d]		
p,p′-di-CH_3	90	25	~143	~282	488	~0.58
p-t-C_4H_9	90	25	5.77	11.4[e]		
p,p′-di-t-C_4H_9	90	25	56.0	110	130	0.85

[a] Lit.[5] 29.6. [b] Lit.[5] 0.65. Ratios of 0.60 and 0.62 were found in the ethanolysis and 2-propanolysis, respectively.[2] [c] Values of 0.328 and 0.251 were observed in the solvolysis in 70% aqueous acetone for the p-chloro and p-bromo compounds, respectively: G. Kohnstam, *J. Chem. Soc.*, 2066 (1960). [d] Lit.[5] 20.6. [e] Lit.[5] 10.9 and 10.5 in 80% acetone at 25°.

liquid sulfur dioxide[7] and the ionization of substituted triphenylmethanols in concentrated sulfuric acid.[8,9]

Experimental Section

The known benzhydryl halides were prepared by literature procedures, and their melting points or boiling points agreed with those reported in the literature. *p,p′*-Di-*t*-butylbenzophenone was prepared from *t*-butylbenzene and carbon tetrachloride[10] and forms white crystals (ligroin) of mp 134.6–134.9° uncor.

Anal. Calcd for $C_{21}H_{26}O$: C, 85.66; H, 8.90. Found: C, 85.66; H, 8.89.

The 2,4-dinitrophenylhydrazone melts at 202–203°.

Anal. Calcd for $C_{27}H_{30}O_4N_4$: C, 68.33; H, 6.37. Found: C, 68.30; H, 6.02.

p,p′-Di-*t*-butylbenzhydrol forms white crystals (ligroin) of mp 102–102.4° uncor.

Anal. Calcd for $C_{21}H_{28}O$: C, 85.08; H, 9.52. Found: C, 85.07; H, 9.52. *p,p′*-Di-*t*-butylbenzhydryl chloride, prepared from the above with dry hydrogen chloride, was recrystallized from ligroin and had mp 122.5–123°.

Anal. Calcd for $C_{21}H_{27}Cl$: C, 80.09; H, 8.64. Found: C, 80.06; H, 8.71.

Acetone was purified by the method of Conant and Kirner.[11] The 80 and 90% acetone were prepared by adding 200 or 100 ml of distilled water to a 1-l. volumetric flask and diluting with acetone to the mark. These solvents contain slightly more acetone than the solvents used by Ingold, *et al.*,[5] who prepared them by mixing appropriate volumes of acetone and water. Solvent batches prepared for runs at different temperatures were not comparable. Rate constants were determined in the usual way by quenching 10-ml samples in 100 ml of ice-cold acetone and titrating with standard $Ba(OH)_2$. They were calculated for each point from the integrated form of the first-order rate equation. The initial concentration of chloride was determined from an infinity titer. The concentrations ranged between 0.035 and 0.04 *M*. Runs were usually conducted in triplicate, and rate constants within one run, as well as in duplicate runs, usually agreed within a few per cent. The rate constants for *p*-methylbenzhydryl chloride in 80% acetone, and those for the *p,p′*-dimethyl compound, in both 80 and 90% acetone, fell as the reaction progressed, those of the dimethyl compound much more than the monomethyl compound, and more in 80% than in 90% acetone.[1] Rate constants were extrapolated to 0% reaction by visually fitting the best smooth line through the points. Because of considerable scatter, the values for *p,p′*-dimethylbenzhydryl chloride are not very precise, but the constant in 80% acetone agrees with the constant obtained similarly by Ingold, *et al.*

Registry No.—*p,p′*-Di-*t*-butylbenzophenone, 15796-82-4; *p,p′*-di-*t*-butylbenzophenone 2,4-dinitrophenylhydrazone, 16607-59-3; *p,p′*-di-*t*-butylbenzhydrol, 16607-60-6; *p,p′*-di-*t*-butylbenzhydryl chloride, 16622-59-6.

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[7] N. C. Deno and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3051 (1955).

[8] N. N. Lichtin, *Progr. Phys. Org. Chem.*, **1**, 75 (1963).

[9] The argument, suggested by a referee, that the results of the solvolysis might be caused by different extents of ion pair return in mono and disubstituted benzhydryl halides, offers an alternate explanation. However, it is much less likely that this argument accounts for the results of the alcoholysis, or the data quoted at the end of the paper.

[10] The procedure was similar to that described for the preparation of benzophenone by C. S. Marvel and W. M. Sperry, "Organic Syntheses," Coll. Vol. I, 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1948, p 95.

[11] J. B. Conant and W. R. Kirner, *J. Amer. Chem. Soc.*, **46**, 232 (1924).

The Synthesis and Anionic Properties of 1,3-Dithiane 1-Oxide

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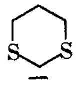
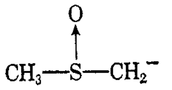
Corey and coworkers have recently developed a variety of reagents for organic synthesis utilizing the properties of sulfur (in various oxidation states) to stabilize carbanions.[2–5] The anion I derived from the title compound, 1,3-dithiane 1-oxide (II), incorporates the structural features of two of these reagents, the "dimsyl anion" (III)[2] and the dithienyl anions (IV),[3] and has been found to undergo reactions common to both.

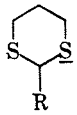


I



$CH_3\text{—}\overset{\overset{\displaystyle O}{\uparrow}}{S}\text{—}CH_2^-$

III



IV

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[1] A National Science Foundation Undergraduate Summer Research Participant, 1967.

[2] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

[3] (a) E. J. Corey and D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1075, 1077 (1965); (b) E. J. Corey, D. Seebach, and R. Freedman, *J. Amer. Chem. Soc.*, **89**, 434 (1967); (c) E. J. Corey and D. Crouse, *J. Org. Chem.*, **33**, 298 (1968); (d) D. Seebach, N. R. Jones, and E. J. Corey, *ibid.*, **33**, 300 (1968).

[4] (a) E. J. Corey and D. Seebach, *ibid.*, **31**, 4097 (1966); (b) E. J. Corey and T. Durst, *J. Amer. Chem. Soc.*, **88**, 5656 (1966).

[5] E. J. Corey and M. Chaykovsky, *ibid.*, **87**, 1353 (1965).