this anion might then combine with more indium ion to form $In[In(C_2O_4)_2(H_2O)_2]_3 \cdot 14H_2O$, or $2In_2(C_2O_4)_3 \cdot 10H_2O$. This would suggest that the compound referred to as the normal oxalate is dimeric with three-fourths of the indium in the complex and thus really a dioxalatoindate. Desiccation of this compound over anhydrous calcium chloride at 25° yields a product corresponding to $In_2(C_2O_4)_3 \cdot 4H_2O$, or $In[In(C_2O_4)_2(H_2O)_2]_3 \cdot 2H_2O$.

The dioxalatoindate complex is not extremely stable, for solutions of the compounds prepared give *nearly* complete precipitation of indium hydroxide when treated with ammonium hydroxide. Furthermore, on digestion with boiling water in quantity insufficient to dissolve it completely, the potassium compound gave a product analyzing for In, 50.17; $C_2O_4$, 27.72; $C_2O_4$/In, 0.72, and probably consisting of a mixture of basic salts resulting from hydrolysis.

A true potassium trioxalatoindate apparently does not result under the conditions employed. The formation of a material of indefinite crystalline structure corresponding to $K_2C_2O_4 \cdot 2K_3In(C_2O_4)_3 \cdot 7H_2O$ seems to be a function of the experimental conditions as already pointed out. This substance readily yields the dioxalato salt, for recrystallization of Sample 70 (Table II) gave a product analyzing for In, 29.10; $C_2O_4$, 44.01; $C_2O_4$/In, 1.975, values closely approaching those calculated for potassium dioxalatoindate. If any trioxalatoindate were present, the reaction could be formulated

$$[In(C_2O_4)_3]^{\equiv} + 2H_2O \longrightarrow [In(C_2O_4)_2(H_2O)_2]^- + C_2O_4^=$$

Furthermore, when a solution of Sample 84 (Table II) was treated with a solution of indium sulfate, a precipitate formed which analyzed for In, 28.49; $C_2O_4$, 43.80; $C_2O_4$/In, 2.001, values which agree almost exactly with those calculated for potassium dioxalatoindate.

## Summary

1. Indium sulfate solution reacts with solutions of sodium, potassium and ammonium oxalates precipitating octahedral crystals of $Na[In(C_2O_4)_2(H_2O)_2] \cdot H_2O$, $K[In(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ and $NH_4[In(C_2O_4)_2(H_2O)_2]$.

2. With oxalic acid, the precipitate corresponds to $In_2(C_2O_4)_3 \cdot 10H_2O$, or *perhaps* $In[In(C_2O_4)_2(H_2O)_2]_3 \cdot 14H_2O$. On drying over anhydrous calcium chloride, this becomes $In_2(C_2O_4)_3 \cdot 4H_2O$, or $In[In(C_2O_4)_2(H_2O)_2]_3 \cdot 2H_2O$. Dimeric formulas are given as *possible* explanations for the compositions of the materials.

3. Attempts to prepare potassium trioxalatoindate have led to an indefinite material approximating $K_2C_2O_4 \cdot 2K_3[In(C_2O_4)_3] \cdot 7H_2O$.

4. Use of the term "neutral" as applied to simple indium salt solutions is seriously questioned.

URBANA, ILLINOIS RECEIVED JULY 8, 1940

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

# Notes on the Preparation and Properties of Some Aliphatic Hydrocarbons

BY LOUIS SCHMERLING, B. S. FRIEDMAN AND V. N. IPATIEFF

Several paraffinic hydrocarbons have been prepared for use in connection with studies in this Laboratory. Their physical constants are presented along with some improved simple methods of preparation. Anti-knock values are also given.

2-Methylpentane was prepared *via* 2-methylpentanol-4 which was obtained by hydrogenating mesityl oxide, a compound which is more readily available than 2-methylpentanol-2 which has been used for the same purpose.[1]

An attempt to use diacetone alcohol as the starting material for the synthesis of the hydrocarbon was unsuccessful. Hydrogenation of the keto-alcohol to the diol was accompanied by hydrogenolysis to isopropyl alcohol. The hydrogenolysis was decreased substantially by use of a lower temperature and of isopropyl alcohol as solvent. However, dehydration of the 2-methylpentanediol-2,4 over activated alumina did not yield methylpentadiene as expected; instead, the product consisted chiefly of acetaldehyde and isobutene. This result may be explained readily as follows:

