

tion from an aqueous solution of the reaction mixture. Solvent was removed with a modified Podbielniak distillation column. The products were analyzed using an Aerograph A-100 gas phase chromatograph equipped with a five-foot Silicone oil-chromosorb column.

The accuracy of the technique was demonstrated by extracting known mixtures of the solvolysis products from acetic acid-sodium acetate-acetic anhydride mixtures. Concentration and volume conditions were identical, with only the relative proportions of olefin and acetate being varied. A direct relationship between area under the effluent peaks and mole fraction was observed.

From *trans*-4-methoxycyclohexyl tosylate there was obtained $67.2 \pm 1.2\%$ 4-methoxycyclohexene (retention time 1 minute 10 seconds) and $32.8 \pm 1.2\%$ 4-methoxycyclohexyl acetate (retention time 5 minutes 5 seconds). A duplicate run gave $65.6 \pm 0.3\%$ and $34.4 \pm 0.3\%$ olefin and acetate, respectively. The acetate fraction gave on hydrolysis a

mixture of *cis*- and *trans*-4-methoxycyclohexanols, which by infrared analysis contained 71.4% *trans* isomer. The acetate fraction showed on a second vapor phase chromatographic analysis 70.9% *trans*-4-methoxycyclohexyl acetate (retention time 28 minutes) and 29.1% *cis*-4-methoxycyclohexyl acetate (retention time 30 minutes). There is thus indicated $66.4 \pm 2\%$ 4-methoxycyclohexene, $24.0 \pm 2\%$ *trans*-4-methoxycyclohexyl acetate and $9.6 \pm 2\%$ *cis*-4-methoxycyclohexyl acetate.

In like fashion, *cis*-4-methoxycyclohexyl tosylate afforded $83.0 \pm 2\%$ (82.4 ± 1 , 83.6 ± 1) 4-methoxycyclohexene and $17 \pm 2\%$ (17.6 ± 1 , 16.4 ± 1) *trans*-4-methoxycyclohexyl acetate, both identified by infrared spectrum. The infrared spectrum of the latter showed *only trans* isomer to be present.

A similar procedure was used for product runs at other temperatures.

BERKELEY 4, CALIF.

(CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY)

Cyclic Diacyl Peroxides. V.¹ Reaction of Phthaloyl Peroxide with Norbornylene

BY FREDERICK D. GREENE AND WILLIAM W. REES²

RECEIVED JULY 24, 1959

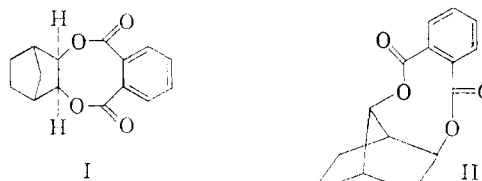
The reaction of phthaloyl peroxide and norbornylene in carbon tetrachloride solution affords the cyclic phthalate of *cis*-*exo*-2,3-bicyclo[2,2,1]heptanediol (I) in 20% yield, the cyclic phthalate of *exo*-2-*syn*-7-bicyclo[2,2,1]heptanediol (II) in 10% yield, phthalic anhydride in 10% yield and the addition product of carbon tetrachloride to norbornylene (IV, 2-chloro-3-trichloromethylbicyclo[2,2,1]heptane). Kinetic data indicate peroxide consumption by bimolecular reaction with norbornylene and establish that peroxide consumption by free radical chain decomposition is unimportant under these conditions. The formation of the 2,7-norbornyl phthalate (II) and earlier data are suggestive of the intervention between reactants and products of configurations possessing considerable positive charge at a carbon atom of the original double bond.

In a previous study³ the reaction of the cyclic diacyl peroxide, phthaloyl peroxide, with olefins was shown to be general and to obey second-order kinetics. The marked similarity observed in the relative reactivity of phthaloyl peroxide, peracetic acid and dibromocarbene toward aliphatic olefins and the available data on product compositions were interpreted in terms of bimolecular reaction of neutral peroxide with olefin. Additional evidence on the nature of the phthaloyl peroxide-olefin reaction is provided by the present study employing norbornylene.

