219 (calcd. 216). The carbon dioxide evolved after hydrolysis of 1.5253 g. of III amounted[14] to 0.3216 g. (104%). No evidence for the presence of a carbonyl group was obtained upon testing III, IV or VI with 2,4-dinitrophenylhydrazine. III was completely hydrolyzed in boiling water during 15 minutes; freeze-drying of the resulting solution gave 100% of the expected amount of methanesulfonamide, m.p. and mixture m.p. 89.5–91.5°. The mol. wt. of IV was 210 (Signer isothermal distillation technique with acetone as solvent; calcd. 244.)

**Sodium Salts of Bis-sulfonylureas.**—The general procedure employed for preparation of the monosodium salts used for pharmacological testing may be illustrated by that used in preparing the salt of I.

1,3-Bis-(benzenesulfonyl)-urea (3.1 g., 0.0091 mole) was mixed with slightly less than an equivalent amount of 1.00 *N* sodium hydroxide, following which the mixture was diluted with water until most of the salt dissolved. Additional sodium hydroxide was then added slowly until the *p*H was 6.9. The mixture was filtered to remove a trace of undissolved solid and the clear filtrate was freeze-dried. The bulky white solid obtained was easily soluble and amounted to 3.11 g. (94%).

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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

# Synthesis of 2,2,4-Trimethyl-4-phenylpentane and 2,2,4-Trimethyl-4-cyclohexylpentane. Reactions of 2,2,4-Trimethyl-4-phenylpentane

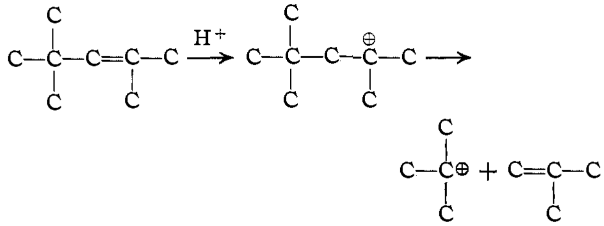
BY HERMAN PINES, RALPH MYERHOLTZ, JR.,[1a] AND V. N. IPATIEFF[1b]

RECEIVED AUGUST 25, 1952

2,2,4-Trimethyl-4-cyclohexylpentane and 2,2,4-trimethyl-4-phenylpentane have been prepared from 2,2,4-trimethyl-4-(*p*-hydroxyphenyl)-pentane. The stability of 2,2,4-trimethyl-4-phenylpentane in the presence of several alkylation catalysts has been determined. In none of the cases studied was there any evidence of appreciable instability under alkylation conditions when sulfuric acid, hydrogen fluoride or ferric chloride were used.

It has previously been reported[2] that depolyalkylation occurred when an attempt was made to alkylate benzene with diisobutylene in the presence of sulfuric acid. The reaction yielded *t*-butylbenzene and *p*-*di*-*t*-butylbenzene rather than the expected 2,2,4-trimethyl-4-phenylpentane (V).

These results may be interpreted in either of two ways: (1) Upon reaction with the catalyst the diisobutylene gives rise to a carbonium ion which may undergo cleavage to give a *t*-butyl carbonium ion and isobutylene.[3] The *t*-butylcarbonium ion as such or as formed from the isobutylene could then condense with benzene to give the products obtained.



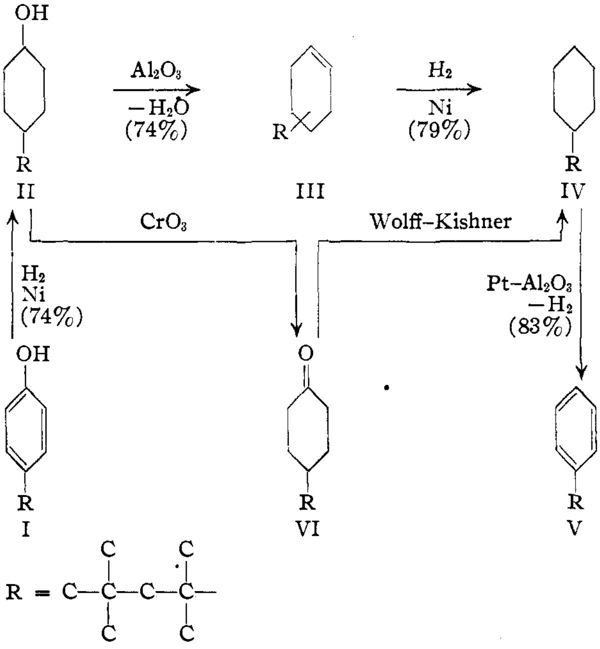
(2) Compound V, if formed, might be reactive under alkylation conditions and undergo a cleavage reaction to give the observed products.

