gave straight lines in each case. The slopes of the lines were 0.079, 0.0481, 0.55 and 0.0604 v., respectively. These results are in essential agreement with the theoretical slope of 0.059 v. (25°) for a reversible potential-determining reaction involving one electron.

## Experimental

The current–voltage curves were determined manually by means of a Fisher Elecdropode after removing dissolved air in the usual way with tank nitrogen. All measurements were made in a thermostat at 25 ± 0.1°. The dropping mercury electrodes used had the following characteristics. Capillary no. 1 at a pressure of 64.5 cm. of mercury, had a drop time of 4.1 seconds in 0.1 *N* potassium chloride (open circuit). The value of *m* was 1.47 mg. sec.$^{-1}$ with a calculated value of $m^{2/3}t^{1/6}$ of 0.669 mg.$^{2/3}$-sec.$^{-1/2}$. Capillary no. 2 at a pressure of mercury of 64.5 cm., had a drop time of 3.9 seconds in 0.1 *N* potassium chloride (open circuit). The value of *m* was 1.84 mg.-sec.$^{-1}$ with a calculated value of $m^{2/3}t^{1/6}$ of 0.800 mg.$^{2/3}$-sec.$^{-1/2}$.

Experiments were carried out in the same manner as has been described in previous work.[7]

**Materials.**—The solutions used had the following compositions and anode potentials[10]: 0.175 *M* tetrabutylammonium iodide, 75% dioxane, anode potential −0.485 volt; 0.175 *M* tetrabutylammonium iodide, 0.052 *M* tetrabutylammonium hydroxide, 75% dioxane, anode potential, −0.590 volt. Stilbene, 1,1-diphenylethylene and fluoranthene were obtained from stock. Dimethylfulvene,[11] diphenylfulvene,[11] dimethylbenzofulvene,[12] diphenylbenzofulvene,[12] benzalfluorene,[8] furfuralfluorene,[8] 9,9′-difluorenyl,[8] biphenylenediphenylethylene,[5] 9-benzhydrylfluorene,[5] cinnamylidenefluorene,[13] γ-phenylpropylidenefluorene,[14] 1-fluorenyl-2-benzylethylene[14] and dibiphenyene-ethylene[15] were prepared by appropriate methods given in the literature.

Triphenylmethyl was prepared in the following manner. To an air-free, dry solution of dioxane containing a few cc. of mercury, triphenylmethyl chloride was added. The resulting mixture was shaken vigorously for fifteen minutes. The yellow solution of triphenylmethyl thus formed was added to an air-free solution of tetrabutylammonium iodide in water. These two substances were present in such amounts that the resulting solution was 0.175 *M* tetrabutylammonium iodide in 75% dioxane. After each analysis air was introduced into the solution and the solution analyzed. The introduction of air caused the yellow color of the free radical to disappear and formed free iodine. Analysis of the resulting solution indicated that the first and third waves originally observed had disappeared. This behavior points conclusively to the presence of triphenylmethyl in solution. The second wave is probably due to the presence of the peroxide. A similar behavior was observed using solid triphenylmethyl prepared by the method of Conant.[16]

## Summary

A polarographic study has been made of olefins which dimerize when treated with sodium.

Most of the compounds investigated were found to dimerize according to the mechanism proposed by Ziegler.

Fluoranthene and cinnamylidenefluorene were found to dimerize according to the mechanism proposed by Schlenk.

Dibiphenylene-ethylene was found to behave like a diradical.

---

[10] Values given in previous work[7] are in error, but the final half-wave potentials are correct.

[11] Thiele, *Ber.*, **33**, 672 (1900).

[12] Thiele and Merck, *Ann.*, **415**, 266 (1918).

[13] Whitby and Katz, THIS JOURNAL, **50**, 1168 (1928).

[14] Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 123 (1928).

[15] Schmidt and Wagner, *Ber.*, **43**, 1796 (1910).

[16] Conant, Small and Taylor, THIS JOURNAL, **47**, 1959 (1925).

IOWA CITY, IOWA RECEIVED JULY 8, 1946

---

[CONTRIBUTION FROM THE VISKING CORPORATION]

# Nitroölefins by the Vapor Phase Catalytic Cleavage of Esters of Nitro Alcohols

BY MARVIN H. GOLD

In the course of certain investigations in these laboratories, it became necessary to produce kilogram lots of several α,β-unsaturated nitroölefins. Since these were relatively large laboratory preparations, a simple and efficient process of preparation was required.

