Ham and Fordyce,[7] on the other hand, found $r_1 = 9$ and $r_2 = 0.083$ for this pair. The earlier work[8] on acrylonitrile and methyl acrylate was done in emulsion but our values are quite close to those reported.

These results indicate clearly that the acrylic acid portion of the ester is totally responsible for the reactivity ratio in the case of these esters.

Experimental

Hydronopyl Acrylate.—A mixture of 210 g. (1.25 moles) of hydronopol, 169 g. (1.35 moles) of dimethylaniline and 200 ml. of dry ethyl ether was warmed until the ether was at reflux temperature, the heating source was removed and 129 g. (1.43 moles) of acrylyl chloride was added at a rate sufficient to maintain a gentle reflux. When the amine hydrochloride began to crystallize, it was necessary to cease adding the acid chloride and cool the flask for a short period. When the reaction slowed down, the remaining acid chloride was added, the mixture was refluxed for about two hours and then cooled. About 200 ml. of water was added to dissolve the amine hydrochloride and the ether layer was separated. It was then washed successively with three 50-ml. portions of cold 10% sulfuric acid solution, then with saturated sodium bicarbonate solution and sufficiently with water. A few crystals of hydroquinone were added, the ether was evaporated and the crude product was distilled (b.p. 107–113° (1.5 mm.), 198 g. 72%, yellow oil, $n^{25}\text{D}$ 1.480), then allowed to stand for 24 hours over a small portion of metallic sodium in order to remove the hydroquinone completely and again distilled under reduced pressure. The yield was 74 g. (27% of the theoretical amount) of a product boiling at 73° under 0.05 mm. pressure, $n^{25}\text{D}$ 1.4800. This material polymerized readily when heated with a small portion of benzoyl peroxide.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.98. Found: C, 75.74; H, 9.95.

Abityl acrylate was not obtained in satisfactory yield from Abitol and acrylyl chloride but was obtained by direct esterification.

Into a 100-ml. 4.6 *M* toluene solution of acrylic acid, 117 g. of Abitol (0.40 mole), 15 g. of hydroquinone and 0.5 g. of *p*-toluenesulfonic acid was suspended a piece of copper wire to help inhibit polymerization, and this solution was heated under a reflux condenser for 22 hours. The condensate was put through a separator to remove water before the toluene was returned to the reaction flask. During this time 7.3 ml. of water was collected. The toluene solution was cooled and most of the hydroquinone crystallized and was removed by filtration. The toluene solution was then washed successively with portions of water until a test portion of the washings no longer gave a yellow color when potassium hydroxide was added. The toluene was removed by distillation (in the presence of copper wire) and the residual ester was distilled twice under reduced pressure. The yield was 80 g. (58%) of a product, b.p. 157–161° (0.5 mm.), $n^{24}\text{D}$ 1.5145. This material polymerized to a colorless polymer when heated at 120° for ten minutes with a little benzoyl peroxide.

Anal. Calcd. for the acrylate ester of a mixture of 15% $C_{20}H_{30}O$, 40% $C_{20}H_{34}O$ and 45% $C_{20}H_{36}O$: C, 80.11; H, 10.61. Found: C, 80.27; H, 10.77.

Other Monomers.—The other monomers which were used in the copolymerization experiments were distilled once to remove inhibitor.

Polymerization.—All polymerizations were carried out in benzene solution with benzoyl peroxide as the initiator. Some were done at 60° and some at 50° as noted in the table. Conversions varied from 1 to 24% and the polymers were purified by reprecipitation with methanol (with abityl acrylate polymers acetone was used) and use of the frozen benzene technique of Lewis and Mayo.[9]

The copolymerization data are presented in Table I and Figs. 1 and 2.

Acknowledgment.—We wish to acknowledge the aid of Mr. Jozsef Nemeth of the University of Illinois, and the Micro-Tech Laboratories, Skokie, Ill., for analytical results reported. We are indebted to Mr. E. L. Patton of the Southern Utilization Research and Development Division of the Agricultural Research Service, Olustee, Florida, for the hydronopol and Abitol used in these experiments.

