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Grignard Reaction and Products. I. 1,4-Addition of Arylmagnesium Bromide to 2-Alkylidenecyclohexanone and the Oxidative Cleavage therein[1)]

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Phenylmagnesium bromide reacted with 2-cyclohexylidenecyclohexanone (I) affording 2-(1-phenylcyclohexyl)cyclohexanone (II) in main, *via* 1,4-addition. Besides, it accompanied 6-(1-phenylcyclohexyl)-6-oxo-hexanoic acid (III) as by-product, even though the reaction was carried out in a stream of nitrogen, using purified ether as a solvent. It was found that (a) III itself did not exist just after the Grignard reaction and appeared after heating of the reaction mixture at 70—80°; (b) the ketone II, even in the enol form, did not produce a substance which convert into III by the absorption of oxygen. This suggested that the III-precursor, presumably a peroxide, was produced in the course of the Grignard reaction, thereafter transformed to III.

Reactions for the identification of III and the Grignard reaction of other α,β-unsaturated ketones were persued.

In general, Grignard reagents react with vinylketones giving alcohols through 1,2-addition and/or ketones through 1,4-addition. The present paper reports the cases where actions of arylmagnesium bromides on 2-alkylidene cyclohexanones mainly resulted in the formation of 1,4-addition products accompanying a small amounts of ketocarboxylic acids formed by oxidative fission of the former.

2-Cyclohexylidenecyclohexanone (I)[3)] was reacted with phenylmagnesium bromide giving 2-(1-phenylcyclohexyl)cyclohexanone (II) in 65—70% yield. Besides, 6-(1-phenylcyclohexyl)-6-oxo-hexanoic acid (III) was formed in 5—7% yield as by-product, even though the reaction was carried out in a stream of nitrogen and in ether befreed of peroxide as possible.

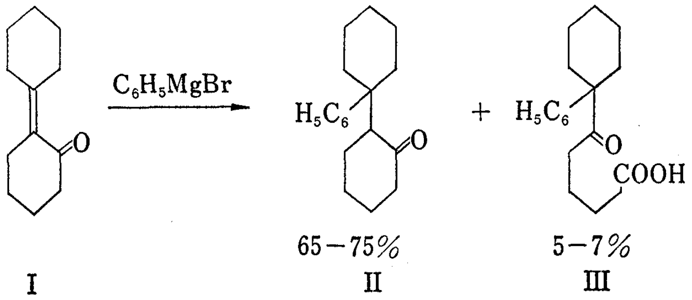

Chart 1

The structure of the ketocarboxylic acid III was established in the following way. The compound III is soluble in a 2N sodium carbonate solution and precipitates by acidification. The infrared (IR) spectrum showed absorption bands at 1717 cm^{-1} (C=O) and at 3200—2500 and 940—920 cm^{-1} (COOH). As shown in Chart 2, III-oxime derived from the ethyl ester

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1) *a*) T. Taguchi, Studies in Stereochemistry. XLIII; *b*) Part XLII: M. Mori, H. Kanayama, K. Tabata and T. Taguchi, *Yakugaku Zasshi*, **89**, 1631 (1969).

2) Location: *Katakasu, Fukuoka*; *a*) Present address: *Faculty of Pharmacy, Fukuoka University, Nanakuma, Fukuoka*; *b*) To whom inquiries should be directed.

3) J. Reese, *Ber.*, **75**, 384 (1942).

of III (IIIa) was converted to adipic acid by the Beckmann rearrangement, followed by hydrolysis. The oxidation of III by chromium trioxide-acetic acid afforded 6-oxo-6-phenylhexanoic acid (IV). III was identical with the compound which was derived *via* two procedures: (a) The Sommlet reaction of 6-(1-phenylcyclohexyl)-6-aminohexanoic acid hydrochloride (VI) which was obtained by the Beckmann rearrangement of II-oxime followed by hydrolysis in a hydrochloric acid solution. (b) Ozone-oxidation of 1-(1-phenylcyclohexyl) cyclohexene (VII), prepared by way of dehydration of DL-*cis*-2-(1-phenylcyclohexyl)cyclohexanol.[4] Reduction of III with sodium borohydride yielded a hydroxy acid (VIII) which was identical with the compound derived from II by the Baeyer–Villiger oxidation.