Since migration of alkyl groups is known to occur when *di*-*t*-butylbenzenes or *di*-*t*-amylbenzenes are treated with sulfuric acid or anhydrous ferric chloride,[4] it seemed of interest to prepare V and investigate its stability in the presence of several alkylation catalysts.

Huston and co-workers have reported the synthesis of V using 2,4,4-trimethyl-2-pentanol and benzene in the presence of aluminum chloride.[5] However, the yield was low; some *t*-butylbenzene was obtained as a by-product and the purity of the product was not determined spectroscopically. In order to obtain a pure sample of V it was decided to prepare it by a previously described method[6] starting with 2,2,4-trimethyl-4-(*p*-hydroxyphenyl)-pentane which is commercially available.

## Discussion of Results

**Synthesis of 2,2,4-Trimethyl-4-phenylpentane (V).**—Compound V was prepared by the sequence of reactions



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[1a] Universal Oil Products Predoctoral Fellow, 1950–1952.

[1b] Deceased November 29, 1952.

[2] V. N. Ipatieff and H. Pines, THIS JOURNAL, **58**, 1056 (1936).

[3] F. G. Ciapetta, S. J. Macuga and L. N. Leum, *Ind. Eng. Chem.*, **40**, 2091 (1948).

[4] V. N. Ipatieff and B. B. Corson, THIS JOURNAL, **59**, 1417 (1937).

[5] R. C. Huston, R. L. Guile, J. J. Sculati and W. N. Wasson, *J. Org. Chem.*, **6**, 252 (1941).

[6] H. Pines, G. J. Czajkowski and V. N. Ipatieff, THIS JOURNAL, **71**, 3798 (1949).

Compound III was prepared by three different methods: (1) dehydration over alumina pellets, (2) dehydration with sulfuric acid according to Niederl[7] and (3) dehydration with aqueous magnesium chloride at elevated temperature.[8] The product of each method was hydrogenated and their infrared spectra compared and found to be identical.

As a further check on the possible occurrence of isomerization, IV was prepared from the corresponding ketone by a Wolff–Kishner reduction and its infrared spectrum compared to that of the product obtained by the hydrogenation of III. The spectra of the octylcyclohexanes prepared by either one of the methods were practically identical. The ketone VI was prepared from II by oxidation with chromic acid.

The octylbenzene (V) was prepared by the dehydrogenation of either III or of IV over platinized alumina. The infrared spectra of V produced by either one of the two methods were identical. Dehydrogenation of IV over chromia-alumina catalyst was accompanied by extensive decomposition and the product was not pure.

That no isomerization occurred during the dehydrogenation over platinum–alumina catalyst was demonstrated by hydrogenation of V and comparison of the infrared spectrum of the hydrogenated product with that of IV; the two spectra were identical.

**Reactions of 2,2,4-Trimethyl-4-phenylpentane.**—When octylbenzene (V) was treated with concentrated sulfuric acid or with hydrogen fluoride under the conditions of dealkylation, no appreciable change occurred. In each case the product was found to be 94–95% pure V on the basis of infrared analysis. However, V was somewhat less stable with respect to ferric chloride. Infrared analysis showed the product from the reaction with benzene and ferric chloride to be at least 90% pure V. No definite conclusion could be reached concerning the structure of the other compounds.

On the basis of these experiments it may be concluded in the reaction of benzene with di-isobutylene and sulfuric acid that depolymerization occurred prior to the alkylation of benzene.

## Experimental

**Synthesis. 2,2,4-Trimethyl-4-(4-hydroxycyclohexyl)-pentane** (II).—Octylphenol (obtained from Rohm and Haas Co., m.p. 69–72°), 224 g., was dissolved in 200 ml. of 95% ethanol and hydrogenated in a one liter autoclave in the presence of 25 g. of nickel-kieselguhr catalyst[9] at 140° and at an initial pressure of 120 atmospheres. The autoclave was recharged several times until the pressure remained constant. The hydrogenated product distilled at 140–145° at 5 mm. and solidified; m.p. 54–55°, yield 74%; literature[7] m.p., 55.5–56°, b.p. 148–150° at 11.5 mm.

