XLIV.—*Condensation of Ketones with Phenols. Part I.*
*Condensation with α -Naphthol.**

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THE condensation of ketones with phenols has already been investigated in some cases (Wittenberg, *J. pr. Chem.*, 1882, [ii], **26**, 76; Dianin, *J. Russ. Phys. Chem. Soc.*, 1891, **23**, 488; Fabinyi and Széki, *Ber.*, 1905, **38**, 2307; Zincke and Gaebel, *Annalen*, 1912, **388**, 299), but no special study appears to have been made with reference to the influence exerted by substituents in the phenols on this type of condensation; further, the position of the linking of the carbonyl carbon with the phenols, particularly naphthols, has not yet been ascertained. The idea of elucidating the latter point led to the present investigation, and it was hoped that by

* For abstract, see P., 1913, **29**, 29.

oxidising the condensation products obtained from ketones and α -naphthol

naphthaxanthenes of known constitution could be prepared, which would, therefore, settle the question in view. Instead, however, of yielding a naphthaxanthone, the oxidation of the anhydrides of 1:1-dihydroxydinaphthylalkylmethanes gave rise to two series of coloured, crystalline substances (P., 1913, **29**, 382). The work directly bearing on the constitution of these being still in progress, and as final conclusions must depend on cumulative evidence based on a large number of experiments, it is proposed to describe in the following pages some new condensation products of α -naphthol with ketones that have come to be studied in this connexion.

The only case of condensation of α -naphthol with a ketone that has hitherto been described, is that with acetone. Dianin (*loc cit.*) employed fuming hydrochloric acid (D 1.19) as the condensing agent, but in course of the present investigation it has been found that phosphoryl chloride serves the purpose decidedly better. The yield is substantially improved, whilst the duration of the experiment is very much shortened, and the reaction can be conducted in an open vessel. The condensation products are obtained in the form of anhydrides, having the general formula

except in the case of *cyclohexanone*, which, in addition to the usual type of compound, yields one having probably the constitution *:

(compare Zincke and Gaebel, *loc. cit.*, p. 300). The production of

* Schmidlin and Lang (*Ber.*, 1910, **43**, 2806) incidentally describe the preparation of a compound, $\text{C}_{26}\text{H}_{22}\text{O}$, which they obtained by the action of concentrated sulphuric acid on a mixture of α -naphthol and *cyclohexanone*, and to which

they attribute the constitution $\text{C}_6\text{H}_{10} < \begin{smallmatrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} > \text{O}$. Their compound has nearly the

same melting point (232°) as that of the above substance (*loc. cit.*), but that it has not the constitution assigned by them will appear from their analysis: "0.1183 gave $\text{CO}_2 = 0.3636$; $\text{H}_2\text{O} = 0.0769$; $\text{C} = 83.82$; $\text{H} = 7.22$ per cent." The correct numbers for $\text{C}_{26}\text{H}_{22}\text{O}$, however, are $\text{C} = 89.15$; $\text{H} = 6.28$ per cent. It should be noted here that although they found the carbon about 2 per cent. lower than what is required by the compound $\text{C}_{32}\text{H}_{32}\text{O}_2$, the percentage of hydrogen obtained by them is in agreement.

this evidently points to the intermediate formation of chlorohydrins in this type of reaction.

The readiness with which this condensation takes place depends, in the first place, on the molecular weight of the ketones generally—the smaller the molecular weight, the more easily is the condensation brought about. Exception, however, is met with in the case of fluorenone, which condenses with α -naphthol as readily as does acetone, although benzophenone gives a yield of 7 per cent. only. Secondly, the nature of the carbon atoms in direct union with the carbonyl group seems to influence the condensation. Thus it is found that tertiary carbon atoms greatly inhibit it, as is seen in the typical case of camphorquinone, which condenses fairly readily with two molecules of phenol, cresol, or catechol (compare P., 1913, **29**, 155), whereas under the same conditions of experiment camphor itself does not undergo condensation. This is probably due, as stated above, to the tertiary carbon atom in direct linking with the carbonyl group of camphor, which, although present in camphorquinone, is there associated with another carbonyl group in direct union with a secondary carbon atom.

EXPERIMENTAL.