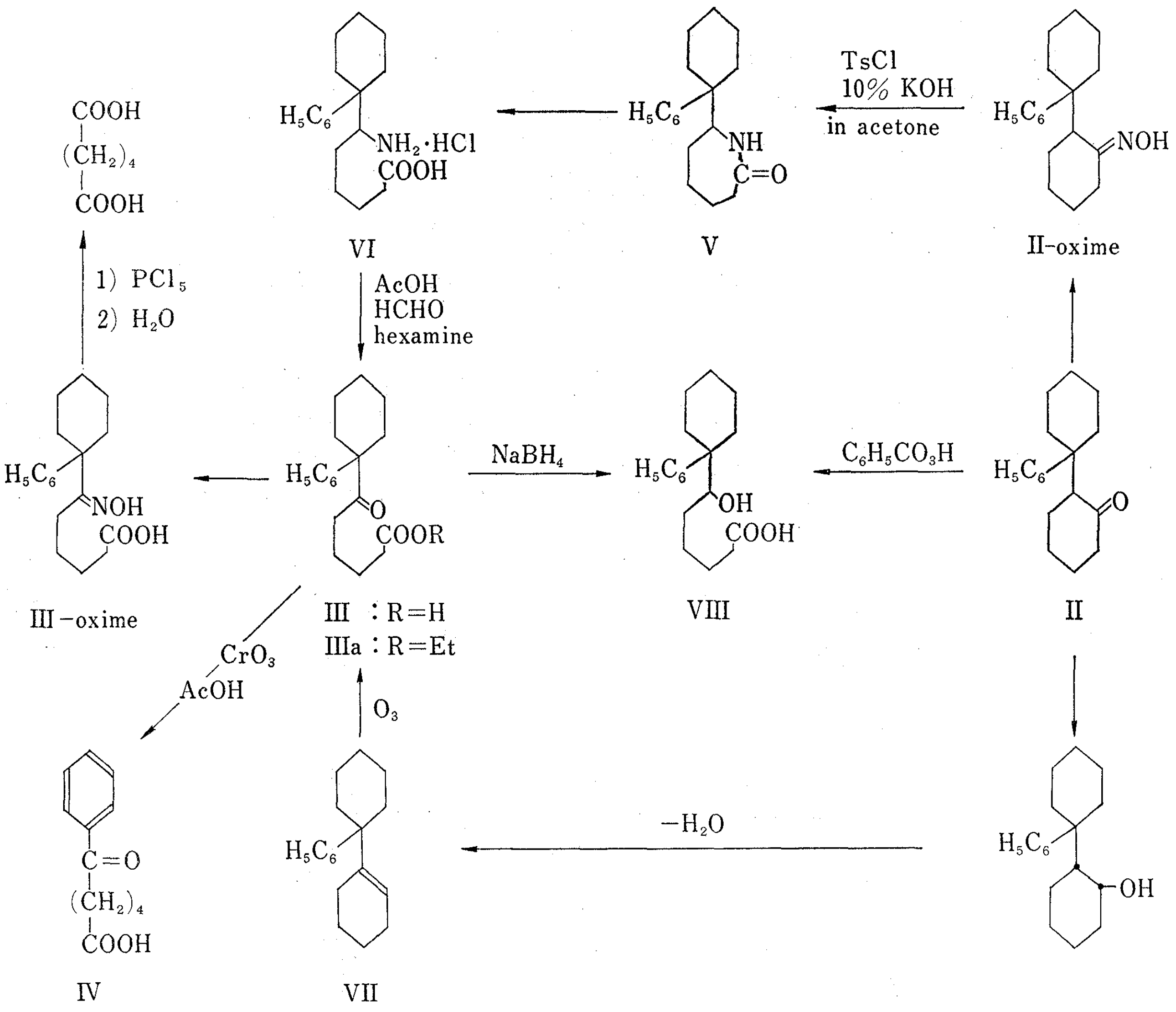

Chart 2

Thus, all the findings agreed with the structure assigned to III.

The oxidative cleavage in the Grignard reaction of ketones has been reported in a minority of literatures. Fuson, *et al.*[5] found the formation of mesitoic acid and 2-phenyl-1-naphthol after a reaction mixture of phenylmagnesium bromide and mesityl-α-naphthyl ketone (IX) had been hydrolyzed and set aside for a few months. The formation of mesitoic acid was attributed to the air-oxidation of the enol form (X) of the normal Grignard product. Kohler,

