[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE USE OF HIGHER DIAZOHYDROCARBONS IN THE ARNDT-EISTERT SYNTHESIS

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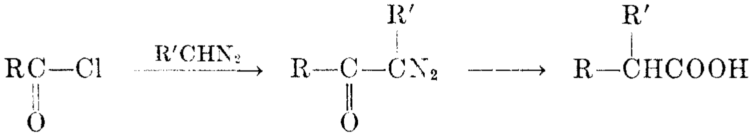
The Arndt-Eistert synthesis (1), involving reaction of an acid chloride with diazomethane followed by rearrangement of the resulting diazoketone, has become a well-established and useful method for converting an acid into a derivative of its next higher homolog. An excellent survey of the reaction and its uses has been made by Bachmann and Struve (2).

The synthesis apparently has not been employed with higher aliphatic diazohydrocarbons; the sole reference to such use which we have found in the literature is the statement by Eistert (3) that the diazoketone from *p*-nitrobenzoyl chloride and diazoethane may be rearranged to the anilide of α-(*p*-nitrophenyl)-propionic acid. Examples are known, however, in which diazoacetic ester has been employed, giving a substituted malonic ester after rearrangement (4). From these, the well-known rearrangement of phenylbenzoyldiazomethane ($C_6H_5COCN_2C_6H_5$) to diphenylketene (5), and the generally accepted mechanism for the Wolff rearrangement involving formation of a ketene intermediate (2, 6), it would be anticipated that higher diazohydrocarbons would give the α-substituted homolog in the Arndt-Eistert reaction.



$$\underset{\underset{\displaystyle O}{\|}}{RC}-Cl \xrightarrow{R'CHN_2} R-\underset{\underset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle R'}{|}}{C}N_2 \longrightarrow R-\overset{\overset{\displaystyle R'}{|}}{C}HCOOH$$

We have investigated the use of diazoethane in this synthesis to determine if this course is taken by the reaction, and to explore the possibilities for using the reaction with the higher diazohydrocarbons as a synthetic tool. Treatment of 1-naphthoyl chloride with diazoethane under the usual conditions gave a yellow, oily diazoketone which evolved nitrogen when refluxed in methanol solution with silver oxide. Saponification of the resulting material gave a solid acid in 26% yield which was shown to be α-1-naphthylpropionic acid (Ia). In another run the acid was obtained in 34% yield, but in ten other attempts the reaction was unsuccessful, only neutral tars and a small amount of the starting acid being isolated. The technique was not at fault, for similar runs with diazomethane gave 1-naphthylacetic acid (Ib) consistently in 70% yield. The reason for these inconsistent results with diazoethane has not been discovered, but from the sequel it is probable that the major fault lay in failure of the diazoketone to undergo rearrangement.

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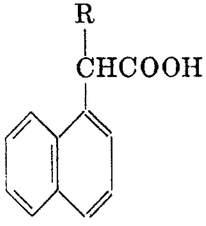
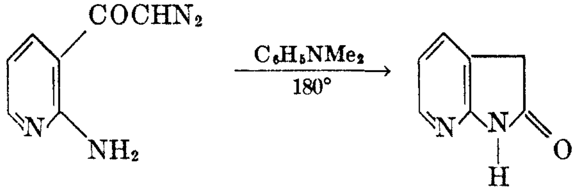
In the work with diazomethane, crystalline diazoketones usually were obtained, while with diazoethane the product was an oil. Even after a method was finally developed which gave crystalline diazoketones from diazoethane and *p*-chlorobenzoyl chloride or *p*-toluyl chloride, attempts to rearrange these pure diazoketones in methanol using silver oxide, silver nitrate, or copper powder met with failure. In all, six different diazoketones were tried. It was then noted that Kägi (7), after unsuccessful attempts to effect the Wolff rearrangement with the diazoketone II in the usual way, was able to rearrange it to the derivative III by heating at 180° with dimethylaniline. Arndt and Eistert (1) have also carried out several rearrangements to anilides by dropping the diazoketone into boiling aniline. In applying this last technique to the diazoketone from *p*-chlorobenzoyl chloride and diazoethane, nitrogen was evolved vigorously and an 85% yield of the anilide resulted. Similar results were obtained with the diazoketones from *p*-toluyl chloride and 1-naphthoyl chloride. Thus, a successful method for effecting the rearrangement was available.



Ia, R = CH_3
Ib, R = H



II

III

In order for the synthesis to be generally useful, however, it was desirable to obtain a derivative more readily hydrolyzed than the anilides. Rearrangement at 170–180° in the presence of dimethylaniline and benzyl alcohol was found to give the benzyl esters which are easily hydrolyzed to the rearranged acids. This procedure has been applied many times to a number of different diazoketones derived from diazomethane, diazoethane, and diazopropane *without as yet a single failure.* Even with diazomethane it is not uncommon for occasional runs, for no apparent reason, to fail in the rearrangement step using the conventional method. This new method, then, appeared to be of considerable general value and was investigated in some detail.

Preparation of the diazohydrocarbons

For preparing diazoethane it has been our experience that the method of Adamson and Kenner (8), employing β-(N-nitrosoethylamino)isobutyl methyl ketone, is less satisfactory than the von Pechmann synthesis (9) using N-nitroso-N-ethylurethan. The latter method has been employed by Nirdlinger and Acree (10) for preparing several of the higher diazohydrocarbons, including diazoethane and 1-diazopropane. We have developed a procedure for preparing diazoethane consistently in 75% yield by fairly rapid addition of the readily available nitrosoethylurethan to a solution of potassium hydroxide in *n*-propyl alcohol. When the addition was slow the yields were decreased to 30–50%. This improved method of preparing diazoethane makes it as readily available for use in organic reactions as diazomethane. In a similar manner 1-diazopropane was prepared in about 57% yield.

Preparation of the diazoketones

In the standard method for preparing diazoketones from diazomethane, the acid chloride is added to an excess (2.5 to 3.0 moles) of diazomethane at 0° and allowed to stand for several hours or even overnight at 0° to room temperature. In all of the runs which we have made with diazomethane this procedure gave practically quantitative yields of the crude crystalline diazoketone.

