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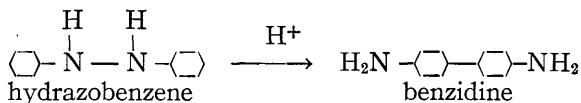
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REARRANGEMENT OF *p*, *p*¹-DISUBSTITUTED BENZILS

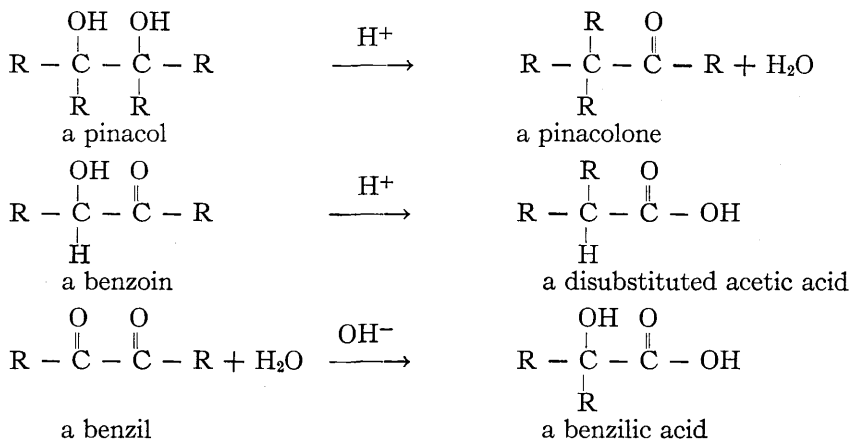
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The term rearrangement, broadly speaking, refers to the shifting of atoms or radicals within a molecule, with or without the elimination of a simple molecule such as water. A new molecule is produced, containing essentially the same atoms as the original, but with a different arrangement. A good illustration is the conversion of hydrazobenzene to benzidine.



This change is induced by treating hydrazobenzene with a concentrated aqueous solution of hydrogen chloride.

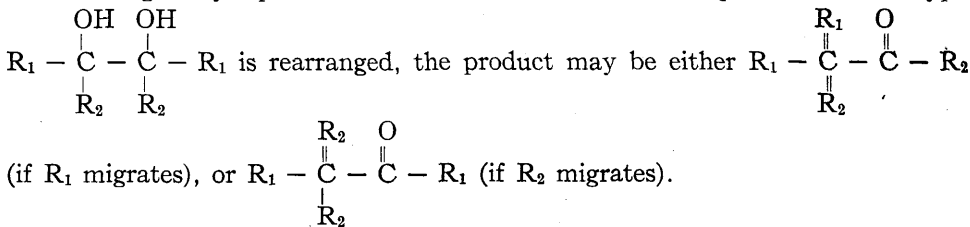
An interesting group of rearrangements consists of the pinacol rearrangement, the benzoin rearrangement, and the benzilic acid rearrangement.



These three rearrangements are similar in that they all involve the migration of a radical from one carbon to an adjacent carbon. They differ in the state of oxidation of the two carbon atoms between which the migration takes place.

A large number of examples of the pinacol rearrangement have been studied. Porter (1928) discusses several of these. R may represent either an aliphatic or an aromatic radical. Examples of the benzilic acid and benzoin rearrangements are less numerous and are restricted principally to compounds in which R represents an aromatic radical.

The pinacol rearrangement has been used as the basis of several studies of relative migratory aptitudes of different radicals. If a pinacol of the type

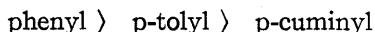


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Bachmann (1934) and others used this preferential migration to determine the relative migratory aptitudes of a large number of radicals, from which the following have been selected, in order of decreasing migratory aptitude, because these same radicals are studied in the present investigation:

p-anisyl,	$\text{---}\langle\bigcirc\rangle\text{---O---CH}_3$
p-phenetyl,	$\text{---}\langle\bigcirc\rangle\text{---O---C}_2\text{H}_5$
p-tolyl,	$\text{---}\langle\bigcirc\rangle\text{---CH}_3$
p-cuminyly,	$\text{---}\langle\bigcirc\rangle\text{---CH(CH}_3)_2$
phenyl,	$\text{---}\langle\bigcirc\rangle\text{---}$
p-chlorophenyl,	$\text{---}\langle\bigcirc\rangle\text{---Cl}$

The benzoin and benzilic acid rearrangements are less well adapted to a study of migratory aptitudes, for in the benzoin rearrangement only one radical can migrate, and in the benzilic acid rearrangement the final product is the same regardless of which radical migrates. In these cases the relative migratory aptitude may be determined by subjecting different benzoinis or benzils to identical conditions encouraging rearrangement, and determining the percent conversion to the rearrangement product. A study of this type was made with benzoinis by James and Lyons (1938), resulting in the following series arranged in order of decreasing migratory aptitude:



It should be noted that this sequence is different from that obtained by the pinacol rearrangement.