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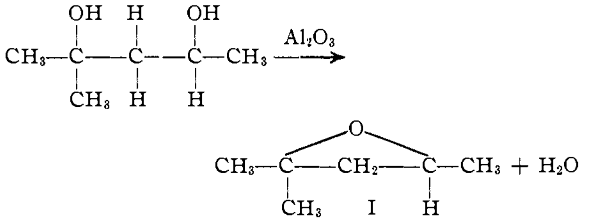
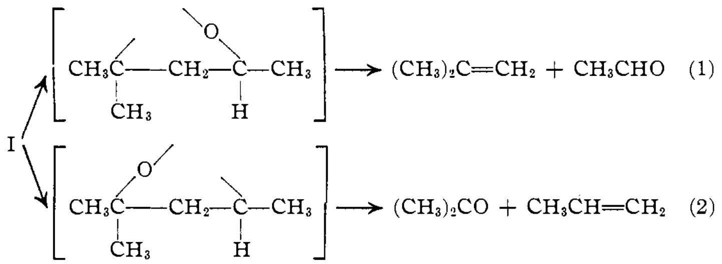
(1) P. L. Cramer and Mulligan, THIS JOURNAL, **58**, 373 (1936).





Reaction (2) occurs to a smaller extent. Analysis of the hydrocarbon gases by Podbielniak[2a] low-temperature fractional distillation and by sulfuric acid absorption[2b] showed that the yield of propene was about 5% of that of isobutene. Acetone was not isolated since it was present in too small amount to be separated from the aldehyde.

Nor could 2-methylpentane be obtained by the direct hydrogenation of the diol in the presence of a nickel-copper catalyst at 200°. Complete conversion to isopropyl alcohol occurred. A similar reaction in the presence of copper-chromium oxide catalyst was observed by Adkins.[3]

2,2-Dimethylbutane was synthesized by the hydrogenation of *t*-butylethylene which was obtained by the pyrolysis of pinacolyl acetate.[4] The intermediate pinacolyl alcohol (*t*-butylmethylcarbinol) was prepared in practically theoretical yield by the hydrogenation of pinacolone in the presence of nickel at 200°.[5] This is more convenient and efficient than the sodium-wet ether method.[6]

The direct replacement of the hydroxyl group of the pinacolyl alcohol by hydrogen offers a possible scheme for obtaining 2,2-dimethylbutane from the alcohol in one step. Hydrogenation in the presence of nickel on kieselguhr, of black nickel oxide or of nickel-alumina mixtures at 200° under 135 atmospheres pressure of hydrogen was unsuccessful and pinacolyl alcohol was recovered quantitatively. On the other hand, at 250°, in the presence of a nickel-copper catalyst, hydrogenation was complete and the theoretical amounts of hydrocarbon layer and water were obtained. However, only about 15% of the hydrocarbon was the desired 2,2-dimethylbutane; the remainder was the rearrangement product, 2,3-dimethylbutane.

2,3-Dimethylbutane was synthesized by two methods. The first consisted in the hydrogenation of the dimethylbutadiene obtained by dehydrating pinacol over alumina at 427°. Pinacolone was a by-product of this reaction. The second method consisted of (a) the reduction of pinacolone to pinacolyl alcohol, (b) the dehydration of the latter by means of oxalic acid[7] to a mixture of tetramethylethylene and *unsym*-methylisopropylethylene, and (c) hydrogenation of these olefins to the desired hexane.

An attempt was made to hydrogenate pinacol in the presence of nickel directly to the 2,3-dimethylbutane. When a nickel-kieselguhr catalyst was used at 250°, the product was a mixture of 2,2- and 2,3-dimethylbutane, the latter being present in greater amount. Similarly, the use of a nickel-copper catalyst resulted chiefly in 2,3,-dimethylbutane along with some of the 2,2-isomer and either pinacolyl alcohol or dimethylisopropylcarbinol.

The carbinols which were intermediates for the preparation of 2,2,3-trimethylbutane, 3,4-dimethylhexane, 2,2,3-trimethylpentane and 2,3,4-trimethylpentane were synthesized by means of the Grignard reaction. They were converted into paraffins (a) by dehydration over alumina to form olefins, followed by hydrogenation, or (b) by simultaneous dehydration and hydrogenation over alumina and nickel by treatment with hydrogen at 250-260°.

## Experimental

Data for the preparation of the intermediates involved in the synthesis of the paraffins are summarized in Table I. The final steps in the syntheses as well as the physical properties of the paraffins are given in Table II.

The hydrogenations were carried out in a rotating Ipatieff type bomb in the presence of about 10% by weight of a nickel-kieselguhr[8] catalyst under 100 kg./sq. cm. initial hydrogen pressure. The alcohols and glycols were dehydrated by passage over activated alumina.

