[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# MOLECULAR REARRANGEMENTS INVOLVING OPTICALLY ACTIVE RADICALS. IX. FURTHER STUDIES ON THE WOLFF REARRANGEMENT OF OPTICALLY ACTIVE DIAZOKETONES

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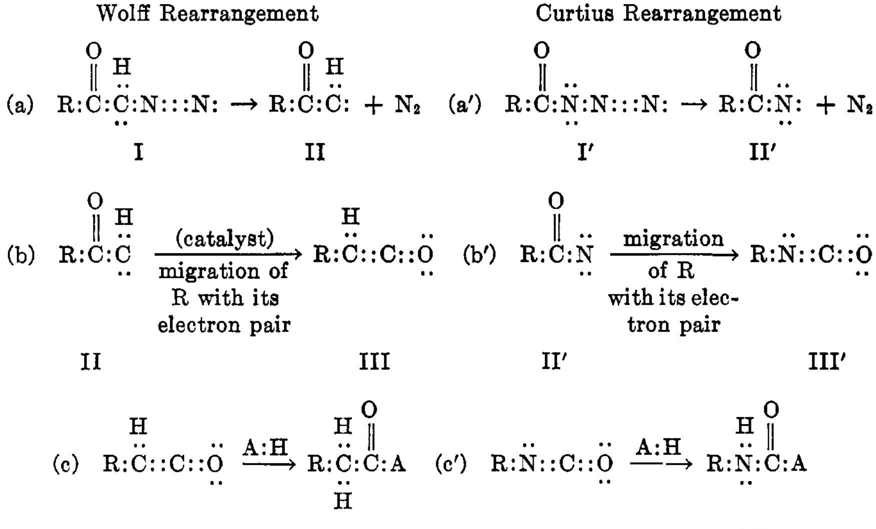
The mechanism for the Wolff rearrangement of diazoketones advanced recently by Eistert (1) and now generally accepted in discussions of this reaction (2) implies a strict similarity in the electronic behavior of the group, R, in both this and the well-known Curtius, Hofmann, and Lossen degradations.



Wolff Rearrangement

Curtius Rearrangement

$$\text{(a)}\quad R{:}\overset{\overset{O}{\|}}{C}{:}\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{C}}}{:}N{:}{:}{:}N{:} \longrightarrow R{:}\overset{\overset{O}{\|}}{C}{:}\overset{H}{\overset{\cdot\cdot}{C}}{:} + N_2 \qquad \text{(a}'\text{)}\quad R{:}\overset{\overset{O}{\|}}{C}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}{:}N{:}{:}{:}N{:} \longrightarrow R{:}\overset{\overset{O}{\|}}{C}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}}{:} + N_2$$

I II I′ II′

$$\text{(b)}\quad R{:}\overset{\overset{O}{\|}}{C}{:}\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{C}}} \xrightarrow[\text{migration of R with its electron pair}]{\text{(catalyst)}} R{:}\overset{H}{\overset{\cdot\cdot}{C}}{:}{:}C{:}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \qquad \text{(b}'\text{)}\quad R{:}\overset{\overset{O}{\|}}{C}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{N}} \xrightarrow[\text{of R with its electron pair}]{\text{migration}} R{:}\overset{\cdot\cdot}{N}{:}{:}C{:}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}$$

II III II′ III′

$$\text{(c)}\quad R{:}\overset{H}{\overset{\cdot\cdot}{C}}{:}{:}C{:}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \xrightarrow{A:H} R{:}\underset{H}{\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{C}}}}{:}\overset{\overset{O}{\|}}{C}{:}A \qquad \text{(c}'\text{)}\quad R{:}\overset{\cdot\cdot}{N}{:}{:}C{:}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}} \xrightarrow{A:H} R{:}\underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{N}}}{:}\overset{\overset{O}{\|}}{C}{:}A$$

III IV III′ IV′

(A: = $OH^-$; $NH_2^-$; $NHR^-$; $OR^-$)

In both rearrangement processes (b) and (b′) the shift of the radical, R, is supposed to occur in such a fashion that the radical remains at all times in complete possession of its electron pair. Such a postulate was shown to explain most readily the complete retention of optical activity in the

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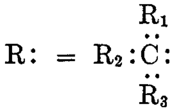
[1] Charlotte Elizabeth Procter Fellow for the year 1940–1941.

