the Friedel–Crafts reaction showed the compounds to be identical. Both esters were hydrolyzed to the same acid, m. p. 280° (dec.).

Ethyl 6-Bromonaphthoate-2.—The ethyl ester of 6-bromonaphthoic acid-2 was prepared by refluxing the acid in absolute ethanol containing sulfuric acid and the product was recrystallized from ethanol, m. p. 67–68°. *Anal.* Calcd. for $C_{13}H_{11}BrO_2$: Br, 28.62. Found: Br, 28.60.

2-(6-Bromonaphthyl)-diphenylcarbinol.—The carbinol was made by treating methyl 6-bromonaphthoate-2 with 100% excess phenylmagnesium bromide in boiling toluene for eighteen hours. Previous attempts using milder conditions gave a material that would not crystallize and would not give a crystalline chloromethane. An attempt was made to prepare the carbinol using phenyl lithium instead of phenylmagnesium bromide, but oily products again resulted. The carbinol crystallized from acetic acid with one mole of acetic acid, m. p. 99–101°. *Anal.* Calcd. for $C_{23}H_{17}BrO\cdot C_2H_4O_2$: Br, 17.80; $C_2H_4O_2$, 13.39. Found: Br, 18.16; $C_2H_4O_2$, 13.66 (by titration).

2-(6-Bromonaphthyl)-diphenylchloromethane.—The crude carbinol was treated with acetyl chloride and converted to the chloromethane. The same compound was produced by passing hydrogen chloride into an ether solution of the carbinol in the presence of calcium chloride. It was recrystallized from an acetyl chloride–petroleum ether mixture, m. p. 118–119°. *Anal.* Calcd. for $C_{23}H_{16}BrCl$: Br, 19.55; Cl, 8.71. Found: Br, 18.90; Cl, 8.32.

1-(2-Bromonaphthyl)-diphenylchloromethane.—The methanol solution after the separation of the solid methyl 6-bromonaphthoate-2, described above, contained methyl 2-bromonaphthoate-1. This ester, a liquid, was treated with a Grignard reagent in a manner similar to that used for the 6-isomer. The chloromethane was produced by treating the crude carbinol with acetyl chloride, m. p. 203–204°. *Anal.* Calcd. for $C_{23}H_{16}BrCl$: Br, 19.55; Cl, 8.71. Found: Br, 18.90; Cl, 9.24.

1-(2-Bromonaphthyl)-diphenylcarbinol.—The preceding chloromethane was hydrolyzed by boiling with dimethylaniline in an acetone–water solution. It was recrystallized from a carbon disulfide–petroleum ether mixture, m. p. 129–131°. *Anal.* Calcd. for $C_{23}H_{17}BrO$: Br, 20.55. Found: Br, 20.38.

Summary

Three bromonaphthyldiphenylchloromethanes have been synthesized which have the bromine atom and carbinol chloride group in the positions corresponding to the oxygen atoms of the three transnuclear naphthoquinones. No evidence of a labile bromine atom could be found when solutions of these compounds in liquid sulfur dioxide were treated with silver chloride and silver sulfate. A sulfur dioxide solution of 1-(2-bromonaphthyl)-diphenylchloromethane likewise showed no evidence of a labile bromine atom and the original material could not be recovered from the sulfur dioxide solution. Sulfur dioxide solutions of *p*-bromophenylchloro-1-naphthylphenylmethane and 1-(4-bromonaphthyl)-diphenylchloromethane gave positive evidence of a labile bromine atom under the same conditions.