Results

Reaction of phthaloyl peroxide with norbornylene in carbon tetrachloride at reflux affords a mixture of products, four of which were obtained in pure form. The major product, isolated in 20% yield of purified material, is a one-to-one adduct of the peroxide and the olefin, m.p. 204–205°. This compound is assigned structure I, cyclic phthalate of *cis*-*exo*-2,3-bicyclo[2,2,1]heptanediol, on the basis of the phthalate absorption in the infrared at 1735, 1300 and 1130 cm^{-1} ; the close similarity in ultraviolet spectrum, λ_{max} 272 ($\log \epsilon$, 3.07), to that of dibutyl phthalate; and alkaline hydrolysis to phthalic acid and *cis*-*exo*-2,3-bicyclo[2,2,1]heptanediol, identified by direct comparison with an authentic sample. A second one-to-one adduct, II, m.p. 142–143°, was isolated from the reaction mixture in 10% yield. The infrared spectrum showed a strong twin-peaked carbonyl band (1737

and 1712 cm^{-1}) and absorption in the carbon-oxygen region at 1300, 1148 and 1125 cm^{-1} . In the ultraviolet the compound showed maxima at 279 $\text{m}\mu$ ($\log \epsilon$ 3.22) and 285 $\text{m}\mu$ ($\log \epsilon$ 3.20). Alkaline hydrolysis of the adduct yielded *exo*-2-*syn*-7-bicyclo[2,2,1]heptanediol in 73% yield, identified by direct comparison with authentic material. On the basis of this evidence, adduct II is assigned the structure of the cyclic phthalate of the 2,7-diol.



Examination of the infrared absorption spectrum of the original product mixture showed absorption in the carbonyl region at 1855 and 1790 cm^{-1} , attributed to phthalic anhydride, and at 1780 cm^{-1} (in addition to the phthalate bands described above). The phthalic anhydride was isolated in 10% yield. The material absorbing at 1780 cm^{-1} was not isolated but is presumed to be lactonic *ortho*-ester, compounds of type III. In the reaction of phthaloyl peroxide with *cis*- and *trans*-stilbene compounds of type III are major products,⁴ showing strong absorption at 1778 cm^{-1} in the infrared.

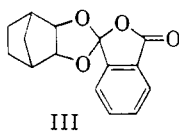
The fourth product isolated from the reaction was a liquid of analysis corresponding to a one-to-one adduct of norbornylene and carbon tetra-

(1) Part IV, F. D. Greene, *THIS JOURNAL*, **81**, 1503 (1959).

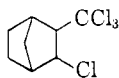
(2) General Electric Fellow 1957–1958. This article is based upon a portion of the Ph.D. thesis of W. W. Rees, 1958.

(3) F. D. Greene and W. W. Rees, *THIS JOURNAL*, **80**, 3432 (1958).

(4) F. D. Greene, *ibid.*, **78**, 2250 (1956).



III



IV

chloride. An adduct of identical physical constants and infrared spectrum was prepared by the benzoyl peroxide-initiated addition of carbon tetrachloride to norbornylene. The compound is considered to be the simple addition product IV (unspecified stereochemistry).⁵

Kinetics.—The reaction of phthaloyl peroxide and norbornylene in carbon tetrachloride at 80° is first order in peroxide and first order in olefin. Within any kinetic run there is a small decrease in the second-order rate constant amounting to a 10–15% decrease in k_2 by 80% completion of reaction.⁶ With the olefins examined previously, the reactions were cleanly second order throughout the entire reaction.³ The decrease in k_2 may be ascribed to the competing process of olefin consumption (formation of adduct IV), a process not of importance with the other olefins investigated. The kinetic data for norbornylene and for other representative olefins are summarized in Table I.