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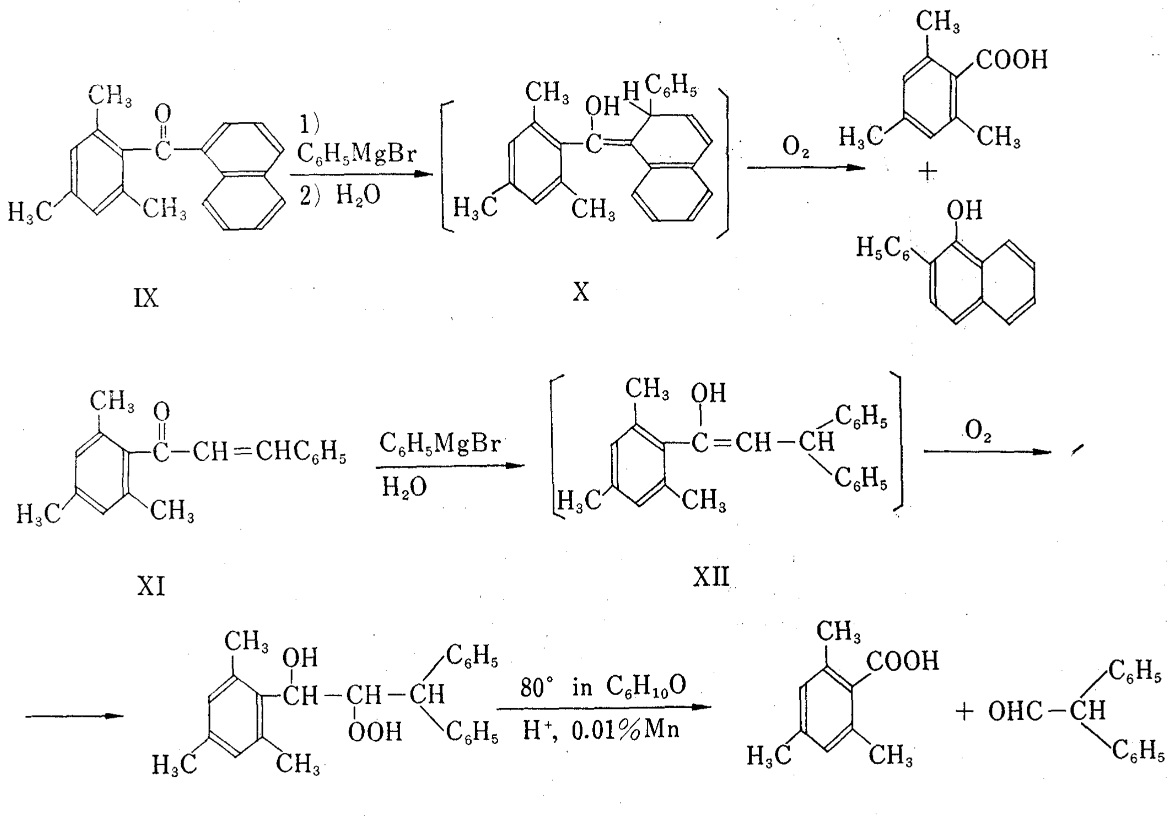
[4] T. Taguchi, T. Kobayashi and Y. Kawazoe, *Chem. Pharm. Bull.* (Tokyo), in preparation.
[5] R.C. Fuson, M.D. Armstrong and S.B. Speck, *J. Org. Chem.*, 7, 297 (1942).

et al.[6] obtained a stable peroxide (XIII) by the air-oxidation of a reaction mixture of phenylmagnesium bromide with benzalacetomesitylene (XI). The reaction was interpreted to proceed through the addition of an oxygen molecule to the enol form (XII). Later, Pritzkow[7] converted XIII into mesitoic acid and diphenylacetaldehyde by thermal decomposition.



IX X XI XII XIII

Chart 3

These example indicated that the oxidative fission occurs only in the case where a ketone produced by the Grignard reaction is stabillized in an enol form by the conjugation with double bond. However, in the other case, any fission has not been found except the examples shown in the present study.

The process of III-formation was precisely examined. As the result, no acidic substance such as III was detected immediately after the hydrolysis of reaction mixture. However, III appeared when the ether layer of the hydrolysis mixture was heated at 70—80° to concentrate, or allowed to stand at room temperature for two days. These facts seem to suggest that III-precursor, for example a peroxide, was formed by air-oxidation not during the reaction but after the reaction and then thermally decomposed into III. To confirm this idea, oxygen gas was introduced to the reaction mixture resulted from the Grignard reaction as Fuson[5] and Kohler[6] attempted. Consequently, it did not result in the increase in yield of III, but in the formations of the hydroxy ketone (XIV) and the vinyl ketone (XV). The structure of XIV was supported by the fact that it was not identical with a hydroxy ketone (XVIII) derived from XVII which was obtained by means of peracid oxidation of the enol benzoate (XVI).

This trial tells us that contrary to the above-stated idea, the air-oxidation of II worked to produce neither III nor III-precursor. Standing on this view, it can be presumed that the

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6) E.P. Kohler, *J. Am. Chem. Soc.*, **57**, 2517 (1935); *ibid.*, **59**, 887 (1937).
7) W. Pritzkow, *Ber.*, **87**, 1668 (1954); *ibid.*, **88**, 572 (1955).

