DERIVATIVES FOR THE IDENTIFICATION OF NITROPARAFFINS

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Although the simpler nitroparaffins are now accessible at low cost, there has been no systematic investigation of means of identifying them. In one research (Hass, Vanderbilt, and Hodge 1936) the products of nitrating paraffins were identified in the following manner:

> "Nitromethane was identified by its boiling point, 101°C., and the formation of the potassium salt of methazonic acid on treatment with concentrated potassium hydroxide.
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> "2-Nitropropane was identified by its physical constants, by conversion to the pseudonitrole, and by a Dumas nitrogen determination.
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> "Nitroethane, 1-nitropropane, 1-nitrobutane, and 2-nitrobutane were identified by their physical constants and starting materials."

This investigation was undertaken to find fusible crystalline derivatives which could all be made by the same simple procedure from common reagents, and which would have a suitable spread of melting points.

The nitroparaffins studied—nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane—were kindly supplied by the Commercial Solvents Corporation, to whom our thanks are due.

One possible approach is to utilize reactions of the nitro group. The use of a Grignard reagent was rejected because Wang (1932) reported a multiplicity of products from the interaction of nitroparaffins and arylmagnesium halides. An attempted reaction between nitroparaffins and 2,4-dinitroaniline, with a view toward splitting out water and forming a 2,4-dinitrophenylazoxyalkane, was unsuccessful, the reagents being recovered unchanged. Reduction of the nitroparaffins with zinc dust and ammonium chloride gave N-alkylhydroxylamines, as indicated by the strong reducing power of the solutions, but no insoluble salts, such as picrates, could be precipitated.

Best results were obtained by vigorous reduction of the nitro group, which has been done by many methods (Houben 1924). In this work granular zinc and concentrated hydrochloric acid were used. The solutions were made alkaline and shaken with benzoyl chloride, *p*-nitrobenzoyl chloride, and benzene sulfonyl chloride, but no suitable derivatives were obtained. The alkaline solution was therefore distilled, according to the procedure of Valton (1924), into an alcoholic solution of 2,4-dinitrochlorobenzene; this gave satisfactory N-alkyl-2,4-dinitroanilines for all four compounds tested.

$$(NO_2)_2C_6H_3Cl + RNH_2 \longrightarrow (NO_2)_2C_6H_3NHR + HCl$$

Other portions of distillate were tested with solutions of picric acid, picryl chloride, ethyl oxalate, and phenyl isothiocyanate. Picric acid gave picrates so soluble as to be nearly useless, and picryl chloride gave no insoluble products. Ethyl oxalate and phenyl isothiocyanate produced quite satisfactory derivatives, the N,N′-dialkyloxamides and N-alkyl-N′-phenylthioureas, respectively.

$$(COOC_2H_5)_2 + 2RNH_2 \longrightarrow (CONHR)_2 + 2C_2H_5OH$$

$$C_6H_5NCS + RNH_2 \longrightarrow C_6H_5NHCSNHR$$

TABLE I

Melting points of derivatives of the amines obtained from nitroparaffins [a]

Derivative	Nitroparaffin			
	CH_3NO_2	$C_2H_5NO_2$	n-$C_3H_7NO_2$	*iso*-$C_3H_7NO_2$
2,4-Dinitroalkylanilines	174°	111°	96°	91°
Beilstein value	175.5	113	95	94
Dialkyloxamides	210	176	162	212
Beilstein value	212	179	162	213
Alkylphenylthioureas	112.5	107	62	102
Beilstein value	113	106	63	101

[a] For comparsion, the literature values for the melting points of derivatives of some butylamines are appended:

2,4-Dinitroalkylanilines: n-butyl 58°, isobutyl 80°
Dialkyloxamides: n-butyl 153°, isobutyl 167°
Alkylphenylthioureas: n-butyl 65°, isobutyl 82°, sec.-butyl 101°.

The other notably reactive part of nitroparaffin molecules is the hydrogen on the alpha carbon atom, and numerous attempts were made to involve this in the formation of solid derivatives. *p*-Nitrosodimethylaniline and nitromethane or nitroethane refluxed together produced only black tars. Coupling of the sodium salt of a nitroparaffin with such high-molecular-weight halides as phenacyl bromide, *p*-bromophenacyl bromide, and *p*-nitrobenzyl chloride seemed to occur but the products were oils. A similar coupling with chloracetic acid gave only water-soluble products.