TABLE I

REACTION OF PHTHALOYL PEROXIDE WITH OLEFINS IN CARBON TETRACHLORIDE AT 80°^a

Olefin	$k_2 \times 10^3, M^{-1} \text{ sec.}^{-1}$
Norbornylene	7.6 ^a
Cyclohexene	6.83
1,1-Diphenylethylene	15.9
<i>trans</i> -Stilbene	13.7
<i>cis</i> -Stilbene	7.18
Allylbenzene	0.077
1-Methylcyclopentene	214

^a Rate constant ($\times 10^3$) decreased from 7.85 at 17% reaction to 7.49 at 57% reaction to 6.95 at 75% reaction in a run initially 0.0137 M in peroxide, 0.0287 M in olefin.

Discussion

In a previous paper³ the facile reaction of phthaloyl peroxide with olefins was considered to be a bimolecular, non-radical reaction. The complexities of the reaction of the peroxide with norbornylene in carbon tetrachloride raise several additional points of interest. Firstly, the formation of the carbon tetrachloride–norbornylene addition product IV is strong evidence for the presence of free radicals in the reaction medium. That the formation of this adduct need have involved only an exceedingly low radical concentration is indicated by a control experiment in which 0.2 mole % of benzoyl peroxide was sufficient to convert norbornylene to the carbon tetrachloride addition product. This finding of long chain length is not generally true for the addition of carbon tetrachloride to olefins but also has been observed with *t*-butylethylene which, like norbornylene, is an olefin lacking activated hydrogen atoms.⁷ The source of these radicals may have

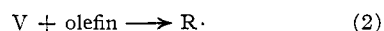
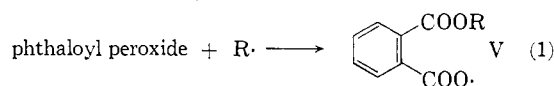
(5) Compound IV exhibited a single peak on a silicone–firebrick vapor phase column.

(6) Rates were determined by iodometric analysis for peroxide and k_2 calculated without taking into account consumption of olefin by the reaction giving the olefin–carbon tetrachloride adduct.

(7) For other evidence concerning the inertness of the hydrogen

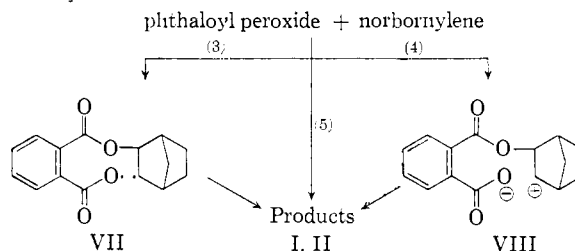
been monomeric phthaloyl peroxide or possibly dimeric phthaloyl peroxide, the presence of which in the monomeric phthaloyl peroxide at a level of 1% or so is not excluded by the evidence at hand.

The certain presence of free radicals in the medium requires a detailed consideration of the role of radicals in the norbornylene–phthaloyl peroxide reaction. Decomposition of benzoyl peroxide in a solution of phthaloyl peroxide (concn. of benzoyl peroxide/concn. phthaloyl peroxide, 1 to 20) in carbon tetrachloride both in the presence and absence of norbornylene does *not* accelerate the rate of disappearance of phthaloyl peroxide. (Both peroxides decompose in carbon tetrachloride alone by first-order processes; $k_{\text{benzoyl}}/k_{\text{phthaloyl}} = 57$ at 80°.) These experiments demonstrate that chain decomposition of olefin and peroxide (*e.g.*, equations 1 and 2) under these conditions is unimportant.⁸



Thus both kinetic and product data point to principal consumption of peroxide by bimolecular reaction with olefin. Of primary importance with respect to the details of this process is the formation of the cyclic phthalate of the *exo*-2-*syn*-7-bicyclo[2,2,1]heptanediol (II). This compound is believed to be a direct product of the reaction rather than a rearrangement product of the *exo*-2,3-cyclic phthalate (I) or lactone III in that subjection of the product mixture to the reaction conditions did not afford an increase in adduct II and subjection of pure I to the reaction conditions led only to recovery of I (83% yield).