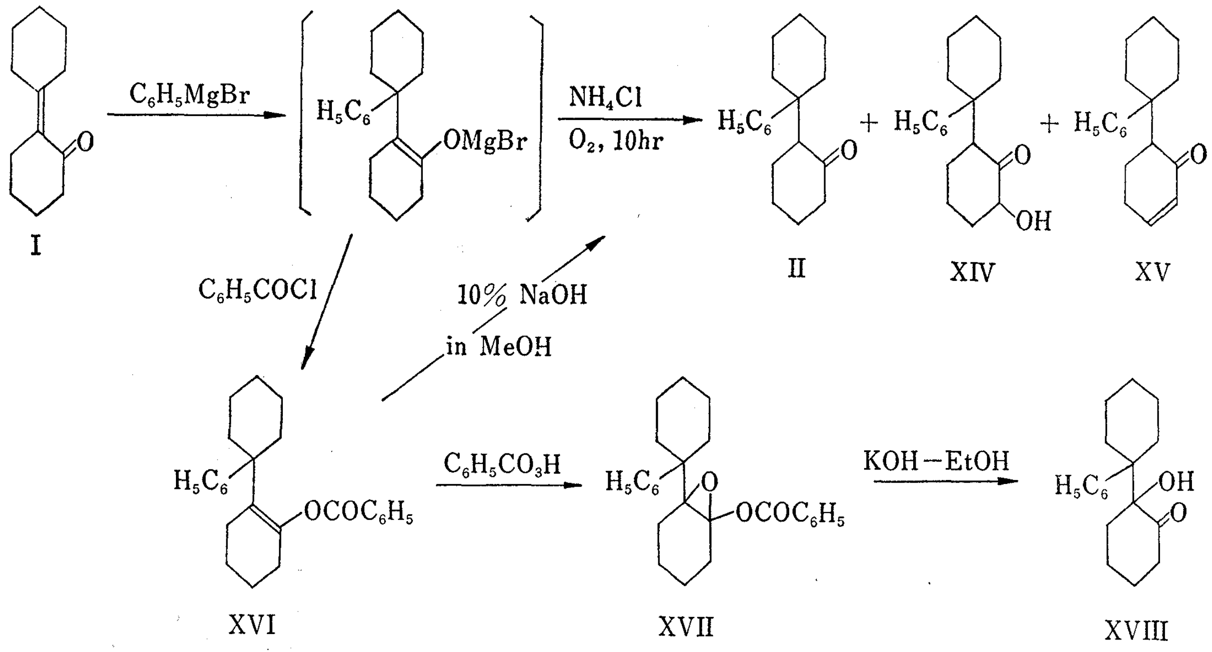

Chart 4

formation of III originated from the process of the Grignard reaction. A few years ago, Stucky and Rundle[8] reported that the ether solution of phenylmagnesium bromide produced $Mg_4Br_6O \cdot 4C_4H_{10}O$ on exposure to a small volume of O_2 and the formation of it during the preparation of Grignard reagent was unavoidable, even if the contact to air was excluded as possible. Besides, it has been reported that chemical species such as ArOMgX, ArOOMgX, MgX_2, $(MgX)_2O$, MgO and *etc.* were found[8] under influence of air in the ether solution of arylmagneisum halide, and they may presumably contribute to produce unexpected products in addition to normal ones.[9a–e] These findings seem to be valid even in the present study, where the reaction was carried out using purified ether in a stream of nitrogen.

These discussions give a reliable suggestion for such a mode as that the peroxidation intervened into the Grignard reaction to produce the III-precursor. And it was indirectly supported by the following finding that the III-precursor might be a kind of peroxides, though its structure has not been elucidated. After the Grignard reaction was completed, a portion of the hydrolysate was titrated by method of iodometry over a period of four days. The consumption of sodium hyposulfite decreased as the time elapsed and almost ceased after two days. This interval was roughly coincident with the time when the III-precursor transformed into III at room temperature as described above.

From this evidence, it could be concluded that not after the reaction, but during the reaction process, oxygen molecule worked causing the formation of III-precursor.

To examine the validity of the by-production of ketoacids, phenylmagnesium bromide was reacted with other α,β-unsaturated ketones, *i.e.* benzalacetophenone (XIX), benzalacetone (XX), furfuralacetone (XXI), 3,5-dimethyl-2-cyclohexene (XXII), 1-benzoylcyclohex-1-ene (XXIII), cholest-4-en-3-one (XXIV), 2-cyclopentylidenecyclopentanone (XXV) and 2-benzalcyclohexanone (XXVI). The reactions were carried out by the method analogous to the case of I, adding cuprous chloride to promote 1,4-addition. However, 1,2-addition proceeded in preference to 1,4-addition. Consequently, ketoacids corresponding to III were undetectable except the case of XXVI.

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8) G. Stucky and R.E. Rundle, *J. Am. Chem. Soc.*, **86**, 4821 (1964).

9) *a*) H. Hock, H. Kopf and F. Ernst, *Angew. Chem.*, **71**, 541 (1959); *b*) C. Walling and S.A. Buckler, *J. Am. Chem. Soc.*, **77**, 6032 (1955); *c*) H. Hock and F. Ernst, *Ber.*, **92**, 2716 (1959); *d*) H. Gillman, *J. Am. Chem. Soc.*, **47**, 2002, 2816 (1925); *ibid.*, **48**, 806 (1926); *e*) A.M. Clover, *J. Am. Chem. Soc.*, **44**, 1107 (1922).

