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# APPLICATION OF THE DARZENS-CLAISEN REACTION TO A β-DIALKYLAMINO KETONE[1]

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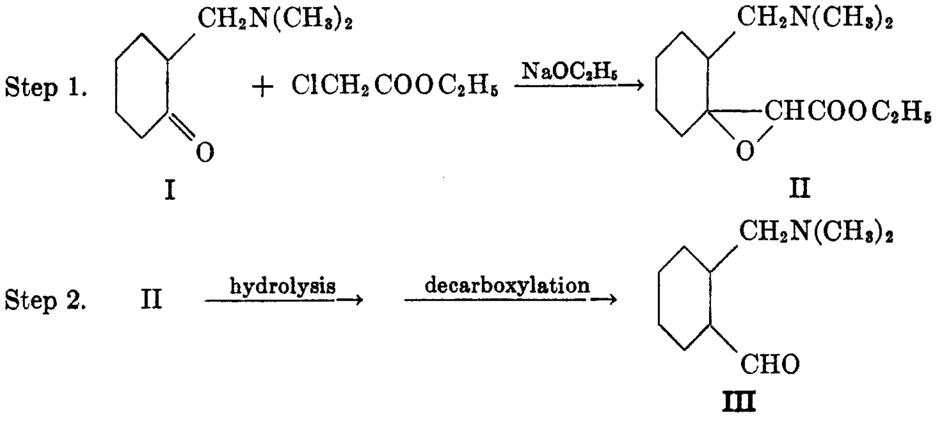
Several years ago a convenient synthesis of 1,3-disubstituted γ-piperidones was developed in these Laboratories (1). The present research was prompted by an interest in methods which might be employed to convert such a piperidone into homomeroquinene.[2] Provided the processes discovered independently by Darzens (4) and by Claisen (5) could be applied to ketones of the γ-piperidone type,[3] one might attach a formyl group to the ketonic carbon of the piperidone and proceed by conventional methods to homomeroquinene or a suitable derivative [*cf.* (2)].

Model β-dialkylamino ketones which could be used in exploring the applicability of the Darzens-Claisen method to our problem are readily provided by the well-known Mannich reaction; the simplest ketone of this type, derived from acetone by the action of dimethylamine and formaldehyde, was abandoned in favor of 2-dimethylaminomethylcyclohexanone (I), similarly derived from cyclohexanone, but in much better yield.

The two steps of the Darzens-Claisen process are illustrated below as applied to the model (I).



Yields of 43–57% of the desired basic glycidic ester (II) were obtained following the simple directions originally published by Darzens (4). The product of

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[1] The contents of this paper were presented before the Pacific Division of the American Association for the Advancement of Science at the Reno, Nevada meeting, June 19, 1946.

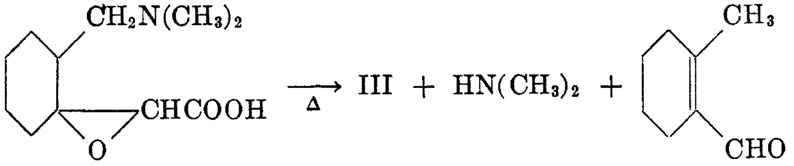
[2] Work on this important intermediate in the synthesis of quinine (2, 3) was interrupted by other investigations of synthetic antimalarial drugs suggested by the Committee on Medical Research; the Woodward-Doering synthesis (3) having appeared in the mean time, we are terminating our work on this problem with this communication.

[3] Clemo and co-workers (6) used this method to obtain a glycidic ester from a basic ketone, but were unable to prepare the desired aldehyde from the ester.

the condensation (step 1) was a mixture of two diastereoisomeric esters (II)[4] which were separated by fractional recrystallization of their dilituric-acid salts.

Refluxing the esters (II) for thirty minutes with concentrated hydrochloric acid gave the desired basic aldehyde (III) in 15% yield; and since it was shown that both the pure isomeric esters (regenerated from the diliturates) gave the same aldehyde[5], the crude mixture served as well for its preparation.

