[CONTRIBUTION FROM THE ROHM AND HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION]

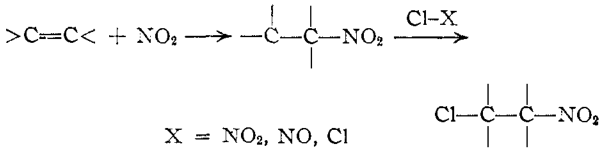
The Reaction of Dinitrogen Tetroxide and Iodine with Olefins and Acetylenes[1]

BY TRAVIS E. STEVENS AND WILLIAM D. EMMONS

RECEIVED AUGUST 15, 1957

Conducting the dinitrogen tetroxide–olefin reaction in ether in the presence of iodine has been found to produce β-nitroalkyl iodides. These experiments not only provide further proof of the radical nature of the dinitrogen tetroxide–olefin reaction but also furnish a convenient synthetic route to the nitroiodoalkanes. β-Iodonitroethylenes were produced from acetylenes.

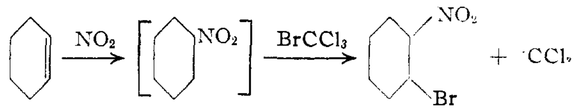
The reaction of dinitrogen tetroxide and an olefin in a weakly basic solvent such as ether to produce dinitroalkanes, nitronitrites or the nitroalcohols derived from them, nitronitrates and other minor products[2] was considered at first to be the result of a heterolytic addition ($NO_2^+ \; NO_2^-$) process.[2,3] Results of recent studies, however, have been interpreted in terms of a homolytic process. Shechter and Conrad[4] have observed that the production of methyl 3-nitroacrylate and methyl 2-hydroxy-3-nitropropionate in the dinitrogen tetroxide–methyl acrylate reaction could not be explained on the basis of heterolytic addition, but was to be expected if a homolytic process were occurring. Brown[5] has shown that olefin nitration under circumstances in which the nitronium ion, NO_2^+, is a logical reactant has characteristics entirely different from those of the dinitrogen tetroxide–olefin reactions. It also has been shown that the reactions of NO_2 and an olefin in the presence of nitryl chloride,[6] chlorine[7] or nitrosyl chloride[7] led to capture of chlorine by the intermediate nitroalkyl radical. The addition of nitryl chloride to an olefin to produce 1-nitro-2-chloroalkanes is well known,[6,8] but the synthetic usefulness of the procedure is sometimes limited by the formation of other products.[9]



$$>C{=}C< + NO_2 \longrightarrow -\overset{|}{\underset{|}{C}}-\overset{|}{C}-NO_2 \xrightarrow{\text{Cl-X}} Cl-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-NO_2$$

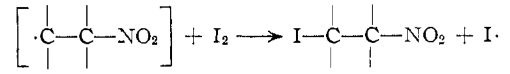
$$X = NO_2,\ NO,\ Cl$$

By studying the reaction of dinitrogen tetroxide and cyclohexene in the presence of bromotrichloromethane, Brand and Stevens[10] found that the normal products, 1,2-dinitrocyclohexane and 2-nitrocyclohexyl nitrite were not formed. Instead, products derived from the interaction of the intermediate β-nitroalkyl radical and the bromotrichloromethane were found.



The product mixture was quite complex, however, due to secondary radical reactions.

By using iodine to trap the intermediate nitroalkyl radical, it has been possible to isolate β-nitroalkyl iodides in good yield.



$$\left[\cdot\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-NO_2\right] + I_2 \longrightarrow I-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-NO_2 + I\cdot$$

The results of these experiments are summarized in Table I. The reactions were carried out by adding the dinitrogen tetroxide slowly in a stream of dry nitrogen to an ether solution of the olefin and excess iodine. These conditions are quite similar to those of the usual dinitrogen tetroxide–olefin reactions, and allow the nitroalkyl radical to be generated in the presence of a large excess of iodine.