(9) F. M. Lewis and F. R. Mayo, *Ind. Eng. Chem.*, *Anal. Ed.*, **17** 134 (1945).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, THE FACULTY OF ENGINEERING, KYOTO UNIVERSITY]

The Preparation of Terephthalic Acid from Phthalic or Benzoic Acid

BY YOSHIRO OGATA, MASARU TSUCHIDA AND AKIHIKO MURAMOTO

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The preparation of terephthalic acid by heating potassium salts of phthalic or benzoic acid has been investigated. It was found that cadmium was the best catalyst cation, zinc the second, and some of the other metals had but inferior catalytic effect. The order of the catalytic efficiency of the anions of cadmium seems to be $I^- > Br^- > Cl^- > CO_3^=$. Dipotassium isophthalate gave the terephthalate more slowly than the phthalate. Several lines of evidence imply an intramolecular mechanism for the rearrangement, but the reaction of dipotassium phthalate catalyzed by radioactive $CdC^{14}O_3$ gave radioactive terephthalic acid, probably *via* carbon isotope exchange between activated reactant and the catalyst. On the other hand, the reaction between potassium benzoate and $CdC^{14}O_3$ gave terephthalic acid with very little radioactivity, suggesting a disproportionation mechanism for the reaction.

A recent patent to Henkel[1] describes a preparation of dipotassium terephthalate in high yield by heating at 400–450° dipotassium phthalate with a catalyst including cadmium or zinc salts and also the similar preparation of the terephthalate from potassium benzoate. In the old literature, similar methods for the preparation of terephthalic acid are recorded, *e.g.*, the fusion of dipotassium *p*-sulfobenzoate with sodium formate[2] or the heating of sodium benzoate,[3] but yields were poor.

The present communication summarizes data on the effect of various conditions and catalysts on the yield of the Henkel process for the terephthalic acid synthesis and also our mechanistic investigation using radioactive carbon isotope.

(1) B. Raecke, *et al.*, to Henkel & Cie, G.m.b.H., German Patents 936,036, Dec. (1955), 945,627 (1956), and additional patents.

(2) I. Remsen, *Ber.*, **5**, 379 (1872).

(3) W. Flight and A. M. Michaelis, *ibid.*, **6**, 1395 (1873).

Experimental

The Preparation of Terephthalic Acid.—Some typical examples are given below.

(1) An intimate mixture of finely powdered dry dipotassium phthalate (1.6 g., 0.00658 mole) and cadmium iodide (0.08 g., 0.000219 mole) was placed in a test-tube equipped with a constricted glass tube connected by means of a rubber stopper. The test-tube was immersed in a metal-bath heated at 415 ± 2° and removed after 2.5 hr. The product, having a carbonized dark surface, was dissolved in 100 ml. of hot water and filtered. To the boiling filtrate hydrochloric acid was added in excess. The resulting white precipitate was filtered while hot, washed thoroughly with hot water and dried. There was obtained 0.930 g. (85.2%) of terephthalic acid, which was identified by converting it into its dimethyl ester, m.p. and mixture m.p. 140° (lit.[4] m.p. 140.8°). In a blank test with dipotassium terephthalate, it was observed that 4–6% of the product was lost during the reprecipitation process. The yields shown in the following synthesis are those uncorrected for this loss; hence the true yields will be higher.

(2) Potassium benzoate (1.6 g., 0.01 mole) and cadmium iodide (0.3 g., 0.000819 mole) were mixed intimately and heated for 4.5 hr. at 448 ± 2° as mentioned in example 1. At the beginning of the reaction, a gas of benzene-like odor was evolved. On processing the raw product there was obtained 0.478 g. (57.6% based on the disproportionation mechanism) of terephthalic acid.

Rate Measurements.—A definite amount of powdered dry potassium salt of phthalic, isophthalic or benzoic acid together with a definite amount of a catalyst was placed in a test-tube as described in example 1 and mixed. These tubes (usually 7–10 tubes) were immersed simultaneously in a metal-bath at constant temperature (±2°). At appropriate time intervals these tubes were withdrawn separately and analyzed for terephthalic acid content as was done in example 1. Figures 1 and 2 show the time–yield curves corrected for the terephthalic acid loss (5%) in the blank work-up. Those runs resulting in low conversion gave on filtration dark colloidal filtrates, containing a fine dispersoid of carbonized materials, which could be removed by precipitating it by the addition of a small amount of zinc sulfate followed by filtration.