Curtius, Hofmann, and Lossen rearrangements where R is an asymmetric group of general structure



$$R: \; = \; R_2 : \overset{R_1}{\underset{R_3}{\ddot{\underset{\cdot\cdot}{C}}}} :$$

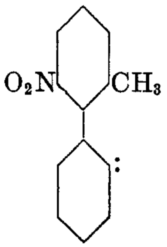
($R_1$ and $R_2$ = alkyl or aryl groups; $R_3$ = H or an alkyl or aryl group)

in the earlier communications of this series (3). In the eighth communication (4), it was pointed out that if the Wolff rearrangement proceeded according to the mechanism outlined above, a similar retention of optical activity by the migrating group would be expected. The results presented in that paper, however, showed conclusively that for the Wolff rearrangement of dextrorotatory benzylmethyldiazoacetone, this was certainly not the case, since partial or complete racemization of the benzylmethylcarbinyl group occurred, depending on the conditions of the experiment.

It is the purpose of this paper to extend the study of the Wolff rearrangement of optically active diazoketones to different types of the radical, R, with a view to establish how far similarity or dissimilarity prevails between the two types of rearrangement, and to determine the cause or causes of the difference in the behavior of the benzylmethylcarbinyl group in the two processes.

In explaining this difference it would seem logical to assume that the group, R, at some time during the step (b) is released as a relatively free fragment and racemizes while in this state. Evidence was obtained by Wallis and Moyer (3d) that for rearrangements of the Curtius, Hofmann, and Lossen types this is not the case, a conclusion further supported by the subsequent investigations of Bell (5). To settle this point a study was made of the Wolff rearrangement of dextrorotatory α-diazo-*o*-(2-methyl-6-nitrophenyl)acetophenone. This compound was chosen since the migrating group would be that shown by Bell (5) to suffer no racemization during the Curtius degradation of the azide of dextrorotatory 6-nitro-2-methyldiphenyl-2′-carboxylic acid,

R: =

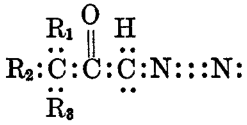


The diazoketone, $[\alpha]_D^{20}$ +115° ($c$ = 6.00 in chloroform), was prepared by the action of diazomethane on the chloride of this acid, $[\alpha]_D^{20}$ +70.0° ($c$ = 1.00 in methanol). Similarly, an optically impure levo-modification, $[\alpha]_D^{20}$ −46.1° ($c$ = 5.99 in chloroform) was prepared from an incompletely resolved levorotatory 6-nitro-2-methyldiphenyl-2′-carboxylic acid, $[\alpha]_D^{20}$ −28.0° ($c$ = 1.00 in methanol).

Portions of the diazoketone were then subjected to the Wolff rearrangement under two sets of conditions. First, the diazoketone was added in small portions to boiling aniline. Rapid rearrangement took place to give dextrorotatory *o*-(2-methyl-6-nitrophenyl)-α-toluanilide, m.p. 124°, $[\alpha]_D^{20}$ +481° ($c$ = 0.96 in chloroform), without any accompanying racemization in detectable amount. Second, a portion of the diazoketone was dissolved in dioxane and treated at 65–70° with an aqueous solution of sodium thiosulfate containing some silver oxide as a catalyst. Rearrangement proceeded smoothly to give dextrorotatory *o*-(2-methyl-6-nitrophenyl)-α-toluic acid, $[\alpha]_D^{20}$ +53.0° ($c$ = 1.00 in chloroform). This acid was then converted to the corresponding anilide, m.p. 123–124°, $[\alpha]_D^{20}$ +485° ($c$ = 1.02 in chloroform), which was identical with the anilide obtained as outlined above.