In the case of the benzilic acid rearrangement, although several substituted benzils had been prepared and rearranged, no systematic comparison of their behavior had ever been made. The first substituted benzils that were studied were cuminil and anisil by Böslér (1881). Since then, perhaps a dozen others have been prepared. In most cases the investigator rearranged the benzil to the benzilic acid, being interested only in obtaining as high a yield as possible. The rearrangement was usually accomplished by refluxing the benzil with an alcohol-water solution of potassium hydroxide, and ordinarily resulted in yields of the rearrangement product of 80 to 95 percent.

That the ease of rearrangement is affected by the position of the substituting group on the benzene nucleus was shown by Schonberg and Keller (1923). A comparison of the rearrangements of 4, 4'-dimethoxybenzil (anisil), 3, 3'-dimethoxybenzil, and 2, 2'-dimethoxybenzil showed that the 4, 4' compound gave the greatest yield of the corresponding benzilic acid, the 3, 3' gave less, and the 2, 2' gave a rather low yield.

In the present study, several p, p'-disubstituted benzils have been prepared, and the relative migratory aptitudes of the substituted phenyl radicals has been found by determining the per cent conversion, under a standard set of conditions, to the corresponding benzilic acids.

EXPERIMENTAL WORK

Preparation of p, p'-disubstituted benzils

1. *Benzil.* $\text{---}\langle\bigcirc\rangle\text{---}\overset{\text{O}}{\parallel}\text{C} \text{---} \overset{\text{O}}{\parallel}\text{C} \text{---}\langle\bigcirc\rangle\text{---}$ Benzil was prepared by the oxidation of benzoin with nitric acid according to the directions of Adams (1921). After recrystallization from 95 percent alcohol it melted at 94.5°C. Literature, 95°.

2. *Tolil.* $\text{CH}_3\text{---}\langle\bigcirc\rangle\text{---}\overset{\text{O}}{\parallel}\text{C} \text{---} \overset{\text{O}}{\parallel}\text{C} \text{---}\langle\bigcirc\rangle\text{---CH}_3$ Tolualdehyde was condensed to toluoin as described by Stierlin (1889). This was oxidized to tolil with nitric acid.

After recrystallization from 95 percent alcohol it melted at 102–103°C. Literature, 105°.

3. *Cuminil*. $(\text{CH}_3)_2\text{CH}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{CH}(\text{CH}_3)_2$ Cuminic aldehyde was condensed to cuminoïn according to the directions of Bösler (1881). The cuminoïn was oxidized to cuminil with chromic acid as described by Widman (1881). After recrystallization from 95 percent alcohol it melted at 82–82.5°C. Literature, 83°.

4. *Anisil*. $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{OCH}_3$ Anisic aldehyde was condensed to anisoïn as described by Bösler (1881). The anisoïn was oxidized by a mixture of copper acetate and ammonium nitrate in glacial acetic acid, according to Weiss and Appel (1948). Recrystallized from 80 percent acetic acid, the crystals had a melting point of 132°C. Literature, 132°.

5. *Phenetil*. $\text{C}_2\text{H}_5\text{O}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{OC}_2\text{H}_5$ Phenetole was condensed with oxalyl chloride in the presence of anhydrous aluminum chloride, as described by Schonberg and Kraemer (1922). It was recrystallized from glacial acetic acid, and melted at 148°C. Literature, 149°.

6. *p, p'*-Dichlorobenzil. $\text{Cl}-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}\text{C}-\overset{\text{O}}{\parallel}\text{C}-\text{C}_6\text{H}_4-\text{Cl}$ The directions of Hodgson and Rosenberg (1930) were used to condense *p, p'*-dichlorobenzaldehyde to *p, p'*-dichlorobenzoin. Without attempting to isolate the benzoin, the mixture was oxidized with nitric acid diluted with acetic acid as suggested by Gomberg and Van Natta (1929). The *p, p'*-dichlorobenzil when recrystallized from acetic acid melted at 192–194°C. Literature, 195°.

Standardization of rearrangement conditions

After some experimentation with different methods of bringing about the rearrangement, it was decided that the classical solution of potassium hydroxide in a mixture of alcohol and water was the most suitable reagent. A series of trials was run to determine the percent conversion of benzil to benzilic acid at 25° C.

