

275. *Mechanism of Reduction of Ethylenic Bonds by Hydrazine.*

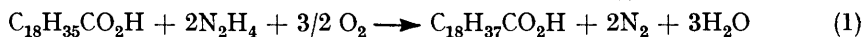
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Stoichiometric data show that two molecules of hydrazine are required to reduce one double bond. According to kinetic and conductometric measurements, a non-ionic oxidation product of the hydrazonium ion is the effective reducing agent of ethylenic bonds. It is suggested that the hydrazonium ion is oxidised to protonated di-imide which gives up its proton to undissociated hydrazine, forming an equivalent mixture of *syn*- and *anti*-di-imide, and that only the *syn*-isomer reacts with the double bond.

Oxidation of hydrazine can be made to follow first-order kinetics, and rate constants were obtained for different alcoholic solvents.

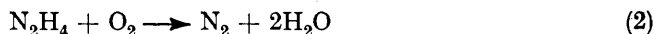
HYDRAZINE reduces ethylenic compounds only in the presence of oxygen.¹ The reaction products consist of the saturated compound, nitrogen, and water. The relationship between the utilised hydrazine and the reduced olefin depends on the supply of oxygen. With high rates of supply, direct oxidation of hydrazine tends to predominate over the hydrogenation of double bonds.

A study has been made of the stoichiometry of the reduction of oleic acid by hydrazine in alcoholic solution. Under conditions of mild aeration, exactly two molecules of hydrazine were required to reduce one double bond (see Table 1). Taking into consideration the nature of the products, the following expression may be written to illustrate the overall stoichiometry:



The validity of expression (1) has been confirmed by a series of closed-system experiments in which the nitrogen liberated and oxygen utilised were measured, together with the changes in the oleic acid and hydrazine concentrations (see Table 2).

The direct oxidation of hydrazine may be represented by:



The ratio of used oxygen to reacted oleic acid shows, in most cases, a slightly higher

¹ Aylward and Sawistowska, *Chem. and Ind.*, 1961, 433.

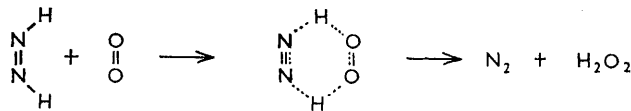
TABLE 1.
Relation between reacted hydrazine and oleic acid in mechanically-stirred mixtures in open vessels at 50°.

Expt.	Reaction time (hr.)	Original oleic acid (mol.)	Original hydrazine (mol.)	Reacted oleic acid (mol.)	Reacted hydrazine (mol.)	Reacted hydrazine / Reacted oleic acid
1	3	0.0209	0.0507	0.0127	0.0253	1.99
2	4	0.0209	0.0507	0.0151	0.0289	1.92
3	5	0.0209	0.0507	0.0161	0.0279	1.76
4	6	0.0209	0.0507	0.0166	0.0308	1.86
5	7	0.0209	0.0507	0.0167	0.0330	1.98
6	8	0.0209	0.0507	0.0171	0.0361	2.11
7	1	0.0212	0.0527	0.0084	0.0211	2.52
8	1	0.0424	0.1054	0.0210	0.0500	2.38
9	2	0.0212	0.0527	0.0104	0.0220	2.19
10	3	0.0212	0.0527	0.0127	0.0258	2.03
11	4	0.0212	0.0527	0.0145	0.0304	2.09
12	5	0.0212	0.0527	0.0153	0.0310	2.03
13	6	0.0212	0.0527	0.0153	0.0304	1.99
14	8	0.0212	0.0527	0.0147	0.0336	2.29

TABLE 2.
Reduction of oleic acid by hydrazine in mechanically-shaken closed vessels at 18° (quantities in mol.).