Virtually none of the usual products of the dinitrogen tetroxide–olefin reaction were found in the examples given in Table I. However, a small amount of the iodoalkyl nitrate recently reported[11] from an apparently similar reaction[12] appeared to form, as evidenced by infrared spectra, in the case of propylene and 1-butene. Due to the very similar boiling points of the nitroiodo compound and the iodonitrate (the iodonitrate is slightly lower boiling), isolation of the latter contaminant was not possible, and complete purification of the rather unstable liquid nitroiodo compound probably was not accomplished. The formation of the iodoalkyl nitrate likely arises from an ionic addition process as indicated by Bachman and Logan,[11] and a small local excess of dinitrogen tetroxide would undoubtedly lead to the production of these compounds. There was no evidence for the formation of a nitrate ester with methyl acrylate, stilbene or camphene, however. Cyclohexene gave a mixture of nitrate ester and nitro compound whose infrared spectrum indicated the latter largely predominated. The products of this reaction were too unstable to purify; considerable iodine was liberated and some 1-nitrocyclohexene was formed on attempted distillation.

The 1,2-diphenyl-2-nitroethyl iodide formed from *trans*-stilbene appeared to be a single isomer. Al-

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[1] Presented at the 131st Meeting of the American Chemical Society, Miami, Fla., April 7–12, 1957.

[2] N. Levy, C. W. Scaife, A. E. Wilder Smith and H. Baldock, *J. Chem. Soc.*, 2627 (1949), and preceding papers.

[3] C. K. Ingold and E. H. Ingold, *Nature*, **159**, 743 (1947).

[4] H. Shechter and F. Conrad, THIS JOURNAL, **75**, 5610 (1953).

[5] J. F. Brown, Jr., paper presented at 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957.

[6] H. Shechter, F. Conrad, A. L. Daulton and R. B. Kaplan, THIS JOURNAL, **74**, 3052 (1952).

[7] J. F. Brown, Jr., private communication.

[8] C. C. Price and C. A. Sears, THIS JOURNAL, **75**, 3275 (1953); J. Ville and G. Dupont, *Bull. soc. chim. France*, 804 (1956).

[9] M. J. Collis, F. P. Gintz, D. R. Goddard and E. A. Hebdon, *Chemistry & Industry*, 1742 (1955).

[10] J. C. D. Brand and I. D. R. Stevens, *ibid.*, 469 (1956).

[11] G. B. Bachman and T. S. Logan, *J. Org. Chem.*, **21**, 1467 (1956).

[12] The reaction reported by Bachman and Logan[11] was similar in the sense that it involved the same reactants. However, their reactions were carried out by adding the olefin to an iodine-dinitrogen tetroxide mixture, conditions which could be expected to produce iodonitrates.

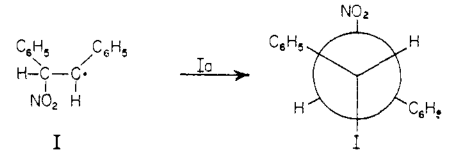
TABLE I

REACTION OF UNSATURATED COMPOUNDS AND DINITROGEN TETROXIDE AND IODINE

Unsaturate	Product	Reaction conditions[a]	Yield, %	B.p., °C. (mm.) or m.p.	Analyses, % Calculated	Found
Propylene	1-Nitro-2-propyl iodide	3 hr., 0°	70[b]	40 (0.2)	C, 16.76	17.02
				1.5374[f]	H, 2.81	3.03
					N, 6.52	6.19
1-Butene	1-Nitro-2-butyl iodide	3 hr., 0°	62[b]	47 (0.4)	C, 20.98	21.23
				1.5295[f]	H, 3.52	3.58
					N, 6.12	6.00
Methyl acrylate	Methyl 3-nitro-2-iodopropionate	6 hr., 25°	75[c]	84 (0.3)	C, 18.55	18.74
				1.5284[f]	H, 2.34	2.39
					N, 5.41	4.86
trans-Stilbene	1,2-Diphenyl-2-nitroethyl iodide	3 hr., 0°	96[d]	147–148[e] dec.	C, 47.61	47.82
					H, 3.43	3.41
					N, 3.97	3.32
cis-Stilbene	1,2-Diphenyl-2-nitroethyl iodide	3 hr., 0°	63[c]	145–146[e] dec.		
Camphene	3-Nitromethyl-3-iodocamphenilane	3 hr., 5°	50[c]	119–120	C, 38.48	39.16
					H, 5.17	5.26
					N, 4.49	4.25
Tolane	*trans*-α-Nitro-α′-iodostilbene	6 hr., 20°	66[d]	176–177	C, 47.90	48.15
					H, 3.08	2.95
					N, 3.99	3.51
	cis-α-Nitro-α′-iodostilbene		15[d]	113–114	C, 47.90	47.76
					H, 3.08	2.94
					N, 3.99	3.51
Phenylacetylene	α-Iodo-β-nitrostyrene	4 hr., 10°	86[c]	49–50	C, 34.93	35.00
					H, 2.20	2.42
					I, 46.14	45.57

