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.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

Aromatic Amines and 3-Nitro-6-fluoronitrostyrene

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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

α-Nitro-β-(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.

α-Bromo-α-nitro-β-(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.

α-Nitro-β-(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

β-DERIVATIVES OF α-NITRO-β-(6-FLUORO-3-NITROPHENYL)-ETHANE

Substance	Formula	M. p., °C.	Analyses, % Calcd. C	Analyses, % Calcd. H	Analyses, % Found C	Analyses, % 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′-(α,α'-Di-(6-fluoro-3-nitrophenyl)-β,β'-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.

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

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