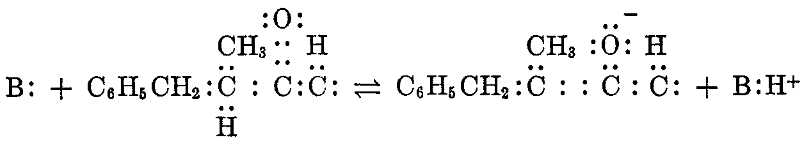
These results indicate quite clearly that release of the migrating group as a free fragment is no more characteristic of the Wolff rearrangement than it is of the Curtius and Hofmann rearrangements. Otherwise racemization would have occurred, since in the free fragment unhindered rotation of the phenyl group about the C—C pivot bond would have taken place. The number of possible explanations for the divergence in behavior of the benzylmethylcarbinyl group during the two types of rearrangement is now reduced to two: (A) The observed racemization is due to a structural peculiarity of the compound studied and is not to be connected with the electronic behavior of the group, R, during the shift in step (b). (B) The racemization is the expression of a real difference in the electronic structure of the asymmetric center during step (b) as contrasted with (b′). Such would be the case, for example, if step (b) proceeded so that at some time the asymmetric center was left with a sextet or septet of electrons (3b, c, e).

As we have pointed out (4), a decision can be made between these possibilities by studying the rearrangement of a diazoketone of the form



$$R_2{:}\overset{R_1}{\underset{R_3}{\ddot{\underset{\cdot\cdot}{C}}}}{:}\overset{O}{\overset{\|}{C}}{:}\overset{H}{\ddot{\underset{\cdot\cdot}{C}}}{:}N{:}{:}{:}N{:}$$

where $R_1$, $R_2$, and $R_3$ are all alkyl or aryl groups. The structural peculiarity of benzylmethyldiazoacetone by which an enolization of the intermediate (II above)



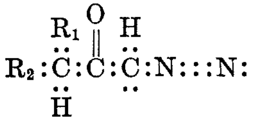
$$B\!: + C_6H_5CH_2\!:\!\overset{CH_3}{\underset{H}{\ddot{C}}}\;:\;\overset{:O:}{\ddot{C}}\!:\!\overset{H}{\ddot{C}}\!: \rightleftharpoons C_6H_5CH_2\!:\!\overset{CH_3}{\ddot{C}}\;:\;:\;\overset{:\ddot{O}:^{-}}{C}\;:\;\overset{H}{\ddot{C}}\!: + B\!:\!H^+$$

(B: = $OH^-$, $NH_3$, etc.)

might cause racemization is thereby eliminated. Racemization of such a trisubstituted diazoacetone then would be due only to electronic changes in step (b) which do not occur in step (b′), *i.e.*, changes by which the asymmetric group assumes a planar structure. Preliminary efforts in this direction were previously discussed (4), but the lack of available material of sufficient optical purity for obtaining conclusive results prevented a definite decision from being made at that time.

Accordingly, a study was made of the rearrangement of dextrorotatory 1-diazo-3-methyl-3-phenylheptan-2-one, $[\alpha]_D^{20}$ +65.0° ($c$ = 14.1 in benzene), obtained by the action of diazomethane on the chloride of dextrorotatory 2-methyl-2-phenylhexanoic acid, $\alpha_D^{20}$ +24.5° (1 dm. tube without solvent). The diazoketone was first rearranged in boiling aniline to give the corresponding anilide. A levorotatory 3-methyl-3-phenylheptanoanilide, $[\alpha]_D^{20}$ −59.5° ($c$ = 2.77 in benzene), m.p. 76°, was obtained. No evidence of accompanying racemization was detected. A subsequent rearrangement of a portion of the diazoketone in aqueous dioxane containing sodium thiosulfate and silver oxide gave an organic acid which was converted by the action of aniline on its chloride to an anilide of m.p. 76–77°, $[\alpha]_D^{20}$ −58.9°, ($c$ = 2.82 in benzene), identical with the preceding product. Similar rearrangements of an incompletely resolved levorotatory diazoketone, $[\alpha]_D^{20}$ −29.4° ($c$ = 15.4 in benzene), prepared from an incompletely resolved levorotatory 2-methyl-2-phenylhexanoic acid, $\alpha_D^{20}$ −10.5° (1 dm. tube without solvent), led to optically impure 3-methyl-3-phenylheptanoanilide from which, on repeated recrystallization, the racemic anilide, m.p. 87°, was obtained.