[a] Includes time of stirring after addition of dinitrogen tetroxide. [b] Based on dinitrogen tetroxide. [c] Based on unsaturated compound. [d] Based on recovered unsaturated compound. [e] Taken by placing the sample in bath at 130° and raising the temperature 2°/min. [f] $n^{20}D$.

though this sample had a decomposition point (about 147°) instead of a melting point, the decomposition temperature did not change on purification. In view of the lack of stereospecificity of the dinitrogen tetroxide–*trans*-stilbene reaction[13] this result was unexpected. The same 1,2-diphenyl-2-nitroethyl iodide was obtained from *cis*-stilbene, iodine and dinitrogen tetroxide, although in lower yield and contaminated by a small amount of an unidentified material. On the basis of the product being a single isomer it appears that the intermediate nitroalkyl radical I must react with iodine in a stereospecific fashion. If this is the case the product is probably the *erythro* isomer



I II

II. Dehydrohalogenation of II gave *cis*-α-nitrostilbene, m.p. 73–74°, and a trace of *trans*-α-nitrostilbene. Since both 1,2-diphenyl-1,2-dinitroethanes give *cis*-α-nitrostilbene on base-catalyzed elimination,[14] this result, while that expected from a *trans*-elimination process for II, is probably of little significance, particularly without comparable information on the other isomer.

Dehydrohalogenation of the nitroalkyl iodides provides a convenient route to α-nitroölefins, and coupled with the addition process is probably the method of choice for converting an olefin to a nitroolefin. Methyl 3-nitro-2-iodopropionate was dehydrohalogenated with sodium acetate in refluxing ether to give methyl 3-nitroacrylate.[6] The 3-iodo-3-(nitromethyl)-camphenilane obtained from camphene gave a good yield (81%) of ω-nitrocamphene on treatment with ethanolic sodium hydroxide.

The last two examples in Table I show the results obtained when a substituted acetylene and dinitrogen tetroxide reacted in the presence of iodine.[15,16] Thus, tolane was found to give a mixture of α-nitro-α′-iodostilbenes in which the higher melting and less soluble *trans* isomer III predominated over the *cis* isomer IV.[17] No trace of the dinitrostilbenes or the nitrophenylisatogen obtained from the tolane–dinitrogen tetroxide reaction[18] could be found. Only one isomer was formed from the

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(13) J. Schmidt, *Ber.*, **34**, 3536 (1901). Conducting the dinitrogen tetroxide–*trans*-stilbene reaction in ether in the absence of iodine in this Laboratory gave a mixture of 1,2-diphenyl-1,2-dinitroethanes in over 50% yield. The isomer melting at 150° predominated by a 3:2 ratio over the 235° isomer.

(14) J. Meisenheimer and F. Heim, *Ann.*, **355**, 269 (1907): A. Angeli and L. Alessandri, *Atti. accad. Lincei*, **19**, I, 784 (1910) [*C. A.*, **4**, 2634 (1910)].