	1	2	3	4	5	6	7	8	9
(i) Original hydrazine	0.0140	0.0168	0.0312	0.0815	0.0647	0.1010	0.0732	0.1070	0.0394
(ii) Reacted hydrazine by expt.	0.0084	0.0108	0.0147	0.0386	0.0274	0.0460	0.0275	0.0402	0.0184
(iii) Liberated nitrogen	0.0081	0.0098	0.0147	0.0400	0.0268	0.0450	0.0278	0.0422	0.0182
(iv) Original oleic acid	0.0063	0.0083	0.0153	0.0400	0.0318	0.0503	0.0364	0.0532	0.0194
(v) Reacted oleic acid by expt.	0.0022	0.0035	0.0055	0.0162	0.0114	0.0130	0.0082	0.0140	0.0076
(vi) Original oxygen	0.0226	0.0226	0.0226	0.0443	0.0443	0.0443	0.0443	0.0443	0.0443
(vii) Reacted oxygen by expt.	0.0073	0.0086	0.0129	0.0342	0.0239	0.0392	0.0241	0.0340	0.0174
(viii) Hydrazine reacted in (1) = 2 (v)	0.0044	0.0070	0.0110	0.0324	0.0228	0.0260	0.0164	0.0280	0.0152
(ix) Hydrazine reacted in (2) = oxygen reacted in (2) = (ii) - (viii)	0.0040	0.0038	0.0037	0.0062	0.0046	0.0200	0.0111	0.0122	0.0032
(x) Oxygen reacted in (1) = (vii) - (ix)	0.0033	0.0048	0.0092	0.0280	0.0193	0.0192	0.0130	0.0218	0.0187
(xi) $\frac{\text{Oxygen reacted in (1)}}{\text{Reacted oleic acid}}$	1.50	1.37	1.67	1.73	1.69	1.48	1.59	1.56	1.87

value than the 3/2 predicted in reaction (1). The higher values were probably due to the formation of hydrogen peroxide. Small quantities of hydrogen peroxide are always formed during the oxidation of hydrazine,² possibly by the interaction of a di-imide molecule with oxygen:



In a closed system this reaction is more favoured than in an open system as, unlike in the reaction $2\text{N}_2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{N}_2 + \text{H}_2\text{O}$, no change in the volume of the gaseous components of the system is involved.

Rao³ and Scholfield and his co-workers⁴ reported that there is no *cis* \longrightarrow *trans* or

² Gilbert, *J. Amer. Chem. Soc.*, 1929, **51**, 2744.

³ Rao, *J. Sci. Ind. Res., India*, 1958, **17**, B, 204.

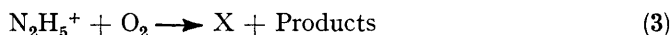
⁴ Schofield, Jones, Nowakowska, Selke, and Dutton, *J. Amer. Oil Chemists' Soc.*, 1961, **38**, 208.

positional isomerisation during the hydrogenation of linolenic acid with hydrazine hydrate. This implies that both hydrogen atoms add to the double bond simultaneously, and they most likely come from the same molecule of the transfer agent. Our study of the kinetics of the hydrogenation step has confirmed these suggestions.

Reduction of neutral ethylenic compounds by hydrazine hydrate is extremely slow. The reaction rate can, however, be considerably increased by the presence of a carboxyl group,^{5a} provided that the solution remains alkaline. Measurements of the conductance of alcoholic hydrazine solutions, in the presence or absence of weak carboxylic acids, indicate that hydrazine salts of such acids are ionised to a much greater extent than hydrazine itself.^{5b} This suggests that the reaction proceeds through the hydrazonium ion and not the hydrazine molecule.

A study of the decomposition of hydrazine provided evidence that an oxidation product of the hydrazonium ion is the effective reducing agent of the ethylenic bond. Fig. 1 shows that hydrazine alone is oxidised very slowly, whereas in the presence of a carboxyl group the rate is considerably increased, whether the ethylenic compound is present or not.

The reaction stages from the oxidation of the hydrazonium ion to the formation of the active intermediate can be summarised as follows:



Consider the kinetics of the two steps in which X is a reactant. For mathematical consideration the rate of reaction (3) is denoted as v_3 , and this represents the velocity of formation of X.

$$v_3 = dx/dt \simeq \Delta x/\Delta t$$

The rate of hydrogenation of the double bond is

$$v_4 = k_4[\text{X}]^m[\text{CH}:\text{CH}] = d[\text{CH}_2\cdot\text{CH}_2]/dt \simeq \Delta[\text{CH}_2\cdot\text{CH}_2]/\Delta t \quad (4)$$

The concentration of oxygen was kept approximately constant, hence the rate of oxidation of X may be expressed as follows:

$$v_5 = k_5[\text{X}]^n = k_6[\text{X}]^n[\text{O}_2] \quad (5)$$

From eqn. (4)

$$\text{X}^m = \Delta[\text{CH}_2\cdot\text{CH}_2]/k_4\Delta t[\text{CH}:\text{CH}] \quad (6)$$