Small amounts of III were also obtained by thermal decomposition of the basic glycidic acids (IV) obtained from II by saponification with barium hydroxide, but the principal products of this reaction were identified as dimethylamine and a non-basic aldehyde tentatively formulated as 2-methyl-3,4,5,6-tetrahydrobenzaldehyde (V);[6] the deep scarlet color of the 2,4-dinitrophenylhydrazone of this aldehyde is in agreement with its postulated conjugated configuration.[7]



IV V

The basic aldehyde (III) is apparently stable when stored under nitrogen, but on exposure to air a crystalline compound is rapidly formed, the properties and composition of which are compatible with those expected of *o*-dimethylaminomethylhexahydrobenzoic acid.

The author wishes to thank Dr. Edwin R. Buchman for suggesting this problem and for guidance throughout its execution.

## EXPERIMENTAL[8]

*2-Dimethylaminomethylcyclohexanone* (*I*) was prepared by the method of Mannich and Braun (10) in yields which seemed to depend on the size of the run; a one-mole experiment gave 71%, three-mole 64.3%, and 6.13-mole 55.2% of colorless, mobile oil boiling at 96–97° at 11.5 mm. [Dimroth, Resin, and Zetzsch (11) give b.p. 93–94° at this pressure]. Contrary to statements of Mannich and Braun, we did not find I to be unusually unstable; redistillation of a sample which had stood at room temperature for almost three years gave a 75% recovery of the basic ketone.

The hydrochloride of I, recrystallized once from ethyl acetate and again from isopropyl

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[4] Four diastereoisomers are theoretically possible; Miescher and Kägi (7) were able to isolate derivatives of four different glycidic acids derived by a somewhat similar process from an asymmetrically-substituted, *non-basic* cyclopentanone (dehydroandrosterone).

[5] This fact must not be taken to indicate that the cis-trans configurations of the cyclohexane-substituent C—C bonds in the two esters are the same, since the degradation (step 2) in aqueous acid probably involves the intermediate formation of the enolic modification of the aldehyde, tautomerism yielding the more stable (probably trans) aldehyde.

[6] Without any proof of structure, Wallach (8) assigned this configuration to an aldehyde prepared by an ambiguous method.

[7] See generalization formulated in these Laboratories by Dr. C. E. Redemann, cited by Buchman *et al.* (9).

[8] All melting points are corrected; microanalyses by Dr. G. Oppenheimer and her staff of this Institute and by the Huffman Microanalytical Laboratories, Denver, Colorado.

ether-ethanol, formed small, glistening, white flakes melting at 139.9–140.6° when heated slowly; the melting point was somewhat higher (145.5°) when the bath temperature was raised more rapidly (Mannich and Braun give m.p. 152°).

*Anal.* Calc'd for $C_9H_{18}ClNO$: C, 56.39; H, 9.46; N, 7.31.
Found: C, 56.69; H, 9.25; N, 7.25.

Mannich and Braun claim to have been unable to prepare the methiodide of I because of its instability; Dimroth and his co-workers prepared the salt in ether solution under nitrogen and reported it stable in the pure crystalline form, m.p. 136–137°, followed by resolidification and decomposition from 200°. We prepared the salt using no special precautions and obtained a product forming, from ethanol, clusters of colorless pyramids in square patterns, m.p. 152–153°, resolidifying at about 160°.

*Anal.* Calc'd for $C_{10}H_{20}INO$: C, 40.41; H, 6.78; N, 4.71.
Found: C, 40.78; H, 6.83; N, 4.80.

Prepared by adding isopropyl-ethereal picric acid to a solution of I in the same solvent, the picrate formed minute yellow needles from isopropyl ether-ethanol, m.p. 147.0–147.2° (Mannich and Braun give m.p. 149°).

Attempts to apply the Reformatsky reaction (with zinc and methyl bromoacetate) to I were apparently complicated by quaternary salt formation, giving only traces of starting material and negligible amounts of higher-boiling basic substances.