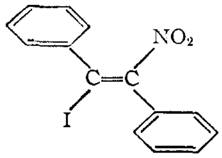
(15) The reaction of diiodoacetylene and dinitrogen tetroxide has been reported to give triiodonitroethylene, apparently *via* iodine liberated during the course of the reaction [H. Biltz, *Ber.*, **30**, 1200 (1897)].

(16) For a discussion of the acetylene–dinitrogen tetroxide reaction see J. P. Freeman and W. D. Emmons, THIS JOURNAL, **79**, 1712 (1957).

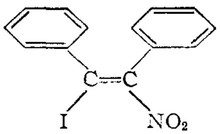
(17) The main evidence for the structural assignments of the *cis* and *trans* isomers was their ultraviolet spectra. The *cis* compound exhibited more intense long wave length (310 mμ) absorption: see J. P. Freeman and T. E. Stevens, *J. Org. Chem.*, in press.

(18) K. N. Campbell, J. Shavel, Jr., and B. K. Campbell, THIS JOURNAL, **75**, 2400 (1953).

phenylacetylene reaction; this appeared to be the one having the phenyl and nitro groups *trans*.[17]

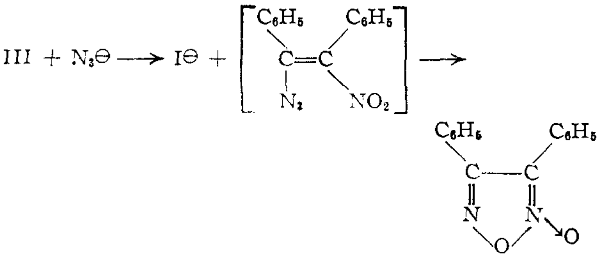


III



IV

Nitroiodoölefins such as III and IV possess an unsaturated system which, similar to that of 1,2-dinitroölefins,[19] is vulnerable to nucleophilic attack. With the nitroiodo compounds, displacement of iodide ion would be expected. An example of this, the reaction of III and sodium azide to give



diphenylfuroxan, is outlined in the Experimental section.

Experimental

All boiling points and melting points are uncorrected. The dinitrogen tetroxide used in this work was obtained from the Matheson Co. and was redistilled before use. The general procedures for the reactions summarized in Table I are illustrated by the examples given below.

Reaction of Dinitrogen Tetroxide, Iodine and an Unsaturated Compound. ***trans*-Stilbene.**—A stirred solution of 5.0 g. (0.028 mole) of *trans*-stilbene and 7.6 g. of iodine in 100 ml. of ether and 100 ml. of methylene chloride was cooled in an ice-bath while 2.0 g. (0.043 mole as NO$_2$) of dinitrogen tetroxide was passed into the solution in a stream of dry nitrogen over 2 hours. The reaction system was protected with a Dry Ice–acetone condenser and a Drierite tube. After addition of the dinitrogen tetroxide, stirring was continued for one hour. The reaction mixture was filtered to remove 6.25 g. of solid material, m.p. dec. 145–146°. The filtrate was washed with aqueous sodium thiosulfate, aqueous sodium bicarbonate and water and dried over magnesium sulfate. The residue obtained on evaporation of the organic solvent was recrystallized from benzene–ligroin to give 2.79 g. of material, m.p. dec. 145–146°. The filtrate was chromatographed on silica gel. Thus 0.13 g. of stilbene was recovered and an additional 0.19 g. of 1,2-diphenyl-2-nitroethyl iodide, m.p. dec. 145–146° (total of 9.23 g., 96.5% based on recovered stilbene) was obtained. After chromatography on silica gel and 5 recrystallizations from ethanol and ligroin–benzene the sample decomposed at 147–148° when it was placed in a bath at 130° and the temperature was raised 2° per minute.