ANN ARBOR, MICHIGAN RECEIVED OCTOBER 21, 1942

[COMMUNICATION NO. 892 FROM THE KODAK RESEARCH LABORATORIES]

The Influence of Addenda on the Inversion of *l*-Menthone with Acids in Benzene (The Effect of Solvents in Chemical Reactions. III)[1]

BY A. WEISSBERGER

The evidence accumulated by various groups of authors demonstrates that the catalytic action of an acid is connected with the transfer of a proton between the catalyst and the substrate.[2] Investigations of the decomposition of diazoacetic ester[3] and of the inversion of *l*-menthone[4] showed that in these processes the reactive complex is of a ternary nature and involves two molecules of the acid per molecule of the substrate. A binary complex between acid and substrate is formed to a rather high degree of completion, and the inversion takes place in the interaction of this complex with a further acid molecule. Solvents which are proton acceptors can be expected to compete with the substrate for the acid, and therefore, to lower the reaction rate. In aprotic solvents such action is absent.

Weissberger and Högen[3] studied the effect of proton acceptors on the *reaction between diazoacetic ester and trichloroacetic acid* with as little change of the medium as possible. Substances like ether, alcohols and ketones were added to the solution of diazo ester and acid in hexane, in amounts equimolar to the reacting compounds. Thus, information was obtained on the protophilic nature of the addenda, which, in many cases, considerably slowed down the formation

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(1) II, Weissberger and Fasold, *Z. physik. Chem.*, **A157**, 65 (1931).

(2) Taylor, *Z. Elektrochem.*, **20**, 201 (1914); Hantzsch, *ibid.*, **29**, 221 (1923); Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924); Hall, *Chem. Rev.*, **8**, 191 (1931); Bell, "Acid–Base Catalysis," Oxford, 1941.

(3) Weissberger and Högen, *Z. physik. Chem.*, **A156**, 321 (1931).

(4) Weissberger, THIS JOURNAL, **65**, 102 (1943).

of the trichloroacetoglycolic ester. On the assumption that the retardation is caused by a virtual elimination of part of the acid through compound formation with the addendum, the amount of acid so eliminated can be determined (Table I, column 6). The explanation of the effect of the addenda by their reaction with the acid was corroborated by a spectroscopic investigation of the influence of the addenda on the *salt formation of trichloroacetic acid with dimethylaminoazobenzene* in benzene. The equilibrium between the red salt of dimethylaminoazobenzene and the yellow free base is shifted by protophilic addenda in favor of the free base (Table I, column 5). The action of the addenda on the equilibrium closely resembles that on the rate of the diazo ester decomposition.

TABLE I

THE EFFECT OF ADDENDA

	Menthone inversion[a]		% Acid eliminated		
Addendum	$(k + k')$ 10^4	ρ_∞ (100-mm. tube)	Menthone reaction	Methyl yellow[b] reaction	Diazo-ester[c] reaction
...	6.51	+2.30	..	..	..
Diphenyl ether	6.25	2.32	2	6	..
Phenol	5.36	2.23	8	0	..
Anisole	5.34	2.22	9	6	..
Diphenylamine	..	..	..	8	..
Tribromoaniline	..	..	..	8	..
Water	..	..	..	12	..
Benzophenone	3.35	1.88	26	14	30
l-Menthol	2.93	1.64[d]	30	..	..
Acetophenone	2.75	1.72	33	14	41
Benzoic acid	..	..	..	23	..
Acetone	2.29	1.57	38	40	45
l-Menthone	2.27[e]	..	38	36	47
p-Chloroaniline	..	..	..	54	..
Ethyl ether	1.35	1.60	52	56	55
Methanol	..	..	..	60	..
Ethanol	..	..	..	67	47
Octanol	..	..	..	..	46
Aniline	..	..	..	89	..

[a] Menthone, 0.5 mole/liter; trichloroacetic acid, 0.5 mole/liter; addendum, 0.5 mole/liter; benzene; 20.0 ± 0.1°. [b] Dimethylaminoazobenzene, 0.002 mole/liter; trichloroacetic acid, 0.002 mole/liter; addendum, 0.02 mole/liter; benzene; 20.0°. [c] Diazoacetic ester, 0.1 mole/liter; trichloroacetic acid, 0.1 mole/liter; addendum, 0.1 mole/liter; hexane; 0.0°. [d] Value after subtraction of the rotation due to the menthol added. [e] $(k + k')10^4$ of a reaction with 0.5 mole/liter of acid and 1.0 mole/liter of menthone.