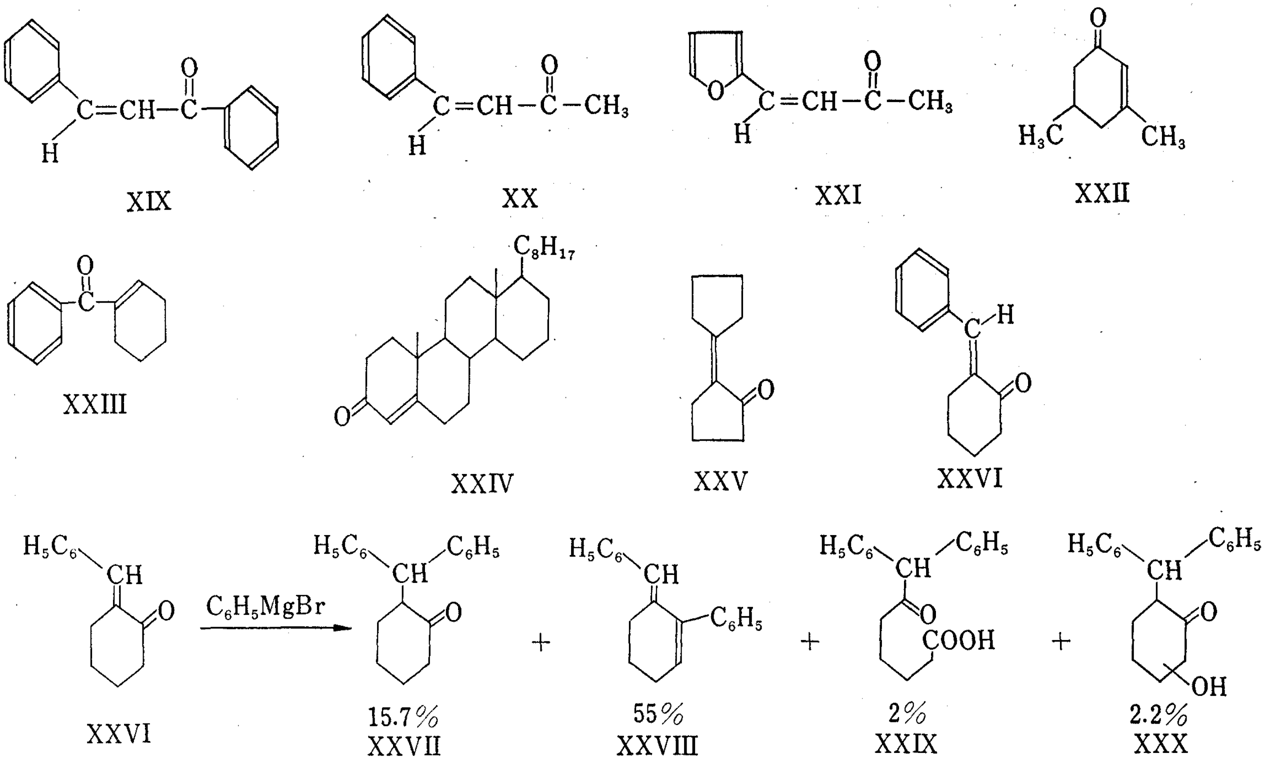

Chart 5

As shown in Chart 5, the reaction of XXVI afforded 2-benzylidene-1-phenyl-6-cyclohexene (XXVIII) in major (50%) through 1,2-addition and 2-benzhydrylcyclohexanone (XXVII) (17%) and the corresponding ketoacid (XXIX) (2%) in minor through 1,4-addition. Thus, these results did not rule the relationship between structure of starting materials and the formation of ketoacids in the Grignard reaction.

Experimental[10]

The Grignard Reaction of 2-Cyclohexylidenecyclohexanone (I)[3] with Phenylmagnesium Bromide—— To polished Mg-cuts (2.5 g) covered with a small amount of peroxide-free absolute ether (abs. ether) was added bromobenzene (16.3 g) diluted with 2—3 times volumes of abs. ether under vigorous stirring in a stream of N_2 and the mixture was refluxed for 1 hr. To the ether solution of the resulting Grignard reagent was added an ether solution of I (15 g, 0.86 eq), maintaining the vessel temperature at 5—10° and then the reaction mixture was stood overnight at room temperature or refluxed for 2 hr. After the contents of the flask was poured into aqueous NH_4Cl solution, the ether layer was separated and the aqueous layer was extracted twice with ether. Combined ether solution was washed with water, dried over Na_2SO_4 and concentrated at 70—80° of bath temperature. The remaining viscous residue was diluted with ether–petr. ether and treated with three 30 ml portions of 2N Na_2CO_3. The alkaline layer was acidified giving an oily substance which crystallized on standing. Recrystallization from petr. benzine gave colorless needles of 6-(1-phenylcyclohexyl)-6-oxo-*n*-hexanoic acid (III), mp 78—80°, yield 5—7%. *Anal.* Calcd. for $C_{18}H_{24}O_3$: C, 74.94; H, 8.39; mol. wt., 288. Found: C, 74.98; H, 8.37; mol. wt. (neutralization method), 276±5. IR $\nu_{\max}^{\mathrm{CCl_4}}$ cm^{-1}: 3200—2500 (COOH), 1717 (C=O).

After separation of the alkaline layer, the ether-petr. ether layer was washed with water and dried over Na_2SO_4. Removal of the solvent left yellow liquid, which crystallized by treating with petr. ether under cooling. Recrystallization from MeOH gave colorless fine needles of 2-(1-phenylcyclohexyl)cyclohexanone (II), mp 64—68°, yield 65—75%. *Anal.* Calcd. for $C_{18}H_{24}O$: C, 84.32; H, 9.44. Found: C, 84.18; H, 9.26. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 1706 (C=O), 704, 739 (benzene). 2,4-Dinitrophenylhydrazone: orange–red granules, mp 160—161° (MeOH). *Anal.* Calcd. for $C_{24}H_{28}O_4N_4$: C, 66.03; H, 6.47; N, 12.84. Found: C, 65.88; H, 6.53; N, 12.92.