*Dimethylaminomethylacetone* was obtained in yields of 3.6 to 13% following the directions of Mannich (12); careful fractional distillation was required to purify the base, b.p. 50–51° at 13 mm., in agreement with Mannich. A small sample of this material subjected to the Darzens-Claisen condensation (see details below) gave 6.1% of the starting material and 4.7% of a pale yellow, viscous oil boiling at 78–91° at 3 mm. An attempt to condense this ketone with ethyl dichloroacetate in the presence of a magnesium amalgam [*cf.* (13)] gave a negligible yield of high-boiling material.

*2-Carbethoxy-4-dimethylaminomethyl-1-oxaspiro[2.5]octane [cf. (14)] (II).* A mixture of 77.6 g. (0.5 mole) of I and 61.25 g. (0.5 mole) of ethyl chloroacetate was cooled in a three-necked 500-cc. flask equipped with a mercury-sealed Hershberg stirrer, a water-cooled Allihn condenser protected by a calcium chloride tube and containing a thermometer dipping into the mixture, and a small conical flask attached to the third neck by a piece of large-bore rubber tubing and containing 34.0 g. (0.5 mole) of freshly-prepared, dry, alcohol-free sodium ethoxide (15). The ethoxide was slowly added at such a rate that the temperature of the mixture did not exceed 20°, requiring about thirty minutes.[9] After stirring overnight at room temperature the light brown paste was heated in a boiling-water bath for three hours, during which it first thickened, then became more mobile and somewhat lighter in color. This paste was cooled in ice, dissolved in 160 cc. of cold 6 *N* hydrochloric acid, washed with ether, carefully basified with potassium hydroxide, and the liberated red-brown oil extracted with two 200-cc. portions of ether; dried over sodium sulfate and stripped of ether, the product was distilled at 0.025 mm. (gauge pressure), yielding 64.4 g. (53.3%) of light yellow oil, b.p. 101–110°. A one-mole run in which the temperature of the mixture was kept under 0° during the addition of the ethoxide gave a 53.8% yield of II, b.p. 110–115° at 1 mm. Other experiments gave yields ranging from 43.5 to 57.5%. For analysis, a sample of II was redistilled at 3 mm., b.p. 127–129°.

*Anal.* Calc'd for $C_{13}H_{23}NO_3$: C, 64.70; H, 9.61; N, 5.81.
Found: C, 64.45; H, 9.60; N, 6.03.

*Separation of isomeric esters (II) with dilituric acid.* One-tenth mole (24.1 g.) of the above ester mixture was dissolved in 300 cc. of absolute ethanol and 22.7 g. (0.1 mole) of dilituric acid trihydrate was added; the mixture was brought to a boil and water added

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[9] As an orienting experiment, these same conditions were applied to cyclohexanone itself (16), giving a 76% yield of 2-carbethoxy-1-oxaspiro[2.5]octane [*cf.* (14)], b.p. 106–112° at 6 mm. [lit. (16), b.p. 128–129° at 17 mm.]; this was saponified with aqueous potassium hydroxide to give the corresponding acid (yield 90%), clusters of short, colorless needles from water, m.p. 125.0–125.7°, analysis for $C_8H_{12}O_3$.

dropwise as long as solid continued to dissolve; a trace of difficultly-soluble white solid was then filtered off. On cooling, 24.7 g. of the α-form of II diliturate crystallized out as small, compact clusters of light yellow plates; this crop was filtered off, washed with ethanol and isopropyl ether, and air-dried. After standing for about a week, the mother liquors deposited 7.1 g. more of the same material. Spontaneous evaporation of a small portion of the first-crop mother liquors gave seed crystals of the β-diliturate, which were added to the mother liquors from the second crop of the α-diliturate, yielding 3.8 g. of the β-form, compact white needle clusters. Evaporation of the filtrate from this crop to dryness left 13.3 g. of material whose melting point could not be raised above 133-134° by repeated recrystallization from ethyl acetate-ethanol, but which gave on regeneration a poor yield of β-II, identified by the methiodide and diliturate (see below).

The α-II diliturate, recrystallized from ethanol-water, melted at 188.6-188.8° dec. After several recrystallizations from ethanol, the β-II diliturate formed clusters of colorless needles with a greenish tinge, m.p. 177.2-178.0° dec.