TABLE I

EFFECT OF TEMPERATURE ON THE PREPARATION OF 1-*p*-CHLOROBENZOYL-1-DIAZOETHANE

TEMP. °C.	YIELD OF CRYSTALLINE DIAZOKETONE, %	YIELD OF OILY DIAZOKETONE, %	TOTAL YIELD, %
5–10	48[a]	—	—
0–10	44	24	68
0	55	16	71
−10	61	12	73
−20	71	8	79
−30	61	10	71

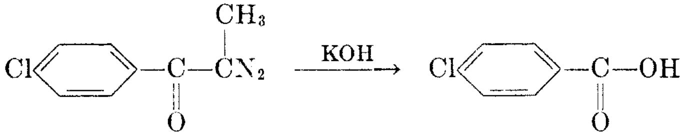
[a] This material contained some of the by-product from further action of diazoethane.

With diazoethane, however, it was found that the reaction conditions were more critical. In Table I are summarized runs with *p*-chlorobenzoyl chloride and diazoethane at various temperatures. The amount of oily diazoketone left in the filtrate was determined by rearrangement using benzyl alcohol and dimethylaniline and isolating the acid. It can be seen that the highest yield, both total and of crystalline material, was obtained at −20°. When the reaction was carried out above 0° a colorless by-product was obtained in addition to the yellow diazoketone. This by-product, $C_{11}H_{11}ClN_2O$, was shown to arise from the reaction of a second mole of diazoethane with the diazoketone with loss of nitrogen. A similar crystalline by-product, $C_{12}H_{14}N_2O$, was obtained from *p*-toluyl chloride. Although the structures of these compounds have not been elucidated, it is apparent that they are not diazoketones, for unlike the latter, they did not evolve nitrogen when treated with hydrobromic acid. We hope to establish the structure of these by-products in the near future.

This type of side reaction apparently is not of importance using diazomethane. Indeed 1-*p*-chlorobenzoyl-1-diazoethane was unaffected by diazomethane under conditions which gave the by-product with diazoethane. There are, however, indications that such by-products may arise in certain cases. Lutz and coworkers (11) found that prolonged reaction of 5-chloro- and 5,8-dichloro-cinchophen acid chlorides with a large excess of diazomethane resulted in mixtures containing considerably more than the expected amount of nitrogen, which suggests reaction with a second mole of diazomethane. Recently Fieser and Turner (12) isolated an anomalous by-product from the reaction of diazomethane with the acid chloride of 9-(2-acetoxy-1,4-naphthoquinonyl-3)-pelargonic acid. Although this compound was formulated as isomeric with the diazoketone, the analysis would also be consistent with a product resulting from addition of a second mole of diazomethane with loss of nitrogen.

Rearrangement of the diazoketones

As mentioned above, the usual silver oxide-methanol procedure was unsuited for rearrangement of a diazoketone from diazoethane, even when the crystalline compound was employed. In several cases, after an attempted rearrangement followed by alkaline hydrolysis, a considerable amount of the starting acid was isolated in addition to dark neutral tars. A separate experiment established the interesting fact that alkali can cleave a diazoketone derived from diazoethane:



Presumably the other fragment is diazoethane which undergoes further reaction, perhaps with the solvent or through decomposition.

For determining the optimum conditions of rearrangement using the benzyl alcohol method, 1-*p*-chlorobenzoyl-1-diazoethane was first heated with a series of high-boiling alcohols in the presence of dimethylaniline (see Table II). In each case the rearrangement took place, even when phenol was used. The best yields seemed to result with benzyl alcohol.

Next the effect of the tertiary amine was investigated, using benzyl alcohol (Table III). The yield was good in each case, ranging from 73 to 90%. The best results were obtained with γ-collidine (85–90%) and isoquinoline (86%). It is interesting to note that a tertiary amine is not essential, since even in its absence a 70% yield of the rearranged acid was obtained. However, the tertiary amine does improve the yields significantly. Triethanolamine and methyldiethanolamine are interesting examples which served both as the tertiary amine and the alcohol, giving 80 and 73% yields, respectively.

For establishing the effect of temperature a series of runs was made using benzyl alcohol and isoquinoline (Table IV). The reaction proceeded rapidly and in good yield at temperatures of 140–200°. At lower temperatures the reaction became slower and the yields dropped, although even at 80° the yield was 68%. The amount of starting acid recovered, though low in any case, was smallest at the highest temperatures. The optimum temperature appears to be around 170–190°.

Finally, to learn if the concentration had any effect, a series of runs was made in which the amount of benzyl alcohol was varied from 1 to 20 moles. The optimum seemed to be about 2–5 moles per mole of diazoketone (80–87% yields).

TABLE II

REARRANGEMENT OF 1-*p*-CHLOROBENZOYL-1-DIAZOETHANE IN THE PRESENCE OF VARIOUS ALCOHOLS

(Using 1 g. of diazoketone, 2.5 cc. of dimethylaniline, approximately 3 cc. of the alcohol, and heating for ten minutes, then hydrolyzing the ester).

ALCOHOL	BATH TEMP. °C	STARTING ACID RECOVERED, MG.	YIELD OF REARRANGED ACID, %
Benzyl	170	—	74–81
Phenylethyl	170	40	53[a]
Octanol-1	170	45	78
Octanol-2	165–170	55	73
2-Ethylhexanol-1	170	60	57
"Hexanol"[b]	150	46	53
Cyclohexanol	160	9	70
Ethylene glycol	170	0	71
Butyl carbitol	170	24	64[c]
Phenol	170	31	71

[a] Part of this product was lost.

[b] A commercial mixture of hexanols.

[c] This product was oily; the others were crystalline solids melting from 52–55° ("hexanol") to 55–57° (benzyl alcohol).

TABLE III

EFFECT OF THE TERTIARY AMINE

(Using 1 g. of 1-*p*-chlorobenzoyl-1-diazoethane, 5 cc. of benzyl alcohol and the tertiary amine at 165–170°)

TERTIARY AMINE (G.)	STARTING ACID RECOVERED, (MG.)	YIELD OF REARRANGED ACID, %
Dimethylaniline (3.8)	15	79
Diethylaniline (4.6)	24	80
γ-Collidine (3.8)	0–3	85–90
Quinoline (4.0)	16	75
Isoquinoline (4.0)	40	86
N-*n*-hexylpiperidine (5.2)	5	78
Triethanolamine[a] (4.6)	10	80
Methyl diethanolamine[a] (3.7)	30	73
None	55	70

[a] No benzyl alcohol used in these runs.