***cis*-Stilbene.**—The procedure outlined above for *trans*-stilbene was followed using 5.0 g. of *cis*-stilbene, n^{20}D 1.6220 (reported[20] n^{20}D 1.6212–1.6218), 8.0 g. of iodine and 2.0 g. of dinitrogen tetroxide. Filtration of the reaction mixture gave 6.02 g. of material, m.p. dec. 115–117° with preliminary darkening. Recrystallization of the sample from ligroin–benzene gave 5.07 g. of material with the same melting point. The sample was then stirred with 40 ml. of warm ethanol (solution was not complete), cooled and filtered to give 4.70 g. of material, m.p. dec. 145–146°. The ethanolic filtrate was diluted with water and was extracted with ether. From the ether extracts was obtained a small amount of dark material showing hydroxyl and carbonyl absorption in the infrared spectrum. From the mother liquor of the first filtration there was obtained after two recrystallizations from ligroin 1.55 g. (total 63%) of 1,2-diphenyl-2-nitroethyl iodide, m.p. dec. 145–146°. The infrared spectrum was identical with that of the product from *trans*-stilbene.

Propylene.—A stirred solution containing 30 ml. of propylene and 31 g. (0.25 mole) of iodine in 200 ml. of ether was cooled to 0°, and 6.9 g. (0.15 mole as NO$_2$) of dinitrogen tetroxide was passed into the solution in a stream of dry nitrogen over 2 hours. The reaction system was protected with a Dry Ice–acetone condenser and a Drierite drying tube. The reaction was stirred an additional hour at 0° after addition of the dinitrogen tetroxide. The ether solution was washed with 15% aqueous sodium thiosulfate until colorless, and was then washed with aqueous sodium bicarbonate and water and dried over magnesium sulfate. The residue obtained on evaporation of the ether at 20° and 30 mm. was distilled through a brown Metroware distilling head to give 22.5 g. (70%) of 1-nitro-2-propyl iodide, b.p. 40–42° (0.5 mm.). Redistillation of the sample through a Holzmann column gave forerun, 1.7 g., b.p. 42–44° (0.45 mm.), n^{20}D 1.5370, and 1-nitro-2-propyl iodide, 18.4 g., b.p. 44° (0.45 mm.), n^{20}D 1.5378. The infrared spectrum of the second fraction exhibited strong absorption at 6.44 μ (nitro group) and very weak peaks at 6.14 and 7.84 μ, indicating a trace of iodonitrate[11] was still present. The nitrate ester peaks were somewhat stronger in the forerun. A sample, redistilled for analysis, had b.p. 40° (0.2 mm.), n^{20}D 1.5374.

Tolane.—The reaction temperature was 20° while 1.3 ml. of dinitrogen tetroxide was added in a stream of dry nitrogen to 5.0 g. (0.028 mole) of tolane and 10 g. of iodine in 150 ml. of ether over 3 hours. When addition was completed the mixture was stirred at 25° for 2 hours. The reaction was filtered to remove 2.49 g. of *trans*-α-nitro-α'-iodostilbene, m.p. 176–177°. The filtrate was washed with aqueous sodium thiosulfate and water and dried over magnesium sulfate. The residue obtained on evaporation of the ether was recrystallized from ligroin 4 times to give an additional 1.38 g. of the *trans* compound, m.p. 171–172°. From the filtrate crystallized an additional 0.60 g. of less pure material, m.p. 163–165° dec. The filtrate was chromatographed on silica gel. Elution of the column with ligroin gave 1.16 g. of recovered tolane, m.p. and mixed m.p. 63–64°. Continued elution with ligroin–benzene (2:1) gave 1.84 g. of nitroiodostilbenes, recrystallization of which from ligroin gave 0.51 g. of the *trans* isomer, m.p. 175–176° (total of 4.98 g., 66% based on recovered tolane). Further concentration of the ligroin filtrate gave 1.10 g. (15%) of *cis*-α-nitro-α'-iodostilbene, m.p. 107–109°. After recrystallization from ligroin and from ethanol the *cis* isomer melted at 113–114°.

Preparation of Nitroölefins from Nitroalkyl Iodides. Methyl 3-Nitroacrylate.—The procedure of Shechter[6] was used, except that the ether solution was refluxed for one hour. From 5.0 g. of methyl 3-nitro-2-iodopropionate was obtained 1.4 g. of methyl 3-nitroacrylate, m.p. 37–38°, reported[6] m.p. 38°.