**2,2,4-Trimethyl-4-(*x*-cyclohexenyl)-pentane** (III).—Prepared by three methods: (1) Compound II, 42 g., was dehydrated according to the method of Niederl[7] using 0.6 ml. of 96% sulfuric acid; b.p. 103–105° at 10 mm., $n^{20}_{D}$ 1.4735, yield 71%. (2) Compound II, 325 g., was dissolved in 900 ml. of *t*-butyl alcohol and dehydrated by passing it over activated alumina pills at 415–420°; b.p. 107–108° at 12 mm., $n^{20}_{D}$ 1.4746, yield 74%. (3) Compound II, 54 g., was treated with a 5% aqueous solution of magnesium chloride. The reaction was made in a 450-ml. capacity rotating autoclave at 250° for 3 hours. The pressure rose to 83 atmospheres. The yield of compound III was 60%; b.p. 118–123° at 16 mm., $n^{20}_{D}$ 1.4745; literature[7] b.p. 113° at 12 mm., $n^{25}_{D}$ 1.4741, $d^{25}_{4}$ 0.8565.

There was no appreciable decomposition inasmuch as no condensable gases were formed.

**2,2,4-Trimethyl-4-cyclohexylpentane** (IV). 1.—The olefin III obtained by the sulfuric acid method was dissolved in 50 ml. of pentane and hydrogenated at 75–80° in the presence of 2 g. of nickel-kieselguhr catalyst and at an initial pressure of 100 atmospheres. The product distilled at 106–112° at 10 mm., $n^{20}_{D}$ 1.4670. The hydrocarbon was redistilled on a Piros–Glover spinning band micro-column of about 40 plates; b.p. 93–94° at 2 mm., $n^{20}_{D}$ 1.4646, $d^{20}_{4}$ 0.8421; $MR_D$ calcd., 63.85, found, 64.20.

*Anal.* Calcd. for $C_{14}H_{28}$: C. 85.63; H, 14.37. Found: C, 85.49; H. 14.10.

A center cut was used to establish the infrared spectrum of IV.

2.—The olefin obtained from the alumina dehydration, 125 g., was hydrogenated according to the method described above. The product distilled at 111–112° at 13 mm., $n^{20}_{D}$ 1.4644, yield 79%. The infrared spectrum of this product was identical to that of the product of (1).

**2,2,4-Trimethyl-4-phenylpentane (V) (Prepared by Two Methods).** 1.—Compound IV, 58 g., was dehydrogenated by passing it over platinized alumina at 280–285°.[10] A sample of the gas evolved was collected over brine and analyzed by mass spectrometer; it was found to contain 98% hydrogen and 1.5% methane. The product was purified by dissolving it in an equal volume of pentane and chromatographing[11] it at 12° on a 45-inch column of Davisson through 200 mesh silica gel. Absolute ethanol was used as eluent; yield 83%.

The aromatic portion was distilled on a Piros–Glover micro column; b.p. 94–95° at 5 mm., $n^{20}_{D}$ 1.4951, $d^{20}_{4}$ 0.8767. A center cut was used to establish the infrared spectrum.

*Anal.* Calcd. for $C_{14}H_{22}$: C, 88.33; H, 11.67; $MR_D$, 63.25. Found: C, 88.24; H, 11.81; $MR_D$, 63.23.

A portion was acetylated according to a previously described method[12] and the following derivatives prepared: **2,4-dinitrophenylhydrazone**, m.p. 185.5–186° (cor.) after crystallization from ethanol-ethyl acetate.

*Anal.* Calcd. for $C_{22}H_{28}N_4O_4$: N, 13.58. Found: N, 13.68.

**Semicarbazone**: m.p. 194–195° (cor.) after crystallization from dilute ethanol.

*Anal.* Calcd. for $C_{17}H_{27}N_3O$: N, 14.51; Found: N, 14.88.

A portion of V was hydrogenated in the presence of nickel-kieselguhr at 120° and 100 atmospheres. The infrared spectrum of the octylcyclohexane thus formed was found to be identical with that of compound IV.

2.—Compound III, 23.5 g. was dehydrogenated over platinized alumina catalyst at 284–286°. The product was purified chromatographically as above. The aromatic fraction was distilled on a Piros–Glover micro-column; b.p. 90–93° at 5 mm., $n^{20}_{D}$ 1.4950. Infrared analysis proved the product to be identical to that obtained by dehydrogenation of IV.

**Synthesis of IV from the Corresponding Ketone. 2,2,4-Trimethyl-4-(4-oxocyclohexyl)-pentane** (VI).—Compound II, 75 g., was dissolved in 300 ml. of acetone and oxidized by a previously described method.[6] The ketone distilled at 130–133° at 5 mm., $n^{20}_{D}$ 1.4746, $d^{20}_{4}$ 0.9212, yield 36%; literature[7,13] b.p. 142–144° at 11 mm., $d^{20}_{4}$ 0.9850, $n^{25}_{D}$

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[7] J. B. Niederl and R. A. Smith, THIS JOURNAL, **59**, 715 (1937).

