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Liquid Phase Nitration

Cycloalkanes with Nitrogen Dioxide

As nitration temperatures are increased, higher yields of nitro compounds are obtained, along with lesser amounts of oxidation products

LIQUID-phase nitration of paraffin hydrocarbons is not a well-defined process, and much confusion exists as to its value, especially in preparing tertiary nitroparaffins. Some experiments indicate that tertiary nitration is simple and straightforward with good yield (7), but others show that this is not always true (6). However, tertiary nitro compounds might be prepared in good yield with proper equipment and technique.

Although the evidence is not complete, this study indicates that introduction of a nitro group into a molecule not only de creases its reactivity toward further nitration (or other freeradical substitution) but increases the difference in reactivity between tertiary and primary and secondary hydrogens. Thus, renitration of 1,4-dimethyl-1-nitrocyclohexane gave an apparently high yield of ditertiary nitro compound.

Equipment

The 1-liter jacketed reactor was equipped with accessory equipment for both batch and continuous operations. Top closure was a tongue and groove flange through which connections were made to the condenser and charging port for batch operation.

Bottom closure was a 1.5 inch-thick stainless steel plug welded in place; it contained two gas-feed inlets, one machined for a 0.25-inch, high-pressure, Amincotype fitting, and the other containing a built-in ball check valve assembly through which a gaseous nitrogen dioxide-nitrogen mixture was admitted. The ball check prevented liquid reaction mixture from entering the gas feed line where an explosive reaction could occur. For continuous operation a product receiver was connected to a flanged stainless steel nozzle on the reactor side. A ball float level controller actuated an automatic valve through which reaction mixture was withdrawn.

Hydrocarbon reactor feed in continuous runs was pumped by a positivedisplacement pump and measured from a graduated cylinder. Feed was preheated with 150-p.s.i.g. steam and an electric heating unit.

Liquid nitrogen dioxide was metered by a positive-displacement pump from a graduated cylinder in an ice bath and vaporized and diluted with nitrogen in a steam-jacketed vaporizer. The mixture was then heated to reactor temperature in an electrically heated preheater. Nitrogen was metered through a highpressure rotameter.

The reactor was heated by hot oil circulated through the jacket and an electrically-heated supply tank. Reactor jacket was also connected to steam, air, and cold-water lines.

All equipment except feed tanks and pumps and nitrogen supply was located behind a steel barricade and was operated by remote controls. The reactor pressure was controlled by a recordercontroller which actuated an automatic valve in the off-gas line from the condenser top. Temperatures were measured by thermocouples.

Procedure

The 1,4- and 1,3-dimethylcyclohexane were obtained by hydrogenating p- and *m*-xylene, respectively, over 5% rhodiumon-carbon catalyst. The 1,4-dimethylcyclohexane boiled at 119.5° to 124° C. $(n_D^{25} = 1.4230)$; 1,3-dimethylcyclohexane boiled at 118° to 120° C. $(n_D^{25} =$ 1.4260). Nitrogen dioxide was supplied by the Matheson Co.

Monotertiary Nitro Compounds. Hydrocarbon to be nitrated was charged to the autoclave, and the reactor was steam-heated to the desired reaction temperature; reaction pressure was maintained by a flow of pure, dry nitrogen through the apparatus. Liquid nitrogen dioxide then was pumped into the preheater and reactor at a predetermined rate (about 4 ml. per minute); the amount used was read from the graduated cylinder containing it. Start of the reaction was indicated by a rise in temperature of the reaction mixture; heat from the reaction was absorbed through the jacket.

After nitrogen dioxide was pumped into the autoclave, about 30 to 40 minutes, the reactor was cooled and the products discharged as a two-phase system. The water layer was separated and discarded. The organic layer (product oil) was weighed and then stirred for 1 hour with 100 ml. of 5% sodium bicarbonate per 100 ml. of product oil. The neutralized product was separated and weighed to give by difference the weight of acids produced (shown in runs above 150° C. to be negligible).

Amounts of primary and secondary nitroparaffins produced were determined then in a similar manner by treating the product oil with 100 ml. of 5% sodium hydroxide per 100 ml. of product oil for 4 hours and weighing the final organic layer. Unreacted hydrocarbon was distilled from the remaining product oil through a 20-inch, glass-helicespacked column at atmospheric pressure; tertiary nitro compound remaining in the still pot was distilled through the same column at reduced pressure.

Mononitro compounds isolated were mixtures of cis- and trans-isomers as demonstrated by the range of refractive indices obtained on distillation cuts shown by infrared analysis to be pure tertiary nitro compound (2, 5). The *cis-*, *trans-*1,4-dimethyl-1-nitrocyclohexane: b.p. 56° to 57° C., 1.5 mm. of mercury; $n_D^{25} = 1.4527$ to 1.4555 (3, 4).

The cis-, trans-1,3-compound boiled at 50° to 51° C., 1.0 mm. of mercury; n_D^{25} 1.4550 to 1.4575 (3).

	Analysis for $C_8H_{15}NO_2$				
	Caled.	Found			
С	61.08	61.20			
H	9.55	9,42			
N	8.91	8.79			

Ditertiary Nitro Compound. The mononitro compound (*cis, trans*-1,4-dimethyl-1-nitrocyclohexane) purified as above was nitrated in the same manner as the hydrocarbons. The product mixture, a slurry of white solid in unreacted mononitro compound, was filtered and the filter cake recrystallized from isopropyl alcohol. Fresh mononitro compound was added to the filtrate and the resultant mixture nitrated again.