ω-Nitrocamphene.—A 2.00-g. sample of 3-iodo-3-(nitromethyl)-camphenilane was shaken with a mixture of 25 ml. of 5% sodium hydroxide and 25 ml. of ethanol for one hour. To this mixture was then added dropwise 25 ml. of ice-cold 15% sulfuric acid. The aqueous solution was extracted with ether. The residue obtained on evaporation of the ether was taken up in ligroin–benzene (1:1) and was placed on 2.2 × 25 cm. silica gel column. Elution of the column with the same solvent gave 0.95 g. (81%) of *dl*-ω-nitrocamphene, m.p. 63–64°, reported[21] 60–62°.

***cis*-α-Nitrostilbene.**—A solution of 1.60 g. of 1,2-diphenyl-2-nitroethyl iodide and 1.5 ml. of pyridine in 50 ml. of benzene was refluxed for 4 hours. The solution was cooled, washed with dilute hydrochloric acid and water and evaporated at reduced pressure. The residue was taken up in ligroin and chromatographed on silica gel. Elution with ligroin gave 0.07 g. of *trans*-stilbene, m.p. 120–122°, and 0.88 g. of α-nitrostilbene, m.p. 66–69°. Recrystallization of the latter from ligroin gave *cis*-α-nitrostilbene, m.p. 73–74°, reported[22] 75°. Slow evaporation of the ligroin filtrate left, in addition to more *cis* isomer, one large prism (15 mg.) of *trans*-α-nitrostilbene, m.p. 127–128°. reported[22] 127–128°.

Preparation of Diphenylfuroxan.—To 0.40 g. of sodium azide suspended in 10 ml. of ethanol was added dropwise 1.00 g. of *trans*-α-nitro-α'-iodostilbene in 50 ml. of warm

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[19] W. D. Emmons and J. P. Freeman, *J. Org. Chem.*, **22**, 456 (1957).

[20] R. E. Buckles and N. G. Wheeler, *Org. Syntheses*, **33**, 88 (1953).

[21] P. Lipp, *Ann.*, **399**, 241 (1913).

[22] F. Heim, *Ber.*, **44**, 2016 (1911).

ethanol. The mixture was stirred at 75° for 80 minutes, and then was poured into water and extracted with ether. The residue obtained from the ether was recrystallized from ethanol to give 0.51 g. (75%) of 3,4-diphenylfuroxan, m.p. 113–115°, reported[19] m.p. 115–117°.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC CO.]

Hydrolysis of Diethyl Methoxyphthalates

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The rate of saponification and acid-catalyzed hydrolysis of the diethyl methoxytere- and methoxyisophthalates have been determined and compared with the previously reported unsubstituted diethyl phthalates. The effect of the methoxyl group is similar to that noted in the methoxybenzoic acid esters.

The effects of the position of substitution of various electron donating and withdrawing groups upon the rates of saponification and acid-catalyzed hydrolysis of substituted ethyl benzoates have been reported.[2] No data of this type are available for the substituted isomeric diethyl phthalates. During a recent study of the esters and polyesters of the isomeric methoxyphthalic acids, it became of interest to determine quantitatively the effect of the position of substitution of the methoxyl group upon the over-all rate of saponification and acid-catalyzed hydrolysis of the diethyl esters of the methoxyiso- and methoxyterephthalic acids. It is the purpose of this paper to report these results and to make a comparison of the over-all rates with those of the unsubstituted diethyl phthalates as well as ethyl benzoate and ethyl anisate.

Experimental

Preparation of the Esters.—The diethyl methoxyphthalates were prepared by the method used by Fosdick[3] for the preparation of diethyl 4-methoxyisophthalate. A mixture of 10 g. of the methoxyphthalic acid, 50 g. of thionyl chloride and several drops of dry pyridine was heated at reflux for four hours after complete solution of the acid had been attained. In several cases this required 18 hours. The excess thionyl chloride was removed by a vacuum flash distillation, followed by an addition of 30 ml. of dry benzene and a second vacuum flask distillation to dryness. Absolute ethanol, 100 ml., was added and the mixture was heated at reflux for 3 hours. The diethyl ester separated as an oil when the alcohol solution was drowned in cold water. The ester was removed from the aqueous suspension by extraction with ether, and the extract was dried over anhydrous calcium chloride. Evaporation of the ether and the subsequent distillation of the dry recovered liquid esters in a Podbielniak spinning-band column gave the compounds listed in Table I.