In order to test the generality of the Arndt-Eistert synthesis with diazoethane as developed in this investigation, the reactions were applied to eight different acids, including one aliphatic and one arylaliphatic as well as aromatic acids (Table V). The over-all yields from the acid chloride ranged from 44 to 70%, and with those examples which were worked out the most carefully they were in the range 55–70%. In three cases, acetic, 1-naphthoic and β-1-naphthylpropionic acids, the structure of the rearranged product was established by direct comparison with an authentic sample and in another case, *p*-nitrobenzoic acid, the melting point of the product was in agreement with that described in the literature.

TABLE IV

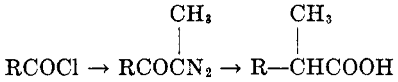
EFFECT OF TEMPERATURE

(Using 1 g. of 1-*p*-chlorobenzoyl-1-diazoethane, 5 cc. of benzyl alcohol and 5 cc. of isoquinoline; theoretical volume of nitrogen = 135 cc.)

BATH TEMP., °C	VOL. OF N_2, CC.	TIME NECESSARY FOR COMPLETION, MIN.	STARTING ACID RECOVERED, MG.	YIELD OF PRODUCT, %
200	140	0.5	6	86
190	135	1	7	87
180	122–135	1–2	13–16	83–84
170	135	2	11	86
160	125	2	6	81
150	130	2	21	81
140	130	4	18	82
120	125	8	24	77
100	122	30	31	76
80	134	420	36	68

TABLE V

ARNDT-EISTERT SYNTHESIS USING DIAZOETHANE



$$RCOCl \rightarrow RCO\overset{CH_3}{\overset{|}{C}}N_2 \rightarrow R-\overset{CH_3}{\overset{|}{C}}HCOOH$$

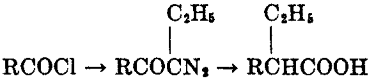
STARTING ACID	YIELD OF DIAZOKETONE	PRODUCT OF REARRANGEMENT	YIELD IN REARRANGEMENT, %	OVER-ALL YIELD, %
Benzoic	(oil)	Anilide	—	55
p-Chlorobenzoic	71% + 7% oil	Acid	85–90	61–70
		Anilide	85	66
p-Toluic	51% + 16% oil	Acid	—	55–70
		Anilide	79	53
p-Nitrobenzoic	76%	Acid	66	50
		Anilide	60	46
1-Naphthoic	(oil)	Acid	—	58
		Anilide	—	36
2-Naphthoic	60%	Acid	67	40–48
β-1-Naphthylpropionic	(oil)	Acid	—	47
Acetic	(oil)	Anilide	—	44

In a similar manner the synthesis was carried out using 1-diazopropane. With this reagent the acids were converted into their next higher homologs with an α-ethyl substituent, in yields ranging from 25 to 58% (see Table VI). The structure of the rearranged product was established in two cases, *p*-nitrobenzoic and *p*-anisic acids, by direct comparison with authentic samples and in a third case, acetic acid, the melting point of the product was in agreement with that reported.

Finally we were interested in making a direct comparison of the benzyl alcohol-tertiary amine method with the usual silver oxide-methanol procedure, using for each the same samples of crystalline diazoketones derived from diazomethane. Four acids were compared with the results summarized in Table VII. In each case the yield using the benzyl alcohol procedure was as good as or superior to that by the silver oxide procedure. In two cases, *p*-anisic and *p*-toluic acids, these particular runs failed using the silver oxide-methanol procedure (although successful ones have been carried out) while the benzyl alcohol procedure gave 76–79% yields. Thus, the new procedure offers the advantage of dependability over the older method, in addition to somewhat higher yields and a much shorter reaction time.

TABLE VI

ARNDT-EISTERT SYNTHESIS USING 1-DIAZOPROPANE



$$RCOCl \rightarrow RCO\overset{C_2H_5}{\overset{|}{C}}N_2 \rightarrow R\overset{C_2H_5}{\overset{|}{C}}HCOOH$$

STARTING ACID	YIELD OF DIAZOKETONE	PRODUCT OF REARRANGEMENT	YIELD IN REARRANGMENT %	OVER-ALL YIELD, %
Acetic	(oil)	anilide	—	25
p-Chlorobenzoic	(oil)	acid	—	58
p-Nitrobenzoic	81%	acid	55	45
p-Anisic	(oil)	acid	—	37

TABLE VII

COMPARISON OF BENZYL ALCOHOL-COLLIDINE PROCEDURE WITH SILVER OXIDE-METHANOL PROCEDURE, USING DIAZOKETONES RELATED TO DIAZOMETHANE

STARTING ACID	YIELD OF REARRANGED ACID, %	
	SILVER OXIDE METHOD	BENZYL ALCOHOL METHOD
p-Chlorobenzoic	64	68
1-Naphthoic	67–75	74
p-Anisic	(unsuccessful)	76
p-Toluic	(unsuccessful)	79

EXPERIMENTAL[2]

Preparation of acid chlorides. Most of the acid chlorides were prepared by heating the acid with thionyl chloride and a drop of pyridine for three hours, removing most of the thionyl chloride under reduced pressure, then adding dry benzene and distilling to facilitate removal of the reagent, and finally distilling the acid chloride under reduced pres-

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[2] All melting points are corrected.

sure. In the case of *p*-nitrobenzoyl chloride the distilled product was recrystallized from benzene. The following table summarizes the results:

ACID CHLORIDE	B.P. (MM.)	YIELD %
p-Chlorobenzoyl	101–102 (12)	85
p-Toluyl	94–95 (11)	87
p-Nitrobenzoyl	m.p. 71–71.5	44
p-Anisoyl	155.5–156 (30)	85
1-Naphthoyl	164–167 (13)	83
2-Naphthoyl	182–185 (25)	73

N-Ethyl-p-toluamide, prepared from the acid chloride and excess 33% aqueous ethylamine, crystallized from dioxane-water as colorless platelets, m.p. 96–97°; reported, 90° (13).