*Anal.* Calc'd for $C_{17}H_{26}N_4O_8$: C, 49.27; H, 6.33; N, 13.52.
Found (α-form): C, 49.60; H, 6.25; N, 13.32.
(β-form): C, 49.63; H, 6.46; N, 12.76.

*Characterization of pure α-II.* A suspension of 10.4 g. of finely-powdered α-II diliturate in 50 cc. of water was warmed just sufficiently to dissolve the salt, cooled in ice, and treated with 7.51 g. (one equivalent) of freshly-distilled anhydrous ethylenediamine [see (17)]; the diamine diliturate was centrifuged down and the crude ester (α-II) (more dense than the aqueous solution) extracted with ether, dried over potassium carbonate, and distilled; yield 3.54 g. (60%) of colorless, very viscous oil, b.p. 95-98° at 1 mm. An aqueous solution of α-II diliturate basified with 4 *N* sodium hydroxide and extracted with ligroin gave 75.5% of α-II, undistilled. A portion of the distilled product was analyzed.

*Anal.* Calc'd for $C_{13}H_{23}NO_3$: C, 64.70; H, 9.61; N, 5.81.
Found: C, 64.61; H, 9.68; N, 5.58.

The basic glycidic acid (α-IV) was obtained by boiling 1.21 g. of pure α-II with 50 cc. of saturated aqueous barium hydroxide for fifteen minutes, a clear solution resulting in five. Careful precipitation of the barium with 6 *N* sulfuric acid followed by evaporation to dryness gave 1.00 g. of colorless solid which, after washing with acetone, melted at 188-190° dec. One recrystallization from acetonitrile-methanol gave very tiny colorless granules, m.p. 202-203° dec.

*Anal.* Calc'd for $C_{11}H_{19}NO_3$: C, 61.94; H, 8.98; N, 6.57.
Found: C, 61.83; H, 8.71; N, 6.42.

Addition of one equivalent of methyl iodide to the ester (α-II) or a concentrated ethanolic solution of it gave the α-II methiodide, which crystallized in either of two forms of different melting point. One form emerged from ethanol in massive clusters of colorless prisms with pyramidic terminations or as diamond-shaped plates thickening into rhomboid figures, m.p. 186.9-187.3°. The other, also recrystallized from ethanol, formed colorless, irregularly-faced, acute pyramids melting at 217.3-218.1°; from ethyl acetate-ethanol, feathered pyramids of m.p. 220.1-220.4° were noted. The form obtained in the absence of seed crystals seemed to be a matter of chance; a warm ethanolic solution of the lower-melting seeded with the higher-melting form gave the latter on cooling.

*Anal.* Calc'd for $C_{14}H_{26}INO_3$: C, 43.87; H, 6.84; N, 3.65.
Found (187°): C, 44.09; H, 6.87; N, 3.17.
(218°): C, 44.26; H, 6.71; N, 3.56.

Prepared in the same way, the ethiodide of α-II crystallized from ethyl acetate-ethanol in beautiful clusters of colorless, stubby needles, m.p. 187.6-188.0°. A mixture of this salt with the lower-melting methiodide (above) had m.p. 186-195°.

*Anal.* Calc'd for $C_{15}H_{28}INO_3$: C, 45.34; H, 7.10; N, 3.53.
Found: C, 45.47; H, 7.52; N, 3.35.

Treatment of α-II with isopropyl-ethereal oxalic acid gave a colorless oil which solidified on standing; after four recrystallizations from isopropyl ether-ethanol, the white rosettes so formed melted at 140.9-141.7° and analyzed as the acid oxalate.

*Anal.* Calc'd for $C_{13}H_{23}NO_3 \cdot C_2H_2O_4$: C, 54.36; H, 7.60; N, 4.23.
Found: C, 54.15; H, 7.60; N, 4.46.

Addition of isopropyl-ethereal solutions of picric and 3,5-dinitrobenzoic acids to α-II gave oily precipitates.

*Characterization of pure β-II.* By the ethylenediamine method detailed above, 3.8 g. of the crude β-II diliturate yielded 1.01 g. (48%) of pure β-II, very viscous, colorless oil, b.p. 93–94° at 1 mm. Liberation of the free base with aqueous sodium hydroxide gave a yield of 43%, undistilled.