The results indicate that the racemization of optically active diazoketones during the Wolff rearrangement is by no means a general phenomenon. Rather it is a special property of diazoketones of the type



$$R_2\!:\!\overset{R_1}{\underset{H}{\ddot{C}}}\!:\!\overset{O}{\overset{\|}{C}}\!:\!\overset{H}{\underset{\cdot\cdot}{\ddot{C}}}\!:\!N\!:\,:\,:\!N\!:$$

where the asymmetric center possesses an enolizable hydrogen. There still remains, however, the problem of reconciling this conclusion with the optical stability of the benzylmethylcarbinyl group during the Hofmann rearrangement (3b). Here, no enolization occurs, though the reaction proceeds in a strongly basic solution at 70–80°. We are inclined to attribute the difference to the effect of the silver ion-silver metal surface of the catalyst present in the Wolff rearrangement. This immediately raises the interesting question of the fate of optically active benzylmethyldiazoacetone in a Wolff rearrangement without a catalyst present. Such a state obtains, of course, in the rearrangements described above where diazoketones are treated with boiling aniline. The temperature of this reaction (184°) is so high, however, that in the basic medium the optical activity of any system of the form $R_1R_2H\overset{|}{C}{-}C{=}O$ would be expected to be short-lived. Such an experiment was in fact carried out on dextrorotatory benzylmethyldiazoacetone, but the β-benzyl-β-methylpropionanilide so obtained was completely optically inactive. So far, we have not found a method of rearranging this compound without the aid of a catalyst at temperatures below 100°. The use of liquid ammonia in a sealed tube at room temperature results in the formation of a black tar from which no recognizable product can be isolated.

We are aware, of course, that such enolization is not the only explanation consistent with the data now at hand. For example, a different mechanism may be involved when the migrating group is secondary than when it is tertiary, as in the solvolysis of secondary and tertiary halides. We contemplate, therefore, a thorough kinetic investigation of the reaction to settle this point.

## EXPERIMENTAL

*Preparation of α-diazo-*o*-(2-methyl-6-nitrophenyl)acetophenone.* This compound was prepared from 6-nitro-2-methyldiphenyl-2′-carboxylic acid. The acid was prepared according to the method of Stoughton and Adams (6). Five grams of the acid was mixed with the calculated amount of phosphorus pentachloride and warmed for one-half hour on the steam-bath. The phosphorus oxychloride was then removed on the steam-bath at 15 mm. pressure, and the residue was recrystallized from a mixture of benzene and light petroleum ether; m.p. 85°. The purified acid chloride was dissolved in 100 cc. of dry ether and added slowly with shaking to a solution of 4 g. diazomethane in 500 cc. of dry ether at −10°. Vigorous evolution of nitrogen set in immediately, but subsided after about twenty minutes. The solution was allowed to stand overnight, filtered, and the ether removed under reduced pressure at 30°. The product, a bright yellow viscous oil, was not obtained crystalline.

For identification, 1 g. of diazoketone was warmed for thirty minutes at 80° with 5 cc. of glacial acetic acid. The mixture was cooled and diluted with light petroleum ether. Orange crystals of crude α-acetoxy-*o*-(2-methyl-6-nitrophenyl) acetophenone separated immediately. These were recrystallized from dilute alcohol. There recrystallizations gave a pure product of m.p. 125°.

*Anal.* Calc'd for $C_{17}H_{15}NO_5$: C, 65.24; H, 4.83; N, 4.47.
Found: C, 65.3; H, 4.8; N, 4.6.

*Rearrangement of α-diazo-*o*-(2-methyl-6-nitrophenyl)acetophenone in aniline.* Two grams of the diazoketone was added in small portions over a period of two minutes to 10 cc. of boiling, freshly distilled aniline. A vigorous reaction ensued, accompanied by rapid darkening of the reaction-mixture. After one minute the mixture was cooled and poured into 150 cc. of 4 *N* hydrochloric acid. The product was taken up in ether and the extract washed well with dilute hydrochloric acid, then with water, and finally with dilute sodium bicarbonate solution. The ether solution was dried over anhydrous sodium sulfate and decolorized with animal charcoal. The product obtained on removal of the ether was recrystallized three times from dilute alcohol; m.p. 137°.