Steady-state conditions were assumed, *i.e.*, that X reacts as soon as it is formed, so that

$$v_5 = v_3 - v_4 \simeq \{\Delta x - \Delta[\text{CH}_2\cdot\text{CH}_2]\}/\Delta t$$

From eqn. (5),

$$\text{X}^n = v_5/k_5 \simeq \{\Delta x - \Delta[\text{CH}_2\cdot\text{CH}_2]\}/k_5\Delta t \quad (7)$$

Taking logarithms and relating eqns. (6) and (7),

$$n \log\{\Delta[\text{CH}_2\cdot\text{CH}_2]/k_4\Delta t[\text{CH}:\text{CH}]\} = m \log\{\{\Delta x - \Delta[\text{CH}_2\cdot\text{CH}_2]\}/k_5\Delta t\} \quad (8)$$

The samples were collected at equal time intervals and, therefore, a plot of $\log\{\Delta[\text{CH}_2\cdot\text{CH}_2]/[\text{CH}:\text{CH}]\}$ against $\log\{\Delta x - \Delta[\text{CH}_2\cdot\text{CH}_2]\}$ ought to give a straight line. This condition was not fulfilled when values of $-\Delta\text{N}_2\text{H}_4$ were taken as Δx .

If two molecules of hydrazine produce only one molecule of X, Δx is equal to $-\frac{1}{2}\Delta\text{N}_2\text{H}_4$. By substituting the values of $-\frac{1}{2}\Delta\text{N}_2\text{H}_4$ for Δx it was found that the numerical value of the expression $\{\Delta x - \Delta[\text{CH}_2\cdot\text{CH}_2]\}$ remained practically constant in the course of each

⁵ Aylward and Sawistowska, *Chem. and Ind.*, (a) 1961, 404; (b) 1962, 484.

TABLE 3.

Summary of data from kinetic experiments on the reduction of oleic acid with hydrazine at 50°.

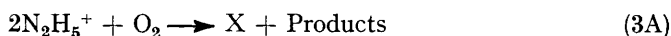
Expt. no.	Original oleic acid (mol.)	Original hydrazine (mol.)	Oxygen rate (ml./l.)	Alkalinity *	$10^3 k_5$ (mol./l. min.)
1	0.271	0.405	600	8.2	0.338
2	0.204	0.484	600	8.3	0.395
3	0.235	0.528	600	8.3	0.384
4	0.278	0.517	600	8.5	0.461
5	0.271	0.518	800	8.5	0.499
6	0.230	0.466	600	8.6	0.630
7	0.248	0.498	600	8.7	0.499
8	0.314	0.812	600	9.0	0.595
9	0.260	0.738	700	9.2	0.990
10	0.312	0.882	700	9.3	0.845
11	0.234	0.980	600	9.5	2.400
12	0.295	1.167	600	9.5	2.400
13	0.312	1.114	600	9.4	2.885
14	0.297	1.178	700	9.5	2.690
15	0.168	1.068	600	9.8	3.485

* The actual pH-meter readings, which have no absolute meaning in a non-aqueous solution.

experiment. It follows that $n = 0$, *i.e.*, the rate of oxidation of X is independent of its concentration. The correct expression for the rate is, therefore:

$$v_5 = k_5 = k_6[\text{O}_2] \quad (5A)$$

Eqn. (3) is modified to:



As two molecules are required to reduce one double bond, it follows that one X reduces one molecule of the olefin and eqn. (4) becomes:

$$v_4 = k_4[\text{X}][\text{CH}:\text{CH}] \quad (4A)$$

Table 3 gives a summary of a number of experiments. Absolute values of k_4 cannot be calculated but those for different olefins can be compared.⁶

Following the consideration of kinetic data, a few general observations can be made. (i) When the value of $-\frac{1}{2}\Delta\text{N}_2\text{H}_4/\Delta t$ approaches that of k_5 the reaction with double bonds is completely arrested. (ii) The values of k_5 do not remain constant, they appear to be affected by alkalinity, and rise steeply at alkalinity 9.5 (see Table 3). Gilbert² observed a similar phenomenon, namely that the rate of oxidation of aqueous solutions of hydrazine, in the presence of sodium hydroxide, increases with alkalinity, reaching a maximum. With even larger amounts of sodium hydroxide the rate falls again, owing to the decrease in the concentration of the hydrazoneium ion.