Simultaneously with these investigations, the effect of addenda on the inversion of *l*-menthone was studied.[5] This stereochemical isomerization is chemically very different from the diazo ester decomposition, and the substrate is free from nitrogen, while both the diazoacetic ester and the dimethylaminoazobenzene are nitrogenous compounds. Benzene was used as a solvent. With hexane, unfavorable solubilities were encountered, while chloroform, in which the solubilities are better, splits off hydrogen chloride in the presence of acid.[4] The materials and techniques employed were those described previously,[3,4] the addenda being added to the menthone solution before adding the acid. The results are given in Tables I and II.

In the experiments recorded in Table I the solutions contained 0.5 mole/liter of menthone, 0.5 mole/liter of trichloroacetic acid, and 0.5 mole/liter of the addendum. In absence of the latter, the reaction rate $(k + k')10^4$, is 6.5. The addenda depressed the rate in all cases (Table I, column 4). Since the dependence of the reaction rate on the concentration of trichloroacetic acid at a menthone concentration of 0.5 mole/liter is known, the acid concentration characteristic for any reaction rate can be read from a graph.[6] The difference between this value and 0.5 mole/liter gives the "acid eliminated" by the addendum (Table I, column 4).

The parallelism in the influence of the addenda in the three very different reactions shows that it is the common component, *viz.*, the acid, which is affected by the addenda, and that the type of the reaction used is of secondary importance only. In the investigation with dimethylaminoazobenzene, the sensitivity of the spectrophotometric measurements permitted the use of the reactants and addenda in rather low concentrations. The latter had to be higher in the present work, and some of the addenda thereby became unsuitable: the amines because they formed insoluble salts, and most of the alcohols because they formed esters and water which made the solutions opaque. However, the nature of the effect is demonstrated most clearly with the amines in the salt formation of dimethylaminoazobenzene (Table I, column 5). Aniline has the greatest influence, introduction of one halogen into the benzene nucleus reduces the effect considerably, as shown by *p*-chloroaniline, and in tribromoaniline the addendum has become quite weak. Diphenylamine acts like tribromoaniline. This order is in agreement with that of the basic ionization constants of these amines (aniline$_{25}$ 4.6×10^{-10}, *p*-chloroaniline$_{25}$ 3.4×10^{-10}, diphenylamine$_{15}$ 7.6×10^{-14}) as can be expected[2] if the effect of the addenda is due to their salt formation with the acid.

In all three reactions, the oxygen-containing

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(5) A. Dörken, Dissertation, Leipzig, 1934.

(6) Weissberger, THIS JOURNAL, **65**, 102 (1943), Fig. 2.

addenda give results which correspond to those with the amines just referred to. Replacement of NH by O lowers the effect, but modifications in the molecules influence the efficiency of the addenda in both series in a similar way. The aliphatic ketones and ethers are more effective than the aromatic, the aliphatic alcohols more effective than phenol. Equimolar concentrations of methanol, ethanol, and octanol have an identical effect, showing that only the alcoholic group is of importance.

Benzoic acid may be mentioned specifically. The effect on the indicator equilibrium resembles that of a ketone. In the menthone inversion, benzoic acid, on account of its solubility, was added in 0.1 molar instead of in 0.5 molar solution. It "eliminated" 5% of the trichloroacetic acid. These results show the protophilic nature of carboxylic acids. The fact that the monomeric acid only is reactive in the menthone inversion and the diazoacetic ester decomposition[4] should be recalled in this connection; by association, the acid "eliminates" itself. Some experiments with 0.1 molar *s*-collidine and *s*-collidine trichloroacetate in the menthone inversion showed that this base "eliminates" more than its equivalent of the acid, presumably because the collidine salt in benzene is highly associated and adsorbs additional acid.