*Anal.* Calc'd for $C_{21}H_{18}N_2O_3$: C, 72.90; H, 5.24; N, 8.08.
Found: C, 72.9; H, 5.2; N, 8.1.

*Rearrangement of α-diazo-*o*-(2-methyl-6-nitrophenyl)acetophenone in aqueous dioxane.* Two grams of the diazoketone was dissolved in 25 cc. of dioxane and added to a mixture of 1.3 g. of silver oxide in 65 cc. of a solution of 3 g. sodium thiosulfate in 100 cc. of water. The mixture was stirred at 65–70° for two hours, then filtered and washed thoroughly with ether to remove impurities insoluble in water. The aqueous solution was then acidified with dilute nitric acid and the product taken up in ether. It was extracted from the ether by washing with several portions of 10% sodium carbonate solution. The extracts were united and acidified with hydrochloric acid. The organic acid was then extracted with ether, washed, dried over sodium sulfate, decolorized with animal charcoal, filtered, and the ether removed. The product, 1 g. of a viscous yellow oil, was not obtained crystalline.

For identification, it was converted to the acid chloride by refluxing for two hours with thionyl chloride. The chloride so obtained was then treated with excess of aniline in benzene solution. After the reaction was complete, the solution was diluted with ether and the excess aniline removed by thorough washing with dilute hydrochloric acid. The solution was then washed several times with 10% sodium hydroxide solution and dried over potassium carbonate. Removal of the solvent gave a product which, after three recrystallizations from dilute alcohol, melted at 136–137°. Mixed melting point with a specimen of *o*-(2-methyl-6-nitrophenyl)-α-toluanilide, 136–137°.

*Preparation of dextrorotatory α-diazo-*o*-(2-methyl-6-nitrophenyl)acetophenone.* Sixty grams of the 6-nitro-2-methyldiphenyl-2′-carboxylic acid described above was resolved into its enantiomorphs according to the method of Bell (5). Fifteen grams of the dextrorotatory acid, $[\alpha]_D^{20}$ +70.0° (*c* = 1.00 in methanol), was obtained. Five grams of this acid was converted to the corresponding diazoketone as described above under the preparation of the racemic form. The dextrorotatory diazoketone was not obtained crystalline. Optical rotation: $[\alpha]_D^{20}$ +115° (*c* = 6.00 in chloroform).

From the mother liquors of the resoltuion was obtained the pure levorotatory acid and an optically impure levo-modification, $[\alpha]_D^{20}$ −28.0° (*c* = 1.00 in methanol). From the latter was prepared an optically impure levo-modification of the diazoketone: $[\alpha]_D^{20}$ −46.1° (*c* = 5.99 in chloroform).

*Rearrangement of the dextrorotatory diazoketone in aniline.* Two grams of dextrorotatory α-diazo-*o*-(2-methyl-6-nitrophenyl)acetophenone was converted into the corresponding anilide by the method described for the preparation of the racemic form. The dextrorotatory *o*-(2-methyl-6-nitrophenyl)-α-toulanilide so obtained had the following physical constants: m.p. 124°; $[\alpha]^{20}_{6563}$ +369°; $[\alpha]^{20}_{5893(D)}$ +481°; $[\alpha]^{20}_{5463}$ +624°; $[\alpha]^{20}_{4861}$ +875° ($c$ = 0.96 in chloroform).

*Anal.* Calc'd for $C_{21}H_{18}N_2O_3$: C, 72.90; H, 5.24; N, 8.08.
Found: C, 73.0; H, 5.2; N, 8.2.

No racemate could be detected in the mother liquors from the recrystallizations.

Rearrangement of the optically impure levorotatory diazoketone gave a product of m.p. 125–134°; $[\alpha]^{20}_{D}$ −137.5° ($c$ = 1.08 in chloroform).

