Nitration of Saturated Hydrocarbons

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Although nitroparaffins were first produced by Victor Meyer[1] in 1872 by the metathesis of alkyl iodides and silver nitrite it was eight years later that Beilstein and Kurbatov[2] first nitrated a paraffin. They were investigating the nature of an American petroleum, and, having previously shown that naphthenes (cycloparaffins) could be nitrated, they treated with nitric acid a fraction boiling in the region of heptane. In this way they were able to isolate pure normal heptane, but they also obtained a product boiling at 196-200°C. which was a mixture of mononitroheptanes.

Since the nitration of aromatic hydrocarbons had proved to be a preparative tool of the first importance, it is not surprising that a number of investigators took up the study of the analagous reactions of the alkanes. Francis and Young, Markovnikov, Konovalov, Nametkin, Worstall, Buc and Hopkins, and Poni and Costachescu are some of the workers who took part in these researches. The paraffins nitrated ranged from isopentane to dodecanes; a number of cycloparaffins and also the aliphatic side-chains of aromatic hydrocarbons were found to be capable of the same reaction. A number of patents[3] describe the nitration of high-boiling petroleum distillates. The constitution of the hydrocarbons comprising these products is still completely unknown so that it is not easy to ascertain to what extent these workers were dealing with nitration of aromatic, olefinic or saturated hydrocarbons.

Results obtained in the liquid-phase nitration of saturated hydrocarbons at temperatures from 20° to the boiling point of nitric acid showed that the ones most readily attacked were those containing a cyclic tertiary carbon atom; these were followed by those with an acyclic tertiary carbon atom and finally by the naphthenes and paraffins free from tertiary carbon atoms. In general, the nitroparaffins obtained contained the same number of carbon atoms as the hydrocarbon nitrated, although Beilstein and Kurbatov[4] isolated a dinitroisobutane from the nitration products of a petroleum fraction boiling from 40°-50°C., which was presumably free from isobutane (b.p. -10.2°C.). The reaction showed a marked selectivity for the substitution of tertiary and secondary hydrogen atoms, in many cases producing substantially only one of the isomeric nitroparaffins theoretically derivable from a given alkane. When isobutane was nitrated in this laboratory in vapor phase at a temperature of 150°C., the product was tertiary nitrobutane of 99%

[1] Meyer, 1872. Ber. 5:203-5, 399.
[2] Beilstein and Kurbatov, 1880. Ber. 13:1818.
[3] Ellis. The chemistry of petroleum derivatives. 1:1052-4.
[4] Beilstein and Kurbatov, 1881. Ber. 14:1620.

purity; the reaction under these conditions behaving as if it were in the liquid phase.

At higher temperatures, however, the vapor-phase reaction gives results quite different from those obtainable under the conditions previously described. Thus n-pentane[5], upon nitration at 400°C., yields all three of the simple substitution products, i.e., 1-nitropentane, 2-nitropentane and 3-nitropentane, but also nitromethane, nitroethane, 1-nitropropane, and 1-nitrobutane. These results are in harmony with those obtained upon every paraffin whose vapor-phase nitration at high temperature has been carefully studied. Every mononitroparaffin is obtained which is theoretically derivable by adding a nitro group to the free radicals obtainable from a given hydrocarbon by fission of a C-H or a C-C bond. Whether or not free radicals are actually involved in the nitration is still not finally decided, but the perfect accuracy of the free-radical mechanism in predicting the identity of the nitro-paraffins obtained lends it an air of probability.

From the viewpoint of the synthetic organic chemist, the ready availability of the primary and secondary nitroparaffins is of interest because of the variety of chemical reactions which these substances will undergo. Thus primary nitroparaffins are hydrolyzed in the presence of strong mineral acids to form first hydroxamic acids and then the carboxylic acids having the same number of carbon atoms as the nitroparaffin used. If desired, the reaction may be stopped at the hydroxamic acid stage. This reaction promises to make hydroxylamine more readily available for large-scale syntheses than has been true in the past.

Both primary and secondary nitroparaffins undergo condensations of the aldol type when allowed to add aldehydes in the presence of a mild base. An illustration of this reaction is the following:

$$CH_3NO_2 \xrightarrow{HCHO} CH_2OH \cdot CH_2NO_2 \xrightarrow{HCHO} (CH_2OH)_2 CHNO_2 \xrightarrow{HCHO} (CH_2OH)_3CNO_2.$$
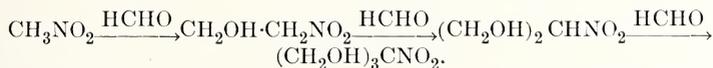
When formaldehyde is used for the reaction, all of the hydrogen atoms attached to the carbon atom holding the nitro group can take part in the condensation. This is also generally true when nitromethane is used regardless of the aldehyde. When nitroparaffins of two or more carbon atoms are condensed with aldehydes of similar complexity, only one molecule of aldehyde reacts per molecule of nitroparaffin. Compounds can be produced, however, of the following type by successive condensations, using formaldehyde and one of its homologs:

$$R \cdot CHOH \cdot C(R') CH_2OH.$$
$$\underset{NO_2}{|}$$
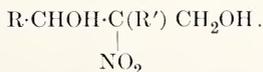
Nitroparaffins, nitroalcohols, nitroglycols, and nitroalkanetriols can all be reduced readily to the corresponding amino compounds. The properties of the hydroxyamines thus obtained are suggestive of those of triethanolamine. They may also be converted to the esters of organic or of inorganic acids. Thus nitration of 2-hydroxymethyl-2-nitro-1,3-propanediol in the usual way with mixed acid yields the trinitrate which is a powerful high explosive.

[5] Hass and Patterson, 1938. Ind. Eng. Chem. 30:67.

Chlorination of nitroparaffins in the presence of a base yields chloronitroparaffins in which the chlorine replaces one or more of the hydrogen atoms attached to the carbon atom holding the nitro group. For example, the chlorination of nitromethane yields chloropicrin which, while no longer of military importance as a toxic vapor, is of distinct value as an insecticide.

Nef[6] showed that the sodium salt of a nitroparaffin would, upon acidification with sulfuric acid under the proper conditions, yield an aldehyde or ketone depending upon whether it is derived from a primary or secondary nitro derivative.

$$2 \cdot R \ CH = NO_2 \cdot Na + H_2SO_4 \rightarrow Na_2SO_4 + 2 \ RCHO + N_2O + H_2O$$

The nitration reaction therefore offers an easy means of converting saturated hydrocarbons to the following classes of substances: nitroparaffins, amines, hydroxamic acids, carboxylic acids, hydroxylamine and its derivatives (such as oximes), nitroalcohols, nitroglycols, nitroalkanetriols, aminoalcohols, aminoglycols, aminoalkanetriols, the esters of the preceding six classes derived from either organic or inorganic acids (including certain high explosives), and the substituted amides derived from any of the amino derivatives, chloronitroparaffins, aldehydes, and ketones. The exploration of this wide field of synthesis is a fascinating research topic for a number of the members of the Department of Chemistry at Purdue.

[6] Nef, 1894.   Ann. **280**:263-91.