Several of the compounds were purified either by distillation in the Podbielniak spinning-band column or by recrystallization: diethyl phthalate, $n^{20}\text{D}$ 1.5021; diethyl isophthalate, $n^{20}\text{D}$ 1.5071; diethyl terephthalate, m.p. 44°; ethyl benzoate, $n^{20}\text{D}$ 1.5049; and ethyl anisate, $n^{20}\text{D}$ 1.5241.

Saponification Procedure.—Reaction mixtures (100 ml.) containing 0.05 equivalent per liter of ethyl ester and of sodium hydroxide in 85% by weight ethanol were prepared. In each case 0.005 equivalent of ester and 40.6 ± 0.2 g. of aqueous ethanol (85% by weight ethanol) were weighed in 250-ml. glass-stoppered flasks and placed in a water-bath maintained at 25 ± 0.1°. At the start of a reaction 50 ml. of 0.1 *N* alcoholic sodium hydroxide (85% by weight ethanol), also adjusted to 25°, was added by pipet to the ester solution. To effect solution the flask was swirled in the bath for about two minutes. Zero time was taken at half the delivery time of the 50-ml. pipet. During a run at least five 10-ml. aliquots of reaction mixture were taken out at intervals and added to 15 ml. of 0.1 *N* aqueous hydrochloric acid which had been cooled in ice to stop the reaction. Sampling time was taken when half the aliquot had been delivered into the acid. The resulting acid solution was promptly titrated with 0.1 *N* aqueous sodium hydroxide to a greenish-blue end-point with brom thymol blue. It was established by direct titration of each of the seven dibasic acids under consideration that in all cases both carboxyl groups are determined quantitatively under the analytical conditions employed. Duplicate saponification runs gave satisfactory checks.

Acid-catalyzed Hydrolysis Procedure.—*p*-Toluenesulfonic acid was chosen as a catalyst for the hydrolysis because of the resistance of this acid to esterification with ethanol and to decomposition under the conditions used. Other strong acids[2e] can react with the solvent. A control run indicated that *p*-toluenesulfonic acid did not change strength within the duration of the present experiments (about 100 hours at 100°).

Reaction mixtures (10 ml.) containing 0.05 equivalent per liter of ethyl ester and of 0.05 equivalent per liter of *p*-toluenesulfonic acid in ethanol (85% by weight ethanol) were prepared. In the case of each ester to be hydrolyzed, 0.005 equivalent of ester was weighed in a 50-ml. volumetric flask and was then made up to 50 ml. with aqueous ethanol (85% by weight ethanol). In each of five heavy-walled Pyrex tubes, capacity about 20 ml., was placed by pipet 5 ml. of stock ester solution and 5 ml. of 0.1 *N* *p*-toluenesulfonic acid in aqueous ethanol (also 85% by weight ethanol). The tubes were cooled in an ice-bath and sealed. The group of five tubes for each ester was placed in a wire basket and submerged at zero time in an oil-bath maintained at 100 ± 0.3°. The reaction mixtures remained homogeneous during the heating period. One tube for each ester was removed from the bath at intervals, cooled in ice, opened, and the contents promptly titrated, at about 0°, with 0.1 *N* aqueous sodium hydroxide to a brom thymol blue end-point. When precipitation occurred during titrations, 15 ml. of 95% ethanol was added to restore homogeneity.

Results and Discussion

Saponification of Ethyl Esters.—In preliminary runs the second-order rate constants were determined for ethyl benzoate and ethyl anisate and were found to agree closely with those previously reported[2b,c]; Table II.

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(1) Locomotive and Car Equipment Department, General Electric Co., Erie, Penna.

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