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[10] All melting and boiling points were uncorrected.

The Grignard Reaction of 2-Benzalcyclohexanone (XXVI)[11] with Phenylmagnesium Bromide——To the ether solution of C_6H_5MgBr (1 eq)—prepared from Mg (5.0 g) and bromobenzene (32.5 g)—was added XXVI (30 g, 0.78 eq) in abs. ether and the mixture was treated just as in the case of I. An acidic substance obtained was recrystallized from ligroin, giving colorless crystals of 6-benzhydryl-6-oxo-*n*-hexanoic acid (XXIX), mp 68—69°, yield 2%. *Anal.* Calcd. for $C_{19}H_{20}O_3$: C, 77.02; H, 6.80. Found: C, 76.83; H, 6.91. IR ν_{max}^{Nujol} cm^{-1}: 3080—2500 (COOH), 1716 (C=O). Semicarbazone: colorless fine needles, mp 186—188° (MeOH). *Anal.* Calcd. for $C_{20}H_{23}O_3N_3$: C, 67.97; H, 6.56; N, 11.89. Found: C, 67.66; H, 6.67; N, 12.01.

After isolation of the acidic substance XXIX, the neutral reaction mass was chromatographed over Al_2O_3. 1) From elution with petr. ether; pale yellow viscous liquid of XXVIII, bp 156—157° (5 mmHg) (lit. bp 150° (0.4 mmHg)[12]), mp 135—137° (decomp.) (EtOH), yield 55%. 2) From elution with benzene; colorless needles of 2-benzhydrylcyclohexanone (XXVII), mp 101—104° (EtOH) (lit. mp 108—110° (EtOH),[12] yield 15.7%. *Anal.* Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.63. Found: C, 86.58; H, 7.77. 3) From elution with EtOH; colorless needles of XXX, after standing the elute for a few months, mp 169—173° (EtOH), yield 2.2%. *Anal.* Calcd. for $C_{19}H_{20}O_2$: C, 81.50; H, 7.20. Found: C, 81.29; H, 7.24. IR ν_{max}^{Nujol} cm^{-1}: 3480 (OH), 1716 (C=O).

5-Benzoyl-*n*-pentanoic Acid (IV)——To a solution of III (1.0 g) in glac. AcOH (30 ml) was added portionwise powdered CrO_3 (3.0 g) under cooling and continued to stir for 1.5 hr at 40—43°. The reaction mixture was diluted with a large volume of water and extracted with ether. The ether layer was shaken with a sat. aqueous $NaHCO_3$ solution. The separated alkaline layer was acidified with dil. HCl and extracted with ether. The ether extract was washed with water, and dried over Na_2SO_4. Removal of the ether gave a small amount of remainder which crystallized by adding petr. benzine. Recrystallization from water afforded colorless glossy needles of mp 77—78°, which was identified as IV by a mixed fusion with an authentic sample.

6-Hydroxy-6-(1-phenylcyclohexyl)-*n*-hexanoic Acid (VIII)——A $CHCl_3$ solution of II (1.0 g) and perbenzoic acid (1.18 eq), containing 5 drops of 10% H_2SO_4–AcOH as catalyst, was allowed to stand for 20 days in a dark and cool place. After the unreacted peracid was removed by treating with alkali, the chloroform layer was washed with water, dried over Na_2SO_4 and evaporated to dryness. The residue was dissolved in MeOH (10 ml) and refluxed for 30 min with 10% NaOH–MeOH (1.0 ml). Through distillation of MeOH and addition of water, unreacted starting material deposited and was filtered off. The filtrate was acidified and extracted with ether. The ether extract was washed with water, dried over Na_2SO_4 and evaporated to dryness giving VIII, colorless crystals on recrystallization from petr. benzine, mp 104—105°, yield 50 mg. *Anal.* Calcd. for $C_{18}H_{26}O_3$: C, 74.45; H, 9.03. Found: C, 74.25; H, 9.05. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3250—3100 (COOH), 1712 (C=O).

Reduction of III with $NaBH_4$——Esterification of III was carried out by dissolving III in a large volume of EtOH with a catalytic amount of conc. HCl and stirring at room temperature for 12 hr. Fractional distillation under reduced pressure gave pale yellow liquid of III-ethylester (IIIa), bp 173° (3 mmHg). To a solution of IIIa (0.5 g) in MeOH (3.0 ml) was added a solution of $NaBH_4$ (0.07 g, 1.18 eq) in MeOH (40 ml) under stirring and cooling. Ten min later, the excess hydride was decomposed with AcOH and a large volume of water was poured into the reaction flask. The reaction mixture was extracted with ether and the ether layer was separated. Removal of the ether, the residue was dissolved in EtOH, added 10% NaOH–EtOH (3.0 ml) and refluxed for 4 hr on a steam bath. On adding water to the reaction mixture, the water-insoluble material was removed by extraction with ether. A substance precipitated by acidifying the alkaline layer was recrystallized from petr. benzine, mp 103—105°, yield 15 mg. It was identified as VIII by a mixed fusion with the sample obtained through the above-stated procedure.