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(2) (a) Podbielniak, *Ind. Eng. Chem.*, *Anal. Ed.*, **5**, 172 (1933); (b) *Cf.* Matuszak, *ibid.*, **10**, 354 (1938).

(3) Adkins, "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 81.

(4) Cramer and Mulligan, *loc. cit.* We wish to thank Dr. Cramer for a private communication, detailing the preparation and the pyrolysis of pinacolyl acetate.

(5) Adkins and H. I. Cramer, THIS JOURNAL, **52**, 4349 (1930).

(6) Cramer and Glasebrook, *ibid.*, **61**, 230 (1939).

(7) Whitmore and Rothrock, *ibid.*, **55**, 1109 (1933).

(8) Ipatieff and Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

TABLE I

INTERMEDIATES

| | Compound | Method | Yield, % | B. p., °C. | $n^{20}D$ |
|---|---|---|---|---|---|
| I | 2-Methylpentanol-4 | $(CH_3)_2C{=}CHCOCH_3 + H_2$ at 150°[a] | 70[b] | 128–131 | 1.4140 |
| II | 2-Methylpentenes | I + $Al_2O_3$ at 427°[c] | (100) | 55–56 | 1.3860 |
| III | 2-Methylpentanediol-2,4 | $(CH_3)_2COHCH_2COCH_3 + H_2$ at 100°[d] | 75 | 194–195 | .... |
| IV | Pinacolyl alcohol | $(CH_3)_3CCOCH_3 + H_2$ at 200°[e] | 100 | 119–120 | 1.4153 |
| V | Pinacolyl acetate | IV + $CH_3COCl$[f] | 92 | 139–140 | 1.4040 |
| VI | 3,3-Dimethylbutene-1 | Pyrolysis of V at 450°[f] | 90 | 41–42 | 1.3768 |
| VII | 2,3-Dimethylbutadiene-1,3 | $(CH_3)_2C(OH)C(OH)(CH_3)_2 + Al_2O_3$ at 427°[g] | 55–70 | 68–70 | 1.4364 |
| VIII | 2,3-Dimethylbutene-1 and -2 | IV + $(COOH)_2$ at 110–120°[h] | 55 | 64–75 | .... |
| IX | 2,2,3-Trimethylbutanol-3[i] | $(CH_3)_3CCOCH_3 + CH_3MgBr$ | 85 | 128–129 | .... |
| X | 3,4-Dimethylhexanediol-3,4 | $CH_3COC_2H_5$ + Mg[j] | 23 | 94–95 at 10 mm. | 1.4540 |
| XI | 2,2,3-Trimethylpentanol-3[k] | $(CH_3)_3CCOCH_3 + C_2H_5MgBr$ | 52 | 68–70 at 35 mm. | 1.4352 |
| XII | 2,3,4-Trimethylpentanol-3 | $(i\text{-}C_3H_7)_2CO + CH_3MgBr$[l] | 81 | 73 at 30 mm. | 1.4350–1.4356 |
| XIII | 2,3,4-Trimethylpentene-2[l] | XII + $Al_2O_3$ at 325° | [m] | 114.5–114.9 at 749.5 mm. | 1.4269 |

[a] Adkins, *loc. cit.*, p. 52. [b] There was also obtained, in 28% yield, methyl isobutyl ketone, b. p. 115–117°; $n^{20}D$ 1.3964 [c] The methyl isobutyl ketone was not removed prior to the dehydration. [d] Isopropyl alcohol (25% by weight of the diacetone alcohol) was used as solvent in order to decrease hydrogenolysis to isopropyl alcohol. In the absence of solvent and at 125° the 2-methylpentanediol-2,4 was obtained in only 57% yield while isopropyl alcohol was isolated in 38% yield. Adkins and H. I. Cramer, *loc. cit.*, report a quantitative yield of the diol at 150°; they did not obtain any isopropyl alcohol. [e] Adkins and H. I. Cramer, *loc. cit.* [f] P. L. Cramer, private communication. [g] German Patent 235,311 (1910). There was also obtained pinacolone in 25–39% yield. [h] Whitmore and Rothrock, *loc. cit.* [i] Edgar and Calingaert, THIS JOURNAL, **51**, 1486 (1929). [j] McCallum and Whitby, *Trans. Roy. Soc. Chem.*, **22**, 39 (1928). [k] Whitmore and Laughlin, THIS JOURNAL, **54**, 4012 (1932). [l] *Idem.*, p. 4392. [m] 450 cc. isolated by distillation through a 100-plate column (footnote *d*, Table II) of the 1510 cc. of the octenes resulting from the dehydration of XII: $d^{20}_4$ 0.7428; $d^{40}_4$ 0.7260; d*D*/d*t*, 0.00084; octane number, 83.