Anal. Calc'd for $C_{10}H_{13}NO$: C, 73.6; H, 8.0.
Found: C, 73.8; H, 8.0.

N-Ethyl-p-chlorobenzamide crystallized from dioxane-water as colorless needles, m.p. 110–111°.

Anal. Calc'd for $C_9H_{10}ClNO$: C, 58.8; H, 5.5.
Found: C, 58.4; H, 5.5.

β-(1-Naphthyl)propionic acid was prepared essentially by the procedure of Fieser and Gates (14) in 60% yield from 1-chloromethylnaphthalene (15). The acid chloride was prepared in benzene solution by warming gently for fifteen minutes with thionyl chloride and a trace of pyridine; several portions of benzene were added and removed under reduced pressure to eliminate the excess reagent.

Preparation of diazohydrocarbons

Diazomethane. For most of the runs the diazomethane was prepared from N-nitroso-N-methylurea as described in *Organic Reactions* (2). The ethereal solution was dried over potassium hydroxide pellets and distilled, giving diazomethane in 66% yield, as estimated by the benzoic acid method (see below).

Diazoethane. (*a*) *From N-nitroso-N-ethylurethan. N-Ethylurethan* was prepared by the method described in *Organic Syntheses* for N-methylurethan (17), except that 270 g. of 33% aqueous ethylamine was substituted for the methylamine. The yield of the colorless liquid was 86–92%, b.p. 59–60° (3 mm.) or 79–80° (14 mm.). The N-ethylurethan (234 g.; 2 moles) was nitrosated as described for the N-methyl derivative (18), resulting in 222–257 g. (76–88%) of pink liquid, b.p. 52.5–53.5° (5 mm.).

Diazoethane was prepared from the nitrosourethan in consistent yields of 75%, when the following procedure was followed closely. A 1-liter, three-necked flask was fitted with a dropping-funnel, mechanical stirrer, and a bent tube leading to a condenser set for downward distillation. The condenser was attached to an adapter which dipped below the surface of a little anhydrous ether in the receiver, a 500-cc. suction flask equipped with a drying-tube and cooled in an ice-bath. Although an all-glass joint apparatus is preferred, good results were obtained using tightly fitting corks coated with paraffin to protect them from the diazoethane. In a typical run 100 cc. of anhydrous ether and a solution of 25 g. of potassium hydroxide in 100 cc. of *n*-propyl alcohol were placed in the three-necked flask and warmed in a water-bath with stirring until the ether began to distill. Then, while the water-bath was held at 50°, a solution of 25 g. of N-nitroso-N-ethylurethan in 75 cc. of anhydrous ether was added rapidly from the dropping-funnel in five minutes or less, at such a rate that frothing was not serious. After addition of the reagent was complete, fresh portions of dry ether were added until the distillate was coming over colorless. The total volume of the deep orange solution was about 400 cc. and contained about 75% (128 millimoles) of the theoretical amount of diazoethane, as estimated by the benzoic acid method (see below).

When the time of addition was lengthened to fifteen minutes the yield decreased to 66%, and when thirty minutes or longer, the yield was 30–50%.

(*b*) *From N-nitroso-β-ethylaminoisobutyl methyl ketone.* This reagent was prepared in 60–67% yields from mesityl oxide and 33% aqueous ethylamine essentially as described previously (8, 16), and observing the necessary precautions during distillation, 100–103° (1 mm.). Several different reagents were tried for the decomposition to diazoethane, including sodium in isopropyl alochol, potassium hydroxide in *n*-propyl or isopropyl alcohol, and sodium in cyclohexanol. The best yields (around 46%) were obtained with the last reagent.

1-Diazopropane. N-n-Propylurethan was prepared by the method described for the N-methyl derivative using 100 g. of *n*-propylamine (Sharples Co.); the yield of colorless liquid, b.p. 92° (22 mm.) was 215 g. (97%). The urethan (215 g.) was nitrosated as described for the lower homolog, except that the product was not distilled;[3] the reddish oil amounted to 258 g. (98% yield) (10). 1-Diazopropane was prepared from the crude reagent using the procedure described above for diazoethane. When the reagent was added in five minutes the yield was 57%; when added in fifteen minutes the yield was 42%. The ether solutions of 1-diazopropane were slightly darker than those of diazoethane.

N-Nitroso-N-isopropylurethan. In a similar manner N-isopropylurethan was prepared from 100 g. of isopropylamine (Eastman Kodak Co.) and obtained in 90% yield as a colorless oil, b.p. 85° (19 mm.). Nitrosation of 199 g. gave 229 g. (94%) of crude, undistilled N-nitroso-N-isopropylurethan.[3]

N-Nitroso-N-n-butylurethan. N-*n*-Butylurethan, prepared in 83% yield, b.p. 71–72° (1 mm.), was nitrosated as before to give the nitrosourethan in 90% yield as a red oil which was not distilled.[3] In a preliminary experiment a sample of the oil was converted to 1-diazobutane using ether and 40% potassium hydroxide as in the preparation of diazomethane from N-nitrosomethylurea (2). The deep orange ethereal solution of diazobutane was identified by reaction with 3,5-dinitrobenzoic acid, giving the *n*-butyl ester which without purification had the m.p. 60–63°; reported, 61–63° (19).

Estimation of the diazohydrocarbons.—The most satisfactory method used for determining the strength of the diazohydrocarbon solutions involved the addition of an aliquot at 0° to a weighed excess of benzoic acid dissolved in 50 cc. of dry ether. After standing for a few minutes 50 cc. of water and two drops of phenolphthalein solution were added and the solution titrated with 0.1 *N* sodium hydroxide with vigorous swirling (19a).

A second method which was used to check the purity of the diazohydrocarbon solution, involved adding an aliquot slowly to a cold solution of excess 3,5-dinitrobenzoic acid in dry ether. After reaction was complete the excess acid was removed by washing with potassium carbonate solution, then the ether solution was dried over potassium carbonate, filtered, and evaporated to dryness. The weight and melting point of the ester gave a measure of the amount of diazohydrocarbon and its purity. The results of duplicate determinations on the same solutions by the two methods are summarized in the following table:

DIAZOHYDROCARBON	BENZOIC ACID METHOD, %	3,5-DINITROBENZOIC ACID METHOD, %
Diazomethane	66	58, m.p. 106–107°
	64	59, (reported for pure ester, 110°)
Diazoethane	56	52, m.p. 92–93°
	59	58, (reported for pure ester 94°) (19)
1-Diazopropane	57	52, m.p. 70–72.5° (reported for pure ester, 75° (19)

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[3] It is reported (10) that N-nitroso-N-*n*-butylurethan explodes when attempts are made to distill it.