As a basis for discussion of mechanism of the phthaloyl peroxide–norbornylene reaction, consider three possibilities: conversion of reactants to products (a) *via* configurations of diradical character [equation 3], (b) *via* configurations of “ion-pair” character [equation 4], (c) directly [equation 5].



With regard to path 3, free radical chain additions of *p*-thiocresol to norbornylene^{9a} and to

atoms in the allylic (but bridgehead) positions of norbornylene, see J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *THIS JOURNAL*, **72**, 3116 (1950).

(8) Although products I and II are not derivable by paths such as 1 and 2, the ascertainment of the relative importance of chain decomposition was desirable in view of the isolation in the form of pure compounds of only 40% of the original phthaloyl units.

(9) (a) S. J. Cristol and G. D. Brindell, *THIS JOURNAL*, **76**, 5699 (1954); (b) J. A. Berson and W. M. Jones, *ibid.*, **78**, 6045 (1956); (c) S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 6039 (1957). For evidence on rearrangement in the addition of thiocresol to norbornadiene, see S. J. Cristol, G. D. Brindell and J. A. Reeder, *ibid.*, **80**, 635 (1958).

substituted norbornylenes^{9b,c} have failed to reveal rearrangement products although a careful search has been made for such products. The failure to observe rearrangement of IX \rightarrow X under condi-

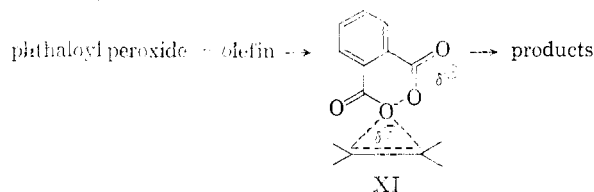


tions in which the lifetime of the radical is that dictated by the energetics of consumption of the radical by a chain transfer reaction is a powerful argument against the formation of the 2,7-adduct II by a rearrangement of VII, in which the lifetime of VII would be that dictated by the energetics of an intramolecular termination reaction. With respect to paths 4 and 5, the unfavorable steric situation for a truly synchronous formation of the 2,7-phthalate II by path 5 and the known propensity of electron deficiency at C-2 in the norbornyl system to lead to 2,7-rearrangement products¹⁰ is strongly suggestive that the reaction of phthaloyl peroxide with olefins proceeds through a stage involving considerable positive charge at a carbon of the original double bond. Further support for this statement is found in the reaction of phthaloyl peroxide *carbonyl-O*¹⁸ with *trans*-stilbene, from which was obtained cyclic phthalate possessing 11% of the excess oxygen-18 at alkyl oxygen.¹ The same distribution of oxygen-18 in cyclic phthalate was obtained from phthaloyl peroxide that had been subjected to 80° in carbon tetrachloride for four days prior to addition of *trans*-stilbene. These results in conjunction with a number of control experiments¹ pointed strongly to oxygen shuffling in the olefin reaction itself rather than in peroxide prior to reaction or in products after formation. Here also incorporation of carbonyl oxygen of peroxide into alkyl oxygen of cyclic phthalate may occur by a cyclic process (a different one from that considered for norbornylene) or by a formulation analogous to VIII in which principal ion-pair collapse occurs to the (closer) peroxygen atom, with some collapse to carbonyl oxygen affording the O¹⁸ in alkyl oxygen of cyclic phthalate.

With respect to the nature of the transition state for the reaction of phthaloyl peroxide with olefins, two considerations indicate that the transition state bears a closer resemblance to reactants than to products: (1) the large value (*ca.* 60–70 kcal./mole) calculated from average bond energies for the exothermicity of the reaction¹¹; and (2) the large *difference* (6 kcal./mole) in the heats of hydrogenation of norbornylene (33.13 kcal./mole) and cyclohexene (27.10 kcal./mole)¹² compared to the closeness in *k*₂ for rates of reaction of these olefins with phthaloyl peroxide. The preferential attack by the peroxide at sites of high electron density [$\rho = -1.65$ (log rel. *k* vs.