Tracer Experiments.—Carbon-14 labeled carbon dioxide was evolved from labeled barium carbonate with hydrochloric acid and absorbed in an aqueous solution of a calculated amount of potassium hydroxide. The solution was evaporated to dryness in vacuum, yielding labeled potassium carbonate. Labeled cadmium carbonate was obtained by mixing the solution of the labeled potassium carbonate and a solution of cadmium chloride; the obtained precipitate was dried in vacuum. The radioactivities of these substances were determined by converting them into barium carbonate.

The methods for the isolation of the product and the recovered reactants are principally the same as those given in example 1; but, in addition, the materials were submitted to four or five recrystallizations from water and then dried in vacuum.

The radioactivity of these materials was counted by means of a Geiger–Müller counter on an "infinitely thick" layer with a surface area of 4.7 cm.^{2}, the counts all being corrected for the background.

Results and Discussion

(A) Terephthalic Acid from Phthalic Acid. The Mechanism.—According to the patent of Henkel,[1] the terephthalic acid synthesis from dipotassium phthalate seems to give better yields under a high pressure of carbon dioxide. Terephthalic acid also can be obtained from potassium benzoate under similar conditions. These facts seem to indicate that dipotassium phthalate initially is decarboxylated to potassium benzoate which again is carboxylated to the terephthalate.

In our hands, however, no evidence was obtained for the intermolecular nature of the phthalate rearrangement. That is, (1) only a small drop in yield was observed when the reaction was carried out at atmospheric pressure. (2) Almost 90% yield was obtained in some experiments (Table II) without the addition of carbon dioxide sources, *i.e.*, by employing cadmium iodide as a catalyst in the absence of carbonate or carbon dioxide. Here, the yield is even higher than in the case of catalysis by cadmium carbonate. (3) Potassium benzoate reacts considerably more slowly than dipotassium phthalate (Fig. 2). (4) As described below, a tracer study confirmed that little radioactivity was detected in the terephthalate obtained from the reaction of benzoate and radioactive cadmium carbonate. The tracer experiments are summarized in Table I. In these experiments, carbon-14 labeled cadmium carbonate was used as a catalyst and the carbon-14 content of the products was estimated. As is seen in the table if one starts with dipotassium phthalate, considerable radioactivity is found in the product. This result, however, does not seem to support the mechanism of the elimination–substitution of carbon dioxide, since no appreciable amount of radioactivity could be detected in the terephthalic acid obtained from the reaction of the potassium benzoate and labeled cadmium carbonate under the same condition.

TABLE I

DATA OF TRACER EXPERIMENTS

Starting material[a]	$CdC^{14}O_3$ added,[b] g.	Temp.,[d] °C.	Time, hr.	Radioactivity,[d,e] counts/min.	Substance counted
p-$C_6H_4(CO_2K)_2$	0.3	450	4	0	p-$C_6H_4(CO_2H)_2$
o-$C_6H_4(CO_2K)_2$	.3	450	3	1105	
o-$C_6H_4(CO_2K)_2$	.2	450	3	485	
o-$C_6H_4(CO_2K)_2$	.1	450	3	312	
o-$C_6H_4(CO_2K)_2$	.2	410	3	677	
o-$C_6H_4(CO_2K)_2$	.2	390	1	646	
o-$C_6H_4(CO_2K)_2$	.2	390	1	56	o-$C_6H_4(CO_2H)_2$
o-$C_6H_4(CO_2K)_2$	.15[c]	410	2	75	
$C_6H_5CO_2K$	.3	450	4	2	p-$C_6H_4(CO_2H)_2$
$C_6H_5CO_2K$	.2	470	2.5	192	
$C_6H_5CO_2K$	.2	410	1	10	$C_6H_5CO_2H$
$C_6H_5CO_2K$	.15[c]	410	2	0	

[a] 1.6 g. of material was used. [b] 5521 counts/min. as $BaC^{14}O_3$. [c] $K_2C^{14}O_3$ (5320 counts/min. as $BaC^{14}O_3$) was used in place of $CdC^{14}O_3$. [d] All values were corrected for the background. [e] Average in duplicate experiments.

The above isotopic exchange may be explained by assuming that the exchange occurs between the phthalate and cadmium carbonate at the initial stage of the reaction, since the recovered phthalic acid was found to be radioactive. The activity is, however, small if compared with that found in the terephthalic acid produced. This is also the case, when labeled potassium carbonate is used in place of labeled cadmium carbonate (Table I).