TABLE II[a]

SYNTHETIC PARAFFINS

| Name | By the hydrogenation of | B. p., °C. | Press., mm. | $d^0_4$ | $d^{20}_4$ | $d^{40}_4$ | d*D*/d*t* | $n^{20}D$ | Octane number[b] |
|---|---|---|---|---|---|---|---|---|---|
| 2-Methylpentane | II at 50° | 59.4–59.6 | 750 | 0.6705 | 0.6529 | .... | 0.00088 | 1.3716 | 71.5 |
| 2,2-Dimethylbutane | VI at 50° | 49.4–49.5 | 753 | .6663 | .6485 | .... | .00089 | 1.3688 | 93 |
| 2,3-Dimethylbutane | VII and VIII | 57.4–57.5 | 745 | .6785 | .6618 | .... | .00084 | 1.3751 | 94 |
| 2,2,3-Trimethylbutane | IX | 80.5–81.0 | 748 | .... | .6895 | 0.6727 | .00084 | 1.3894 | 100 |
| 3,4-Dimethylhexane | X | 118–118.3 | 750 | .... | .7193 | .7035 | .00079 | 1.4041 | 84.5 |
| 2,2,3-Trimethylpentane | XI | 110–110.5[c] | 749 | .... | .... | .... | ..... | 1.4030 | 100 |
| 2,3,4-Trimethylpentane | XIII | 112.3–112.4[d] | 736 | .... | .7187 | .7027 | .00080 | 1.4050 | 94.5 |

[a] *Cf.* Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Company, New York, N. Y., 1939, Vol. I. [b] C. F. R. motor method; "A. S. T. M. Standards on Petroleum Products and Lubricants," American Society for Testing Materials, Baltimore, Md., 1938, p. 153. [c] Separated by careful fractionation of the mixture of octanes resulting from the simultaneous dehydration–hydrogenation of XI. This purified fraction amounted to 48.5% by volume of the total octanes. [d] 100-plate bubble-cap still, Bruun and Faulconer, *Ind. Eng. Chem., Anal. Ed.*, **9**, 192 (1937); b. p. determined in modified Cottrell reboiler, Bruun and Hicks-Bruun, *Bur. Standards J. Research*, **6**, 871 (1931).

As an example of the *simultaneous dehydration* and *hydrogenation* of the alcohols (IX and XI) and the glycol (X), the formation of 3,4-dimethylhexane from (X) is described. Three hundred cc. of the diol, 50 cc. of isopentane, 2 g. of powdered activated alumina and 18 g. of nickelic oxide was heated for ten hours at 250–260° in a 3-liter rotating bomb under 100 kg./sq. cm. initial hydrogen pressure. The hydrocarbon layer was then separated from the resulting water and the catalyst, dried over sodium and fractionated.

**Dehydration of 2-Methylpentanediol-2,4 (III).**—Forty grams of the diol was passed during forty minutes over 50 cc. of activated alumina in a tube at 427°. There was obtained 7 cc. of water, 6 cc. of a viscous upper layer which was not further investigated, and 36 cc. of material condensed at −78°. The latter was redistilled by warming to room temperature, bubbling the gas through water into a trap immersed in dry-ice–acetone mixture. A low temperature Podbielniak[2a] distillation gave the following as the composition of the water insoluble condensate: $C_3H_6$, 4.1%; $C_3H_8$(?), 0.7%; $i$-$C_4H_8$, 81.0%; $n$-$C_4H_8$, 6.9%; $C_4H_{10}$(?), 1.2%; $C_5^+$, 1.5%. There was also found 4.6% of material boiling at −23 to −20°. The aqueous solution contained acetaldehyde, which was identified as the *p*-nitrophenylhydrazone, m. p. 128°.[9]

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(9) Hyde, *Ber.*, **32**, 1813 (1899).

## Summary

The synthesis of three hexanes, one heptane and three octanes is described. Their boiling points, refractive indices, densities, and octane numbers are given.

2,2,3-Trimethylbutanol-3, 3,4-dimethylhexanediol-3,4 and 2,2,3-trimethylpentanol-3 may be simultaneously dehydrated and hydrogenated to yield the corresponding paraffin.

Dehydration of 2-methylpentanediol-2,4 over activated alumina yields chiefly acetaldehyde and isobutene.

