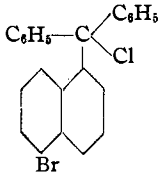
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Quinoidation of Triaryl Compounds—Bromonaphthyldiphenylchloromethanes

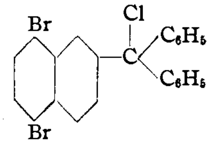
BY LEIGH C. ANDERSON AND DERLAND JOHNSTON[1]

The purpose of this investigation was to synthesize compounds whose chemical reactions might provide evidence for a quinonoid structure across both rings in the naphthalene nucleus. 1,5-, 1,7- (or 2,8-) and 2,6-naphthoquinones may be cited as examples of the three transnuclear quinonoid structures which are theoretically possible. Anderson and Thomas[2] have reviewed the evidence for the existence of the transnuclear naphthoquinones and have attempted to isolate compounds having these structures from hydroxynaphthyldiphenylcarbinols. No colored crystalline compounds were isolated but the relative permanency of the color of acid solutions of the carbinols indicated that the transnuclear quinonoid structures were present for a limited time. It was presumed that the failure to isolate the desired naphthofuchsones was due to their instability as well as to the competition of other reactions, as oxidation, polymerization and fluorenation.

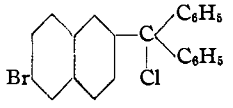
It has been shown by Gomberg and co-workers[3] that *p*-bromotriarylmethyl halides can assume a quinonoid structure when dissolved in a suitable solvent such as sulfur dioxide or nitrobenzene. In the case of 1-(4-bromonaphthyl)-diphenylchloromethane, the bromine in the 4-position becomes labile when the chloromethane becomes quinonoid, and in the presence of silver chloride or silver sulfate a reaction takes place in which silver bromide is formed. The work of Anderson and Thomas has indicated that the naphthoquinonoid structures may be present in some solutions. Since the reaction with silver salts does not require the isolation of a compound having a naphthoquinonoid structure, it seemed probable that a study of bromonaphthyldiphenylchloromethanes might provide evidence concerning these structures and the three compounds shown below were synthesized.



1-(5-Bromonaphthyl)-diphenylchloromethane



2-(5,8-Dibromonaphthyl)-diphenylchloromethane



2-(6-Bromonaphthyl)-diphenylchloromethane

When this investigation was nearly completed, Lund and Berg[4] reported a study of bromopyrenediphenylcarbinol chlorides in which they attempted to find evidence of quinoidation in the pyrene series. They were unable to isolate any of the original compounds from sulfur dioxide solutions, and silver bromide was not produced when the solutions were treated with silver chloride or silver sulfate.

The reaction between silver salts and the bromonaphthyldiphenylchloromethanes prepared in this investigation was studied by shaking sealed tubes containing the two materials with liquid sulfur dioxide as a solvent. After shaking for periods ranging from two days to a month, the tubes were opened and the silver halides were separated from the other materials. The amount of silver bromide in the salts was determined by ascertaining the loss in weight that occurred when the silver halides were fused in a chlorine atmosphere. Nitrobenzene, dimethyl sulfate and cyanobenzene were also tried as solvents with two of the chloromethanes and the results were similar to those obtained with sulfur dioxide.

Six naphthyldiphenylchloromethanes were tested in the above manner and the results are shown in Table I. The first three compounds, the 1-(5-bromonaphthyl)-diphenylchloromethane, 2-(5,8-dibromonaphthyl) - diphenylchloromethane and 2-(6-bromonaphthyl)-diphenylchloromethane might be expected to show transnuclear quinonoidation. The fourth compound, 1-(2-bromo-

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[1] The material presented in this paper constitutes a portion of a dissertation submitted by Derland Johnston to the Horace H. Rackham School of Graduate Studies of the University of Michigan in partial fulfillment of the requirements of the Ph.D. degree, June, 1942.

[2] Anderson and Thomas, THIS JOURNAL, **65**, 234 (1943).

