[Contribution from the Department of Chemistry, Purdue University]

# Nitration Studies. XIV. Effects of Peroxides, Ultraviolet Irradiation, and Silent Electric Discharge in the Vapor Phase Nitration of Hydrocarbons[1]

G. BRYANT BACHMAN and NORMAN W. STANDISH[2]

*Received May 16, 1960*

In seeking agents for the promotion of vapor phase nitration of hydrocarbons, we have found that ozonized oxygen is outstanding in its ability to raise conversions and yields, to lower reaction temperatures, and to alter the distribution of products. The effects observed are greater than can be explained solely from increases in the rate of generation of alkyl radicals and appear to involve also removal of the nitration inhibitor, nitric oxide, as rapidly as it is formed. Organic peroxides, hydrogen peroxide, ultraviolet irradiation, and silent electric discharge all reduce conversions in nitrations and cause minor variations in the distributions of products formed. The mechanisms by which these effects are probably exerted are discussed

Numerous attempts have been made in the past to find catalysts for the vapor phase nitration of aliphatic hydrocarbons,[3] but marked success has been achieved only with oxygen,[4] halogens, and oxygen-halogen combinations.[5] Analysis of the effects of these additives has led to clearer insight into the mechanisms of the processes occurring during nitration, and has shown that the principal value of these catalysts is to increase the rate of formation of alkyl radicals from hydrocarbons.

Since peroxides are probable intermediates when oxygen is the catalyst, it seemed likely that the addition of preformed peroxides to the reaction mixture would serve the same purpose as the addition of oxygen itself and lead to increased yields of and conversions to nitroalkanes and to useful variations in the distribution of products. It was anticipated that reactions of dissociation (1) and hydrogen abstraction (2, 3) might occur and lead

$$\mathrm{ROOH} \longrightarrow \mathrm{RO\cdot} + \mathrm{\cdot OH} \qquad (1)$$

$$\mathrm{RO\cdot} + \mathrm{RH} \longrightarrow \mathrm{ROH} + \mathrm{R\cdot} \qquad (2)$$

$$\mathrm{HO\cdot} + \mathrm{RH} \longrightarrow \mathrm{HOH} + \mathrm{R\cdot} \qquad (3)$$

to approximately two alkyl groups per peroxide molecule. However, the addition of 0.16 mole of *t*-butyl hydroperoxide per mole of nitric acid in the vapor phase nitration of propane not only failed to improve nitration results, but actually decreased both conversions and yields (especially in the presence of added oxygen) and increased the amounts of carbon oxides formed. Furthermore a brown film soon covered the reactor walls and still further decreased the conversion to nitro alkanes. With cumene hydroperoxide and di-*t*-butyl peroxide these effects were amplified, and after short times formation of nitro alkanes ceased entirely. The introduction of 0.05–0.23 mole of hydrogen peroxide per mole of nitric acid gave similar results, although brown film formation did not occur with this reagent. The use of a slightly higher ratio of hydrogen peroxide to nitric acid led to a violent explosion and destruction of the reactor.

The failure of peroxides to promote nitration can probably be explained on the basis of relative oxidation-reduction potentials. Thus, while peroxides can oxidize hydrocarbons and many other substances, they reduce nitric acid. Mixtures of nitric acid and hydrogen peroxide evolve nitrogen dioxide rapidly or even explosively if concentrated. This type of reaction apparently supersedes the reaction of peroxides with hydrocarbons in vapor phase nitration.