RIVERSIDE, ILLINOIS RECEIVED JUNE 22, 1940

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

# Aromatic Amines and 3-Nitro-6-fluoronitrostyrene

BY DAVID E. WORRALL AND HENRY T. WOLOSINSKI

The relatively weak tendency of nitrostyrene to form addition compounds with certain organic bases is slightly strengthened by the introduction of a nitro group into the aromatic nucleus.[1] It is also true that the additive tendency toward other bases, hydroxylamine or aniline for example, is lost, perhaps from an increased tendency for destructive oxidation–reduction reactions. The first effect is increasingly enhanced by the presence of chlorine, bromine, and iodine in the nitrated aromatic ring,[2] while the inhibitory factor is correspondingly diminished. The present communication completes the series of halogen derivatives in which it seems clear that fluorine is the least effective in promoting these addition reactions.

## Experimental

**$\alpha$-Nitro-$\beta$-(2-fluorophenyl)-ethylene** (I).—A mixture of fluorobenzaldehyde prepared by hydrolysis of *o*-fluorobenzalbromide with an equivalent amount of nitromethane containing a small portion of triethylamine[1,2] after cooling and standing for several hours was steam distilled in the presence of hydrochloric acid; yield, approx. 60%. (I) separated from ligroin as narrow yellow plates, m. p. 56.5–57.5°.

*Anal.* Calcd. for $C_8H_6FNO_2$: C, 57.5; H, 3.6. Found: C, 57.3; H, 3.7.

**$\alpha$ - Bromo - $\alpha$ - nitro - $\beta$ - (2 - fluorophenyl) - ethylene.**—A small portion of I was brominated in hot chloroform solution and the residue treated with an equivalent amount of alcoholic potassium acetate, avoiding the application of heat. After pouring the mixture into water, the residue crystallized from alcohol as yellow prismatic needles, m. p. 89–90°.

*Anal.* Calcd. for $C_8H_5BrFNO_2$: C, 39.0; H, 2.0. Found: C, 38.6; H, 2.4.

It formed an addition product with *p*-phenylene-diamine, also with benzidine, the latter separating as orange crystals, m. p. 134–135°.

*Anal.* Calcd. for $C_{28}H_{24}F_2N_4O_4$: C, 64.9; H, 4.6. Found: C, 64.8; H, 5.1.

**$\alpha$-Nitro-$\beta$-(6-fluoro-3-nitrophenyl)-ethylene** (II).—A small portion of I was nitrated at ordinary temperatures using fuming acid. The product, precipitated by means of ice water, crystallized from alcohol as slender pale yellow needles, m. p. 142–143°.

*Anal.* Calcd. for $C_8H_5FN_2O_4$: C, 45.3; H, 2.8. Found: C, 45.4; H, 2.7.

It has been assumed that the nitro group has the same position in the ring as with the derivatives previously studied. The same procedure previously used was followed in preparing the addition compounds, which were slow in forming.

TABLE I

$\beta$-DERIVATIVES OF $\alpha$-NITRO-$\beta$-(6-FLUORO-3-NITROPHENYL)-ETHANE

| Substance | Formula | M. p., °C. | Analyses, % Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|---|---|
| Anilino | $C_{14}H_{12}FN_3O_4$ | 134–135 | 55.1 | 3.9 | 54.5 | 4.0 |
| *m*-Toluidino | $C_{15}H_{14}FN_3O_4$ | 105–106 | 56.4 | 4.4 | 56.7 | 4.7 |
| *p*-Toluidino | $C_{15}H_{14}FN_3O_4$ | 116–117 | 56.4 | 4.4 | 56.1 | 4.6 |
| Phenylhydrazino | $C_{14}H_{13}FN_4O_4$ | 103–104 | 52.5 | 4.1 | 52.8 | 4.5 |

Negative results were obtained with *o*-toluidine, the anisidines, hydroxylamine, *p*-tolylhydrazine, and ammonia.

**N,N′ - ($\alpha,\alpha'$ - Di - (6 - fluoro - 3 - nitrophenyl) - $\beta,\beta'$-dinitrodiethyl)-benzidine.**—Yellow granular crystals appeared eventually on mixing an alcohol solution of the nitro derivative of I with benzidine, m. p. 139.5–140.5°.

*Anal.* Calcd. for $C_{28}H_{22}F_2N_6O_8$: C, 55.3; H, 3.6. Found: C, 55.0; H, 4.0.

## Summary

3-Nitro-6-fluoronitrostyrene has been prepared and its behavior examined toward aromatic amines. It is less active in forming addition compounds than analogous derivatives previously examined.

MEDFORD, MASS. RECEIVED JULY 2, 1940

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[1] Worrall and Benington, THIS JOURNAL, **60**, 2844 (1938).

[2] Worrall and Benington, *ibid.*, **62**, 493 (1940).