The Anhydride of β -1:1-Dihydroxydinaphthylpropane,

A mixture of 28.8 grams of α -naphthol, 5.8 grams of acetone, and 2—3 c.c. of phosphoryl chloride was heated at 100° for five minutes, when a brisk action occurred, at the end of which the liquid set to a crystalline mass. To ensure complete reaction about 1 c.c. of acetone was further added, and the flask heated another five minutes. The crystalline mass was digested with alcohol, which dissolved out any unchanged α -naphthol and decomposed the unchanged phosphoryl chloride, leaving the condensation product in a white, crystalline state. The yield at this stage amounts to about 65 per cent. of the theoretical, and, on recrystallisation from alcohol, about 58 per cent. By Dianin's method, using fuming hydrochloric acid as the condensing reagent, the yield scarcely exceeds 50 per cent. The substance crystallises in lustrous, quadratic plates, melting at 186° (as stated by Dianin). It is sparingly soluble in alcohol, readily so in acetone, chloroform, carbon disulphide, pyridine, or benzene. (Found, C=89.4; H=5.86. Calc. C=89.03; H=5.8 per cent.)

The *picrate*, prepared in benzene solution, crystallises in dark red prisms, melting at 164—165°. It is soluble in most solvents; almost insoluble in ether:

0.2500 gave 17.4 c.c. N_2 at 18.5° and 744 mm. $N = 7.88$.

$C_{23}H_{18}O, C_6H_5O, N_3$ requires $N = 7.79$ per cent.

The *dichloro*-derivative, $\begin{matrix} CH_3 \\ \diagup \\ C \\ \diagdown \\ CH_3 \end{matrix} < \begin{matrix} C_{10}H_5Cl \\ C_{10}H_5Cl \end{matrix} > O$, was prepared by saturating with dry chlorine a solution of the anhydride in carbon tetrachloride. The solid residue left after expelling the solvent was crystallised twice from pyridine diluted with a few drops of water. It is very sparingly soluble in alcohol, readily so in carbon disulphide, chloroform, pyridine or acetone, and melts at 262° :

0.2264 gave 0.1680 AgCl. $Cl = 18.32$.

$C_{23}H_{16}OCl_2$ requires $Cl = 18.73$ per cent.

The *dibromo*-derivative was prepared by adding the requisite quantity of bromine dissolved in carbon disulphide to the anhydride also dissolved in the same solvent. When the evolution of hydrogen bromide ceased, the carbon disulphide was expelled, and the residue crystallised from pyridine diluted with a few drops of water. It is sparingly soluble in alcohol or acetic acid, but readily so in acetone, carbon disulphide or pyridine. It crystallises in rhombic prisms, melting at $287-289^\circ$:

0.3374 gave 0.2675 AgBr. $Br = 33.73$.

$C_{23}H_{16}OBr_2$ requires $Br = 34.1$ per cent.

The *Mononitro*-derivative, $\begin{matrix} CH_3 \\ \diagup \\ C \\ \diagdown \\ CH_3 \end{matrix} < \begin{matrix} C_{10}H_5(NO_2) \\ C_{10}H_6 \end{matrix} > O$. — Three grams of the anhydride were suspended in about 50 c.c. of glacial acetic acid, and the temperature kept below 5° ; 3 c.c. of fuming nitric acid were next added drop by drop with constant shaking; towards the latter part of the addition of nitric acid, most of the nitro-compound separated from the solution. After allowing the mixture to remain at the ordinary temperature for about a quarter of an hour, the yellow precipitate was collected, washed several times with alcohol or water, and crystallised from boiling glacial acetic acid, from which it separates in long, yellow needles, melting at 225° . It is sparingly soluble in almost all solvents, but dissolves readily in hot nitrobenzene or pyridine. It can be further brominated or chlorinated, whilst the dinitro-derivative described below cannot be further brominated at the ordinary temperature:

0.2615 gave 9.25 c.c. N_2 at 16.8° and 746 mm. $N = 4.1$.

$C_{23}H_{17}O_3N$ requires $N = 3.94$ per cent.