6-(1-Phenylcyclohexyl)-6-oxo-*n*-hexanoic Acid Oxime (III-Oxime)——IIIa (1.0 g) and $NH_2OH \cdot HCl$ (1.0 g) dissolved in pyridine–EtOH (1:1) (10 ml) were refluxed for 5 hr on a steam bath. The residue, after removal of the solvent, was refluxed with 10% KOH–EtOH for 2 hr. Reaction mixture was poured into water and washed with ether. The aqueous layer was acidified with dil. HCl and followed by extraction with ether. The ether extract was washed with water and dried over Na_2SO_4. Removal of ether left III-oxime, colorless needles after recrystallization from ether–petr. ether, mp 127—128°, yield 0.7 g. *Anal.* Calcd. for $C_{18}H_{25}O_3N$: C, 71.26; H, 8.31; N, 4.62. Found: C, 71.44; H, 8.48; N, 4.88. IR ν_{max}^{Nujol} cm^{-1}: 3535, 3357—3275 (OH), 3200—2500 (COOH), 1717 (C=O), 1646 (C=N).

The Beckmann Rearrangement of III-Oxime——To a solution of III-oxime (3.0 g) in ether (40 ml) was portionwise added PCl_5 powder under stirring and cooling, until no more PCl_5 was consumed. Brownish liquid, obtained after removal of the solvent, was refluxed for 8 hr with 25% HCl (25 ml) on direct fire. Before the reaction flask was cooled, the unreacted substance was removed by filtration, and the filtrate was concentrated *in vacuo*, giving colorless crystal. By repeated recrystallization from acetone gave 0.1 g of adipic acid which was identified by IR spectrum and a mixed fusion with an authentic sample.

2-(1-Phenylcyclohexyl)cyclohexanone (II) Oxime——To a mixture of II (50 g) and $NH_2OH \cdot HCl$ (50 g) in EtOH(1000 ml) was added KOH (80 g) dissolved in a small amount of water, and the mixture was refluxed

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11) D. Vorländer and K. Küze, *Ber.*, **59**, 2078 (1926).

12) J.P. Freeman, *J. Am. Chem. Soc.*, **80**, 1926 (1958).

for 3 hr on a steam bath. After removing a large portion of EtOH, water was added to the remainder and crystals precipitated were filtered off. Recrystallization from EtOH gave colorless granules of II-oxime, mp 127—128°, yield 90.5%. *Anal.* Calcd. for $C_{18}H_{25}ON$: C, 79.66; H, 9.26; N, 5.16. Found: C, 79.59; H, 9.28; N, 4.85. IR ν_{max}^{Nujol} cm^{-1}: 3330—3100 (OH), 1663 (C=N), 956, 917 (N–O).

δ-(1-Phenylcyclohexyl)caprolactam (V)——To an acetone solution (150 ml) of II-oxime (7.2 g) was added 8% aqueous NaOH (20 ml) and subsequently a cool solution (20 ml) of TsCl (5.7 g) in acetone (20 ml) under ice-cooling. After standing overnight, NaCl was removed by filtration and the filtrate was concentrated *in vacuo* at 40°. The residual crystals were subjected to fractional recrystallization from EtOH and separated into two different kind of crystals at a yield ratio of 2.5/1; one, mp 68—70°, and the other, mp 116—120°. The former was transformed into the latter by drying over P_2O_5 at 65° under reduced pressure. Recrystallization from EtOH gave colorless crystals of V, mp 118—120°, yield 76%. *Anal.* Calcd. for $C_{18}H_{25}ON$: C, 79.66; H, 9.29; N, 5.16. Found: C, 79.46; H, 9.29; N, 5.25.

6-Amino-6-(1-phenylcyclohexyl)-*n*-hexanoic Acid·HCl (VI)——V (2.0 g) was refluxed with 25% aqueous HCl (100 ml) for 6 hr on direct fire. After removal of undissolved materials by filtration in warm and the filtrate was cooled to precipitate colorless crystals. Filtration and recrystallization from 25% HCl gave colorless scales of VI, mp 202°, yield 94%. *Anal.* Calcd. for $C_{18}H_{28}O_2NCl$: C, 66.31; H, 8.66; N, 4.30. Found: C, 66.16; H, 8.55; N, 4.29. IR ν_{max}^{Nujol} cm^{-1}: 3247, 3196 (OH), —3120, 2800—2300, 1610, 1506 (NH_3^+), 1728 (C=O).

The Sommlet Reaction of VI——A mixture of VI (5.5 g), hexamine (4.0 g), 40% HCHO (2.5 ml) and AcOH (24 ml) was refluxed for 2 hr. The reaction mixture was concentrated *in vacuo* and added water to liberate an oil which was extracted with ether. The ether extract was washed with water, dried over Na_2SO_4 and evaporated to dryness. Recrystallization from petr. benzine gave crystals of mp 79°, which was identified as III by a mixed fusion and comparison of IR spectra with the sample obtained by the Grignard reaction above-stated.