[3] Gomberg and others, (a) *Ber.*, **40**, 1846 (1907); (b) **42**, 406 (1909); (c) THIS JOURNAL, **33**, 531 (1911); (d) **35**, 1035 (1913); (e) **45**, 1765 (1923).

[4] Lund and Berg, *Kgl. Danske Videnskab. Selskab, Math.-fys. Medd.*, **18**, no. 9 (1941).

TABLE I

Compound (0.2 g.)	Silver salt, g.	Solvent (30 cc.)	Color of solution		Shaking time, days	AgBr found	Organic residue at end of shaking
			Start	End			
1-(5-Bromonaphthyl)-diphenylchloromethane	AgCl 0.4	SO_2	Deep green	Red	16	None	Red, amorphous
	Ag_2SO_4 .6	Dimethyl sulfate	Deep green	Light orange	6	None	Red, amorphous
	Ag_2SO_4 .6	Nitrobenzene	Deep green	Light orange	6	None	Red, amorphous
2-(5,8-Dibromonaphthyl)-diphenylchloromethane	AgCl .4	SO_2	Light red	Light red	30	None	Chloromethane
	Ag_2SO_4 6	SO_2	Deep red	Deep red	30	None	Chloromethane
	Ag_2SO_4 .6	Nitrobenzene	Deep green	Deep green	30	None	Red, amorphous
	Ag_2SO_4 .6	Dimethyl sulfate	Colorless	Reddish-brown	30	None	Red, amorphous
	Ag_2SO_4 .6	Cyanobenzene	Colorless	Colorless	30	None	....
2-(6-Bromonaphthyl)-diphenylchloromethane	AgCl 4	SO_2	Cherry-red	Light red-orange	14	None	Red, amorphous
	Ag_2SO_4 .6	SO_2	Cherry-red	Light red-orange	14	None	Red, amorphous
1-(2-Bromonaphthyl)-diphenylchloromethane	AgCl .4	SO_2	Deep red (green in thin layers)	Light red-orange	10	None	Red, amorphous
	Ag_2SO_4 .6	SO_2		Light red-orange	14	None	Red, amorphous
1-(4-Bromonaphthyl)-diphenylchloromethane	AgCl 4	SO_2	Deep violet	Green	2.5	55%	Red, amorphous
p-Bromophenylchloro-1-naphthylphenylmethane	AgCl .4	SO_2	Deep green	Blue-green	2.5	65%	Red, amorphous

naphthyl)-diphenylchloromethane, was tested because, theoretically, it can possess an ortho quinonoid structure in one naphthalene ring. The fifth compound, 1-(4-bromonaphthyl)-diphenylchloromethane, and the sixth compound, *p*-bromophenylchloro-1-naphthylphenylmethane, were tested in order to show that quinonoidation in chloromethanes containing a naphthalene nucleus could be detected when sulfur dioxide was used as a solvent. Gomberg and Blicke[3e] have previously demonstrated a quinonoid structure for these last two compounds when nitrobenzene was used as a solvent. Samples of these latter two compounds were supplied through the courtesy of Dr. Blicke.

Several conclusions can be drawn from the table. Taking the formation of silver bromide as a criterion, a quinonoid structure has been demonstrated in the case of the last two compounds only. With these two compounds, as no attempt was made to remove the bromine quantitatively, the solutions were shaken for only a few days. However, the fact that more than 50% of the bromine was removed in two and a half days, seemed to indicate that the reaction between the solid silver salts and the dissolved chloromethanes was fairly rapid. Since the other chloromethanes were shaken for several weeks, it is reasonable to believe that some silver bromide should have been produced if these compounds had been present in the postulated quinonoid forms.