Conductometric study provided evidence of the existence of one or more conducting intermediates, apart from the hydrazoneium ion. Fig. 2 represents the change in conductance of an actual reaction mixture and of an artificial reaction mixture.

TABLE 4.

Relationship between the rate constant K and the dielectric constant ϵ of the solvent alcohol.

Alcohol	ϵ at 25°	ϵ at 50°	$K = k_0 k_1 [\text{RCO}_2\text{H}][\text{O}_2]$ (min. ⁻¹)
Methanol.....	32.6	27.5	4.40
Ethanol.....	24.3	20.9	4.94
Propan-1-ol.....	20.1	16.2	7.32
Propan-2-ol.....	18.3	~15.2	8.80
2-Methylpropan-1-ol.....	17.7	~14.7	8.48
Butan-1-ol.....	17.1	~14.2	8.18
2-Methoxyethanol.....	16.0	~13.3	7.58
3-Methylbutan-1-ol.....	14.7	~12.2	5.14
Hexan-1-ol.....	13.3	~11.1	4.94

⁶ Sawistowska, Ph.D. Thesis, London, 1962.

The oxidation of hydrazine was investigated in several alcohols. Table 4 represents the relation between the rate constant and the dielectric constant of the solvent. The optimum reaction conditions appear to be achieved in alcohols of dielectric constant between 14 and 16.

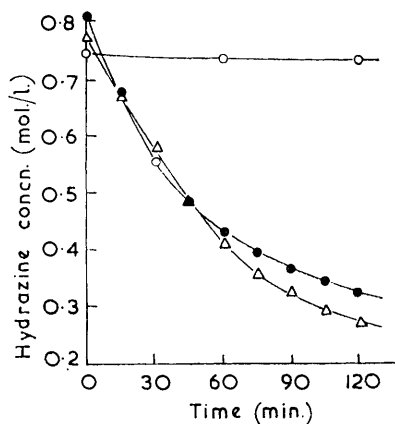


FIG. 1. Decomposition of hydrazine in propan-1-ol.

○ Alone; △ in the presence of decanoic acid; ● in the presence of decanoic acid and oleyl alcohol.

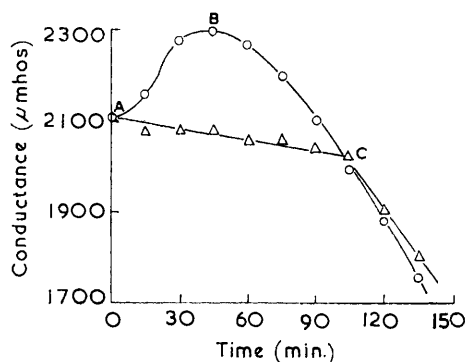
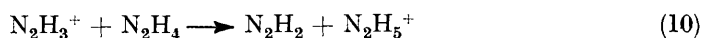
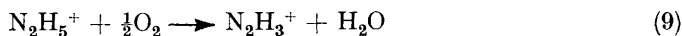


FIG. 2. Conductance curves.

○ Actual reaction mixtures; △ artificial mixtures.

DISCUSSION

Consideration of the nature of the products from hydrazine leads us to the conclusion that the initial step must involve a transfer of two electrons.⁷ It follows that the unknown conducting intermediate (Fig. 2) is probably the protonated form of di-imide, formed by direct oxidation of the hydrazonium ion. The mechanism of oxidation of hydrazine to di-imide may be represented,



In Fig. 2, the portion AB of the conductance curve for the actual mixture appears to correspond to an interval of time during which reaction (9) is faster than reaction (1). It is likely that the rise in conductance is due to the increase in the total number of ions. The concentration of the hydrazonium ion is a function of the concentration of hydrazine and of the carboxyl group.

$$[\text{N}_2\text{H}_5^+] = k_1[\text{N}_2\text{H}_4][\text{RCO}_2\text{H}] \quad (11)$$

Although the protonated di-imide is formed at the expense of the hydrazonium ion, a certain amount of undissociated hydrazine ionises during the reaction to satisfy the above relation.