Preparation of diazoketones

Diazoketones from diazomethane. These were prepared in the usual manner (2) by adding a solution of the acid chloride in dry ether dropwise to an ethereal solution of diazomethane (using 3 moles per mole of acid chloride). The solution was allowed to stand for two to twelve hours at 0–10° and then evaporated to dryness in the cold under reduced pressure. The crude solid diazoketones were used without purification. The following results were obtained:

p-Chlorobenzoyldiazomethane, crude yield 101%, m.p. 112–115°. A sample purified by recrystallization from petroleum ether (60–68°) as light yellow needles, m.p. 114–115°, gave low values for nitrogen (Found: N, 13.8; 13.8). When a sample was sublimed at 70° and 0.05 mm. followed by recrystallization from petroleum ether, m.p. 113–114.5°, satisfactory values were obtained.

Anal. Calc'd for $C_8H_5ClN_2O$: N, 15.5; Found (micro-Dumas): N, 15.1.

p-Toluyldiazomethane, crude yield 102%, m.p. 45–50°. Recrystallization from petroleum ether gave light yellow needles, m.p. 48–51°.

Anal. Calc'd for $C_9H_8N_2O$: N, 17.5; Found: N, 17.1.

p-Anisoyldiazomethane was obtained in 102% crude yield, m.p. 84–88°; reported for the pure compound, 90–91° (20).

1-Naphthoyldiazomethane was obtained in 100% crude yield, m.p. 48–50°; reported for the pure compound, 54–55° (1).

1-p-Chlorobenzoyl-1-diazoethane. The following procedure represented the optimum conditions in this case, and was typical for the preparation of diazoketones from diazoethane. To 355 cc. of an ethereal solution containing 131 millimoles of diazoethane, cooled to −20° in a Dry-Ice-alcohol bath (see Table I) was added dropwise with mechanical stirring a solution of 11.0 g. (62 millimoles) of *p*-chlorobenzoyl chloride in 50 cc. of anhydrous ether. The addition required fifteen minutes and the solution was stirred at −20° for an additional fifteen minutes, after which the excess diazoethane was removed under reduced pressure, still keeping the solution at −20°. When the excess diazoethane was gone (as indicated by the lightening in color of the solution) the remainder of the solvent was removed at 0°. The residual diazoketone, which crystallized, was triturated with ice-cold petroleum ether, giving 7.87 g., m.p. 50–52.5°. Additional crops obtained by cooling, finally to −80°, amounted to 0.55 g., m.p. 50–52°, and 0.26 g., m.p. 49–51°, bringing the total to 71%. By recrystallization from petroleum ether yellow prisms, m.p. 56–57.5°, were obtained.

Anal. Calc'd for $C_9H_7ClN_2O$: N, 14.4; Found, N, 14.4.

The oily residue from the filtrate, dissolved in 7 cc. of benzyl alcohol and 8 cc. of dimethylaniline, was heated in an oil-bath at 170° for five minutes and worked up as described below. In addition to 0.28 g. (3%) of *p*-chlorobenzoic acid, m.p. 236–237°, 0.88 g. (8%) of α-(*p*-chlorophenyl)propionic acid was obtained, m.p. 52.5–55.5°, indicating the total amount of diazoketone to be at least 79%.

α-Bromo-p-chloropropiophenone. To a solution of 0.5 g. of the above diazoketone in ether was added 48% hydrobromic acid dropwise until the evolution of nitrogen ceased. From the ether layer by evaporation and crystallization of the residue from dilute alcohol was obtained 0.52 g. (82%) of the bromoketone as colorless plates, m.p. 77–79°; reported, 77.5° (21).

Alkaline cleavage of 1-p-chlorobenzoyl-1-diazoethane. To 1 g. of the diazoketone was added 5 cc. of 45% potassium hydroxide and 5 cc. of methanol. There was a distinct warming of the solution with evolution of nitrogen and formation of a black insoluble tar. When the solution was warmed further another gas with an ethereal odor was evolved (methyl ethyl ether?). After refluxing for four hours the diluted solution was extracted with ether to remove the non-acidic fraction. The alkaline solution was acidified, extracted with ether, evaporated and the residue was digested with hot petroleum ether (60–68°), giving 0.28 g. (35%) of *p*-chlorobenzoic acid, m.p. 235–237°. From the filtrate was obtained an additional 0.05 g., m.p. 180–200°.

1-p-Toluyl-1-diazoethane was prepared from 2.09 g. of *p*-toluyl chloride as described for the *p*-chloro derivative, allowing the reaction mixture to stand at −20° for one hour after addition was complete. The product, a yellow oil, was crystallized from petroleum ether by cooling with Dry-Ice-ether, giving 1.15 g. (49%) of the crystalline derivative, m.p. 51–52°. Recrystallization from petroleum ether gave yellow prisms, m.p. 52–53°.

Anal. Calc'd for $C_{10}H_{10}N_2O$: N, 16.1; Found; N, 15.9.

α-Bromo-p-methylpropiophenone was prepared from the above diazoketone by treating a dioxane solution with 48% hydrobromic acid and crystallizing the product from dilute alcohol; yield 65%, m.p. 70–75°. Recrystallization from petroleum ether raised the m.p. of the solid to 78–78.5°; reported, 76–77° (22).

1-(p-Nitrobenzoyl)-1-diazoethane was prepared from 10 g. of *p*-nitrobenzoyl chloride as described above for *p*-chloro derivative. The diazoketone crystallized from the reaction mixture, 7.49 g., m.p. 109–110° dec., and from the filtrate by concentration under reduced pressure was obtained an additional 0.76 g., m.p. 106.5–108° dec., and 0.22 g., m.p. 105–107° dec., for a total of 76%. Recrystallization from ether gave yellow needles, m.p. 109.5–110° dec.

Anal. Calc'd for $C_9H_7N_3O_3$: N, 20.5; Found: N, 20.8.

