[Contribution from the Department of Chemistry, Purdue University]

Nitration Studies. VIII. The Nitration of Cyclohexane[1]

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Study of the vapor phase nitration of cyclohexane with nitric acid has shown that chlorine alone, but not in combination with oxygen is an effective agent for promoting higher conversions to nitrocyclohexane. Conversions are also increased by increases in the C_6H_{12}/HNO_3 ratios. Thus, a conversion of 37% was obtained with a $C_6H_{12}/HNO_3/Cl_2$ mole ratio of 17/1/0.2. The findings are correlated and compared with the nitration mechanisms previously proposed for the acyclic alkanes.

INTRODUCTION

Nitration of cyclohexane has been studied by various workers, although only a few have directed their attention to the reaction in the vapor phase. Shechter[3] reacted cyclohexane with nitric acid at temperatures in the range of 430–455° using C_6H_{12}/HNO_3 ratios of about 4/1 and found conversions[4] of 17–21%. Quilico and Fusco[5] found a 15% conversion at the lower temperature of 370°, employing a C_6H_{12}/HNO_3 ratio of 2/1. In view of the low conversions so reported it was decided to attempt to better them by a study of the reaction. Nitrocyclohexane is not only of interest as a solvent and high energy fuel, but is also easily converted by reduction to cyclohexanone oxime, which by Beckmann rearrangement, and hydrolysis is converted to 6-aminocaproic acid, a valuable intermediate for the synthesis of polyamides.

Bachman and Pollack[6] showed that oxygen-chlorine combinations and chlorine alone promote better conversions in the nitration of propane with nitric acid, and furthermore, that chlorine alone serves to decrease the degree of degradation of this hydrocarbon during nitration, thereby increasing the amounts of nitropropanes relative to the lower nitroparaffins also formed. It would be expected that these effects of chlorine would be retained in the nitration of higher hydrocarbons such as cyclohexane. Accordingly it was decided first to study the chlorine-promoted nitration of cyclohexane with nitric acid and also to investigate the effect of higher hydrocarbon/nitric acid ratios on the conversions.

EXPERIMENTAL

Apparatus. The apparatus was of glass construction similar to that employed in the nitration of propane.[7] A tube designed to vaporize the cyclohexane was constructed of 18 mm. OD Pyrex tubing, 4 feet in length, packed with $^1/_4$ inch ID glass helices and heated by Chromel wire. The liquid cyclohexane was introduced through a calibrated jet, under constant nitrogen pressure to the top of the vaporizer which was set in a vertical position. The vaporized hydrocarbon issuing from the bottom of the tube was passed directly into the preheater, where it was mixed with nitric acid and chlorine, and thence into the reactor.

Product analysis. The condensed product, containing excess cyclohexane was neutralized with solid sodium bicarbonate after aliquot portions had been taken for acid and carbonyl analysis. The neutralized material was dried, an aliquot portion was taken for Kjeldahl analysis, and then was fractionally distilled under reduced pressure, the nitrocyclohexane being collected at 85–92°, (8–12 mm.).

DISCUSSION

Fig. 1 shows the effect of increasing C_6H_{12}/HNO_3 ratios on conversions in the absence and presence of chlorine. High cyclohexane concentrations appear to have a beneficial effect on conversion. A 30% conversion was obtained in the absence of chlorine

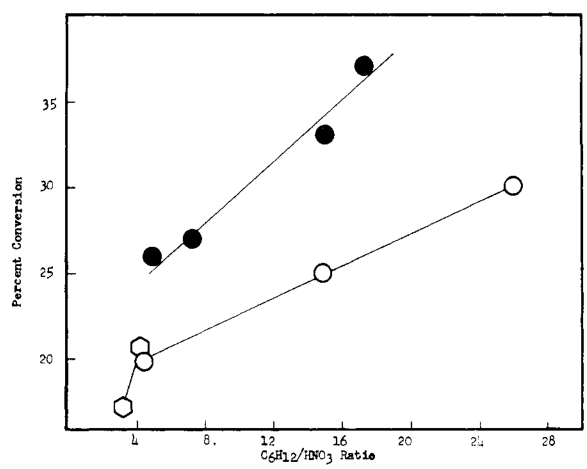

Fig. 1.—Nitration of C_6H_{12}: The Effect of C_6H_{12}/HNO_3 Ratios on Conversion in the Presence and Absence of Chlorine, O—uncatalyzed, 2–4 seconds contact time, 415–417°; ⬡—uncatalyzed, 1 second contact time, 455° (Shechter[3]) ●—Cl_2/HNO_3 = 0.12–0.7, 2–4 seconds contact time, 415–423°.

(1) Abstracted in part from a dissertation submitted by John P. Chupp to the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, February, 1955.

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(3) H. Shechter, Ph.D. thesis, Purdue University, 1946.

(4) Conversion, unless otherwise indicated, means the mole per cent of nitroparaffin produced per mole of nitrating agent introduced.

(5) A. Quilico and R. Fusco, *Chimica, e industria (Milan)*, **30**, 137 (1948).

(6) G. B. Bachman and M. Pollack, *Ind. Eng. Chem.*, **46**, 713 (1954).