The case of 1-(2-bromonaphthyl)-diphenylchloromethane is interesting and may provide an explanation of some of the results obtained for the first three compounds. This type of compound is capable of existing in a 1,2-naphthoquinonoid structure. Gomberg and Sullivan[5] have shown previously that the very similar 1-(2-hydroxynaphthyl)-diphenylcarbinol can exist in a colored quinonoid form in the solid state. As shown in the table, however, no silver bromide was produced when a sulfur dioxide solution of 1-(2-bromonaphthyl)-diphenylchloromethane was shaken with silver salts. The organic residue after shaking yielded a red amorphous material rather than the chloromethane that had been added to the tube originally. The red amorphous material indicates that unknown reactions took place, and the absence of silver bromide indicates that these reactions precluded quinonoidation.

The data obtained from reactions of 1-(5-bromonaphthyl)-diphenylchloromethane and 2-(6-bromonaphthyl)-diphenylchloromethane have to be explained on the basis of the results obtained for 1-(2-bromonaphthyl)-diphenylchloromethane. Solutions of these three chloromethanes were similar in that, after being shaken for about seven days, the colors of the solutions changed from a deep red to a light orange and the organic residue consisted of red amorphous materials. These data indicated that side reactions had probably proceeded to completion faster than the formation of any possible quinonoid forms involving the bromine atom.

The color of the 2-(5,8-dibromonaphthyl)-diphenylchloromethane solutions did not change appreciably during the shaking and some of the original chloromethane was recovered from the organic residue after the shaking period. In this case, since apparently side reactions were not predominant and since no silver bromide was

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(5) Gomberg and Sullivan, THIS JOURNAL, **42**, 1864 (1920).

formed, it must be concluded that quinonoidation did not occur.

Experimental

1-(5-Bromonaphthyl)-diphenylcarbinol and 1-(5-Bromonaphthyl)-diphenylchloromethane.—The carbinol was made by the reaction of phenylmagnesium bromide on methyl-5-bromonaphthoate-1 in boiling toluene. Attempts to obtain pure carbinol directly from this reaction gave poor results. The crude carbinol was converted to the chloromethane by means of acetyl chloride. A yield of 62% was obtained for the over-all conversion of the methyl ester to the chloromethane. The chloride was recrystallized from acetyl chloride; m. p. 172–174°. *Anal.* Calcd. for $C_{23}H_{16}BrCl$: Br, 19.55; Cl, 8.71. Found: Br, 19.20; Cl, 8.98.

Pure carbinol was prepared by boiling the chloride with dimethylaniline in an acetone–water solution and was crystallized from a carbon disulfide–petroleum ether mixture; m. p. 150–151°. *Anal.* Calcd. for $C_{23}H_{17}BrO$: Br, 20.55. Found: Br, 20.31. Attempts to prepare the carbinol by the reaction of phenylmagnesium bromide on 5-bromonaphthoic acid-1 or its chloride gave low yields. The attempt to convert the carbinol to the chloromethane by means of hydrogen chloride acid in ether also gave poor results.

2-(5,8-Dibromonaphthyl)-diphenylcarbinol and 2-(5,8-Dibromonaphthyl)-diphenylchloromethane.—2-(8-Bromonaphthyl)-diphenylchloromethane was desired in order to demonstrate the 2,8-naphthoquinonoid structure. The intermediate required for this chloromethane is 8-bromonaphthoic acid-2. This acid has not been described to date and attempts to isolate it were not successful. However, 5,8-dibromonaphthoic acid-2 has been described and a carbinol and chloromethane were made from this acid. Since a conjugated system ending at the 2 and 5 positions is not possible, the additional bromine atom at the 5 position is of no consequence and only the bromine in the 8 position is in a possible quinonoid position with respect to the chloromethane attached at the 2 position.

2-(5,8-Dibromonaphthyl)-diphenylcarbinol was made in 77% yield from the ethyl ester of 5,8-dibromonaphthoic acid-2, while an attempt using the acid chloride gave poor results. The material from the ester reaction gave a residue that crystallized after a few washings with petroleum ether, while that from the acid chloride reaction gave an oil that could not be crystallized. The carbinol was recrystallized from acetic acid, m. p. 127–128°. *Anal.* Calcd. for $C_{23}H_{16}Br_2O$: Br, 34.25. Found: Br, 34.15. The crude carbinol from the ester reaction was converted to the chloromethane by means of acetyl chloride, the yield being 84.5%. It was recrystallized from pure acetyl chloride, m. p. 163–164°. *Anal.* Calcd. for $C_{23}H_{15}Br_2Cl$: Br, 32.90; Cl, 7.28. Found: Br, 32.69; Cl, 7.37.