The comparatively fast oxidation of the hydrazonium ion, under the experimental conditions, may possibly be connected with the alkalinity of the reaction mixture. We have noted that the rate of oxidation of di-imide increases with alkalinity (see values of k_5 in Table 3). It is conceivable that the activity or "effective concentration" of oxygen is affected by alkalinity.

By decreasing the concentration of hydrazine it is possible to make step (9) slower from the start. Under such conditions the initial part of the reaction is first-order with

⁷ Higginson, *Chem. Soc. Special Publ.*, No. 10, 1957, 95.

respect to hydrazine. This is in accordance with the proposed mechanism. The rate of step (9) may be expressed,

$$v_9 = k_9[\text{N}_2\text{H}_5^+][\text{O}_2] \quad (12)$$

Combining eqns. (11) and (12),

$$v_9 = k_9k_i[\text{N}_2\text{H}_4][\text{RCO}_2\text{H}][\text{O}_2] \quad (13)$$

As the concentrations of carboxyl group and oxygen remain constant, eqn. (13) simplifies to:

$$v_9 = K[\text{N}_2\text{H}_4]$$

Hünig *et al.*⁸ and Corey *et al.*⁹ suggested that di-imide is the actual hydrogenating agent of ethylenic bonds, during reduction with hydrazine. This reduction is stereospecifically *cis*, and it follows that the reducing entity must have a *syn*-configuration.^{8,9} The protonated di-imide also satisfies the condition of possessing a *syn*-configuration. Stoichiometric and kinetic data indicate, however, that it cannot be the reducing entity. We suggest that the di-imide cation loses its proton to molecular hydrazine with the formation of equivalent quantities of *syn*- and *anti*-di-imide, of which only the *syn*-isomer is capable of reducing double bonds. Considering the structure of protonated di-imide, the formation of an equivalent mixture of *syn*- and *anti*-di-imide appears plausible, as the loss of a proton seems equally likely to produce either form. Further evidence that deprotonation occurs before the reduction step was obtained from conductometric measurements. The conductance changes during the oxidation of hydrazine follow similar patterns whether an olefinic compound is present or not.

Final proof of the non-ionic nature of the hydrogenation step was obtained in the reduction of oleyl alcohol by azodiformic acid ethyl ester, at pH 5.

Corey *et al.*⁹ found that the presence of copper ions greatly accelerated the reduction of olefinic linkages by hydrazine. We found this to be the case only when the carboxyl group is absent. The mechanism possibly involves oxidation of hydrazine to di-imide in two univalent stages, namely through the hydrazyl radical. The copper(II) ion appears to be the oxidant; oxygen, which passes through the solution constantly, regenerates it from the cuprous state. The presence of hydrazyl radicals is indicated by the formation of ammonia.⁷

EXPERIMENTAL

Mild Aeration Experiments.—Stock solutions, in ethanol, of oleic acid and hydrazine were prepared and aliquots of these mixed together. Reactions were carried out at 50° in gas-jars immersed in a thermostatically heated bath. The mixtures were stirred mechanically, at speeds varying from 100 to 300 r.p.m. and periodically topped up with ethanol to the original volume. In experiments 1–6 oleic acid was determined with Wijs iodine, on aliquot samples which had been acidified with 30% sulphuric acid and extracted with ether. Hydrazine was determined in the sulphuric acid extract by the indirect iodate method. In experiments 7–14 oleic acid was determined in the residues obtained after passing the samples through an Amberlite I.R.-120(H) column and evaporating to dryness. Hydrazine was titrated with 0.1N-perchloric acid, in glacial acetic acid, using Methyl Violet as indicator.

Closed-system Experiments.—Volumetric flasks of known volume were filled with oxygen. Samples, consisting of oleic acid and hydrazine in ethanol were then introduced, and the flasks were sealed with stoppers through which tubes provided with taps were inserted. The closed flasks were mechanically shaken for 3–4 hr. at room temperature. The tubes were then connected to gas-burettes, opened, and the increases in volume which had taken place during the reaction were measured. Analyses of the gases showed that they consisted of nitrogen and oxygen, or nitrogen only. To determine the oxygen, samples of the gases were mixed with an excess of hydrogen, and exploded, and decreases in volume were measured. Residual oleic

⁸ Hünig, Müller, and Thier, *Tetrahedron Letters*, 1961, **11**, 353.