Samples each containing 2.10 g (0.01 mols) of benzil, 2.10 g (0.038 mols) of potassium hydroxide, 4.20 g of water and 4.20 g of alcohol were allowed to stand at 25°C for periods varying from 8 to 72 hours, with occasional shaking. During the course of the rearrangement a violet color appeared rather early in all samples. This color quickly darkened to a deep violet, and upon standing the color began to fade, until at about 50 hours it approached the yellow color present at the start of the experiment. At this stage, a cream-white precipitate was present, presumably potassium benzilate. At the end of the period of standing, water was added to dissolve the potassium benzilate. Filtration of this alkaline solution removed unchanged benzil and other non-acidic materials. The filtrate was then acidified with dilute hydrochloric acid, and the precipitated benzilic acid filtered onto a weighed sintered glass filter. After drying for 6 hours at 70–75°C, the filters were reweighed to obtain the weight of the benzilic acid (table 1). It should be mentioned that a slight precipitate often occurred just at the neutralization point and before the benzilic acid was precipitated. When this happened, it was removed by filtration before precipitating the benzilic acid.

Here and throughout the investigation samples were run in triplicate. Results were generally in good agreement, most of the figures falling within one percent of the average of the three trials. In all cases but one the melting point of the benzilic acid was 144° or higher, as compared to 150° for pure benzilic acid. Since the melting points were uniformly close to that of pure benzilic acid, further purification was not considered to be necessary.

A delicate test for benzoic acid is available. Even small amounts of benzoic acid impart an intense red color to concentrated sulfuric acid. This test was used to determine how completely the benzoic acid had been precipitated by acidification of the potassium benzoate solution. The precipitate of benzoic acid was filtered off, and a few drops of the filtrate were added to a few drops of concentrated sulfuric acid. Only a pale pink color appeared, so it was assumed that precipitation of benzoic acid was practically complete.

TABLE 1
Percent conversion of benzil to benzoic acid at 25° C.

Time (hours)	Average conversion	Time (hours)	Average conversion
8	30.3%	42	82.0%
12	42.0%	48	87.3%
24	69.2%	50	88.8%
30	74.1%	60	94.3%
32	76.4%	72	91.5%

Treatment of anisil, tolil, and phenil with potassium hydroxide in the proportions described above was carried out for twenty-four hours at 25°C. Acidification of the reaction mixture did not give any precipitate of the expected disubstituted benzoic acids. A few drops, when added to concentrated sulfuric acid, did give an intense red color, showing that at least traces of the substituted benzoic acids had been formed.

Having failed to obtain any appreciable amount of rearrangement of substituted benzils at 25°, a series of samples was run at 40° with unsubstituted benzil. Other conditions were the same as before. Flasks containing the reaction mixture were suspended in a water bath with a stirrer maintained at a temperature of 40 ± 1° by an immersion heater equipped with a rheostat. Each flask was removed and shaken occasionally during the heating period. On the basis of the results of these trials, 15 hours at 40° was selected for another trial with anisil and tolil. Just as before, however, no precipitate of the substituted benzoic acids was obtained, though the solution did cause an intense red color to form with concentrated sulfuric acid.

The temperature was then increased to 60° and a series of samples run with unsubstituted benzil. The results are shown in table 2. In these trials the amounts of alcohol, water, and potassium hydroxide were doubled, because experience had shown that the volume of liquid used before was so small that mixing by shaking was difficult.

On the basis of these results and our previous experience, 6 hours at 60°C was chosen for the next trials with substituted benzils. Under these conditions anisil rearranged to anisilic acid to the extent of 8.1 percent, and tolil to tolicilic acid with a yield of 37.4 percent. Since these results were satisfactory, the same conditions were used for rearrangement of the other substituted benzils as described in detail below.

TABLE 2
Percent conversion of benzil to benzoic acid at 60° C.

Time (hours)	Average conversion
2	88.9%
6	87.0%
9	87.3%

Rearrangement of p, p'-disubstituted benzils

Reaction mixtures were made up in the following proportion: 0.01 mols of the substituted benzils, 4.20 g (0.075 mols) of potassium hydroxide, 8.40 g of water and 8.40 g of alcohol. These were well mixed in 125 ml Erlenmeyer flasks which were then suspended in a water bath maintained at $60 \pm 1^\circ$ for six hours. The flasks were removed and shaken occasionally. At the end of the heating period the flasks were removed from the bath, filtered to remove unchanged benzil, and the filtrate acidified with dilute hydrochloric acid until red to litmus paper. The benzilic acids which precipitated were filtered onto weighed sintered glass filters, washed, dried at $70\text{--}75^\circ$ for 6 hours, and weighed.