*Rearrangement of the dextrorotatory diazoketone in aqueous dioxane.* Two grams of dextrorotatory α-diazo-*o*-(2-methyl-6-nitrophenyl)acetophenone was dissolved in 25 cc. of dioxane and treated as described above under the corresponding rearrangement of the racemic form. The resulting *o*-(2-methyl-6-nitrophenyl)-α-toluic acid, $[\alpha]^{20}_{D}$ +53.0 ($c$ = 1.00 in chloroform), was not obtained crystalline. For identification it was converted to the corresponding anilide as described under the identification of the racemic acid. The product so obtained had the following physical constants: m.p. 123–124°; mixed m.p. with a specimen of dextrorotatory *o*-(2-methyl-6-nitrophenyl)-α-toluanilide: 123–124°; $[\alpha]^{20}_{6563}$ +363°; $[\alpha]^{20}_{5820(D)}$ +485°; $[\alpha]^{20}_{5463}$ +625° ($c$ = 1.02 in chloroform). Again no racemate could be detected in the mother liquors of the recrystallizations.

*Preparation of dextrorotatory 1-diazo-3-methyl-3-phenylheptan-2-one.* This compound was prepared from dextrorotatory 2-methyl-2-phenylhexanoic acid. The acid, b.p. 145°/2 mm., was prepared by the method of Conant and Carlson (7), and was resolved by their method into its enantiomorphs. Four grams of the dextrorotatory acid, $\alpha^{20}_{D}$ +24.5° (1 dm. tube without solvent), $[\alpha]^{20}_{5463}$ +14.0° ($c$ = 2.40 in alcohol), was refluxed four hours with an excess of thionyl chloride. The thionyl chloride was then removed at 15 mm. pressure on the steam-bath, and the acid chloride was dissolved in 50 cc. of dry ether. This solution was then added slowly and with shaking to a solution of 4 g. diazomethane in 500 cc. of dry ether at −10°. The mixture was allowed to stand overnight, filtered, and the ether removed at 30° under diminished pressure. The bright yellow diazoketone was not obtained crystalline. $[\alpha]^{20}_{D}$ +65.0 ($c$ = 14.1 in benzene).

Similarly, an optically impure levo-modification, $[\alpha]^{20}_{D}$ −29.4° ($c$ = 15.4 in benzene), was prepared from an incompletely resolved levorotatory acid, $\alpha^{20}_{D}$ −10.5° (1 dm. tube without solvent).

*Rearrangement of the dextrorotatory diazoketone in aniline.* One and one-half grams of dextrorotatory 1-diazo-3-methyl-3-phenylheptan-2-one was added in small portions to 10 cc. of boiling, freshly distilled aniline over a period of two minutes. After five minutes the reaction-mixture was cooled and poured into 200 cc. of 4 *N* hydrochloric acid. The product was then treated by the same methods used for the isolation of dextrorotatory *o*-(2-methyl-6-nitrophenyl)-α-toluanilide. Three recrystallizations from dilute alcohol gave a product having the following physical constants: m.p. 76°; $[\alpha]^{20}_{6563}$ −47.2°; $[\alpha]^{20}_{5893(D)}$ −59.5°; $[\alpha]^{20}_{5463}$ −72.2°; $[\alpha]^{20}_{4861}$ −96.0° ($c$ = 2.77 in benzene).

*Anal.* Calc'd for $C_{20}H_{25}NO$: C, 81.36; H, 8.54; N, 4.75.
Found: C, 81.3; H, 8.5; N, 4.7.

No racemate could be detected in the mother liquors of the recrystallizations.

Similarly, 2 g. of the optically impure levorotatory diazoketone was converted into an optically impure dextro-modification. This product, after two recrystallizations from dilute alcohol showed a rotation $[\alpha]_D^{20}$ +9.30° ($c = 9.80$ in methanol). Three more recrystallizations gave the racemic anilide, m.p. 87°.