[8] V. N. Ipatieff and H. Pines, *ibid.*, **66**, 1120 (1944). Dehydration with magnesium chloride was carried out by Y. Ben-Levi, presently at Research Council of Israel, Jerusalem, Israel.

[9] V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

[10] H. Pines, R. C. Olberg and V. N. Ipatieff, THIS JOURNAL, **70**, 533 (1948).

[11] B. J. Mair and A. F. Forziati, *J. Research Natl. Bur. Standards*, **32**, 151, 165 (1944).

[12] H. Pines, A. Weizmann and V. N. Ipatieff, THIS JOURNAL, **70**, 3859 (1948).

[13] Using the physical constants of Niederl and Smith,[7] one obtains a value of 60.35 for the molar refraction of this compound, a figure which is not in good agreement with the theoretical value of 64.66. Since the analytical data reported by these authors also deviates from the calculated percentages for carbon and hydrogen, it would appear that their product was impure.

1.4768. *Anal.* (Literature cited) Found: C, 79.3; H, 12.3. *Anal.* Calcd. for $C_{14}H_{26}O$: C, 79.93; H, 12.46; $MR_D$, 64.66. Found (our values): C, 80.00; H, 12.55; $MR_D$, 64.14.

**The 2,4-dinitrophenylhydrazone** of VI melted at 107–108° after crystallization from dilute ethanol.

*Anal.* Calcd. for $C_{20}H_{30}N_4O_4$: N, 14.36. Found: N, 14.43.

**The oxime** of VI melted at 146.5–148° (cor.) after crystallization from dilute ethanol; literature[7] m.p. 152° (uncor.). *Anal.* (Literature cited, ref.[7]) Calcd. for $C_{14}H_{27}NO$: C, 74.66; H, 12.00; N, 6.23. Found (our values): C, 74.60; H, 12.21; N, 6.17. *Anal.* Calcd. for $C_{14}H_{27}NO$: N, 6.26. Found (our value): N, 6.31.

**2,2,4-Trimethyl-4-cyclohexylpentane** (IV).—Compound VI, 21 g., was reduced to the hydrocarbon by the modified Wolff–Kishner[14] method using 10 g. of potassium hydroxide, 75 ml. of diethylene glycol, and 7.5 ml. of 85% hydrazine hydrate. A 51% yield of hydrocarbon was obtained, $n^{20}\mathrm{D}$ 1.4650, whose infrared spectrum was practically identical to that of compound IV obtained by dehydration of II followed by hydrogenation.

**Reactions of Compound V. Sulfuric Acid and Benzene.**—The procedure of Ipatieff and Corson[4] was followed using 10 g. of V, 16 g. of benzene and 19 g. of 96% sulfuric acid. The reaction mixture was maintained at 50–60° for 4 hours. The organic layer was separated, extracted with 5% sodium hydroxide, washed with water and dried. The product was distilled at 5 mm. on a Piros–Glover micro column, giving the following fractions: (a) 83–91° 0.3 ml., $n^{20}\mathrm{D}$ 1.4890; (b) 92–93°, 3.0 ml., $n^{20}\mathrm{D}$ 1.4938; (c) 93–94°, 2.9 ml., $n^{20}\mathrm{D}$ 1.4940. A composite sample of fractions (b) and (c) was analyzed by means of infrared spectra; found 94 ± 3% pure compound V.

**Hydrogen Fluoride and Benzene.**—Compound V, 8 g., 125 ml. of benzene and 30 g. of hydrogen fluoride were stirred for an hour in a copper reactor maintained at 0°. The organic layer was separated, washed with 5% potassium hydroxide followed by water, and dried. Distillation on a Piros–Glover micro column at 4 mm. gave the following fractions: (a) 83–88°, 0.3 ml., $n^{20}\mathrm{D}$ 1.4900; (b) 88–90°, 0.9 ml., $n^{20}\mathrm{D}$ 1.4938; (c) 90–91°, 4.7 ml., $n^{20}\mathrm{D}$ 1.4942. A composite sample of fractions (b) and (c) was submitted for infrared analysis; found 95 ± 3% pure compound V.