The above results indicate that the only peroxides which might be added to promote vapor phase nitration would be those which are more powerful oxidizing agents than nitric acid itself. One readily available and easily volatilized substance of this

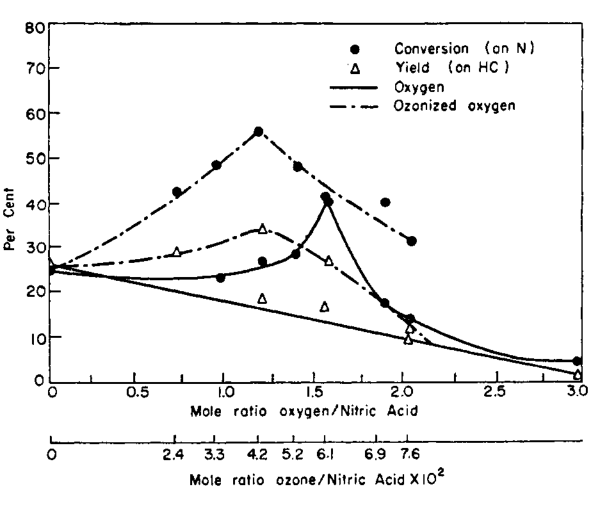

Fig. 1. Effect of adding oxygen and ozonized oxygen to the vapor-phase nitration of propane. Mole ratio propane/nitric acid 10, temperature 425°, and contact time 2.0 to 2.5 seconds

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[1] From the Ph.D. thesis of Norman W. Standish, Purdue University, January 1960.

[2] Commercial Solvents Corporation Research Assistant. Present address: The Standard Oil Company of Ohio, Cleveland, Ohio.

[3] A. V. Topchiev, *Nitration of Hydrocarbons and Other Organic Hydrocarbons*, Pergamon Press, New York, N. Y., 1959.

[4] H. B. Hass and L. G. Alexander, *Ind. Eng. Chem.*, **41**, 2266 (1949); U. S. 2,609,401 (1954).

[5] G. B. Bachman, *et al.*, *J. Org. Chem.*, **17**, 906, 914, 928, 935, 942 (1952); **21**, 465, 655 (1956); *Ind. Eng. Chem.*, **46**, 713 (1954); U. S. 2,597,698 (1952).

TABLE I

Vapor Phase Nitration of Propane

| Experiment No. | H-8 | H-49 | H-76 | H-11 | H-14 | H-108 | H-90 | H-117 |
|---|---|---|---|---|---|---|---|---|
| Temperature | 425 | 425 | 425 | 425 | 425 | 350 | 425 | 425 |
| Contact time, sec. | 2.59 | 2.80 | 2.08 | 2.26 | 2.32 | 2.25 | 2.39 | 2.04 |
| S/V, cm.$^{-1}$ | 3 | 3 | 3 | 3 | 3 | 3 | 4 | 100 |
| Reactants, mole ratio | | | | | | | | |
| $C_3H_8$ | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| $HNO_3$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| $H_2O$ | 1.05 | 1.05 | 5.32 | 1.05 | 1.05 | 1.05 | 1.05 | 1.05 |
| $H_2O_2$ | ... | ... | 0.23 | ... | ... | ... | ... | ... |
| $(CH_3)_3COOH$ | ... | 0.16 | ... | ... | ... | ... | ... | ... |
| $O_2$ | ... | ... | ... | 1.59 | 1.20 | 1.20 | ... | ... |
| $O_3$ | ... | ... | ... | ... | 0.042 | 0.042 | ... | ... |
| Ultraviolet | ... | ... | ... | ... | ... | ... | Yes | ... |
| Silent electrical discharge, 130 watts | ... | ... | ... | ... | ... | ... | ... | Yes |
| Conversion (on N), % | 24.8 | 2.0 | 18.1 | 40.0 | 56.4 | 69.8 | 24.4 | 20.9 |
| Yield (on HC), % | | | | | | | | |
| $RNO_2$ | 25.0 | 3.5 | ... | 16.7 | 32.5 | ... | 38.6 | 22.6 |
| $CO_2$ | 2.5 | 17.9 | ... | 1.9 | 2.5 | ... | 14.1 | 6.2 |
| CO | 9.6 | 17.9 | ... | 12.5 | 14.3 | ... | 11.0 | 20.3 |
| $C_3H_6$ | 28.8 | 38.8 | ... | 27.9 | 20.1 | ... | 23.1 | 32.9 |
| $C_2H_4$ | 19.3 | 16.1 | ... | 10.6 | 10.7 | ... | 7.4 | 7.8 |
| Carbonyl | 14.8 | 5.7 | ... | 30.4 | 19.9 | ... | 5.6 | 10.1 |
| Distribution $RNO_2$, % | | | | | | | | |
| $CH_3NO_2$ | 13.1 | ... | ... | 26 | 17 | 18.8 | 4.6 | 9.9 |
| $C_2H_5NO_2$ | 16.6 | ... | ... | 18 | 22 | 21.8 | 13.7 | 12.9 |
| 2-$C_3H_7NO_2$ | 33.7 | ... | ... | 9 | 16 | 20.7 | 39.7 | 30.1 |
| 1-$C_3H_7NO_2$ | 36.0 | ... | ... | 48 | 45 | 39.9 | 41.5 | 47.0 |