*Anal.* Calc'd for $C_{13}H_{23}NO_3$: C, 64.70; H, 9.61; N, 5.81.
Found: C, 64.88; H, 9.62; N, 5.63.

By the method described above, the acid (β-IV) was obtained in quantitative yield, crude m.p. 196° dec.

β-II methiodide formed clumps of colorless granules from ethanol, m.p. 173.4–173.6°.

*Anal.* Calc'd for $C_{14}H_{26}INO_3$: C, 43.87; H, 6.84; N, 3.65.
Found: C, 43.37; H, 7.21; N, 3.53.

Recrystallized from isopropyl ether- or ethyl acetate-ethanol, the ethiodide of β-II formed clusters of fine colorless needles or blades with a micaceous luster, m.p. 134.9–135.3°.

*Anal.* Calc'd for $C_{15}H_{28}INO_3$: C, 45.34; H, 7.10; N, 3.53.
Found: C, 45.37; H, 6.97; N, 3.13.

The picrate of β-II was obtained as a red oil which could not be induced to crystallize.

*o-Dimethylaminomethylhexahydrobenzaldehyde (III).* One-eighth mole (30.2 g.) of the ester mixture (II) was treated with 104 cc. of 12 *N* hydrochloric acid and refluxed for one-half hour, giving a deep wine-red, slightly cloudy solution and a small amount of dark green oil. After cooling in ice, the solution was basified by the slow addition of 30% aqueous potassium hydroxide, the solution turning yellow at about the neutral point. The product was extracted with isopropyl ether (freshly-distilled), dried over potassium carbonate, and distilled at 1 mm., yielding 3.20 g. (15.2%) of colorless liquid boiling at 61.6–62.3°; about an equal amount of brown oil remained in the boiler. The aldehyde (III) had a characteristic terpene-like odor, was insoluble in water, and was fairly stable when not exposed to the air (see below).

*Anal.* Calc'd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31; N, 8.28.
Found: C, 71.11; H, 11.30; N, 8.32.

Small amounts (2.2 and 1.1 g., respectively) of the pure esters (α- and β-II) subjected to this same procedure gave the same aldehyde (III), identified in the case of the α-ester as the picrate, in that of the β-ester as the air-oxidation acid; these derivatives are described below.

Hydrolysis of another one-eighth mole of the mixed esters (II) with 500 cc. of 1.68 molar sulfuric acid, refluxing overnight, gave 0.79 g. (3.7%) of III.

On cooling a solution of the picrate of III in hot ethanol-acetonitrile, the salt emerged as dendritic, bright yellow needle-clusters which slowly changed into larger, darker yellow blades; both forms had the same melting point (168.6–169.4°), which was not depressed by admixture.

*Anal.* Calc'd for $C_{16}H_{22}N_4O_8$: C, 48.23; H, 5.57; N, 14.06.
Found: C, 48.30; H, 5.82; N, 13.68.

The methiodide of III, prepared in ethanol and recrystallized from ethyl acetate-acetonitrile, formed irregular clusters of colorless bars, m.p. 213.8–214.0°; this melting point was somewhat higher when the heating was rapid.

*Anal.* Calc'd for $C_{11}H_{22}INO$: C, 42.45; H, 7.13; N, 4.50.
Found: C, 42.58; H, 7.07; N, 4.27.

An attempt to prepare the 2,4-dinitrophenylhydrazone of III by the usual method (18) gave instead the hydrochloride of the desired derivative, clusters of light or orange-yellow needles from acetonitrile, m.p. 221.5–221.8° dec.

*Anal.* Calc'd for $C_{16}H_{24}ClN_5O_4$: C, 49.81; H, 6.27; N, 18.16.
Found: C, 50.36; H, 6.50; N, 18.44.

Basifying an aqueous solution of this salt with aqueous sodium hydroxide gave the free

2,4-dinitrophenylhydrazone, also recrystallized from acetonitrile, beautiful clusters of light orange rods, m.p. 146.9–147.4°.

*Anal.* Calc'd for $C_{16}H_{23}N_5O_4$: C, 55.00; H, 6.63.
Found: C, 55.28; H, 6.36.

