

a few hours, shaking frequently, the mixture was allowed to stand overnight, all of the alcoholate remaining in solution. The next day, the solution was boiled for ten hours. The clear solution gradually became black, due to the formation of tarry matter. At the end of the ten hours, all the metal had disappeared. Now after cooling, 35 cc. of methyl alcohol was added, the mixture shaken well, and distilled directly. The material b. p. 65–185° was fractionated through column B twice. About 2 g. of the original carbinol was thus obtained, b. p. 138–143°, n_D^{20} 1.4118. The optical activity was unchanged, $[\alpha]_D^{25} -0.82^\circ$. There had been, therefore, decomposition apparently but no racemization.

Summary

1. Levo methylisopropyl- and levo methylpropylcarbinols are configurationally related.

2. A tertiary alcoholate was not racemized by heating at 190° for ten hours; this supports Hückel's mechanism of racemization and rearrangement of alcoholates.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TORONTO]

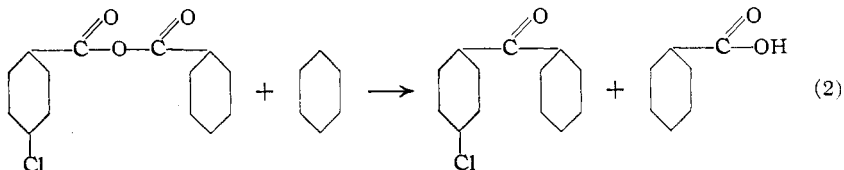
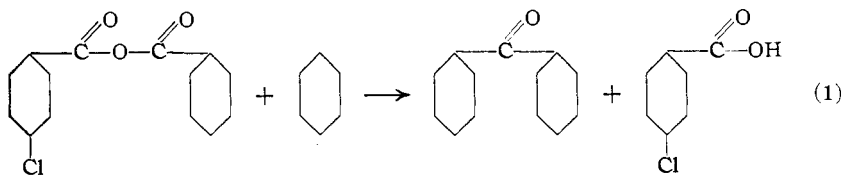
THE FRIEDEL AND CRAFTS REACTION. SOME UNSYMMETRICAL ACID ANHYDRIDES AND THEIR BEHAVIOR WITH BENZENE AND ALUMINUM CHLORIDE

BY J. M. ZEAVIN AND A. M. FISHER

RECEIVED MAY 23, 1932

PUBLISHED SEPTEMBER 5, 1932

Previous research in this Laboratory on the Friedel and Crafts reaction—the production of acids and ketones from anhydrides, aromatic hydrocarbons and aluminum chloride—has been concerned with anhydrides of single acids. The purpose of the present research was to determine the course of the reaction using anhydrides which would give two acids on hydrolysis. With mono-*p*-chlorobenzoic anhydride, for example, there are three possibilities



(3) The ketones might be a mixture of benzophenone and mono-*p*-chlorobenzophenone. In this paper a number of such anhydrides have

been prepared and their behavior with benzene and aluminum chloride has been investigated.

A. Preparation of the Anhydrides.—Attempts were made to prepare the anhydrides from the sodium salts of suitable acids and an acid chloride but this method was found to be satisfactory only in a few cases. Direct bromination of anhydrides failed to give the desired product. A modification of the method of Einhorn and Seuffert¹ for the preparation of anhydrides of substituted salicylic acid was used to prepare most of our anhydrides. A general outline of the modified method is as follows.

The acid required was dissolved in cold ether and pyridine and to this a cold ethereal solution of the molecular quantity of the acid chloride was added slowly. After standing at 0° a precipitate of pyridine hydrochloride was formed. This, together with the excess pyridine, was removed by two washings with 25 cc. of concd. hydrochloric acid and ice and then with 7% sodium hydroxide and ice. The solution was then washed with cold water and dried at 0° with anhydrous sodium sulfate, filtered, the ether evaporated and the anhydride, if impure, recrystallized from suitable solvents.

In some cases it was found more satisfactory to perform the first part of the experiment at room temperature and to shake the mixture instead of keeping it at 0°. Though most of the anhydrides were quite stable when once prepared, still the yield was decreased considerably by hydrolysis during the course of preparation, especially in ethereal solutions, and, therefore, to inhibit hydrolysis, benzene was used instead of ether. In so doing, it was unnecessary to dry the solution with anhydrous sodium sulfate. Also, when benzene was a better solvent for the anhydride, it was used instead of ether. Details concerning each of the anhydrides are given in the table.

Stability of the Anhydrides.— α -Naphthoicacetic anhydride and β -naphthoicacetic anhydride decompose very readily at room temperature.