type is ozone. Introduction of ozonized oxygen or air into our nitration system immediately increased yields and conversions, and after careful study, led to the best nitration results ever attained in these laboratories (Table I and Fig. 1). Ozone lowers the optimum temperature of nitration from about 425° to about 350°. Relative to ordinary oxygen the ozonized oxygen produces less carbonyl compounds and less of the lower nitro alkanes.

In attempting to account quantitatively for the effects of ozone, we soon found that ozone must do more than merely increase the rate of formation of alkyl radicals. Under optimum conditions the increase in moles of nitro paraffins produced per mole of ozone introduced amounts to about 7.5, while the maximum effect predicted by the equation

$$6\ RH + O_3 \longrightarrow 6\ R\cdot + 3\ H_2O \qquad (4)$$

is 6.0, assuming (very improbably) that none of the oxygen atoms become bonded to carbon atoms. Furthermore, similar calculations show that ozone produces a decrease in carbonyl compound formation amounting to about 6.6 moles per mole of ozone. While these results are only very roughly quantitative, they suggest that part of the effectiveness of ozone is the result of a process which hinders carbonyl compound formation. We believe that this process involves the reaction of NO with hydrocarbon radicals, *e.g.*,

$$RCH_2\cdot + NO \longrightarrow RCH_2NO \qquad (5)$$

$$RCH_2NO \longrightarrow RCH{=}NOH \qquad (6)$$

$$2\ RCH{=}NOH + NO_2 \longrightarrow 2\ RCH{=}O + NO + N_2 + H_2O \qquad (7)$$

An equation similar to (7) has been proposed[6] to account for the results obtained in the reaction of benzaldoxime with nitrogen tetroxide. It will be noted that the above equations (5–7) provide a simple explanation for the inhibiting effect of nitric oxide in vapor phase nitration, which has often been observed in this laboratory. Furthermore, if it can be established that ozone removes nitric oxide from the reaction mixture, then they will also explain why ozone is more effective in promoting nitration than would be expected from its ability to produce alkyl radicals from hydrocarbons.

The oxidation of nitric oxide to nitrogen dioxide by ozone has been shown to be a very fast reaction,[7] much faster than the decomposition of nitrogen dioxide to nitric oxide and oxygen. Furthermore ozone catalyzes the oxidation of nitric oxide by oxygen, so that this also becomes a very fast reaction[7b]

$$NO + O_3 \longrightarrow NO_2 + O_2 \text{ very fast} \qquad (8)$$

$$NO_2 \longrightarrow NO + 1/2\ O_2 \text{ slow} \qquad (9)$$

$$NO + 1/2\ O_2 \xrightarrow{O_3} NO_2 \text{ very fast} \qquad (10)$$

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[6] S. S. Novikov, L. I. Khmel'nitsku, and O. V. Lebedev, *J. Gen. Chem.* (*U.S.S.R.*), **28,** 2333 (1958). See also J. H. Boyer and H. Alul, *J. Am. Chem. Soc.*, **81,** 4237 (1959).