⁹ Corey, Mock, and Pasto, *Tetrahedron Letters*, 1961, **11**, 347.

acid and hydrazine were determined by the iodine-value method and titration with 0.1N-perchloric acid in glacial acetic acid, respectively.

Kinetic Study.—The apparatus consisted of a 700-ml. open-neck reaction flask (Quickfit FR 700 F), equipped with a three-necked lid (Quickfit MAF 5/22). A gas-inlet, provided with a sintered distribution disc of 30 mm. diameter and porosity 1, was inserted through one of the side-necks. Oxygen was supplied to the system through a flowmeter. The other side-neck was fitted with a reflux condenser. The middle neck was reserved for either a stirrer or the electrodes of a conductance bridge. The vessel was immersed in a thermostatically controlled bath.

Oleic acid and solvent propan-1-ol were introduced into the reaction vessel and oxygen was passed for 30 min. at not less than 600 ml./min. Mechanical stirring at 400 r.p.m. was applied. After 30 min. hydrazine hydrate was introduced. Approximately 3 min. were necessary for the contents to mix completely and at this stage the volume of the mixture was about 500 ml. Every 5 min., two 5 ml. samples were withdrawn through the side-neck, while the reflux condenser was momentarily removed. Hydrazine was determined on one aliquot, by titration with perchloric acid. The other sample was passed through an Amberlite I.R.-120(H) column, which was washed with chloroform (30 ml.). Ethylenic bonds were determined on the combined sample and washings by Wijs iodine method.

Values of k_s were found from plots of $\Delta[\text{CH}_2\cdot\text{CH}_2]$ against $-\frac{1}{2}\Delta\text{N}_2\text{H}_4$. When $\Delta[\text{CH}_2\cdot\text{CH}_2] = 0$, $-\frac{1}{2}\Delta\text{N}_2\text{H}_4 = k_s\Delta t$.

The alkalinity was measured on a Cambridge pH-meter at the start of the runs.

Reaction Rates in Different Alcohols.—Solutions of hydrazine (0.480M) and decanoic acid (0.450M) were oxidised at 50° by passing in oxygen at the rate of 600 ml./min. Samples were collected every 15 min. and analysed as previously described. The mixtures contained 10 g. of sodium perchlorate per 500 ml. to minimise any changes in the ionic strength.

Conductometric Study.—The reaction was conducted under the conditions used for the study of kinetics except that at zero time the readings and samples were taken under nitrogen, and only then was the passage of oxygen started. At times when samples were taken for analysis, the conductance was measured by means of a Mullard conductivity bridge, Type E 7566. Artificial mixtures of reactants and products, corresponding to different stages of reduction, were prepared under nitrogen, and their conductances measured at 50°. The amount of water to be added to the artificial reaction mixtures was calculated on the assumption that complete oxidation of the utilised hydrazine to nitrogen had occurred. Table 5 gives the concentrations observed in the course of the reaction.

TABLE 5.

Concentrations of hydrazine and oleic acid during the conductometric study of real and artificial reaction mixtures.

Time (min.)	0	15	30	45	60	75	90	105	120	135
Hydrazine (mol.)	0.835	0.812	0.676	0.552	0.489	0.430	0.395	0.368	0.346	0.325
Oleic acid (mol.)	0.320	0.311	0.251	0.202	0.171	0.161	0.147	0.145	0.141	0.139

For comparison of changes in conductance during the reaction in presence and in absence of ethylenic compounds, the conductance traces were automatically recorded by means of a type R.I.O.C. Electrolytic Conductivity Recorder (Electronic Switchgear) during the oxidation of propanol solutions of (1) hydrazine (0.758M), decanoic acid (0.250M), and oleyl alcohol (0.213M), and (2) hydrazine (0.776M) and decanoic acid (0.255M). To the second solution, methyl tetradecanoate (50 ml.) was added, to lower the original conductance to a level comparable to that recorded in the presence of oleyl alcohol.

Reduction of Oleyl Alcohol with Azodiformic Acid Ethyl Ester.—To a mixture of oleyl alcohol (16.978 g., 0.0634 mol.), azodiformic acid ethyl ester (7.3936 g., 0.0402 mol.), and propan-1-ol (10 ml.), 0.1N sodium hydroxide (7 ml.) was added gradually while the solution was heated to 50°. The final pH was 5. After the evolution of nitrogen was complete, the iodine value of the recovered alcohol indicated a reduction of 31.1%.

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