The *Dinitro*-derivative.—One part of the anhydride was dissolved in 12 parts of glacial acetic acid by boiling. The solution was allowed to cool to $80-90^\circ$, and 8 parts of fuming nitric acid were added. The mixture was allowed to remain at 100° for about an hour, and then poured into water. The dinitro-derivative separ-

ated in an almost theoretical yield. When crystallised from hot nitrobenzene, it is obtained in golden-yellow, prismatic needles, which remain unmelted at 327°. It is sparingly soluble in the ordinary solvents, more readily so in boiling acetone, carbon disulphide or pyridine:

0.2758 gave 16.4 c.c. N_2 at 20° and 763 mm. $N=6.84$.

$C_{23}H_{16}O_5N_2$ requires $N=7.0$ per cent.

The Anhydride of β -1:1-Dihydroxydinaphthylbutane,

Three grams of methyl ethyl ketone and 14.4 grams of α -naphthol were heated with 2 c.c. of phosphoryl chloride in an open flask for about half an hour, when the contents solidified to a crystalline mass. If, however, the phosphoryl chloride is added in excess, the mass is usually pasty, but, on boiling with alcohol, a white, crystalline residue is left behind which is almost pure. On crystallisation from glacial acetic acid, the compound separates in lustrous, rhombic or prismatic plates, melting at 154—155°. The yield is about 65 per cent. The solubility of the compound is analogous to its previous homologue:

0.1168 gave 0.3803 CO_2 and 0.0639 H_2O . $C=88.87$; $H=6.07$.

0.6839, in 10.1244 naphthalene, gave $\Delta t = -1.452^\circ$. $M.W.=330.3$.

$C_{24}H_{20}O$ requires $C=88.88$; $H=6.17$ per cent. $M.W.=324$.

The *dichloro*-derivative prepared by direct chlorination crystallises from pyridine, diluted with a few drops of water, in small, colourless needles, melting at 221°:

0.1664 gave 0.1244 $AgCl$. $Cl=18.49$.

$C_{24}H_{18}OCl_2$ requires $Cl=18.06$ per cent.

The *dibromo*-derivative crystallises from pyridine in plates, melting at 250°:

0.1802 gave 0.1420 $AgBr$. $Br=33.5$.

$C_{24}H_{18}OBr_2$ requires $Br=33.2$ per cent.

The *dinitro*-derivative crystallises from glacial acetic acid in golden-yellow, prismatic needles, melting at 262—265°:

0.1986 gave 12.0 c.c. N_2 at 18° and 742 mm. $N=6.93$.

$C_{24}H_{18}O_5N_2$ requires $N=6.76$ per cent.

The *picrate* is very soluble in benzene, and crystallises in red needles, melting at 142—143°.

The Anhydride of γ -1:1-Dihydroxydinaphthylpentane,

4.3 Grams of diethyl ketone and 14.4 grams of α -naphthol were dissolved in 35 c.c. of glacial acetic acid, and fuming hydrochloric acid was added until the precipitation of α -naphthol just began. The bottle was heated for about 6 hours at 100° , when crystals began to appear. The heating was continued for two hours more, and the product was crystallised as usual from glacial acetic acid, from which it was obtained in colourless plates, melting at 166 — 167° . The yield is about 30 per cent. of the theoretical. The alternative preparation by the use of 2—3 c.c. of phosphoryl chloride takes about an hour, with a yield amounting to about 55 per cent.:

0.1261 gave 0.4116 CO_2 and 0.0736 H_2O . C=88.89; H=6.48.

$\text{C}_{25}\text{H}_{22}\text{O}$ requires C=88.75; H=6.58 per cent.

The *dibromo*-derivative crystallises in plates, melting at 258° :

0.3140 gave 0.2333 AgBr. Br=31.6.

$\text{C}_{25}\text{H}_{20}\text{OBr}_2$ requires Br=32.22 per cent.

The *dichloro*-derivative crystallises in prisms, melting at 238 — 239° :

0.3072 gave 0.2136 AgCl. Cl=17.19.

$\text{C}_{25}\text{H}_{20}\text{OCl}_2$ requires Cl=17.44 per cent.

The *dinitro*-derivative crystallises from glacial acetic acid or hot nitrobenzene in golden-yellow, prismatic needles, becoming discoloured at 290° , sintering at 298° , and decomposing and melting at 301 — 302° :

0.1590 gave 9.5 c.c. N_2 at 23° and 769.2 mm. N=6.85.