[7] (a) H. S. Johnston and D. M. Yost, *J. Chem. Phys.*, **17,** 386 (1949); (b) T. V. Zabolotskii, *J. Gen. Chem.* (*U.S.S.R.*), **20,** 1449 (1950); (c) H. S. Johnston and J. H. Crosby, *J. Chem. Phys.*, **19,** 799 (1951); **22,** 689 (1954); (d) H. W. Ford, G. J. Doyle, and N. Endow, *J. Chem. Phys.*, **26,** 1337 (1957).

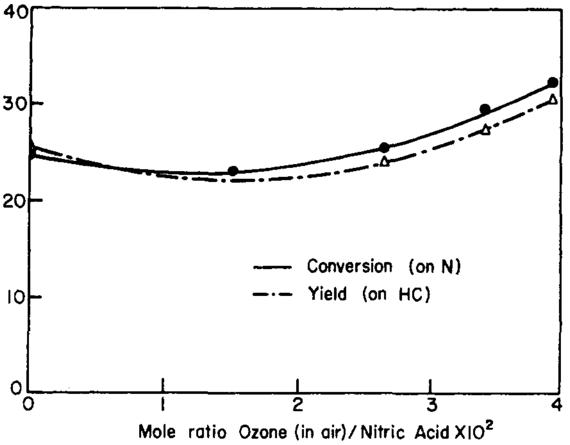

Fig. 2. Effect of adding ozonized oxygen (as air) to the vapor-phase nitration of propane. Mole ratio propane/nitric acid 10, temperature 425°, and contact time 2.0 to 2.5 seconds

The net result of these kinetic differences is that ozonized oxygen is an excellent scavenger for nitric oxide, especially in processes proceeding under non-equilibrium conditions, such as vapor phase nitration (about 2 seconds contact time).

Increased amounts of ozone give increasingly better results in nitration (Fig. 2) within the limits of concentration we were able to achieve with our ozonizer. The probable reason for this lies in reactions with hydrocarbon radicals which lower the concentration of ozone below the optimum scavenging range. We attempted to absorb considerable amounts of ozone in nitric acid (70%), but found that such a solution, saturated at ice bath temperatures, contained less than $10^{-5}$ mole per liter (by colorimetric titration with nitrogen dioxide in nitric acid). Nitric acid saturated with ozone gave only slight improvements in nitration results. We wish to call attention to the desirability of developing a method for removing oxygen selectively from an ozone-oxygen stream and so concentrating the ozone.

Ozone is extremely unstable at elevated temperatures and decomposes to oxygen atoms which may also be effective agents in promoting nitration of hydrocarbons. Oxygen atoms can be produced from oxygen molecules without the intermediate formation of ozone molecules, as, for example, by photo excitation or by silent electric discharge. It seemed desirable, therefore, to test the possibility of promoting nitration in the presence of oxygen by these forms of physical energization. Accordingly the nitration apparatus was redesigned to accommodate either a high intensity mercury arc or an electrode so placed at the center of the reactor (Fig. 3) that all of the emission from these sources passed through the hot reactants continuously. The arc and the electrode were enclosed in a quartz tube and a glass tube respectively.