Attempts to prepare the semicarbazone of III were unsuccessful.

*Exposure of III to air* resulted in the rapid deposition of colorless bobbin-clusters, apparently *o*-dimethylaminomethylhexahydrobenzoic acid; washed with ligroin or isopropyl ether and recrystallized from ethyl acetate-ethanol, this compound melted at 154–155°; it was readily soluble in water, giving a weakly basic solution (*p*H about 8).

*Anal.* Calc'd for $C_{10}H_{19}NO_2$: C, 64.83; H, 10.34; N, 7.56.
Found: C, 64.24; H, 10.37; N, 7.60.

When this acid was stirred with an ethereal solution of diazomethane at 0°, the acid slowly dissolved, nitrogen was evolved, and a white flakey solid separated from the solution. Evaporation of the ether and excess diazomethane left a colorless oil. This was treated with isopropyl-ethereal picric acid, giving a red oil which solidified on standing and scratching; recrystallized from isopropyl ether-ethyl acetate, the picrate of the methyl ester formed rugged orange bipyramids, m.p. 114–115° after some softening from 112°.

*Anal.* Calc'd for $C_{17}H_{24}N_4O_9$: C, 47.66; H, 5.65; N, 13.08.
Found: C, 47.80; H, 5.69; N, 13.04.

*Thermal decomposition of the basic glycidic acids (IV)*, derived as described above from the mixed esters (II), was accomplished by heating to 200° in a vessel evacuated to 1 mm.; a vigorous evolution of gases ensued, leaving a frothy, tan solid which was extracted with isopropyl ether and treated with picric acid in the same solvent; the picrate thus obtained was identified as that of III by m.p. and mixed m.p.

In a similar experiment with an 0.83-g. sample of α-IV, about 0.4 cc. of a light yellow-green liquid was trapped out with dry ice; redistillation of this material gave 0.2 cc. of colorless oil, b.p. *ca.* 80° (bath temperature) at 4 mm. This oil gave a 2,4-dinitrophenylhydrazone, deep scarlet needles from acetonitrile, m.p. 192.4–192.7°, analyzing as that of 2-methyl-3,4,5,6-tetrahydrobenzaldehyde (V).

*Anal.* Calc'd for $C_{14}H_{16}N_4O_4$: C, 55.26; H, 5.30; N, 18.41.
Found: C, 55.45; H, 5.13; N, 18.88.

Another portion of this redistilled product derived from α-IV gave a picrate, yellow needles from isopropyl ether-ethanol, m.p. 147.8–148.1°, in amount too small for analysis.

The crude product trapped out in another thermal decomposition of a sample of α-IV was treated directly with isopropyl-ethereal picric acid; the crude picrate was recrystallized from isopropyl ether-ethanol, giving a mixture of yellow needles and red blades which were separated mechanically. The yellow needles crystallized in clusters from ethanol, m.p. 193.4–193.9° to a black liquid, found: C, 49.49, 49.71; H, 5.07, 5.37; N, 15.80, 15.66. The red blades formed orange lattices from ethanol, m.p. 159.9° after some sintering from 155°, unaffected by admixture with an authentic sample of dimethylamine picrate [Jerusalem (19) gives m.p. 158–159°].

*Anal.* Calc'd for $C_8H_{10}N_4O_7$: C, 35.04; H, 3.68; N, 20.43.
Found: C, 35.30; H, 3.73; N, 20.21.

A 0.47-g. sample of β-IV thermally decomposed in the same way gave, on redistillation of the trapped-out material, 0.07 g. of a colorless oil having a strong terpene-like odor and boiling at 66–76° at 10 mm.; the picrate prepared from this oil could not be induced to crystallize, but the 2,4-dinitrophenylhydrazone formed deep scarlet needles or bars from acetonitrile, m.p. and mixed m.p. identical with that of the derivative similarly obtained from α-IV (see above), presumably of V.

## SUMMARY

The Darzens-Claisen reaction has been applied successfully to the conversion of a typical β-dialkylamino ketone into a mixture of two basic glycidic esters;

these have been separated as their diliturates and degraded to the same basic aldehyde.

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