*Rearrangement of the dextrorotatory diazoketone in aqueous dioxane.* One and one-half grams of dextrorotatory 1-diazo-3-methyl-3-phenylheptan-2-one was dissolved in 15 cc. of dioxane and treated with 40 cc. of a mixture of 2 g. of silver oxide and 100 cc. of an aqueous solution of 3 g. sodium sulfate, according to the method described above under the corresponding rearrangement of α-diazo-*o*-(2-methyl-6-nitrophenyl)acetophenone. The organic acid so obtained was converted to the corresponding anilide by the usual method. This anilide had the following physical constants: m.p. 76–77°; mixed m.p. with a specimen of levorotatory 3-methyl-3-phenylheptanoanilide: 76–77°; $[\alpha]_{6563}^{20}$ −46.5°; $[\alpha]_{5893(D)}^{20}$ −58.9°; $[\alpha]_{5463}^{20}$ −71.3°; $[\alpha]_{4861}^{20}$ −95.0° ($c = 2.82$ in benzene). No racemate could be detected in the mother liquors of recrystallization.

In the same way, an optically impure dextro-modification of the anilide resulted from treatment of the optically impure levorotatory diazoketone by these methods. This showed essentially the same properties as the optically impure anilide described in the preceding paragraph. Repeated recrystallization from dilute alcohol yielded ultimately the racemic anilide, m.p. 87°.

*Rearrangement of dextrorotatory benzylmethyldiazoacetone in aniline.* This compound was prepared from dextrorotatory benzylmethylacetic acid, $\alpha_D^{20}$ +22.7° (1 dm. tube without solvent), by a method previously described (4). The diazoketone had a rotation $\alpha_D^{20}$ +134° (1 dm. tube without solvent). Two grams of the diazoketone was added slowly in small portions to 10 cc. of boiling, freshly distilled aniline. The reaction was complete after about two minutes. The mixture was then cooled and the product worked up by the method described above for the isolation of the other anilides. The product so obtained was completely optically inactive. Three recrystallizations from benzene and light petroleum ether gave the racemic anilide, m.p. 102°.

*Anal.* Calc'd for $C_{17}H_{19}NO$: C, 80.65; H, 7.57; N, 5.53.
Found: C, 81.0; H, 7.6; N, 5.6.

In conclusion we wish to thank Merck and Co., Rahway, New Jersey, for the analyses published here; E. I. duPont de Nemours and Co., Wilmington, Delaware, for the grant of a fellowship to the junior author for the year 1939–1940, during which part of this work was accomplished; and Dr. E. M. May, Newark, New Jersey, for the preparation and resolution of the 2-methyl-2-phenylhexanoic acid used in certain of these experiments.

## SUMMARY

α-Diazo-*o*-(2-methyl-6-nitrophenyl)acetophenone has been prepared in the racemic, pure dextro, and mixed levo-modifications.

From the racemic modification, α-acetoxy-*o*-(2-methyl-6-nitrophenyl)-acetophenone results on treatment with glacial acetic acid.

Evidence is submitted to show that on treatment of the optically active modifications of this compound with boiling aniline, a Wolff rearrangement takes place to give optically active *o*-(2-methyl-6-nitrophenyl)-α-tolu-

anilide without any accompanying racemization in appreciable amount. Similarly, on treatment with water in the presence of a catalyst, a Wolff rearrangement occurs to give optically active *o*-(2-methyl-6-nitrophenyl)-$\alpha$-toluic acid without appreciable racemization.

1-Diazo-3-methyl-3-phenylheptan-2-one has been prepared in the pure dextro and mixed levo-modifications. Treatment of this compound with boiling aniline gives optically active 3-methyl-3-phenylheptanoanilide without appreciable racemization. Treatment with water and a catalyst gives optically active 3-methyl-3-phenylheptanoic acid without appreciable racemization.

Dextrorotatory benzylmethyldiazoacetone has been prepared and subjected to the Wolff rearrangement in boiling aniline. The resulting $\beta$-methyl-$\beta$-benzylpropionanilide is completely optically inactive.

A discussion of these results is given with special reference to the relation of the detailed mechanism of the Wolff rearrangement to that of the Curtius, Hofmann, and Lossen rearrangements. It is concluded that the partial or complete racemization of the products resulting from the Wolff rearrangement of optically active benzylmethyldiazoacetone under different conditions is due to the presence of an enolizable hydrogen on the asymmetric center. That enolization and racemization occur in the Wolff rearrangement and not in the Hofmann rearrangement where the benzylmethylcarbinyl group is involved, is attributed to the presence of the metallic catalyst in the former reaction.

PRINCETON, N. J.

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