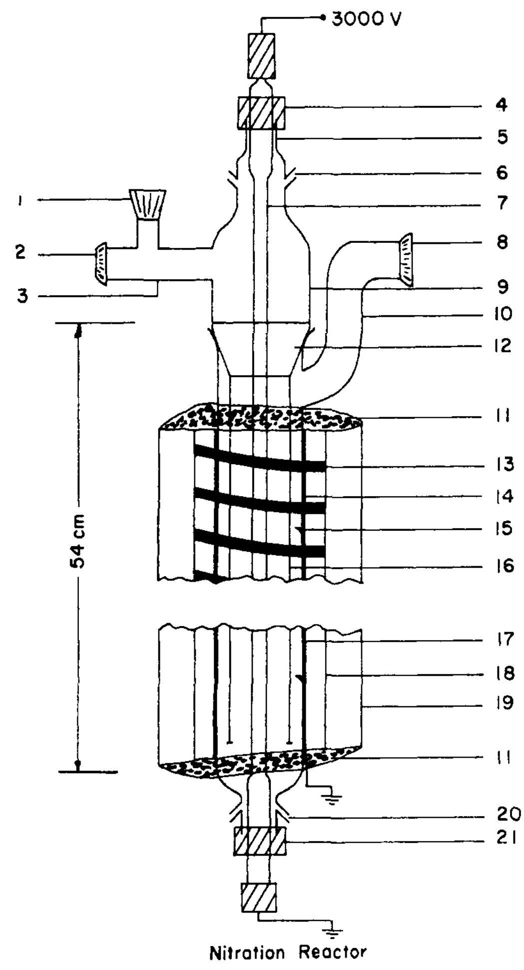

Fig. 3. 1. Outer glass joint, 10/30. 2. Inner ball joint, 18/9. 3. Pyrex glass tubing, 12 mm. O.D. 4. Tygon bushing. 5. Pyrex glass tubing, 16 mm. O.D. 6. Ball joint, 28/15. 7. Ultraviolet lamp, 6 mm. O.D. 8. Outer ball joint, 18/9. 9. Pyrex glass tubing, 22 mm. O.D. 10. Pyrex glass tubing, 12 mm. O.D. 11. Asbestos end plate. 12. Glass joint, 24/40. 13. Nichrome heating ribbon, $^{1}/_{16}$ inch, 11 feet. 14. Aluminum foil electrode. 15. Thermocouple well. 16. Pyrex glass tubing, 18 mm. O.D. 17. Pyrex glass tubing, 35 mm. O.D. 18. Pyrex glass tubing, 42 mm. O.D. 19. Pyrex glass tubing, 54 mm. O.D. 20. Ball joint, 28/15. 21. Tygon bushing

Ultraviolet irradiation lowered conversions (based on nitrating agent) slightly, raised yields (based on hydrocarbon) appreciably, decreased yields of oxidation products, and altered distributions of nitro paraffins obtained in favor of the higher molecular weight homologs. Maximum conversions occurred at 425° as in normal nitration. Nitrations with added oxygen or halogen present and nitrations using nitrogen dioxide in place of nitric acid showed similar influences. It is concluded that ultraviolet irradiation is without major beneficial effects in vapor phase nitration probably because the energy so introduced is primarily absorbed by other molecules than the oxygen, and other reactions than nitration are promoted. Thus nitro paraffins absorb at 2000–3000 Å and are converted to aldehydes,[8] nitrogen dioxide absorbs at 2200 and 2459

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[8] E. N. Hirschlaff and R. G. N. Norrish, *J. Chem. Soc.*, 1580, (1936).

Å and is converted to nitric oxide and oxygen,[9] and nitric oxide absorbs at 1860–1990 Å and is converted to nitrogen and oxygen.[10] Several Russian investigators[11] have shown that ultraviolet irradiation has little effect in the nitration of benzene, hexane, and cyclohexane using nitrogen dioxide at 60° and relatively minor effects in the nitration of toluene. Harris and Siegel[12] found no effect at 300° in nitrating methane with nitrogen dioxide, although Rohr and Noyes[13] found that ethane gave small amounts of nitroethane with nitrogen dioxide at 160°.