σ^+) for reaction of the peroxide with substituted *trans*-stilbenes in carbon tetrachloride at 80°³; see also the relative reactivity data in Table I] points to a transition state involving partial charge transfer from the π -electron cloud to the peroxide moiety. The closeness in *k*₂ for the reaction with norbornylene and with cyclohexene (Table I) is further suggestive that the transition state is closer in structure to the reactants than to representations such as VII or VIII. If at the transition state the double bond were disrupted in a manner represented by VII or VIII, norbornylene might have been expected to be substantially more reactive than cyclohexene (relative reactivity of norbornylene and cyclohexene to attack by the thiocresyl radical, 45 to 1^{9a}; relative reactivity in acetolysis of *exo*-norbornyl brosylate and cyclohexyl brosylate at 25°, 500 to 1).¹³

The simplest representation of the olefin-phthaloyl peroxide reaction that embraces the facts presented here and earlier^{1,3,4} is association of phthaloyl peroxide with the double bond, followed by conversion of the complex XI to products, in which the diversity of products is suggestive of the interconversion between XI and the products of configurations involving considerable positive charge at a carbon atom of the original double bond (for which VIII represents an electronic extreme).¹⁴



Experimental

Phthaloyl peroxide was prepared by the methods described previously.⁴ Material of at least 97% purity, obtained by recrystallization from methylene chloride, was used throughout.

Reaction of Phthaloyl Peroxide with Norbornylene (Bicyclo[2.2.1]heptene-2).—A solution of 0.882 g. (5.38 mmoles) of phthaloyl peroxide and 1.12 g. (11.9 mmoles) of norbornylene (a commercial sample, freshly sublimed) in 125 ml. of carbon tetrachloride was heated at reflux for 19 hr. The colorless acrid-smelling solution was cooled to 25° and evaporated to dryness under reduced pressure. Trituration of the resulting semi-solid with ether afforded 0.277 g. of crystalline material of m.p. 203–205°, a 20% yield of the cyclic phthalate of *cis-exo*-2,3-bicyclo[2.2.1]heptanediol (I). Two recrystallizations from carbon tetrachloride afforded felted needles of m.p. 205–206°; ultraviolet absorption, λ_{\max} 272 (log ϵ 3.07) in ethanol; infrared absorption (KBr pellet), 1735, 1300, 1130 cm.⁻¹.

Anal. Calcd. for C₁₅H₁₄O₄: C, 69.74; H, 5.46. Found: C, 69.54; H, 5.50.

The ether filtrate was evaporated to dryness. The fluid residue was dissolved in carbon tetrachloride and cooled, affording 0.077 g. (10% yield) of phthalic anhydride, m.p. 126.5–128°, mixed m.p. 126.5–128°.

The oil resulting from evaporation of the carbon tetrachloride filtrate was chromatographed on 50 g. of Florisil (100–200 mesh). Elution with petroleum ether–benzene (9:1) yielded 1.023 g. (35%) of carbon tetrachloride–norbornylene addition product, *n*_D²⁰ 1.5269, of identical infrared absorption spectrum with the one-to-one adduct of

(13) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan and H. Marshall, *ibid.*, **74**, 1127 (1952).

(14) For other examples of heterolytic reactions in inert media and in the gas phase, see C. K. Ingold, *J. Chem. Soc. (Proc.)*, 279 (1957).

(10) (a) H. Kwart and L. Kaplan, *THIS JOURNAL*, **76**, 4072 (1954); (b) H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954); (c) H. M. Walborsky and D. F. Loncrini, *ibid.*, **76**, 5396 (1954); (d) K. B. Wiberg and K. A. Saegbarth, *ibid.*, **79**, 6256 (1957); (e) K. Alder, H. Wirtz and H. Koppelberg, *Ann.*, **601**, 138 (1956).