Since the observed carbon-14 isotope effect in the decarboxylation of malonic acid is very small (3–5%),[5] this effect may be neglected in this rather qualitative discussion of our results.

Dipotassium isophthalate produces terephthalic acid considerably more slowly than the phthalate (Fig. 2), and hence the isophthalate should not be an intermediate of this reaction.

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(4) M. T. Bogert and C. P. Harris, THIS JOURNAL, **41**, 1676 (1919)

(5) P. E. Yankwich, N. Promislow and R. F. Nystrom, *ibid.*, **76**, 5893 (1954).

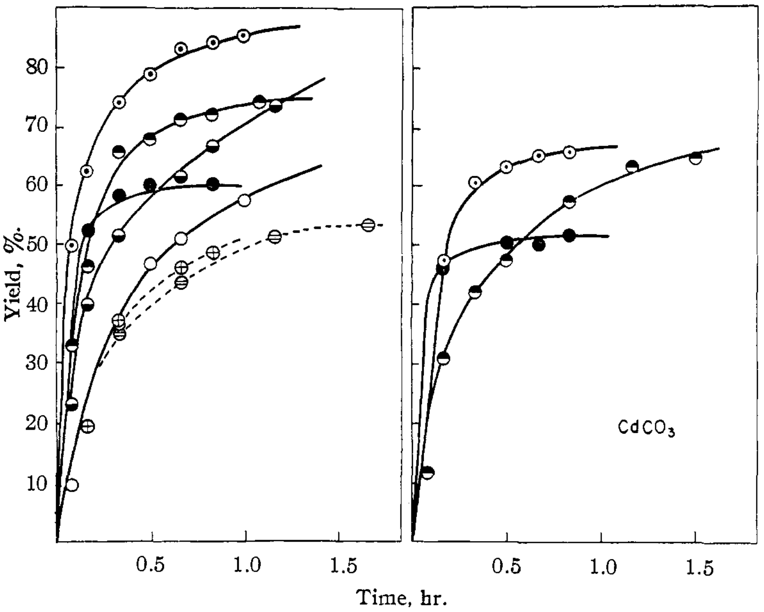

Fig. 1.—Rates of formation of terephthalic acid from dipotassium phthalate using various catalysts at varying temperatures: the reactant and catalysts are 2.9×10^{-4} and 6.6×10^{-3} mole, respectively; ○ 385°, ◒ 400°, ◓ 415°, ● 430°, ⊙ 415°. The catalyst quantity was duplicated in the last case. Left figure, CdI_2, solid line; $CdBr_2$, 385°, ---⊕---; $CdCl_2$, 385°, ---⊖---.

The Effect of Catalysts.—Typical examples of the preparation of terephthalic acid are given in Table II. In general, the maximum yield varies with the nature of the catalyst anion as well as the catalyst cation. Of the various catalyst cations studied, cadmium is the most effective (maximum yield *ca.* 90%), zinc is the second (*ca.* 50%) and then strontium, barium, calcium and magnesium (*ca.* 25%), manganese, copper, iron, aluminum, lead, mercury, cerium, zirconium and thorium (*ca.* 15%) in decreasing order Tin, cobalt, titanium, lanthanum, bismuth, vanadium, sodium, potassium and lithium have no catalytic effect but are harmless. Therefore, it is apparent that metals of group II in the periodic chart are more or less effective as catalyst cations. Nickel salts are harmful and facilitate unfavorable decompositions. Oxidative as well as reductive reagents (*e.g.*, $KMnO_4$, K_2CrO_4 and Na_2SO_3, H_2S, H_2) are harmful. Disodium phthalate gives only a poor yield of terephthalate in the same conditions, even if cadmium iodide catalyst was used.

The influence of the anionic portion of catalysts on the yield is unexpectedly large; halides were found to be most effective, and the decreasing order of the effectiveness was $I^- > Br^- > Cl^- > CO_3^=$ (Fig. 1). The oxides and sulfates of cadmium are also useful, but the nitrates are unsatisfactory. A graphical representation of the rates of the reaction using various catalysts is given in Fig. 1.