Ozone is customarily produced by passage of air or oxygen through a silent electric discharge at room temperature or below. In the hope of generating ozone, oxygen atoms, or some form of activated oxygen molecules, we passed electric discharges through our nitration reaction mixtures at temperatures ranging from 350° to 425°, at wattages of 25 to 250, and with oxygen and oxygen-halogen mixtures present or absent. It was found that minor changes very similar to those observed with ultraviolet irradiation occurred. Zabolotskii[7b] and others[14] have shown that neither induction discharges, high and low frequency fields, nor corona discharges accelerate the oxidation of nitric oxide when passed through mixtures of this gas with oxygen, but marked acceleration occurs when the oxygen is energized in the same way before mixing with the nitric oxide. This may explain the absence of pronounced promotional effects of silent discharges in vapor phase nitrations. On the other hand it has been reported[15] that benzene is nitrated by oxides of nitrogen in a glow discharge, although yields and other data needed for comparisons were not given. We observed that a definite glow appeared in the reactor when the silent discharge was passed through mixtures in which the nitrating agent was nitrogen dioxide. This was absent with mixtures in which the nitrating agent was nitric acid.

## EXPERIMENTAL

The general equipment and procedures described in previous papers in this series[6] were employed in this research except as noted below. The reactor (Fig. 3) consisted basically of a mixing chamber with a long throat and an electrically heated and thermostatically controlled reaction chamber surrounding the throat. The vapors passed downward through the throat and then upward through the reaction chamber and out the top. Two such reactors were used in series to obtain the necessary contact times. A third such reactor was used as a preheater for the hydrocarbon vapors. It was also used as a reactor in experiments requiring longer contact times.

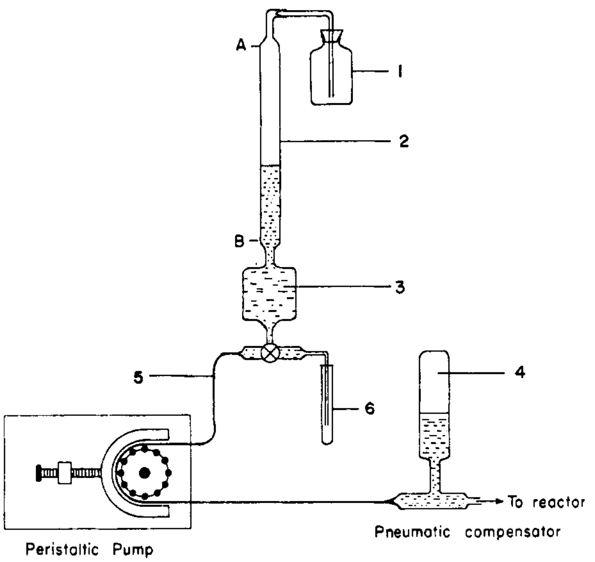

Fig. 4. Nitric acid metering system. 1. Nitric acid supply bottle, 500 ml. (polyethylene). 2. Inverted gas buret, 100 ml. 3. Nitric acid. 4. Pyrex glass tubing, 12 mm. O.D. 5. Polyethylene tubing, 1.25 mm. 6. Waste receiver

The exit gases were passed through a water-cooled condenser to collect products which were liquid at room temperatures and then through two Dry Ice condensers to remove other condensible products. The remaining gases were measured volumetrically through a wet test meter (Precision Scientific Company, Chicago, Ill.) and then collected over a 10% sulfuric acid solution saturated with sodium sulfate for analysis, or vented as desired.

In the experiments with ultraviolet irradiation a specially designed high intensity, quartz tube mercury vapor arc lamp (Engelhard Industries Inc., Newark, N. J.) was inserted through the center of the reactor and extended out the top and out the bottom for the electrical connections. Its dimensions were 76.2 × 0.6 cm., and it was operated on a 3000 v., 30 ma. current provided by a high capacitance transformer. In experiments with silent electric discharge a center electrode of No. 24 copper wire encased in a 6 mm. glass tube was similarly inserted through the center of the reactor. The external electrode consisted of a 3 × 50 cm. copper strip extended lengthwise along the outside wall of the reactor, the whole being wrapped with aluminum foil and held in place with copper wire. These electrodes were connected to a 25,000 v. transformer (Thordarson Electric Manufacturing Company, Chicago, Ill.) whose wattage could be varied. During these latter experiments the space between the throat and the reactor casing was packed with glass helices to prevent electrical breakdown of the reaction chamber walls.