1. *Tolil*. In the rearrangement of tolil to tolilic acid a dark brown solution was formed, which at the end of the heating period was diluted with water and filtered. The filtrate was acidified with dilute hydrochloric acid, forming a dark-brown gummy mass which solidified on standing. This was filtered onto a sintered glass funnel, washed, dried, and weighed. The melting point of the crude tolilic acid was found to be $120\text{--}125^\circ$. This was dissolved in dilute sodium carbonate solution and reprecipitated with hydrochloric acid, and then melted at $127\text{--}130^\circ$. The literature melting point (Gattermann, 1906) is $133\text{--}135^\circ$. An average yield of 37.4 percent was obtained.

2. *Cuminil*. The usual heating period was followed by acidification, giving a cream-white solid which melted at $110\text{--}113^\circ$. Dissolving in dilute sodium carbonate solution and reprecipitating gave a cream-white powder melting at $115\text{--}118^\circ$. Repeating the process gave a melting point of $118\text{--}119^\circ$. According to Bösler (1881) the melting point of cuminilic acid is $119\text{--}120^\circ$. The yield was 19.0 percent.

3. *Anisil*. Acidification of the reaction mixture in this case gave a cream-yellow precipitate. This was filtered, washed, dried and weighed. The average percent conversion of the three samples was 8.1 percent. The melting point of the crude acid was $149\text{--}153^\circ\text{C}$. Dissolving the crude acid in sodium carbonate solution and acidifying gave an almost white powder melting at $157\text{--}159^\circ$. A second recrystallization raised the melting point to $158\text{--}160^\circ$. According to Bösler (1881) the melting point of anisilic acid is 164° .

4. *Phenetil*. When phenetil was treated in the same manner, the amount of precipitate upon acidification was so slight that attempts to isolate it by filtration onto a sintered glass funnel resulted in loss of the sample. The addition of a few drops of the reaction mixture to a few milliliters of concentrated sulfuric acid resulted in the formation of an intense red color, showing that some rearrangement had taken place.

5. *p, p'-Dichlorobenzil*. When *p, p'*-dichlorobenzil was treated in the same way as the others, acidification produced a gummy mass. This was filtered, washed, dried, and weighed. The average percent conversion was 96.7. The crude material was dissolved in sodium carbonate solution and re-acidified. The product, when dry, melted at $159\text{--}162^\circ$. Again it was dissolved in alkali and acidified. The mass was still slightly gummy. After drying, a melting point of $158\text{--}165^\circ$ was obtained. To get a reliable melting point further purification would no doubt have been necessary. Although this seemed to be the expected benzilic acid since it gave a red color with concentrated sulfuric acid and gave a positive Beilstein test for the presence of halogen, the melting point does not agree with that given by Montagne (1902) who claimed that *p, p'*-dichlorobenzilic acid melted at 101.75° .

SUMMARY AND CONCLUSIONS

The results of this investigation are summarized in table 3. On the basis of this data, it may be seen that the relative ease of migration of substituted radicals

in the benzoic acid rearrangement follows that of the benzoin rearrangement as determined by James (1938) rather than that of the pinacol rearrangement as

TABLE 3
Conversion of various benzils to the corresponding benzoic acids.

Benzil	Average conversion
Anisil	8.1%
Benzil	87.0%
Cuminil	19.0%
p, p'-Dichlorobenzil	96.7%
Phenetil	very small
Tolil	37.4%

determined by Bachmann (1934). The order of decreasing migratory aptitudes in the three types is as follows:

<i>Benzoic acid</i>	<i>Benzoin</i>	<i>Pinacol</i>
p-chlorophenyl	phenyl	p-anisyl
phenyl	p-tolyl	p-phenetyl
p-tolyl	p-cuminylyl	p-tolyl
p-cuminylyl		p-cuminylyl
p-anisyl		phenyl
p-phenetyl		p-chlorophenyl

These results are surprising since both the pinacol and the benzoin rearrangements are acid-catalyzed while the benzoic acid rearrangement is base-catalyzed. It should be pointed out, however, that the same method of determining percent conversion was used in the two series which agree with one another, while an entirely different method of determining migratory aptitudes was involved in the studies with the pinacol rearrangement.

Another interesting comparison may be made of this series with that of Kharasch and Reinmuth (1928) of decreasing electronegativity of radicals. In almost every case the migratory aptitude of the radicals in the benzoic acid rearrangement increases as the electronegativity decreases.

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