Since the condensation of nitroparaffins with aldehydes and ketones is a well-known reaction, such carbonyl compounds as benzaldehyde, cinnamaldehyde, salicylaldehyde, and piperonal were treated with each of the nitroparaffins separately in the presence of sodium methoxide, but only uncrystallizable oils resulted. Cyclohexanone and benzalacetophenone were also tried with the same results except that the latter did form addition products with nitromethane, m.p. 103°, and 1-nitropropane, m.p. 167°. These compounds and melting points have been obtained before by Kohler (1916).

Phenyl isocyanate reacts with the sodium salt of a nitroparaffin to yield a variety of products (Hantzsch and Schultze 1896, Michael 1905, Steinkopf and Daege 1911). When this reaction was tested, using pyridine as catalyst instead of the sodium salt, an exothermic reaction occurred, but the crystalline solid isolated proved to be *sym*-diphenylurea in every case. Phenyl isothiocyanate gave no evidence of undergoing any similar reaction.

Primary and secondary nitroparaffins have long been known to couple with diazonium salts according to the equation

$$C_6H_5N_2Cl + RCH_2NO_2 \longrightarrow C_6H_5NH{-}N{=}C(NO_2)R + HCl$$

This structure for the product is preferred to the possibly tautomeric form $C_6H_5N{=}N{-}CH(NO_2)R$. In the present work the sodium salts of the nitroparaffins were treated with the diazonium salts derived from aniline, *p*-toluidine, *p*-nitroaniline, and 2-naphthylamine. Nearly all the compounds resulting from the coupling are brilliantly colored crystalline substances with sharp melting points; some of their properties are set forth in Table II. Most of these compounds gradually decompose on long exposure to air and light, and the spread of melting points is not all that might be desired.

TABLE II

Derivatives of nitroparaffins obtained by diazonium couplings

Diazotized amine	Melting point and color[a] of product with			
	CH_3NO_2	$C_2H_5NO_2$	*n*-$C_3H_7NO_2$	*iso*-$C_3H_7NO_2$
Aniline	oil	141°:OY	97-98°;O	oil
Beilstein value	74.5-75.5°; 84.5-85.5	141-142; 136.5	98.5-99.5	oil[b]
p-Toluidine	oil	137;YO	88-89;OR	oil
Beilstein value	....	133 d.	....	20°[b]
p-Nitroaniline	159;OR, shade 1	157;OY	139-140;OR	104;Y
Beilstein value	....	....	....	....
2-Naphthylamine	oil	159;OR	138;OR	73-74;OY, tint 1
Beilstein value	....	145 d	....	67[b]

[a] Colors are named by the color chart in Mulliken (1904).

[b] According to Feasley with Degering (1943).

No modification of the Kjeldahl procedure could be made to give theoretical values of nitrogen in the compounds in Table II, nor did titration with standard titanous chloride yield results that could be interpreted.

Two familiar type reactions offering some possibilities were not investigated in the present work: nitrosation and hydrolysis. The former is known to yield nitrolic acids with primary nitro compounds and pseudonitroles with secondary, and hydrolysis could be made to produce an aldehyde or ketone, which might be distilled into some appropriate characterizing reagent.

EXPERIMENTAL

In reducing the nitroparaffins, about 5 ml of the nitroparaffin and 10 g of granular zinc were treated under reflux with concentrated hydrochloric acid portionwise until the top layer disappeared; the acid was added rapidly enough to keep the solution boiling. The reaction mixture was cooled, made strongly alkaline with concentrated sodium hydroxide solution while cooling was continued, and distilled into the reagent chosen. About 2 g of reagent was employed, 2,4-dinitrochlorobenzene in saturated alcohol solution, diethyl oxalate, or phenyl isothiocyanate undiluted. The precipitated derivative was isolated by filtration and recrystallized from ethanol. For use in characterizations amounts as small as one-tenth those specified may be employed.

For coupling nitroparaffins with diazonium salts, the latter were prepared in the usual manner. The nitroparaffin was treated in the cold with concentrated sodium methoxide solution until the odor of the nitro compound could not be detected. To this salt solution an equimolar amount of the freshly prepared diazonium salt solution was added with vigorous shaking. Occasionally small additional amounts of sodium methoxide were needed to cause complete solidification of the product. This was isolated by filtration, washed with a little dilute hydrochloric acid to destroy any sodium salt that remained, and recrystallized from ethanol.

CONCLUSIONS

The most satisfactory method studied for converting nitroparaffins to solid identifying derivatives is to reduce them to primary amines and characterize these. The N-alkyl-2,4-dinitroanilines are believed best for this purpose, but the N, N′-dialkyloxamides and N-alkyl-N′-phenylthioureas are also serviceable. The only alternative procedure found is to couple the sodium salts of nitroparaffins with diazonium salts, but this method is less general and otherwise less satisfactory.

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