Ozone Oxidation of 1-(1-Phenylcyclohexyl)cyclohexene (VII)[4]——Ozone was bubbled into a solution of VII (0.5 g) in $CHCl_3$ (5.0 ml) under ice-cooling. End-point of reaction was checked by thin-layer chromatography (TLC). To the remainder, after removal of $CHCl_3$ *in vacuo*, H_2O_2 (2.0 ml) and AcOH (2.0 ml) was added and the mixture was stirred for 3.5 hr at 80°. After removal of AcOH, excess 10% Na_2CO_3 was added and the insoluble substance was removed. Acidifying the alkaline layer, colorless crystals precipitated. Recrystallization from petr. benzine gave III, mp 80°, which was identified by comparison of IR spectra and mixed fusion with the sample obtained by the Grignard reaction, yield 32%.

The Grignard Reaction of I and Treatment of the Reaction Mixture with Oxygen——The Grignard reaction of I (12 g) and C_6H_5MgBr—prepared from Mg (2.0 g) and bromobenzene (13.0 g)—was carried out as stated above. From 10 min before the subsequent hydrolysis, O_2-bubbling into reaction mixture was begun. During and after hydrolysis, the bubbling was continued for additional 10 hr. The ether layer was treated just as stated before and 0.5 g of an acidic substance (PhOH) was isolated. Distillation of the remainder gave 5 g of distillate, bp 142—148° (1 mmHg) and 3 g of which was chromatographed over Al_2O_3. 1) From elution with ether–petr. ether (1:9); 0.6 g of II. 2) From elution with ether–petr. ether (3:7); (a) colorless fine needles, mp 74—77° (petr. ether), of 2-(1-phenylcyclohexyl)cyclohex-6-enone (XV), yield 0.7 g. *Anal.* Calcd. for $C_{18}H_{22}O$: C, 84.94; H, 8.85. Found: C, 84.99; H, 8.72. IR ν_{max}^{Nujol} cm^{-1}: 1670 (C=C–C=O). (b) colorless columns, mp 58—60° (petr. ether), as 2-(1-phenylcyclohexyl)-6-hydroxycyclohexanone (XIV), yield 0.2 g. *Anal.* Calcd. for $C_{18}H_{24}O_2$: C, 79.48; H, 8.89. Found: C, 79.46; H, 8.98.

2-(1-Phenylcyclohexyl)-1-benzoyloxycyclohexene (XVI)——The Grignard reaction of I (18.0 g) with C_6H_5MgBr—prepared from Mg (3.0 g) and bromobenzene (19.5 g)—was performed as usual. To the reaction mixture was added benzoylchloride (15.0 g) maintaining the vessel temperature at 5—10°. The reaction mixture was heated on reflux for 1 hr, and extracted with ether after hydrolysis. The ether extract was washed with 2N $NaHCO_3$ and then water, and dried over Na_2SO_4. Removal of ether followed by recrystallization from EtOH gave colorless granules of XVI, mp 94—96°, yield 73%. *Anal.* Calcd. for $C_{25}H_{28}O_2$: C, 83.28; H, 7.83. Found: C, 83.32; H, 7.89. IR ν_{max}^{Nujol} cm^{-1}: 1724 (C=O), 1690 (C=C), 1280, 1130 (ester).

2-(1-Phenylcyclohexyl)-2-hydroxycyclohexanone (XVIII)——A mixture of XVI (1.0 g) and perbenzoic acid–$CHCl_3$ solution (8 ml, containing 0.098 g/ml of peracid) was stood in a dark for 7 days. After removal of the excess peracid with 10% NaOH, the chloroform layer was washed with water, dried over Na_2SO_4 and evaporated to dryness. Recrystallization from MeOH gave colorless fine needles of 2-(1-phenylcyclohexyl)-1,2-epoxy-1-benzoyloxycyclohexane (XVII), mp 85—88°, yield 96%. *Anal.* Calcd. for $C_{25}H_{28}O_3$: C, 79.73; H, 7.49. Found: C, 79.58; H, 7.55. IR ν_{max}^{Nujol} cm^{-1}: 1735 (C=O), 1280—1250, 1130 (ester), 877, 818 (epoxy).

To a solution of XVII (0.5 g) in EtOH (40 ml) was added 10% KOH–EtOH (0.5 ml) and the solution was stirred for 2 hr at room temperature. After removing off EtOH by distillation, water was added to the residue and the mixture was extracted with ether. The ether layer was washed with water, dried over Na_2SO_4 and evaporated to dryness. Recrystallization from petr. ether gave colorless needles of XVIII, mp 56—61°, yield 0.2 g. *Anal.* Calcd. for $C_{18}H_{24}O_2$: C, 79.39; H, 8.88. Found: C, 79.26; H, 9.00. IR ν_{max}^{Nujol} cm^{-1}: 3440 (OH), 1709 (C=O).