Nitric acid was metered through a system (Fig. 4) consisting of an inverted gas buret, polyethylene tubing, peristaltic action pump (American Instrument Company, Silver Springs, Md.), and a pneumatic pulse-compensator. The pump could be set to deliver from 0.2 to 25 ml. per minute. Gaseous reactants were metered through Precision Bore Flowrator Tubes (Matheson Company, East Rutherford, N. J.) of suitable sizes. Ozone was produced with a Welsbach T-23 ozonator (The Welsbach Corporation, Philadelphia, Pa.). The ozone content was measured by

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(9) R. G. N. Norrish and R. G. Griffiths, *Proc. Roy. Soc.*, **139A**, 147 (1933).

(10) J. Y. MacDonald, *J. Chem. Soc.* 1, (1928).

(11) P. D. Shorigin and A. Topchiev, *Ber.*, **67B**, 1362 (1934): A. I. Titov and A. N. Boryshnikova, *J. Gen. Chem.* (*U.S.S.R.*), **6**, 1855 (1936); *Chem. Abstr.*, **31**, 4286 (1937).

(12) L. Harris and B. M. Siegel, *J. Am. Chem. Soc.*, **63**, 2520 (1941).

(13) T. M. Rohr and W. A. Noyes, Jr., *Can. J. Chem.*, **33**, 843 (1955).

(14) N. Kobozev, M. Temkin, and S. Fraiberg, *J. Gen. Chem.* (*U.S.S.R.*), **3**, 534 (1933).

(15) D. Avanesov and I. Vyalskin, *Khim. Referat. Zhur.*, **2**, No. 5, 43 (1939); *Chem. Abstr.*, **34**, 2262 (1940).

passing the gas into a saturated potassium iodide solution, acidifying, and then titrating with standard thiosulfate solution to a starch endpoint. Minor liquid reactants, such as the organic peroxides, were vaporized into a bypassed fraction of the hydrocarbon stream and were metered by controlling the temperature of the container according to previously prepared calibration curves. Hydrogen peroxide was introduced directly into the reactor throat as a liquid and was metered through a calibrated capillary and the flow rate controlled by varying the air pressure on the liquid in a closed container.

Product analysis was done for carbonyl compounds (in each layer), nitro paraffins (total nitrogen by the Kjeldahl method, distribution by gas chromatographic and mass spectrographic methods), strong acid, weak acid, and the gases carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, ethylene, and propylene (in an Orsat absorption apparatus) as previously described.[5]

Some 134 nitration experiments were completed and form the basis for the conclusions drawn in the discussion part of this paper. However, only a few pertinent data are included in Table I to illustrate the effects observed.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IDAHO STATE COLLEGE AND AVERY LABORATORY, THE UNIVERSITY OF NEBRASKA]

# The Reaction of *N*-Bromosuccinimide with *p*-Bromophenyl Benzyl Ether[1]

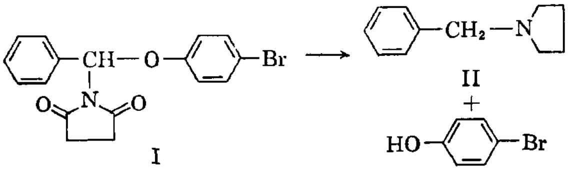
LOREN L. BRAUN[2] AND J. H. LOOKER

*Received May 23, 1960*

*p*-Bromophenyl benzyl ether, on treatment with an equimolar quantity of *N*-bromosuccinimide, yields a small amount of DL-*N*-$\alpha$-(*p*-bromophenoxy)benzylsuccinimide. A structure proof of the latter compound is presented. Yields are increased by increasing the molar ratio of *N*-bromosuccinimide to *p*-bromophenyl benzyl ether, provided bromine is distilled from the reaction mixture. A mechanism for the reaction is proposed.