A number of methods appear in the literature for the preparation of the lower molecular weight nitroölefins. Thus, nitroethylene[1] was first made by dehydrating 2-nitroethanol with sodium bisulfate or phosphorus pentoxide. Similarly 1-chloro-1-nitroethylene[2] was synthesized by heating 2-chloro-2-nitroethanol with phosphorus pentoxide at 170°. The same authors also treated 2-chloro-2-nitroethyl nitrate with sodium bicarbonate in refluxing ether to give the chloro nitroethylene. Schmidt and Rutz[3] used this latter principle in preparing nitroölefins and chloro nitroölefins. They synthesized a number of these compounds, from the nitropropenes through to the nitroöctenes. Their reactions were conducted by refluxing the acetate esters of the nitro alcohols with an ether suspension of potassium bicarbonate. This reaction operated efficiently but the yields of lower molecular weight nitroölefins were sharply decreased by polymerization. Other means of preparation have been described. Thus Haitinger[4] showed that the action of nitric acid on tertiary alcohols gave rise to branched chain nitroolefins. This work was amplified by Bouveault and Wahl[5] who show that highly branched olefins are nitrated under anhydrous conditions to give branched nitroölefins. The authors[6] also prepared

---

[1] Wieland and Sakellarios, *Ber.*, **52B**, 898 (1919); **53B**, 201 (1920).

[2] Wilkendorf and Trenal, *ibid.*, **57B**, 306 (1924).

[3] Schmidt and Rutz, *ibid.*, **61B**, 2142 (1928).

[4] Haitinger, *Ann.*, **193**, 366 (1878).

[5] Bouveault and Wahl, *Bull. soc. chim.*, [3] **25**, 910 (1901); [3] **29**, 517 (1903).

[6] Bouveault and Wahl, *Comp. rend.*, **134**, 1227 (1902); *Bull. soc. chim.*, [3] **29**, 643 (1903).

a few primary nitroölefins by dehydration of the corresponding nitro alcohol with zinc chloride.

In the past few years a number of patents have been issued on the preparation of various nitroolefins. Schwarz and Nelles[7] claim to be able to produce good yields of nitroölefins by heating acylated esters of nitro alcohols with catalytic quantities of mildly alkaline agents, under reduced pressure. The nitroölefin and acid thus distil from the reaction mixture as they are formed. Hasche[8] claims a process whereby formaldehyde and a nitroparaffin are condensed over a catalyst in the vapor phase to produce nitroölefins directly. Still another group of patents[9] claim that $\alpha,\beta$-dinitroparaffins and nitrate esters of $\beta$-nitro alcohols when refluxed with alcohols give the nitroolefins and inorganic esters of the alcohol used as reaction medium.

In this Laboratory it has been found that acetate esters of $\beta$-nitro alcohols, and $\beta$-chlorinated nitroparaffins undergo cleavage in the vapor phase. These reactions are illustrated by the equations.

$$\text{(a)}\quad CH_3CO{-}O{-}CH_2CH_2NO_2 \xrightarrow{\Delta H} CH_3COOH + CH_2{=}CHNO_2$$

$$\text{(b)}\quad ClCH_2CH_2NO_2 \xrightarrow{\Delta H} HCl + CH_2{=}CHNO_2$$

The exception to this reaction, of course, occurs in those cases where the nitro group is tertiary and no hydrogen is available for elimination of the acid.

Although a straight vapor-phase pyrolysis gives fairly good yields it was deemed advisable to find some catalysts which would lower the cleavage temperature and increase both the yields and conversions. A number of such satisfactory catalysts have been found. In addition to those shown in Figs. 1 and 2, aluminum phosphate and silica gel have been found to have good activity. It will be noted that the most efficient catalysts are neutral salts of alkaline earths and mineral acids. Compounds which are alkaline in nature (such as activated alumina or sodium acetate deposited on pumice) caused a great deal of gasification, thereby lowering the yields considerably.

For the preliminary trials to determine the best catalysts 2-nitrobutyl-1 acetate was chosen. This compound is obtained by esterification of the commercially available 2-nitro-1-butanol.[10]

It was found that a substance which showed high catalytic activity for one nitro compound, was generally of similar activity for all the others. However, the compounds containing a primary nitro group were more temperature sensitive than those containing a secondary nitro group. Thus, the optimum cleavage temperature for a primary nitro ester would be about 50° lower than for a secondary nitro ester.

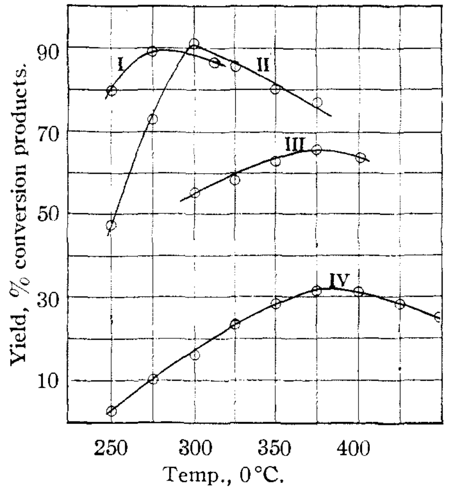

Fig. 1.—Pyrolysis of 2-nitro-1-butyl acetate: catalysts used; I, 90% Ca–10% Mg phosphates; II, $CaSO_4$; III, $CaCl_2$; IV, $CaCO_3$.