$\text{C}_{25}\text{H}_{20}\text{O}_5\text{N}_2$ requires N=6.55 per cent.

The Anhydride of β -1:1-Dihydroxydinaphthylpentane,

This compound was prepared by using hydrochloric acid as the condensing reagent, the yield amounting to 40 per cent. of the theoretical. The alternative preparation with phosphoryl chloride gave a yield of 62 per cent. It crystallises in plates, melting at 162 — 163° :

0.1041 gave 0.3374 CO_2 and 0.0596 H_2O . C=88.38; H=6.34.

$\text{C}_{25}\text{H}_{22}\text{O}$ requires C=88.75; H=6.58 per cent.

The *dichloro*-derivative melting at 178—179° was obtained in colourless, rhombic plates:

0.3134 gave 0.2146 AgCl. Cl=17.03.

$C_{25}H_{20}OCl_2$ requires Cl=17.44 per cent.

The *dibromo*-derivative melts at 196°:

0.1566 gave 0.1175 AgBr. Br=31.93.

$C_{25}H_{20}OBr_2$ requires Br=32.22 per cent.

The *dinitro*-derivative crystallises from hot nitrobenzene in yellow, prismatic needles, melting at 260—263°:

0.4321 gave 24 c.c. N_2 at 23° and 768 mm. N=6.32.

$C_{25}H_{20}O_5N_2$ requires N=6.55 per cent.

The Anhydride of β -1:1-Dihydroxydinaphthyl-octane,

6.4 Grams of methyl hexyl ketone and 14.4 grams of α -naphthol were heated with 2 c.c. of phosphoryl chloride at 100° for one-half to three-quarters of an hour. The resulting paste was boiled with small portions of alcohol to remove any unchanged α -naphthol, and the residue was boiled with about 30 parts of alcohol and the solution allowed to cool gradually. As the solution cools, a gummy deposit is observed on the sides of the beaker, when the solution is carefully decanted into another dry beaker. After several minutes, if the sides of the second beaker are found coated with any gummy deposit, the solution is decanted into a third, and so on, until the first appearance of a crystalline solid is noticed. On allowing the solution now to remain for two to three hours, pure crystals can be collected, melting at 96—97°, which after recrystallisation from glacial acetic acid or alcohol, melt at 99°, appearing in well-defined prisms. The yield scarcely exceeds 25 per cent. of the theoretical. The substance is markedly more soluble in alcohol or acetic acid than its homologues:

0.1039 gave 0.3386 CO_2 and 0.0690 H_2O . C=88.89; H=7.37.

$C_{28}H_{28}O$ requires C=88.42; H=7.36 per cent.

The *dichloro*-derivative melts at 162°:

0.2078 gave 0.1354 AgCl. Cl=16.12.

$C_{28}H_{26}OCl_2$ requires Cl=15.81 per cent.

The *dibromo*-derivative melts at 193° and crystallises in rhombic plates:

0.1720 gave 0.1231 AgBr. Br=30.46.

$C_{28}H_{26}OBr_2$ requires Br=30.88 per cent.

The *dinitro*-derivative crystallises in golden-yellow, prismatic needles, melting at 228—229°:

0.2160 gave 11.8 c.c. N_2 at 18.5° and 754 mm. $N=6.28$.

$C_{28}H_{26}O_5N_2$ requires $N=5.95$ per cent.

The Anhydride of α -1:1-Dihydroxydinaphthylethylbenzene,

Four grams of acetophenone and 9 grams of α -naphthol were dissolved in about 4 c.c. of glacial acetic acid, and the liquid was saturated with dry hydrogen chloride in the cold. The mixture was then heated in a stoppered bottle for six hours at 100°, when crystals began to appear, and the contents of the bottle soon solidified. On recrystallisation from glacial acetic acid, the substance is obtained in rhombic plates, melting at 167°. The yield amounts to about 47 per cent. of the theoretical; using phosphoryl chloride as the condensing reagent, it rose on one occasion to 60 per cent.:

0.1001 gave 0.3324 CO_2 and 0.05 H_2O . $C=90.8$; $H=5.54$.

$C_{28}H_{20}O$ requires $C=90.32$; $H=5.38$ per cent.