**Ferric Chloride and Benzene.**—The procedure of Ipatieff and Corson[4] was followed using 10 g. of V, 88 g. of benzene and 6 g. of freshly prepared anhydrous ferric chloride.[15] The mixture was refluxed with stirring for 4 hours; hydrogen chloride was evolved. The reaction mixture was then washed with 5% hydrochloric acid followed by water until the washings were neutral. After drying, the product was distilled at 3 mm. on a Piros–Glover micro column. Fractions collected: (a) 78–86°, 0.6 ml., $n^{20}\mathrm{D}$ 1.4910; (b) 86–87°, 1.5 ml., $n^{20}\mathrm{D}$ 1.4938; (c) 87–88°, 5.8 ml., $n^{20}\mathrm{D}$ 1.4942. Fraction (a) and a composite sample of (b) and (c) were submitted for infrared analysis; found fraction (a) contained 90% compound V. The composite sample was about 98% pure compound V.

Microanalyses were performed by J. Sorensen and C. Brauer, Northwestern University.

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[14] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[15] H. F. Walton, "Inorganic Preparations," Prentice-Hall Publishers, Inc., New York, N. Y., 1948, p. 113.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE ROLLIN H. STEVENS MEMORIAL LABORATORY OF THE DETROIT INSTITUTE OF CANCER RESEARCH]

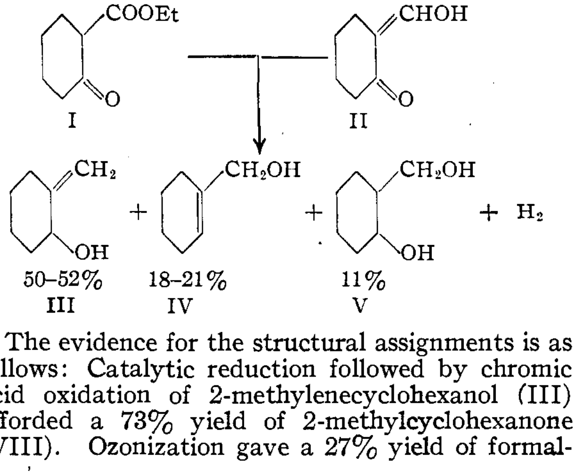
# Reduction of Some Enolizable β-Dicarbonyl Compounds to Unsaturated Alcohols by Lithium Aluminum Hydride. I. Monocyclic β-Ketoesters and α-Hydroxymethylene Ketones[1]

BY ANDRE S. DREIDING AND JOHN A. HARTMAN

RECEIVED APRIL 15, 1952

The lithium aluminum hydride reduction of four β-dicarbonyl compounds was found to give primarily unsaturated alcohols 2-Methylenecyclohexanol and 1-cyclohexenemethanol were the main products of the reduction of both 2-carbethoxycyclohexanone and 2-hydroxymethylenecyclohexanone. A small amount of 2-hydroxymethylcyclohexanol was also formed. The corresponding results were obtained with the related compounds in the five-membered ring series. The structures of the unsaturated alcohols were proven by their reactions and in some cases by alternative synthesis. A mechanism is suggested.

The action of lithium aluminum hydride on partially enolized β-dicarbonyl compounds has been reported to give low yields of the 1,3-diols as the only organic products.[2] While the evolved hydrogen has been determined quantitatively,[3] the nature of the major product(s) has not been reported. Our investigation showed that an excess of lithium aluminum hydride in boiling ether reduced 2-carbethoxycyclohexanone (I), and the structurally related 2-hydroxymethylenecyclohexanone (II), to give a mixture of 2-methylenecyclohexanol (III), 1-cyclohexenemethanol (IV) and 2-hydroxymethylcyclohexanol (V) in a 5:2:1 ratio. The physical properties and the derivatives of III and IV are shown in Table I.



The evidence for the structural assignments is as follows: Catalytic reduction followed by chromic acid oxidation of 2-methylenecyclohexanol (III) afforded a 73% yield of 2-methylcyclohexanone (VIII). Ozonization gave a 27% yield of formal-

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[1] (a) A part of this work was presented at the 118th Meeting of the American Chemical Society. (b) This work was supported in part by a Research and Development Contract between the Detroit Institute of Cancer Research and the United States Atomic Energy Commission. Additional support was provided by institutional grants from the Michigan Cancer Foundation, the American Cancer Society, Inc., and the S. S. Kresge Foundation.

[2] M. Viscontini and C. Ebnoeter, *Helv. Chim. Acta*, **34**, 116 (1951); C. S. Marvel and H. W. Hill, Jr., THIS JOURNAL, **73**, 481 (1951); V. Boekelheide and S. Rothchild, *ibid.*, **71**, 879 (1949), and E. Buchta and H. Bayer, *Ann.*, **71**, 227 (1951).

[3] J. A. Krynitsky, J. E. Johnson and H. W. Carhart, THIS JOURNAL, **70**, 486 (1948); F. A. Hochstein, *ibid.*, **71**, 305 (1949).