(11) G. S. Hammond, *THIS JOURNAL*, **77**, 334 (1955).

(12) R. B. Turner, W. R. Meador and R. E. Winkler, *ibid.*, **79**, 4116 (1957).

carbon tetrachloride and norbornylene formed under benzoyl peroxide initiation. Elution with benzene-ether (4:1) yielded an oil which sublimed slowly at room temperature. Sublimation at 110–115° (0.25 mm.) afforded 0.143 g. (10% yield) of the cyclic phthalate of *exo-2-syn-7-bicyclo[2,2,1]-heptanediol* (II), m.p. 138–140°. A second sublimation raised the melting point to 141.5–143°; ultraviolet absorption in ethanol, λ_{\max} 231 m μ ($\log \epsilon$ 3.91), 279 (3.22), 285 (3.20); infrared absorption (potassium bromide pellet) 1737, 1712, 1300, 1270, 1148 and 1125 cm.⁻¹.

Anal. Calcd. for C₁₅H₁₄O₄: C, 69.74; H, 5.46. Found: C, 69.53; H, 5.62.

Carbon Tetrachloride-Norbornylene Addition Product (IV).—A solution of 1.095 g. (0.117 mole) of norbornylene and 0.272 g. (0.00113 mole) of benzoyl peroxide in 125 ml. of reagent carbon tetrachloride was heated at reflux for 19 hr. The acrid-smelling mixture was washed with aqueous sodium carbonate solution, with water and then dried over magnesium sulfate. Concentration followed by distillation yielded 1.61 g. (56% yield) of a colorless liquid, b.p. 132–135° (9 mm.), n_D^{20} 1.5298. Vapor phase chromatography on a silicone-firebrick column afforded a single uniform peak, suggestive of the presence of a single isomer.

Anal. Calcd. for C₈H₁₀Cl₄: C, 38.74; H, 4.06; Cl, 57.19. Found: C, 39.01; H, 4.13; Cl, 56.88.

In a separate experiment, 10 mg. (4.13 × 10⁻⁵ mole) of benzoyl peroxide sufficed to convert 1.17 g. of norbornylene in 125 ml. of carbon tetrachloride into the 1:1 adduct in 50% yield, b.p. 130–133° (10 mm.), n_D^{20} 1.5263. Only a faint cloudiness developed after several hours at 25° upon subjection of the liquid to 2% alcoholic silver nitrate solution.

Stability of 2,3-Norbornyl Phthalate to Conditions of Formation.—A solution of 0.058 g. of *exo-2,3-norbornyl* phthalate (I), 6.5 mg. of benzoyl peroxide and 0.257 g. of norbornylene in 25 ml. of carbon tetrachloride was heated at reflux for 20 hr. The colorless acrid-smelling solution was cooled and concentrated under reduced pressure, yielding a semi-solid residue. The residue was treated with ether and filtered yielding 0.042 g. (73%) of recovered cyclic phthalate of m.p. 201.5–204°. Concentration of the ether filtrate, chromatography on 2 g. of Florisil, and elution with petroleum ether-benzene (9:1) yielded the 1:1 solvent addi-

tion product. Elution with benzene-ether (1:1) afforded 0.006 g. of *exo-2,3-norbornyl* phthalate, m.p. 193–198°, total recovery 0.048 g. (83%). None of the 2,7-norbornyl phthalate could be isolated or detected.