The *dibromo*-derivative melts at 279—280°:

0.1897 gave 0.1296 $AgBr$. $Br=29.6$.

$C_{28}H_{18}OBr_2$ requires $Br=30.18$ per cent.

The *dichloro*-derivative crystallises in white needles, melting at 242°:

0.1407 gave 0.0919 $AgCl$. $Cl=16.15$.

$C_{28}H_{18}OCl_2$ requires $Cl=16.1$ per cent.

The *dinitro*-derivative becomes red above 250°, and melts at 308—309°:

0.1457 gave 8.0 c.c. N_2 at 18° and 765 mm. $N=6.3$.

$C_{28}H_{18}O_5N_2$ requires $N=6.05$ per cent.

The Anhydride of Diphenyl-1:1-dihydroxydinaphthylmethane,

The condensation between benzophenone and α -naphthol could not be appreciably brought about in glacial acetic acid solution by means of hydrochloric acid, even after heating two days at 100°. With phosphoryl chloride, however, although the condensation product is easily obtained pure, the yield is only 7 per cent. of that required by theory.

Four grams of benzophenone and 6.3 grams of α -naphthol were melted together on the water-bath, and 1—1½ c.c. of phosphoryl

chloride added. Any excess of the condensing reagent must be avoided, or complicated products, difficult to purify, are produced. After heating for two hours, a dark-coloured, viscid mass is obtained, which is treated with alcohol to remove the unchanged α -naphthol and benzophenone, leaving about 0.7 gram of the condensation product. It is best crystallised from a hot solution in pyridine diluted with a few drops of water, when snow-white needles are obtained, melting at 274–275° (compare Clough, T., 1906, **89**, 771) (Found, C=91.09; H=5.15. Calc., C=91.2; H=5.07 per cent.). It is very sparingly soluble in boiling alcohol or acetic acid, but fairly so in benzene, chloroform, or acetone.

The *dichloro*-derivative crystallises from pyridine in plates melting at 302–303°:

0.1884 gave 0.1090 AgCl. Cl=14.37.

$C_{33}H_{20}OCl_2$ requires Cl=14.11 per cent.

The *dibromo*-derivative sinters at about 309° and melts at 311–312°:

0.2012 gave 0.1255 AgBr. Br=26.55.

$C_{33}H_{20}OBr_2$ requires Br=27.02 per cent.

The Anhydride of Diphenylene-1:1-dihydroxydinaphthylmethane,

Two grams of the ketone and 3.2 grams of α -naphthol were heated with 1 c.c. of phosphoryl chloride for about eight minutes at 100°, when the liquid set to a mass of crystals. The product was washed with hot alcohol, when the condensation product was left behind as a colourless, crystalline mass. The yield at this stage amounted to 3½ grams, corresponding with 70 per cent. of the theoretical. When crystallised from pyridine, it was obtained in colourless, prismatic needles, melting at 290°:

0.1164 gave 0.3910 CO₂ and 0.0495 H₂O. C=91.49; H=4.72.

0.3354, in 10.6283 naphthalene, gave $\Delta t = -0.560^\circ$. M.W.=400.1.

$C_{33}H_{20}O$ requires C=91.66; H=4.63 per cent. M.W.=432.

The *dinitro*-derivative crystallises from hot nitrobenzene in golden-yellow, prismatic needles, which remain unmelted at 340°:

0.3751 gave 15.8 c.c. N₂ at 20° and 763 mm. N=5.16.

$C_{33}H_{15}O_5N_2$ requires N=5.36 per cent.

Condensation of cycloHexanone with α -Naphthol.

Cyclic ketones also condense readily with α -naphthol, although secondary reactions seem considerably to diminish the yield (*Ber.*,

1896, **29**, 1595), in the presence of fuming hydrochloric acid or other such condensing reagents. The purification of the condensation product is therefore often attended with some difficulty. *cyclo*Hexanone itself gives two products with α -naphthol, namely, (1) the normal product, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{C} \begin{smallmatrix} \text{C}_{10}\text{H}_6 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} \text{O}$. and (2) a compound probably having a constitution represented by the formula **a**:

the mechanism of the formation of which has already been discussed (*loc. cit.*).