(7) G. B. Bachman, H. B. Hass, and L. M. Addison, *J. Org. Chem.*, **17**, 914 (1952).

at a C_6H_{12}/HNO_3 ratio of 26/1. The effect of high ratios of hydrocarbon/nitric acid has been noted and explained by Bachman and Kohn.[8] Chlorine also shows a positive effect on conversion as is seen in the shift towards higher conversions at lower C_6H_{12}/HNO_3 ratios in the line representing chlorine-promoted nitration. The highest conversion (37%) obtained in this study was at a $C_6H_{12}/HNO_3/Cl_2$ ratio of 17/1/0.2, and reflects the beneficial effects of both high hydrocarbon ratios and chlorine.

With cyclohexane there is an optimum conversion at a Cl_2/HNO_3 ratio of about 0.2 (Fig. 2) while with propane the conversion increases continuously up to a Cl_2/HNO_3 ratio of 0.6 and possibly beyond.[7] This suggests that all hydrocarbons will be found to show optimal Cl_2/HNO_3 ratios although the ratios may differ from hydrocarbon to hydrocarbon. This is not unexpected since at some concentration of chlorine, the competition for alkyl radicals must become overwhelmingly in favor of the chlorine over the nitrating agent.

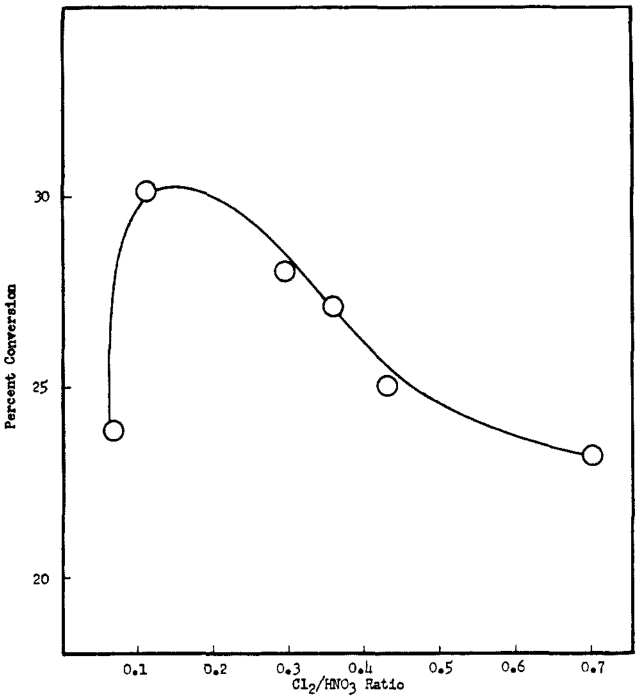


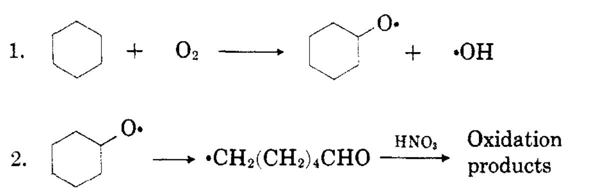
FIG. 2.—NITRATION OF C_6H_{12}: THE EFFECT OF Cl_2/HNO_3 RATIOS ON CONVERSIONS. O—C_6H_{12}/HNO_3 = 6.4–8.34/1.

A few chlorine-promoted reactions were run in the presence of oxygen. Table I shows that conversions are not noticeably increased by the use of oxygen-chlorine combinations, although the decrease actually observed may be partially due to slightly lower C_6H_{12}/HNO_3 ratios. The lack of a promoting effect of oxygen on conversions is thus different from the effect of oxygen-chlorine combinations in nitration of propane,[6] where conversions are markedly increased. This is not so surprising as it might at first seem. Oxygen not only catalyzes nitration, it also causes degradation to lower alkyl radicals. With cyclohexane this would lead to products other than simple nitro compounds. Since such products were not isolated and identified, only a hypothetical explanation of their formation can be put forth at this time:

TABLE I

STUDY OF THE EFFECT OF OXYGEN ON CONVERSIONS IN CHLORINE-PROMOTED NITRATION OF CYCLOHEXANE WITH HNO_3

Experiment No.	G-24	G-34	G-35	G-36
Conditions				
Temp., °C of reactor bath	423	423	423	423
Cont. time, sec	2.4	2.0	2.0	2.0
S/V cm.$^{-1}$	2.2	2.2	2.2	2.2
Reactants, relative moles				
C_6H_{12}	6.4	8.4	7.8	6.53
HNO_3 (70%)	1	1	1	1
Cl_2	0.11	0.21	0.2	0.16
O_2	0.0	0.25	0.5	0.8
Products, RNO_2				
Convs. (on N), %	30.2	27.8	27.0	21.0



In accord with equations 1 and 2, the formation of alkoxy radicals through reaction with oxygen would lead to ring opening and the production of bifunctional aliphatic compounds susceptible to oxidation by the nitrating agent.

LAFAYETTE INDIANA

(8) G. B. Bachman and L. Kohn, *J. Org. Chem.*, **17**, 942 (1952).