1-(2′-Naphthoyl)-1-diazoethane, prepared as above from 2.43 g. of 2-naphthoyl chloride, gave 1.37 g. of bright yellow needles, m.p. 109–110° dec., from the original reaction mixture and an additional 0.54 g., m.p. 98–104° dec., and 0.17 g., m.p. 85–95° dec., from the filtrate for a total yield of 78%. The melting point of the material in the first crop was not raised by further recrystallization from petroleum ether.

Anal. Calc'd for $C_{13}H_{10}N_2O$: C, 74.3; H, 4.8.
Found: C, 74.1; H, 4.8.

Other diazoketones from diazoethane. In a similar manner were prepared the diazoketones from diazoethane and acetyl chloride, benzoyl chloride, 1-naphthoyl chloride and β-(1-naphthalene)propionyl chloride. These diazoketones were obtained as yellow oils and were used in the rearrangement step without purification.

By-product from p-toluyl chloride and diazoethane. (a) Prepared from toluyl chloride. When a solution of 1.5 g. of *p*-toluyl chloride was added to excess diazoethane solution at 0° and allowed to stand at room temperature for sixteen hours before removing the ether, crystallization of the product from petroleum ether gave 0.45 g. (25%) of colorless needles, m.p. 78–80°.

(*b*) *From the diazoketone and diazoethane.* When 0.7 g. of 1-*p*-toluyl-1-diazoethane and a solution of 18 millimoles of diazoethane in 50 cc. of ether were allowed to stand at room temperature for two and one-half hours, crystallization of the residue gave 0.11 g. (14%) of the by-product as colorless needles, m.p. 78–80°. On further crystallization the m.p. of the sample was raised to 80.5–81°. The compound decomposed to an oil with evolution of gas upon standing at room temperature for fifteen to twenty hours. Unlike the diazoketone it did not evolve nitrogen when treated with hydrobromic or acetic acid.

Anal. Calc'd for $C_{12}H_{14}N_2O$: C, 71.3; H, 7.0; N, 13.9.
Found: C, 70.9, 71.0, 71.1; H, 6.8, 6.9, 6.9; N, 13.4.

By-product from p-chlorobenzoyl chloride and diazoethane. (a) Prepared from the acid chloride. From 1.5 g. of *p*-chlorobenzoyl chloride and diazoethane as described above for the *p*-toluyl derivative was obtained 0.52 g. (27%) of pale yellow needles, m.p. 86–86.5°.

(*b*) *From the diazoketone and diazoethane.* When 1 g. of 1-*p*-chlorobenzoyl-1-diazoethane and a solution of 18 millimoles of diazoethane in 50 cc. of ether were allowed to stand at room temperature for four hours, a total of 0.47 g. (41%) of the by-product could be crystallized from petroleum ether, m.p. 88.5–90°. Recrystallization of a sample from petroleum ether gave colorless needles, m.p. 90.5–91°, which decomposed to an oil upon standing at room temperature, but evolved no gas when treated with acid.

Anal. Calc'd for $C_{11}H_{11}ClN_2O$: C, 59.3; H, 5.0; N, 12.6.
Found: C, 59.0, 59.3, 59.6; H, 5.0, 4.9, 5.1; N, 12.4.

(*c*) *Action of diazomethane on 1-p-chlorobenzoyl-1-diazoethane.* When 1 g. of the diazoketone (m.p. 52–54°) was treated with ethereal diazomethane and allowed to stand at room temperature for twenty hours, 88% of the diazoketone was recovered, m.p. 51–54°, with an additional 10% of yellow oil which evolved nitrogen vigorously when treated with acid. This indicated no appreciable reaction between this diazoketone and diazomethane under these conditions.

1-p-Nitrobenzoyl-1-diazopropane.—To a solution of 20 millimoles of diazopropane in 230 cc. of ether at −20° was added with stirring 1.85 g. (10 millimoles) of *p*-nitrobenzoyl chloride in 30 cc. of dry ether over a fifteen-minute period. After an additional thirty minutes at −20° the solution was concentrated under reduced pressure to about 150 cc. and filtered, giving 1.39 g. of yellow needles, m.p. 97–98° dec. From the filtrate was obtained 0.39 g., m.p. 96.5–98° dec., and 0.07 g., m.p. 83–87° dec. The first two crops corresponded to a yield of 81%. The analytical sample crystallized from petroleum ether as yellow prisms, m.p. 97.5–98.5° dec. The compound dissolved in acetic acid with slow evolution of nitrogen.

Anal. Calc'd for $C_{10}H_9N_3O_3$: N, 19.2; Found: N, 18.9.

Other diazoketones from 1-diazopropane. In a similar manner were prepared the diazoketones from 1-diazopropane and acetyl chloride, *p*-chlorobenzoyl chloride, and *p*-anisoyl chloride. These derivatives, obtained as yellow oils, were used for rearrangement without purification.

Rearrangement of the diazoketones—general methods

The benzyl alcohol-tertiary amine method.—The benzyl alcohol used here was purified by shaking for one hour with saturated sodium bisulfite solution and allowing to stand overnight. The benzyl alcohol layer was then shaken with 45% potassium hydroxide, dried over potassium carbonate and distilled under reduced pressure, collecting the fraction b.p. 92–94° (12 mm.).

For the rearrangement reaction, the diazoketone (1.0 g.) was dissolved in a mixture of purified benzyl alcohol (about 5 cc.) and a high-boiling tertiary amine (about 5 cc.). The solution was heated rapidly to the desired temperature by immersing the flask (attached to reflux condenser) in a preheated oil-bath, usually at 170–190°. After an induction period of a few seconds a vigorous evolution of nitrogen occurred. The reaction was usually over in a few minutes at 170° or higher. After heating about five minutes, the solution was cooled, ether added, and the extract washed twice with dilute hydrochloric acid. Following removal of the ether the oily ester was hydrolyzed by heating with methanol (5 cc.) and 45% potassium hydroxide (5 cc.) for two to four hours. (In the case of the nitro compounds the hydrolysis was effected by heating with 10 cc. of hydrochloric and 10 cc. of acetic acids for eighteen to twenty-four hours.) The methanol was then evaporated and the alkaline solution extracted twice with ether before acidifying. Ether extraction gave the crude acid which was purified by recrystallization or evaporative distillation.