The 1,4-dimitro-1,4-dimethylcyclohexane isolated melted at 178° to 179° C. and appeared to be a single compound, possibly the trans isomer.

Analysis for C₈H₁₄N₂O₄

	Caled.	Found
С	47.50	47.50
н	6.94	7.07
N	13.86	13.44



Nitration reactor was fabricated from a 12-inch length of 3-inch diameter, Schedule 80, 304 stainless steel pipe, and its full-length jacket was made from 5-inch diameter, Schedule 40 steel pipe

Results

Nitration of 1,3- and 1,4-Dimethylcyclohexane. Hydrocarbon consumption (total hydrocarbon charged minus unreacted material), in general, was about 50% at a 1 to 1 mole ratio of nitrogen dioxide to hydrocarbon, regardless of reaction temperature or pressure, but decreased to 27% at a 1 to 2 mole ratio (Table I).

At the 1 to 1 ratio, pressure had little effect in the 50- to 300-p.s.i. range, but in the one run at 400 p.s.i., extensive tar formation took place. At the 1 to 2 ratio, increasing pressure decreased the yield of tertiary nitro compound and increased the amount of primary and secondary compounds. Increased reaction temperatures definitely increased total yield of nitrocycloalkane produced and yield of tertiary nitrocycloalkane. Below 150° C. there was considerable acid formation, but above 150° C. very little acid was produced.

In general, decreasing the nitrogen dioxide-hydrocarbon ratio had little effect on yield of either tertiary or primary plus secondary nitro com-pounds. Catalysts such as alumina, silica, charcoal, copper(II) oxide, or iron(III) oxide had little effect on the nitration; iodine and bromine inhibited the reaction almost completely. In nearly all runs highest yield of tertiary nitrocycloalkane (66% by infrared analysis, 53.6% isolated) and one of the highest tertiary to primary-secondary ratios (3.5) was obtained with a 1 to 2 ratio at 190° C. and 100 p.s.i.g. pressure. Results with 1,3-dimethylcyclohexane were almost identical.

Nitration of 1,4-Dimethyl-1-nitrocyclohexane. Nitration of 1,4-dimethyl-1nitrocyclohexane, did not occur below 175° C. (25 to 50 p.s.i.g.), but proceded smoothly above this temperature; pressures higher than 50 p.s.i.g. were not used. The 1,4-dimethyl-1,4-dinitro-cyclohexane was isolated in about 15 to 20%

Table I. Nitration of 1,4-Dimethylcyclohexane (DMC)

Highest yield of tertiary nitrocycloalkane was obtained at 190° C. and 100 p.s.i.g.

Mole Ratio			DMC	Yields %		Ratio
1,4-DMC/ NO ₂	°C.	Pressure, P.S.I.G.	Consumed, %	Prim. + sec.	Tert	Tert/prim. + sec.
			Effect of Pre	ssure		
1 1 2 2 2	190 190 190 190 190 190	100 200 300 100 175 200	54.5 51 48.8 27 27.2 27.2	16.4 15 18 15.3 14.8 20.8	41 46 47.5 53.6 49.2 43.8	2.5 3.0 3.8 3.5 3.3 2.5
		1	Effect of Temp	erature		
1 1 1 1 1	125 140 150 190 200 220	200 200 200 200 200 200	46.4 45.5 41 51 48 48	21.6 31.4 34 15 17.6 19	25.1 32.2 35.6 46.0 51.5 47.5	1.16 1.02 1.02 3.0 3.4 2.5

Mechanism. A plausible mechanism for nitration of aliphatic compounds by nitrogen dioxide has been proposed (7):

$$\begin{array}{l} \mathrm{RCH}_3 + \mathrm{NO}_2 \longrightarrow \mathrm{RCH}_2. \ + \ \mathrm{HONO} \ \ (1) \\ \mathrm{RCH}_2. \ + \ \mathrm{NO}_2(\mathrm{N}_2\mathrm{O}_4) \longrightarrow \end{array}$$

 $RCH_2NO_2 + RCH_2ONO$ (2)

Reaction of the hydrocarbon free radical formed in Equation 1 with nitrogen dioxide leads to a nitro compound, whereas reaction with dinitrogen tetroxide produces a nitrite ester. Under usual liquidphase nitration conditions the nitro compound is stable, but the nitrite ester is oxidized or decomposed to acids or carbonyl compounds. Thus, nitration product yields should be improved by high temperature and low pressure, as this would shift the $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium toward a higher concentration of nitrogen dioxide. Ease of removing hydrogen from hydrocarbons during nitration (or other free radical reactions) is well established to be primary <secondary < tertiary. However, at high temperatures, where there may be sufficient energy to exceed the activation energy of all hydrogens, reactivity of primary and secondary hydrogens might be closer to that of tertiary hydrogens in a tertiary alkyl hydrocarbon; a higher proportion of primary and secondary nitro compounds would be obtained.

The data verify that as nitration temperatures are increased, higher yields of nitro compounds are obtained, along with lesser amounts of oxidation products. However, when temperature was increased from 125° C. to 190° to 200° C., a lower rather than higher proportion of primary and secondary nitro compounds was obtained. Highest ratios of tertiary to primary-plus-secondary nitro compounds were obtained at the highest practical operating temperature, although the reason is not clear.

Results with dimethylcyclohexanes would not necessarily apply to other aliphatic hydrocarbons.

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