Although bromination with *N*-bromosuccinimide has been the subject of numerous investigations,[3] both from the standpoint of its mechanism and its synthetic utility, only a few studies[4] have reported the isolation of succinimidyl derivatives from the products of the reaction. A recent study on the synthesis of aldehydes from benzyl ethers by Markees[5] has reported the formation of DL-*N*-$\alpha$-methoxy-*p*-nitrobenzylsuccinimide from *N*-bromosuccinimide and *p*-nitrobenzyl methyl ether. In the present investigation, a similar starting material, *p*-bromophenyl benzyl ether, has yielded DL-*N*-$\alpha$-(*p*-bromophenoxy)benzylsuccinimide(I). This unexpected product was obtained in small yield (*ca.* 5%), along with benzaldehyde[6] and a copious evolution of hydrogen bromide, when the reaction was carried out in carbon tetrachloride, under reflux, with an equimolar ratio of *N*-bromosuccinimide to ether.

Evidence for the structure of I was provided by elementary analysis, molecular weight determination, infrared spectrum (with an imide carbonyl peak at 1700 cm.$^{-1}$), and degradative reduction studies.[7] Lithium aluminum hydride reduction resulted in the formation of *N*-benzylpyrrolidine (II, isolated as the picrate) and *p*-bromophenol (III, isolated as the *N*-$\alpha$-naphthylcarbamate). Thus both the fact that a succinimidyl group has been incorporated into the molecule, and that its point of attachment is at the *alpha* carbon atom by



I II III

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(1) This investigation was supported in part by a research grant (E-1703) from the National Institute of Allergic and Infectious Diseases, Public Health Service.

(2) Department of Chemistry, Idaho State College, Pocatello, Idaho.

(3) Several reviews of the reactions of *N*-bromosuccinimide have appeared in the literature. See (a) L. Horner and E. H. Winkelmann, *Angew. Chem.*, **71**, 149 (1959); (b) C. Djerassi, *Chem. Rev.*, **43**, 271 (1948); (c) W. Ringli, *Bromierungen mit Bromsuccinimid*, Leeman, Zurich, 1948; (d) T. D. Waugh, *NBS, Its Reactions and Uses*, Boulder, Colo., Arapahoe Chemicals, Inc., 1951; (e) N. P. Buu-Hoï, *Record Chem. Prog.*, **13**, 30 (1952).

(4) (a) H. L. Dryden, Jr., and Bill E. Burgert, *J. Am. Chem. Soc.*, **77**, 5633 (1955) have obtained *N*-(cyclohepta-2,4,6-trienyl)succinimide in high yield from *N*-bromosuccinimide and cycloheptatriene. (b) D. R. Howton, *J. Am. Chem. Soc.*, **69**, 2060 (1947) and (c) E. R. Buchman and D. R. Howton, *J. Am. Chem. Soc.*, **70**, 2517 (1948) have reported the formation of *N*-phenylsuccinimide when methylenecyclobutane is brominated with *N*-bromosuccinimide in benzene solution. Also (d) H. Schmid and P. Karrer, *Helv. Chim. Acta*, **29**, 573 (1946) and (e) H. Schmid and W. E. Leutenegger, *Helv. Chim. Acta*, **30**, 1965 (1947) have observed the formation of bromo- derivatives of 9-succinimidyl acridine on the reaction of *N*-bromosuccinimide with acridine.

(5) D. G. Markees, *J. Org. Chem.*, **23**, 1490 (1958).

(6) The formation of aldehydes on the treatment of benzyl ethers with *N*-bromosuccinimide was reported by M. Okawara, H. Sato, and E. Imoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, **58**, 924 (1955). Their observation that phenyl ethers are brominated in the *para* position by *N*-bromosuccinimide has also been confirmed by our conversion of phenyl benzyl ether to *p*-bromophenyl benzyl ether (45% yield).

(7) Several attempts at cleavage by hydrogenation with a palladium on charcoal catalyst at various temperatures and pressures failed to yield a pure isolable product.