With large runs it was advantageous to add the solid diazoketone in portions to the hot alcohol-amine mixture, since in this way the rate of evolution of gas could be controlled.

Aniline method. A solution of the diazoketone (1.0 g.) in freshly distilled aniline (5 cc.) was immersed in an oil-bath preheated to 180°. After the vigorous reaction was over, the mixture was poured onto ice and concentrated hydrochloric acid, and the anilide was purified by recrystallization.

Silver oxide-methanol method. This procedure was essentially as described in *Organic Reactions* (2).

Rearrangement of diazoketones related to diazomethane

The results are summarized in Table VIII. For the four runs in which the silver oxide-methanol and benzyl alcohol-γ-collidine methods are compared, the same sample of diazoketone was used for each method.

Rearrangement of diazoketones related to diazoethane

Using 1-p-chlorophenyl-1-diazoethane. For the alcohol-tertiary amine method the results using different alcohols are given in Table II, with different amines in Table III and varying the temperature in Table IV. For each of these runs the standard procedure with 1 g. of diazoketone was followed except for the variation noted in the Tables. The crude acidic product was digested with 10–12 cc. of hot petroleum ether (60–68°), allowed to stand at room temperature and filtered to remove *p*-chlorobenzoic acid. The acid in the filtrate was evaporatively distilled at 100–120° (0.1 mm.) giving crystalline α-*p*-chlorophenylpropionic acid in the yield reported. The analytical sample crystallized from petroleum ether as colorless crystals, m.p. 57–58°.

TABLE VIII

REARRANGEMENT OF DIAZOKETONES RELATED TO DIAZOMETHANE

DIAZOKETONE $RCOCHN_2$ RCO =	WEIGHT G.	METHOD OF REARRANGEMENT	PRODUCT ISOLATED (RCH_2COOH ETC.)	% YIELD	M.P. °C.	M.P. REPORTED (REF.) °C
Benzoyl	[a]	Silver oxide-ethanol	Acid	40	76–77	76–77
p-Nitrobenzoyl	[b]	Silver oxide-methanol	Methyl ester	62	50.5–51	54 (24)
p-Chlorobenzoyl	1	Silver oxide-methanol	Acid	64	100–103[c]	105–106 (25)
"	1	Benzyl alcohol-γ-collidine	Acid	68	104–105	105–106 (25)
p-Toluyl	1	Silver oxide-methanol	Unsuccessful	0	—	94 (26)
"	1	Benzyl alcohol-γ-collidine	Acid	79	87–91.5	94 (26)
p-Anisyl	1	Silver oxide-methanol	Unsuccessful	0	—	85–87 (20)
"	1	Benzyl alcohol-γ collidine	Acid	69–76[d]	80–84	85–87 (20)
1-Naphthoyl	1	Silver oxide methanol	Acid	67	131–133	131.5 (27)
"	1	Benzyl alcohol-γ-collidine	Acid	74	130–133	131.5 (27)

[a] From 10 g. of benzoyl chloride; crude diazoketone, m.p. 44–46°.

[b] From 5 g. of *p*-nitrobenzoyl chloride.

[c] About one-third of product m.p. 93–102°.

[d] The higher yield was obtained when the solid diazoketone was added to the hot alcohol-amine mixture.

A larger run, carried out by adding 9 g. of the solid diazoketone to a hot (150–180°) mixture of 28 g. of γ-collidine and 25 g. of benzyl alcohol gave an 83% yield of the rearranged acid, m.p. 47–55°.

Another run in which the diazoketone from 3.25 g. of *p*-chlorobenzoyl chloride was not isolated but the entire product rearranged gave 0.21 g. (7%) of *p*-chlorobenzoic acid, m.p. 236–238°, and 2.08 g. (61%) of α-*p*-chlorophenylpropionic acid, m.p. 50–55°.

Using 1-p-nitrobenzyl-1-diazoethane. In one run, starting with 2.4 g. of the diazoketone

TABLE IX

Rearrangement of Diazoketones Related to Diazoethane

(Using benzyl alcohol-tertiary amine method except where noted)

DIAZOKETONE $RCO\overset{CH_3}{\overset{\vert}{C}}N_2$ RCO =	WEIGHT G.	TERTIARY AMINE	TEMP. °C	PRODUCT ISOLATED $R\overset{CH_3}{\overset{\vert}{C}}HCOOH$	YIELD %[a]	M.P. °C	M.P. °C REPORTED (REF)	ANAL. FOUND	
								C	H
Benzoyl	[b]	Aniline[c]	190	Anilide	55[d]	131 -132	—	80.0[e]	7.0[e]
p-Chlorobenzoyl	1	γ-Collidine (see Table III)	170	Acid	85–90	57 -58	—	58.6[f]	4.8[f]
"	0.5	Aniline[c]	165	Anilide	78	154.5–155	—	69.4[g]	5.6[g]
p-Toluyl	[h]	γ-Collidine	190	Acid	70[d]	not completely pure	34 -35 (28)	—	—
"	0.7	Aniline[c]	170	Anilide	79	132.5–133	—	80.3[i]	7.1[i]
p-Nitrobenzoyl	1	γ-Collidine	160	Acid	66	88 -89	87 -88 (29)	—	—
"	1	Aniline[c]	165	Anilide	60	159 -159.2	—	66.4[j]	5.4[j]
1-Naphthoyl	[k]	γ-Collidine	180	Acid	58[d]	146 -148[l]	148 -149 (30)	—	—
"	[m]	Aniline[c]	150	Anilide	38[d]	150 -154[l]	154.5–155.5[q]	—	—
2-Naphthoyl	[n]	γ-Collidine	190	Acid	48[d]	129.5–130	—	78.1[r]	5.8[r]
β-1-Naphthylpropionyl	[o]	γ-Collidine	190	Acid	47[d]	83 -83.5[l]	83 -84 (31)	—	—
Acetyl	[p]	Aniline[c]	165	Anilide	44[d]	104 -105[l]	104.5–105.5[q]	—	—

[a] The yield is for material melting within a few degrees of the purest samples unless otherwise noted.

[b] Using the oily diazoketone from 2.06 g. of benzoyl chloride.