Some of the anhydrides are unstable when heated to their melting points. When mono-*p*-chlorobenzoic anhydride was first heated, it melted at 66.5–70.0°. Cooling this molten material produced another solid which melted at 126–144°. It seems probable that the decomposition indicated in the change of the melting point may account for failure to obtain a sharper melting point for some of the anhydrides. Another example of similar instability is the behavior of mono-*p*-bromobenzoic anhydride. This anhydride melted at 82–83°, began to solidify at 86° and melted again at 165–182°. A sample of it was heated to its melting point and precipitated fractionally from benzene with petroleum ether. It was found to consist of benzoic anhydride and *p*-dibromobenzoic anhydride. A similar transformation took place when a concentrated solution of the anhydride in benzene was heated to boiling. This was not evident in dilute solutions.

B. The Friedel and Crafts Reaction. The Acid Anhydrides with Benzene and Aluminum Chloride.—Working with phthalic anhydride, benzene and aluminum chloride, Rubidge and Qua² found that maximum yields of *o*-benzoylbenzoic acid were obtained when the anhydride and aluminum chloride were used in amounts proportional to their formula weights (using Al₂Cl₆ for aluminum chloride). In all experiments in the present research, this practice was followed. Excess benzene was used both as a reagent and as a solvent.

¹ Einhorn and Seuffert, *Ber.*, **43**, 2993 (1910).

² Rubidge and Qua, *THIS JOURNAL*, **36**, 732 (1914).

TABLE I
PREPARATION AND PROPERTIES OF THE ANHYDRIDES

Anhydride	Reactants		Solvent	Yield, %	M. p., °C.	Remarks
	Acid	Chloride				
1 Mono- <i>o</i> -benzoxybenzoic	Salicylic	Benzoyl	Benzene	88	67.0-67.8	Recryst. warm Bz ^a
2 Mono- <i>o</i> -methoxybenzoic	<i>o</i> -Methoxybenzoic	Benzoyl	Ether	77	76.3-77.2	Recryst. large plates, warm Bz
3 Mono- <i>p</i> -chlorobenzoic	<i>p</i> -Chlorobenzoic	Benzoyl	Ether	69	66.5-70.0	See "Stability of the Anhydrides" ^b
4 Mono- <i>p</i> -bromobenzoic	<i>p</i> -Bromobenzoic	Benzoyl	Benzene	80	82.0-83.0	
5 Mono- <i>o</i> -nitrobenzoic	<i>o</i> -Nitrobenzoic	Benzoyl	Ether	75	65.0-65.5	Recryst. Bz and pet. ether ^c
6 Mono- <i>m</i> -nitrobenzoic	<i>m</i> -Nitrobenzoic	Benzoyl	Benzene	75	101-103	Diff. method by Gerhardt ^d
7 Mono- <i>p</i> -nitrobenzoic	<i>p</i> -Nitrobenzoic	Benzoyl	Benzene	65	130-130.5	Diff. method by Kahn, ^e m. p. 130°
8 3,5-Dinitrobenzoic	3,5-Dinitrobenzoic	Benzoyl	Benzene	60	115.5
9 α -Naphthoicbenzoic	α -Naphthoic	Benzoyl	Ether	69	89.5-90.3	Recryst. Bz and pet. ether
10 β -Naphthoicbenzoic	β -Naphthoic	Benzoyl	Benzene	..	54.0-57.5	^f
11 α -Naphthoicacetic	α -Naphthoic	Acetyl	Benzene	85	Clear brown oil, dec. readily
12 β -Naphthoicacetic	β -Naphthoic	Acetyl	Benzene	83	50.5-51.0
13 Dibenzoiophthalic	Sodium phthalate and benzoyl chloride heated at 120° for twelve hours gave better results. The mixture was shaken with warm benzene and filtered hot. Addition of petroleum ether to the cooled filtrate produced long white needles which melted at 131.0-132.0°; yield, 75%.					

^a *Anal.* Calcd. for C₂₁H₁₄O₅: C, 72.8; H, 4.08. Found: C, 72.7; H, 4.21. Einhorn and Seuffert report m. p. 74-75°.

^b *Anal.* Calcd. for C₁₄H₉O₃Br: Br, 26.20. Found: Br, 26.14.

^c *Anal.* Calcd. for C₁₄H₉O₃N: N, 5.17. Found: N, 5.16.

^d Gerhardt, *Ann.*, 87, 158 (1853).

^e Kahn, *Ber.*, 36, 2536 (1903).

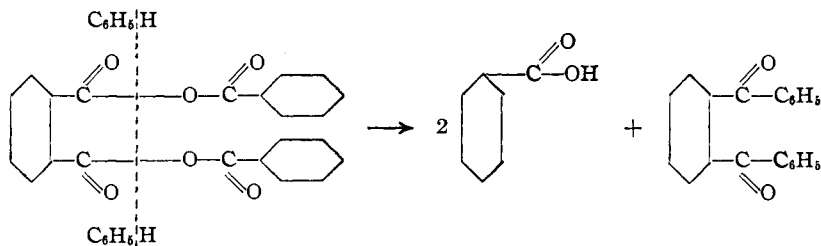
^f An oily residue which formed crystals when precipitated from cold benzene with petroleum ether.