Although the reason for the remarkable catalytic effect of the iodide ion is still obscure, it is interesting to note a related observation that iodide ion accelerates the decarboxylation of ethyl hydrogen isopropylidenemalonate[6]; the loosening of the carbon–carbon bond between carboxyl group and benzene nucleus seems to be facilitated in the presence of iodide just as in the decarboxylation process. This catalytic effect of halides was observed with zinc halides as well as cadmium halides, but potassium iodide or iodine was ineffective.

(B) Terephthalic Acid from Benzoic Acid. The Mechanism.—As is evident from Table I, heating of potassium benzoate with labeled cadmium carbonate did not produce radioactive terephthalic acid (except at higher temperature where a little activity is observed in the product), and the recovered benzoic acid is also inactive, which shows that this reaction differs in the mechanism from the phthalate rearrangement.

The facts indicate that both carboxyl groups in the product are derived from benzoic acid. On the basis of this finding as well as the following observations: (1) that the reaction carried out under higher carbon dioxide pressure (150–200 atm.)[1] shows no substantial increase in the yield; that cadmium iodide is a better catalyst than the carbonate both in the yield and the rate; (2) that the yield of the reaction under no condition exceeds 50%, if assumed that one mole of the benzoate produces one mole of the terephthalate; and (3) since the reaction produces benzene a disproportionation may be suggested for the course of this reaction.

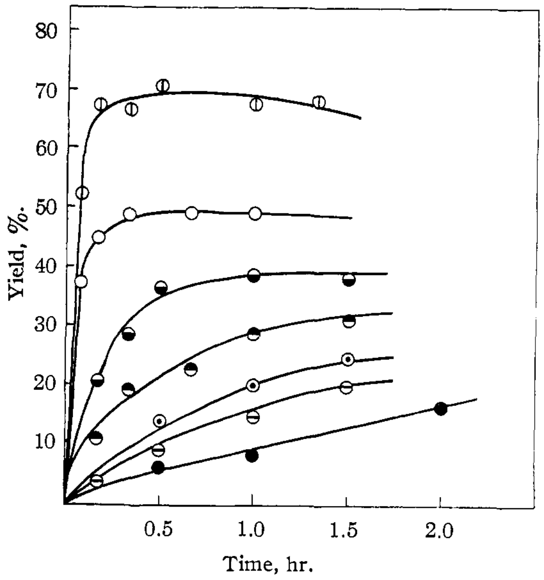

Fig. 2.—Rates of formation of terephthalic acid from benzoic acid using various catalysts at 425°: the reactant and catalysts are 1.00×10^{-2} and 5.80×10^{-4} mole, respectively; ○ CdI_2, ◒ $CdBr_2$, ◓ $CdCl_2$, ⊙ $CdCO_3$, ● CdI_2 but in a half amount, ⦶ CdI_2, a reaction of the phthalate, ⊖ CdI_2, a reaction of the isophthalate.

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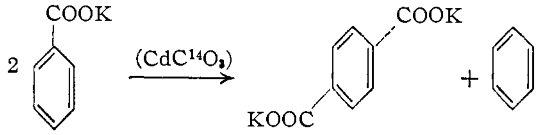
[6] E. J. Corey, THIS JOURNAL, **74**, 5897 (1952).



The rate of this reaction is slower than that of the phthalate (Fig. 2) and a larger amount of catalyst and a higher temperature are required.