Attention may be drawn to the fact that with falling reaction rates (column 2), *i. e.*, rising amounts of "acid eliminated" (column 4), the rotation of the equilibrium mixtures (column 3) becomes lower. The sinking of the final values of rotation with falling acid concentrations has been described and discussed previously.[4]

Experiments with varying concentrations of ether and acetone are recorded in Table II.

TABLE II

Trichloroacetic acid 0.5 mole/liter; menthone 0.5 mole/liter; benzene; temperature 20.0 ± 0.1°

Addendum	Mole/liter	$(k + k')10^4$	% Acid eliminated	Mole acid eliminated per mole addendum	K_3
Ether	0.1	4.43	16	0.80	86
Ether	.25	2.62	34	.68	61
Ether	.5	1.35	52	.52	45
Ether	1.0	0.62	72	.36	45
Acetone	0.1	4.67	14	.70	50
Acetone	.25	3.38	26	.52	27
Acetone	.5	2.29	38	.38	19

In qualitative agreement with the mass action law, the effect per mole decreases with rising concentration of the addendum. For a quantitative examination, we call the total concentrations of acid, menthone and addendum a, m and e, respectively. M signifies the monomeric menthone; A, the monomeric acid; E, the monomeric addendum; A_2, the dimeric acid; MA, the binary acid menthone complex; EA, the binary acid addendum complex, and [ ] denotes concentrations. Other binary complexes, solvation effects and any ternary complexes are neglected. In a solution containing menthone, acid and a protophilic addendum, the following equilibria exist

$$[A_2] \rightleftarrows 2[A]$$

$$K_1 = [A]^2/[A_2] \qquad (1)$$

$$[MA] \rightleftarrows [M] + [A]$$

$$K_2 = [M][A]/[MA] \qquad (2)$$

$$[E] + [A] \rightleftarrows [EA]$$

$$K_3 = [EA]/[A][E] \qquad (3)$$

To calculate K_3[7] we need [EA], [E] and [A].

$$[EA] = a\,\frac{\text{"\% Acid eliminated"}}{100}$$

$$[E] = e - [EA]$$

$$a = [A] + [MA] + [EA] + 2[A_2] \qquad (4)$$

$$m = [M] + [MA] \qquad (5)$$

From (1) and (5) we obtain

$$[MA] = \frac{m[A]}{K_2 + [A]}$$

Substituting [MA] and $[A_2]$ from (5) and (1) in (4), we obtain

$$a = [A] + \frac{m[A]}{K_2 + [A]} + [EA] + \frac{2[A]^2}{K_1}$$

and, clearing fractions and collecting terms

$$[A]^3 + \frac{K_1 + 2K_2}{2}[A]^2 + \frac{K_1}{2}(K_2 + m - a + [EA])[A] - \frac{K_1K_2}{2}(a - [EA]) = 0 \qquad (6)$$

The values for a and m are known. For the reciprocals of the association constant of trichloroacetic acid, K_1, and of the formation constant of the binary acid menthone complex, K_2, we choose 0.04.[4] These values are substituted in (6) which is solved for [A], using, in turn, each experimental value for [EA].

The trend of the values of K_3 in Table II may be caused by the association of the acid-addendum complex, which was shown by cryoscopic measurements.[1] Such factors will influence the results of the "addenda method," which, however, may be considered as an additional means for the determination of the proton affinity of weak bases.[8]

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[7] For these calculations I am indebted to Mr. D. S. Thomas, Jr., of these Laboratories.

[8] Hammett, *Chem. Rev.*, **13**, 61 (1933).

In the experiments with trichloroacetic acid, none of the addenda tested caused an acceleration of the reaction rate. With hydrogen chloride in benzene, Tubandt[9] showed that small amounts of alcohols accelerate the inversion of *l*-menthone. A few experiments with hydrogen chloride (Table III) show that ether lowers the activity of this acid, while phenol, like the aliphatic alcohols, causes a strong increase of the reaction rate and of the rotation of the final equilibrium.[4] According to Tubandt, the reaction rates sink again if larger amounts of the alcohols are added. The evidence available at present appears insufficient for an adequate interpretation of these effects.