In order to obtain the latter compound, 3 grams of *cyclohexanone* and 9 grams of α -naphthol were dissolved in about 25 c.c. of glacial acetic acid, and 15—18 c.c. of fuming hydrochloric acid added. The clear solution soon became turbid on heating at 100°, and minute drops of oil began to separate. The heating was continued for about one and a-half hours with frequent shaking, when the oil set almost completely to a crystalline cake. This was treated with boiling alcohol, when a snow-white, crystalline mass, weighing about 2½ grams, remained behind. It is best crystallised from a saturated solution in boiling glacial acetic acid, in which it is sparingly soluble. On allowing to cool gradually, small, colourless, rectangular plates melting at 236° are obtained :

0.1103 gave 0.3454 CO₂ and 0.0708 H₂O. C=85.4; H=7.12.*

0.2144, in 10.72 naphthalene, gave $\Delta t = -0.336^\circ$. M.W. = 422.7.

$C_{39}H_{39}O_9$ requires C=85.71; H=7.14 per cent. M.W.=448.

A *mononitro*-derivative is obtained by suspending the anhydride in glacial acetic acid, heating to 80°, and adding a slight excess of fuming nitric acid. The suspended solid dissolves, and on cooling, small, yellow, prismatic needles appear, melting at 266—267°:

0.2175 gave 5.5 c.c. N_2 at 20° and 762 mm. $N = 2.93$.

$$\text{C}_{32}\text{H}_{31}\text{O}_4\text{N} \text{ requires N} = 2.84 \text{ per cent.}$$

The Anhydride of 1:1-Dihydroxydinaphthylcyclohexane,

If instead of heating the mixture of *cyclohexanone* and α -naphthol in an open vessel, as in the previous case, the same proportions are heated in a sealed tube for eight to ten hours at 100–105°, a

* A second analysis gave C=85.99; H=7.15.

viscid, black oil is obtained. This is washed once with cold alcohol, and once or twice with small portions of hot alcohol, which removes a great part of the impurities, leaving the condensation product in the form of a brown paste. This is dissolved in a small quantity of ethyl acetate, and left for a day or two, when dark-coloured, prismatic needles appear. These are collected and washed with a minimum quantity of light petroleum, which leaves the crystals much brighter. On crystallising twice from a hot solution in pyridine, diluted with alcohol, colourless, thin prisms or needles are obtained, melting at 146° . In a subsequent preparation, the solution of the brown paste in ethyl acetate was sown with a few crystals from the first crop, when the condensation product separated in the course of a few hours. The yield is extremely poor. From 3 grams of *cyclohexanone* about 0.3 gram of the condensation product was obtained:

0.1089 gave 0.3570 CO_2 and 0.0612 H_2O . $\text{C}=89.39$; $\text{H}=6.24$.

0.1464, in 7.4984 naphthalene, gave $\Delta t = -0.390^{\circ}$. $\text{M.W.}=355.4$.

$\text{C}_{26}\text{H}_{22}\text{O}$ requires $\text{C}=89.15$; $\text{H}=6.28$ per cent. $\text{M.W.}=350$.

Condensation of 1-Methylcyclohexan-3-one with α -Naphthol.

Two grams of 1-methylcyclohexan-3-one and 4 grams of α -naphthol were heated with 1 c.c. of phosphoryl chloride for two hours in a stoppered bottle at 100° . The paste so obtained was boiled several times with fresh portions of alcohol, until it set into a solid. It was then repeatedly crystallised from small portions of acetone until it melted at 164 – 165° :

0.1394 gave 0.4531 CO_2 and 0.0826 H_2O . $\text{C}=88.66$; $\text{H}=6.59$.

$\text{C}_{27}\text{H}_{24}\text{O}$ requires $\text{C}=89.01$; $\text{H}=6.59$ per cent.

It is markedly more soluble in glacial acetic acid than the other members of the series.

The *dinitro*-derivative melts at 282° :

0.1355 gave 7.45 c.c. N_2 at 20° and 759 mm. $\text{N}=6.25$.

$\text{C}_{27}\text{H}_{22}\text{O}_5\text{N}_2$ requires $\text{N}=6.16$ per cent.

Further investigation regarding the oxidation and hydrolysis of the products described above is in progress.

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