[c] No benzyl alcohol used here.

[d] Over-all yield from acid chloride (or acid in some cases).

[e] Calc'd for $C_{15}H_{15}NO$: C, 80.0; H, 6.7.

[f] Calc'd for $C_9H_9ClO_2$: C, 58.5; H, 4.9.

[g] Calc'd for $C_{15}H_{14}ClNO$: C, 69.4; H, 5.4.

[h] Using the entire diazoketone from 2.23 g. of *p*-toluyl chloride.

[i] Calc'd for $C_{16}H_{17}NO$: C, 80.3; H, 7.1.

[j] Calc'd for $C_{15}H_{14}N_2O_3$: C, 66.7; H, 5.2.

[k] Using the oil diazoketone from 4.25 g. of 1-naphthoyl chloride.

[l] Mixed m.p. with an authentic sample undepressed.

[m] Using oily diazoketone from 2.5 g. of 1-naphthoyl chloride.

[n] Using the entire diazoketone from 2.52 g. of 2-naphthoic acid through the acid chloride.

[o] Using the oily diazoketone from 2.82 g. of β-1-naphthylpropionic acid through the acid chloride.

[p] Using the oily diazoketone from 1.38 g. of acetyl chloride.

[q] Pure sample prepared from the acid.

[r] Calc'd for $C_{13}H_{12}O_2$: C, 78.0; H, 6.0.

and heating with 1.2 g. of benzyl alcohol and 6 g. of γ-collidine at 180° for three minutes, the intermediate benzyl ester was isolated by washing the ether extract of the reaction mixture with dilute acid and water, and then distilling. The fraction, b.p. 173–179° (0.1 mm.) was redistilled at 140–150° (0.05 mm.) to give 1.87 g. (59%) of *benzyl α-(p-nitrophenyl)propionate.*

Anal. Calc'd for $C_{16}H_{15}NO_4$: C, 67.4; H, 5.3.
Found: C, 67.4; H, 5.3.

Hydrolysis of a sample of the ester by heating with hydrochloric and acetic acids for eighteen hours, gave the acid, m.p. 86–87.5°.

With other diazoketones. The results are summarized in Table IX.

The following derivatives were prepared for comparison starting with acid chloride from authentic α-(1-naphthyl)propionic acid (30):[4]

Amide, colorless needles from dioxane-water, m.p. 127–128°.

Anal. Calc'd for $C_{13}H_{13}NO$: C, 78.4; H, 6.6.
Found: C, 78.2; H, 6.5.

TABLE X

REARRANGEMENT OF DIAZOKETONES RELATED TO 1-DIAZOPROPANE

DIAZOKETONE $RCO\overset{C_2H_5}{\overset{\vert}{C}}N_2$ RCO =	WEIGHT	TERTIARY AMINE	TEMP. °C	PRODUCT ISOLATED $R\overset{C_2H_5}{\overset{\vert}{C}}HCOOH$	YIELD %	M.P. °C	M.P. °C REPORTED (REF.)
Acetyl	[a]	Aniline[b]	170	Anilide	25[c]	109.5–110.5	110–111 (32)
p-Chlorobenzoyl	[d]	γ-Collidine	200	Acid	58[c]	crude 76–81 pure 81.5–82.5	
p-Nitrobenzoyl	1 g	γ-Collidine	165	Acid	56	crude 112–118 pure 120–121.5[g]	121–122.5 (33)
p-Anisoyl	[f]	γ-Collidine	165	Acid	37[c]	crude 52–58 pure 62–63.5[g]	66–67 (33)

[a] Using the oily diazoketone from 2.6 g. of acetyl chloride.

[b] No benzyl alcohol used here.

[c] Over-all yield from acid chloride.

[d] Using oily diazoketone from 1.86 g. of *p*-chlorobenzoyl chloride.

[e] *Anal.* Calc'd for $C_{10}H_{11}ClO_2$: C, 60.4; H, 5.6. Found: C, 60.6; H, 5.8.

[f] Using oily diazoketone from 5.53 g. of anisoyl chloride.

[g] Mixed m.p. with an authentic sample undepressed.

Anilide, colorless needles from 80% alcohol, m.p. 154.5–155.5°.

Anal. Calc'd for $C_{19}H_{17}NO$: C, 82.9; H, 6.2.
Found: C, 82.7; H, 6.1.

Attempts to use the silver oxide-methanol method. In eleven attempts to use this method with the oily diazoketone from 1-naphthoyl chloride and diazoethane, the reaction was successful in two trials, giving 26% and 34%, respectively, but in nine other attempts it was unsuccessful, probably because the diazoketone did not undergo rearrangement. In these cases large amounts of neutral tar and in several runs some 1-naphthoic acid were obtained. In one run a small amount (10%) of the amide of the rearranged product was prepared using silver nitrate and ammonium hydroxide in dioxane solution.

The silver oxide-methanol rearrangement was also unsuccessful using the crystalline

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[4] This acid was synthesized by Richard S. Schiefelbein (B.S. Thesis, University of Wisconsin, 1943) by a method similar to that published subsequently by Blicke and Feldcamp (30).

1-*p*-chlorobenzoyl-1-diazoethane (32% of *p*-chlorobenzoic acid obtained after alkaline hydrolysis), with 1-*p*-toluyl-1-diazoethane (42% of *p*-toluic acid obtained), 1-*p*-nitrophenyl-1-diazoethane, 1-(2′-naphthoyl)-1-diazoethane and the oily 1-(β-1′-naphthyl-1-propionyl)-1-diazoethane.

Rearrangement of diazoketones related to 1-diazopropane

These reactions, carried out with benzyl alcohol and γ-collidine by the standard procedure, are summarized in Table X. There is some indication that the *n*-propylamine used to prepare the 1-diazopropane was not entirely pure, which may account in part for the lower yields and less pure products in this series.

SUMMARY

1. Procedures have been developed which make it possible to use the Arndt-Eistert reaction with higher diazohydrocarbons.

2. The reaction has been employed with diazoethane and 1-diazopropane to prepare α-methyl and α-ethyl homologs, respectively, of the starting acid.

3. An improved method for effecting rearrangement of the diazoketones was developed, involving heating at 180–190° with benzyl alcohol and a tertiary amine.

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