TABLE III

Hydrogen chloride 0.032 mole/liter; menthone 0.5 mole/liter; benzene; temperature 20.0 ± 0.1°

Addendum, 0.5 mole/liter	ρ_∞ (100-mm. tube)	$(k + k')10^4$
...	−1.58°	198
Phenol	−2.84°	795
Ethyl ether	−1.41°	101

Summary

The inversion of *l*-menthone with trichloroacetic acid in benzene was studied in the presence of small amounts of various protophilic compounds. The results are compared with those obtained by adding such compounds to solutions of diazoacetic ester or dimethyl yellow and trichloroacetic acid in aprotic solvents.

All of these addenda, including benzoic acid, retard the rate of reaction. This effect is explained with the elimination of part of the catalyzing acid by compound formation with the addendum. The addenda method represents an additional means for the determination of the proton affinity of weak bases. The elimination of part of the acid is also indicated by the rotation of the equilibrium mixtures.

The inversion of *l*-menthone with hydrogen chloride is retarded by ether and accelerated by phenol.

ROCHESTER, N. Y. RECEIVED NOVEMBER 17, 194

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[9] Tubandt, *Ann.*, **354**, 259 (1907).

[COMMUNICATION NO. 893 FROM THE KODAK RESEARCH LABORATORIES]

The Inversion of *l*-Menthone and the Reaction of Diazoacetic Ester with the Chloroacetic Acids

BY A. WEISSBERGER

Hantzsch attributed both the catalytic activity and the ionization of acids to their salt formation, in the former case with the substrate, in the latter case with the solvent.[1] As a substrate for the investigation of the activity of acids in non-aqueous solvents, diazoacetic ester was chosen. The work of other authors agrees with the fundamental idea.[2] A connection between the catalytic activity of acids and their ionization, other than the untenable assumption of an exclusive activity of free hydrogen ions, had been suggested by Taylor,[3] and was most successfully formulated in the Brönsted relation.[4] However, the use of the decomposition of diazoacetic ester in non-aqueous solvents for the comparison of different acids encountered unabated criticism,[5] because the reaction product varies with the acid HX

$$HX + N_2CHCO_2C_2H_5 \longrightarrow XCH_2CO_2C_2H_5 + N_2$$

The inversion of *l*-menthone to *d*-isomenthone, on the other hand, was accepted for the comparison of different acids.[6] In the latter reaction, the product is qualitatively independent of the catalyst, inasmuch as it is always *d*-isomenthone. However, *l*-menthone and *d*-isomenthone are not true optical antipodes, but diastereoisomers and the final equilibrium between the isomers shifts with the concentration and the nature of the catalyzing acid.[7] Therefore, the difference between the decomposition of diazoacetic ester and the inversion of *l*-menthone is not one of principle but only of degree of deviation from the ideal.

The mechanism of both reactions,[7,8] as revealed by their kinetics, is of a striking similarity. In both cases, the reactive complex is built up of one molecule of the substrate, menthone or ester, and two molecules of the monomeric acid. This similarity seemed to indicate that the above-mentioned criticism of the use of the diazo ester

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[1] Hantzsch, *Z. Elektrochem.*, **29**, 221 (1923).

[2] Hammett, THIS JOURNAL, **50**, 2666 (1928).

[3] Taylor, *Z. Elektrochem.*, **20**, 201 (1914).

[4] Brönsted and Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

[5] R. P. Bell, "Acid-Base Catalysis," Oxford, 1941.

[6] Bell and Caldin, *J. Chem. Soc.*, 382 (1938).

[7] Weissberger, THIS JOURNAL, **65**, 102 (1943).

[8] Weissberger and Högen, *Z. physik. Chem.*, **A156**, 321 (1931).