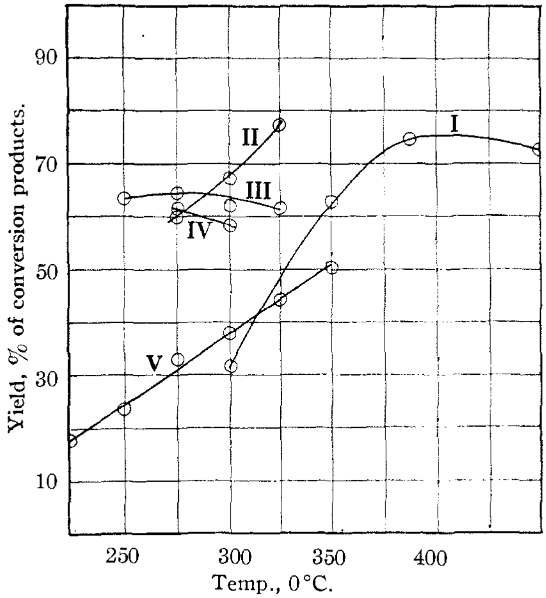

Fig. 2.—Pyrolysis of 2-nitroethyl acetate: catalysts used; I, glass beads; II, $Al_2(SO_4)_3$; III, $CaSO_4$; IV, $AlPO_4$; V, 20% $Al_2(SO_4)_3$ on pumice.

The preparation of nitroölefins by this method has several advantages:

1. The method gives high yields and conversion.
2. Relatively large quantities of nitroölefins can be obtained in a short time.
3. The reaction can be operated either continuously or intermittently.
4. The catalyst is easily regenerated by burning out with an air stream.
5. The lower molecular weight nitroölefins are not exposed for long periods to polymerizing

---

[7] Schwarz and Nelles, U. S. Patent 2,257,980.

[8] Hasche, U. S. Patent 2,298,375.

[9] Smith, Scaife and Stanley, U. S. Patents 2,384,050 and 2,385,111.

[10] Purchased from Commercial Solvents Corp., Terre Haute, Ind.

influences. In fact, they are obtained in equimolar mixture with acids, which inhibit their polymerization. Thus, the distilled acid–nitroölefin mixture may be stored in a refrigerator for extended periods and be separated just before use.

## Experimental

**Apparatus.**—The pyrolysis unit consisted of a vertically mounted Hevi Duty tubular electric furnace, which was thermostatically controlled by a Wheelco "Capacitrol" instrument. The pyrolysis chamber was a 1-in. Pyrex tube with a male standard taper at the bottom leading to an air condenser, followed by a water condenser and receiver. The catalyst was supported by means of indentations in the lower part of the tube. Above the catalyst portion the tube was packed with glass beads to act as a heat transfer medium. In operation a stream of nitrogen gas at the rate of 200 cc./min. was kept flowing through the system, while the nitro ester was dropped in at the top. At the completion of the addition the system was swept through with a rapid stream of nitrogen until no more vapors were condensed. Then the temperature of the furnace was raised to about 400 to 450° and the catalyst "burned out" with a stream of air.

**Catalysts.**—The catalysts which were tried were used in their regular commercial form wherever available. Thus, the calcium carbonate was a good grade of marble chips. The calcium chloride was regular anhydrous 4 to 8 mesh drying reagent. The calcium sulfate was 4 to 6 mesh Drierite.

The 90% calcium-10% magnesium phosphate catalyst was prepared in the following manner: A solution of 200 g. of anhydrous calcium chloride and 19 g. of anhydrous magnesium chloride in 300 cc. distilled water was acidified with 90 cc. of 85% phosphoric acid. The resulting warm suspension was treated with ammonium hydroxide to a phenolphthalein end-point to neutralize the liberated hydrochloric acid. The resulting mixed precipitate of ammonium chloride and calcium and magnesium phosphates was separated by filtration, placed in a large evaporating dish and dried in an oven at 100°. The cake was then broken up into large pieces and ignited on a wire gauze over a Meker burner. When most of the ammonium chloride had been volatilized a hard product of porous structure remained. These large pieces were crushed to smaller size and the ignition was completed in an electric muffle at cherry red heat.