With the anhydrides listed above as numbers 2, 3, 4, 6, 7, 8, 9 and 10 the procedure was as follows.

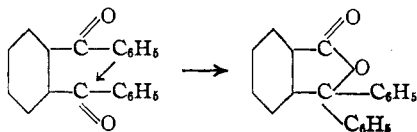
Five grams of the anhydride was dissolved in 50 cc. of benzene and the molecular quantity of aluminum chloride was added slowly. After standing for about one hour, the mixture was heated on a steam-bath in a flask fitted with a reflux condenser and calcium chloride tube until evolution of hydrogen chloride ceased (usually between eight and ten hours); 75 cc. of 5% hydrochloric acid was added slowly and the benzene removed by steam distillation. The contents of the distilling flask were cooled and filtered and the residue was warmed with 7% sodium hydroxide solution, cooled and filtered. The acids were recovered from the filtrate on the addition of concd. hydrochloric acid. Benzophenone was obtained from the portion insoluble in sodium hydroxide by steam distillation or by recrystallization from alcohol or ether. In the case of mono-*m*-nitrobenzoic anhydride, a slight trace of mono-*m*-nitrobenzophenone was found.

With α -naphthoicacetic anhydride and β -naphthoicacetic anhydride the only ketone produced was acetophenone.

With dibenzoicphthalic anhydride the products of the reaction were benzoic acid and diphenylphthalide, whereas *o*-benzoylbenzophenone was expected.



This is probably due to a rearrangement, as



In working with the nitro derivatives of benzoic anhydride, it was found that a tarry material was produced if the mixture was not kept at room temperature for at least twenty hours before heating on the steam-bath.

The authors' thanks are due to Mr. F. E. Beamish for the analyses recorded and to Professor F. B. Allan under whose direction this investigation was performed.

Summary

1. Ten new anhydrides have been prepared, *viz.*, mono-*o*-methoxybenzoic anhydride, mono-*p*-chlorobenzoic anhydride, mono-*p*-bromobenzoic anhydride, mono-*o*-nitrobenzoic anhydride, 3,5-dinitrobenzoic anhydride, α -naphthoicbenzoic anhydride, β -naphthoicbenzoic anhydride, α -naphthoicacetic anhydride, β -naphthoicacetic anhydride and dibenzoicphthalic anhydride.

2. A new method of preparation for mono-*m*-nitrobenzoic anhydride and for mono-*p*-nitrobenzoic anhydride has been described.
3. The stability of some of these anhydrides has been discussed.
4. The behavior of eleven of the anhydrides with benzene and aluminum chloride has been investigated and the products of the reaction identified.

TORONTO, CANADA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

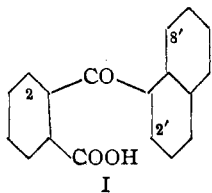
REARRANGEMENTS IN THE CONDENSATION OF METHYLATED DERIVATIVES OF α -NAPHTHOYL-2-BENZOIC ACID

BY LOUIS F. FIESER AND MARY A. PETERS

RECEIVED MAY 24, 1932

PUBLISHED SEPTEMBER 5, 1932

While 1,2-benzanthraquinone is the sole condensation product formed by the action of sulfuric acid on α -naphthoyl-2-benzoic acid (I), the quinone is accompanied by about 10% of an isomeric substance when molten sodium aluminum chloride is used as the condensing agent.¹ The isomer, which has the properties of a lactone, is probably formed either by a Scholl benzanthrone condensation between positions 2 and 8' or by intramolecular addition of position 8' to the carbonyl group to give a substance of the type formed by 2'-hydroxy-1-naphthoyl-2-benzoic acid.^{1b} In order to study this matter further and to determine if possible which type of *peri* condensation actually takes place, we have investigated the behavior of a few substituted acids with which it seemed reasonable to expect a higher proportion of the abnormal reaction product.



By blocking position 2' with a methyl group we hoped to prevent entirely the formation of an anthraquinone, but this expectation was not realized. On heating 2'-methyl-1-naphthoyl-2-benzoic acid (III) in sodium aluminum chloride at 150°, there was produced a yellow substance having the composition and the properties of a methyl-1,2-benzanthraquinone. Such a compound could be formed from an acid of the structure indicated only as the result of a rearrangement. In view of the unexpected results, it seemed advisable to establish beyond question the structure of the starting material. There can be little doubt on this point, for Scholl and Tritsch, who prepared the acid by condensing phthalic anhydride with β -methyl-naphthalene, noted that the substance is not converted into an anthraquinone by concentrated sulfuric acid.² More positive evidence was

¹ (a) I. G. Farbenind., English Patent 303,375 (1930); (b) Fieser, *THIS JOURNAL*, **53**, 3546 (1931).

² Scholl and Tritsch, *Monatsh.*, **32**, 997 (1911).