TABLE II

TYPICAL EXAMPLES OF THE TEREPHTHALIC ACID SYNTHESES

Catalysts and their wt., g.	Time, hr.	Temp., °C.	Yield, %
	Starting material,[a] o-$C_6H_4(CO_2K)_2$		
$CdCO_3$, 0.10	2	430	73.8
$CdCO_3$, 0.10	4	400	67.7
$CdCl_2$, 0.10	4	400	70.0
$CdBr_2$, 0.14	4	400	72.7
CdI_2, 0.20	1	415	81.6
CdI_2, 0.08	2.5	415	85.2
CdI_2, 0.10	5	375	88.9[b]
$CdCO_3$, 0.05 $ZnBr_2$, 0.05	7	425	79.5
$CdCO_3$, 0.05 ZnI_2, 0.05	7	425	74.1
$CdCO_3$, 0.05 ZnI_2, 0.05	5	375	85.4[b]
$ZnBr_2$, 0.20[c]	7	425	48.3
ZnI_2, 0.20[c]	7	425	53.4
$ZnBr_2$, 0.025 $BaCO_3$, 0.05	4	425	58.1
$SrCl_2$, 0.05	7	425	24.0
$BaCO_3$, 0.20	7	425	19.7
$CuCl_2$, 0.05	3	450	13.9
	$C_6H_5CO_2K$		
$CdBr_2$, 0.20	5	375	49.8[b]
CdI_2, 0.30	4	448	57.6[b]
$CdCO_3$, 0.10 ZnI_2, 0.10	5	375	76.6
ZnI_2, 0.05[c]	2	425	15.4
SrI_2, 0.05	7	440	15.8
	p-$C_6H_4(CO_2K)_2$		
None	4	425	97.4
CdI_2, 0.50	4	425	60.5
$CdCO_3$, 0.20	2	425	89.1
	m-$C_6H_4(CO_2K)_2$		
CdI_2, 0.10	1.5	425	31.4

[a] 1.6 g. of each material was used. [b] The reaction mixture was placed in a test-tube with a constricted upper end (without stopper) and heated in an autoclave under 1–2 atmospheric pressure. Introduction of carbon dioxide had no appreciable effect. [c] Zinc halides are very hygroscopic. Hence, although the presence of a small amount of water had little effect on the yield, the catalyst mixing was insufficient and seemed to result in a considerable drop in the yield.

The Effect of Catalysts.—Typical examples of the preparation are listed in Table II. Of all the catalyst metals investigated, cadmium was the best and zinc the second as in the case of the phthalate rearrangement. Other metals tested have only a little catalytic effect and the order of the effectiveness is almost in accord with that observed in the case of the phthalate.

Also in this reaction, iodide is most effective and the efficiency decreases in the order $I^- > Br^- > Cl^- > CO_3^=$. A recent report[7] that benzoic anhydride is produced from bromo- or chlorobenzene under high carbon monoxide pressure in the presence of nickel carbonyl or other nickel salts and alkali metal salts is very interesting in relation to the accelerating effect of halides found in the present study. But our attempted reaction of potassium *p*-iodo- or *p*-bromobenzoate with cadmium carbonate for the terephthalate failed. There seems an apparent difference in mechanism between these two reactions.

Acknowledgments.—The authors wish to thank Profs. R. Oda, R. Goto, R. Nakai and Mr. K. Ogata for their aid in these experiments.

[7] W. W. Prichard, THIS JOURNAL, **78**, 6137 (1956).

KYOTO, JAPAN

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

The Dinitrogen Pentoxide–Olefin Reaction[1]

BY TRAVIS E. STEVENS AND WILLIAM D. EMMONS

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The reaction of dinitrogen pentoxide and several olefins has been investigated. The simple acyclic olefins gave 1,2-nitronitrates and a mixture of α- and β-nitroölefins. Cyclohexene gave a complex mixture that included 1,3- and 1,4-nitronitrates indicating that nitration by the nitronium ion may have been occurring. In the presence of excess nitrate ion added to suppress nitronium ion formation, *cis*-addition of dinitrogen pentoxide was found to occur. The *cis*-addition process is postulated as involving molecular dinitrogen pentoxide in a cyclic transition state.

Earlier investigations[2,3] of the dinitrogen pentoxide–olefin reaction indicated that the corresponding dinitrate was the principal product of the reaction and that dinitroalkanes, nitroalcohols and nitronitrates were produced also. However, in most cases neither the identity of the products nor the ratio in which they were formed was established definitely. This study was undertaken to determine the products formed from the dinitrogen pentoxide–olefin reaction and to elucidate their manner of formation.

Dinitrogen pentoxide, a volatile unstable white solid, reacts violently with many organic compounds.[2] Accordingly, the olefin reactions reported here were carried out by adding an approx-

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[1] This research was carried out under Army Ordnance Contract W-01-021-ORD-3341

[2] L. B. Haines and H. Adkins, THIS JOURNAL, **47**, 1419 (1925).

[3] N. Y. Demyanov, *Compt. rend. acad. sci., U.R.S.S.*, **1930A**, 447 (1931) [*C. A.*, **25**, 1215 (1931)]; *Ann. l'Inst. Agron., Moscow*, **4**, 155 1898) [*Chem. Zentr.*, **70, I**, 1064 (1899)].