Alkaline Hydrolysis of the Norbornyl Cyclic Phthalates.
A. 2,7-Isomer.—A mixture of 0.16 g. of cyclic phthalate, m.p. 138–140°, 1 g. of sodium hydroxide and 10 ml. of 75% ethanol was heated at reflux for 12 hr. The slightly yellow mixture was cooled, diluted with 3 ml. of water saturated with sodium chloride and extracted with seven 30-ml. portions of ether. Concentration of the dried ether solution and two sublimations of the residual solid at 130–135° (15 mm.) afforded 57 mg. (73% yield) of white solid, m.p. 163–168°, which gave a negative periodic acid test. Recrystallization from ether-petroleum ether yielded pure diol of m.p. 172–174°, *exo-2-syn-7-bicyclo[2,2,1]heptanediol*, no depression upon admixture with an authentic sample prepared by the method of Walborsky and Loncrini.^{10c}

The alkaline phase was diluted with 40 ml. of water, acidified with hydrochloric acid and extracted with ethyl acetate. Concentration of the dried organic phase yielded 64 mg. (62%) of phthalic acid, identified by sublimation to phthalic anhydride.

B. 2,3-Isomer.—A sample of 0.171 g. of cyclic phthalate of m.p. 204–205° was subjected to the above hydrolytic conditions. Three sublimations at 105–110° (15 mm.) afforded pure *cis-exo-2,3-bicyclo[2,2,1]heptanediol*, m.p. 137–139°, mixture m.p. of 136–138.5° with an authentic sample prepared by the oxidation of norbornylene by permanganate.¹⁵

The alkaline phase was worked up in the manner described previously, yielding 95 mg. of phthalic acid identified by conversion to phthalic anhydride.

Kinetics.—The rate of reaction of phthaloyl peroxide with olefin was followed by the method described previously³ (iodometric analysis for peroxide).

Acknowledgment.—We wish to thank the Research Corporation for a Frederick Gardner Cottrell grant which was of great assistance to this research.

(15) K. B. Wiberg and K. A. Saegerbarth, *THIS JOURNAL*, **79**, 2822 (1957).

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

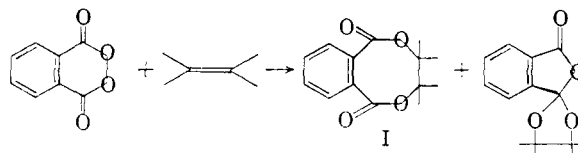
Cyclic Diacyl Peroxides. VI.¹ Reaction of Phthaloyl Peroxide with Diarylacetylenes

BY FREDERICK D. GREENE AND WILLIAM W. REES²

RECEIVED JULY 24, 1959

Phthaloyl peroxide reacts with diphenylacetylene and with di-*p*-methoxyphenylacetylene in carbon tetrachloride by a process involving over-all consumption of two moles of peroxide per mole of acetylene. The principal products from acid hydrolysis of the product mixture from peroxide and di-*p*-methoxyphenylacetylene are anisil, isolated in 32% yield, and phthalic acid. Kinetic evidence is presented for rate-determining formation of a one-to-one adduct of peroxide and acetylene followed by rapid reaction of adduct with peroxide. Possible complications in the tolan reactions are considered with reference to the reaction of phthaloyl peroxide with tetraphenylethylene and with a series of olefinic and non-olefinic compounds.

Phthaloyl peroxide previously has been shown to undergo a stereospecific reaction with olefins in a process that is kinetically first order in peroxide and first order in olefin to afford mixtures of products in which cyclic phthalates (I) and lactonic *ortho*-esters (II) are major components.³ In this paper the results of an investigation of the reaction of phthaloyl peroxide with two compounds possessing a carbon-carbon triple bond are presented.



Results and Discussion

The acetylenic compounds employed in this study were diphenylacetylene (tolan) and di-*p*-methoxyphenylacetylene. The reaction of phthaloyl peroxide with the acetylenes was carried out in carbon tetrachloride at 80°. With both acetylenes orange-red coloration developed during the reaction. The infrared spectra of the crude

(1) Part V, F. D. Greene and W. W. Rees, *THIS JOURNAL*, **82**, 890 (1960).

(2) General Electric Fellow, 1957–1958. This article is based upon a portion of the Ph.D. thesis of W. W. Rees, 1958.

(3) (a) F. D. Greene, *THIS JOURNAL*, **78**, 2250 (1956); (b) F. D. Greene and W. W. Rees, *ibid.*, **80**, 3432 (1958).