A 20% aluminum sulfate on pumice catalyst was prepared by stirring 61.5 g. of 3 to 8 mesh pumice into a solution of 24 g. of aluminum sulfate octadecahydrate in 30 cc. of distilled water. The mixture was heated with constant stirring in an evaporating dish until dry. Then it was placed in a pyrolysis tube in the furnace and heated to 450° while passing a constant stream of air through the mass. After holding at 450° for twenty minutes the furnace was allowed to cool and the catalyst was ready for use.

A solid aluminum sulfate catalyst was prepared by adding 133.5 g. of anhydrous aluminum chloride to a solution of 198 g. of ammonium sulfate in 375 cc. of distilled water. The well-stirred solution was evaporated to dryness. The dry cake was then broken up into large pieces and ignited in an electric muffle at 400 to 600° to volatilize out the ammonium chloride. This left a very porous aluminum sulfate which was then broken to proper size and the fine particles removed by screening.

The aluminum phosphate catalyst was prepared by adding 114.5 g. (1 mole) of 85% phosphoric acid to a solution of 241.5 g. (1 mole) of aluminum chloride hexahydrate in 150 cc. distilled water. This well-stirred solution was then neutralized by the careful addition of 225 cc. of concentrated ammonia, to give a thick gelatinous precipitate. The precipitate was separated by filtration, spread out in an enameled pan, and dried in an oven at 100°. The resulting hard cake was then heated on a wire gauze over a Meker burner to remove occluded ammonium chloride by volatilization. The ignition was finally completed at about 600° in the electric muffle. This gave a light porous material which was broken to size for use as a catalyst.

**Preparation of Reagents.**—The acetate esters were all prepared according to the method of Tindall.[11] Nitroethanol was prepared by the method of Gorski and Makarov[12] using a 10 to 1 molar ratio of nitromethane to paraformaldehyde. The two nitropropanols were prepared by the general method of Hass and Vanderbilt.[13] 2-Chloronitroethane and 1-chloro-2-nitropropane were special preparations obtained from Prof. E. T. McBee, Purdue University.

The data shown in Figs. 1 and 2 were obtained by packing the reaction tube with 50 cc. of catalyst and filling the remainder of the tube with glass beads. Then when the furnace had come to equilibrium at the desired temperature 25 cc. of nitro compound was dropped into the tube over a period of twenty-five to thirty minutes. After the completion of the pyrolysis, the liquid condensate was distilled under reduced pressure to give two fractions. The first fraction consisted mainly of an equal molar mixture of acetic acid and the nitroölefin. The second fraction was the unchanged ester. The points on the curves indicate the per cent. of fraction I obtained, based on the quantity of starting material. In addition to the pyrolysis plotted in Figs. 1 and 2, the results of a miscellaneous group of runs are listed in Table I.

TABLE I

| Nitro ester | Catalyst | Temp., °C. | %, yield |
|---|---|---|---|
| 1-Nitropropyl-2 acetate | Mixed 90% Ca<br>10% Mg phosphates | 285 | 79 |
| 2-Nitropropyl-1 acetate | | 285 | 85 |
| 1-Chloro-2-nitropropane | Silica gel | 325 | 51 |
| 2-Chloro-1-nitroethane | Calcium chloride | 250 | 26.5 |
| 2-Chloro-1-nitroethane | Calcium carbonate | 275 | 15.8 |
| 2-Chloro-1-nitroethane | Calcium carbonate | 300 | 20.2 |
| 2-Chloro-1-nitroethane | Calcium carbonate | 375 | 27 |
| 2-Chloro-1-nitroethane | Calcium carbonate | 400 | 30 |
| 2-Chloro-1-nitroethane | Calcium carbonate | 450 | 7 |

A number of large batch pyrolyses were made using the 2-nitrobutyl-1 acetate over calcium sulfate catalyst. In these cases the nitrobutene was separated from the acetic acid by washing with several portions of saturated salt solution and finally with bicarbonate, the resulting oily fraction boiled constantly over a range of 56–58° (50 mm.).

*Anal.* Calcd. for $C_4H_7NO_2$: N, 13.86. Found: N, 13.25.

## Summary

A means is described for the preparation of conjugated nitroölefins by the vapor phase cleavage of esters of $\beta$-nitro alcohols.

The types and preparation of materials which may act as catalytic agents to produce nitroölefins are described.

CHICAGO, ILLINOIS RECEIVED AUGUST 19, 1946

---

(11) Tindall, *Ind. Eng. Chem.*, **33**, 65 (1942).

(12) Gorski and Makarov, *Ber.*, **67B**, 996 (1934).

(13) Hass and Vanderbilt, *Ind. Eng. Chem.*, **32**, 34 (1940).