6-Bromonaphthyl-2-methyl Ketone and 2-Bromonaphthyl-1-methyl Ketone.—Both of these compounds are formed in the Friedel–Crafts reaction between acetyl chloride and 2-bromonaphthalene. Dziewonski and Sternbach[6] reported carrying out this reaction in carbon disulfide, and separated the ketones by fractional crystallization of the phenylhydrazones. No data concerning yields appear in the article, so that the relative amounts of each ketone were not known. A trial run using carbon disulfide under the conditions described in the article gave an amount of the 6-bromonaphthyl-2-methyl ketone which indicated that it had been formed in the reaction in a ratio of one to ten of the 2-bromonaphthyl-1-methyl ketone.

In the method finally adopted for the preparation of 6-bromonaphthyl-2-methyl ketone, the reaction with acetyl chloride was carried out in nitrobenzene solution. Previous experiments had shown that the separation of the isomeric ketones was unsatisfactory. As a result, the mixture of isomers was carried through the later stages of the synthesis before a satisfactory separation was found. Data acquired when the isomers were finally separated indicated that the isomeric ketones had been formed in the Friedel–Crafts reaction in nitrobenzene in a 1:1 ratio. This marked effect of solvent upon the relative proportions of isomers formed in the Friedel–Crafts reaction has been reported for other compounds.[7]

6-Bromonaphthoic Acid-2 and 2-Bromonaphthoic Acid-1.—The mixture of ketones from the reaction with acetyl chloride was subjected to a haloform oxidation using potassium hypochlorite. The reaction gave a practically quantitative conversion of the ketones to the acids. Attempts were made to separate the isomeric acids but none was successful.

Methyl 6-Bromonaphthoate-2 and Methyl 2-Bromonaphthoate-1.—The mixture of acids from the oxidation reaction, upon treatment with diazomethane, was converted to a mixture of the corresponding methyl esters. The esters were distilled under reduced pressure and were separated by recrystallization from boiling methanol; both esters were soluble in the hot solvent while methyl 6-bromonaphthoate-2 was insoluble in the cold solvent. The amount of the latter ester corresponds to a yield of 42%. Unsuccessful attempts were made to separate the isomers by fractional crystallization of the ethyl esters and by fractional distillation of the methyl and ethyl esters. Methyl 6-bromonaphthoate-2 was obtained pure after two recrystallizations from methanol, m. p. 123–124.5°. *Anal.* Calcd. for $C_{12}H_9BrO_2$: Br, 30.15. Found: Br, 30.25.

Other methods of synthesizing 6-bromonaphthoic acid-2 were tried and in all cases except one the acid was not obtained because of low yields in the intermediate stages. A small amount of the acid was obtained by a series of reactions starting with 6-bromonaphthol-2.[8] 6-Bromonaphthol-2 was heated with ammonium hydroxide and ammonium sulfite for twenty-four hours at 190° in a sealed tube; a 95% yield of 6-bromonaphthylamine-2 was obtained. Running this reaction for ten hours at 150° gave only a 5% conversion to the amine. Attempts to diazotize the amine and to introduce the cyano group by means of the Sandmeyer reaction gave very low yields. The small amount of 6-bromonaphthonitrile-2 that was obtained was hydrolyzed to the acid and the acid treated with diazomethane to give the ester. A mixed melting point of this methyl ester with the ester prepared through

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(6) Dziewonski and Sternbach, *Bull. acad. polonaise*, **A**, 59 (1931).

(7) Haworth and Sheldrick, *J. Chem. Soc.*, 864 (1934); Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1941, pp. 271–280.

(8) Koelsch, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1940, Vol. 20, p. 18.

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) H. 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).