Reactions of *t*-Butyl Peresters. IX. The Reaction of Diphenylphosphinous Chloride with *t*-Butyl Peresters[1]

GEORGE SOSNOVSKY AND DAVID J. RAWLINSON

University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201

Received September 4, 1968

The reaction of diphenylphosphinous chloride, Ph_2PCl (**1**) with *t*-butyl peresters, *t*-BuOO(O)CR (**5a**, R = Ph; **5b**, R = Me), in refluxing benzene produces a complex mixture containing diphenylphosphinic anhydride, $Ph_2P(O)O(O)PPh_2$ (**2**), carboxylic anhydride, RC(O)O(O)CR, carboxylic acid chloride, diphenylphosphinic acid, $Ph_2P(O)OH$ (**6**), carboxylic acid, *t*-butyl chloride, and isobutylene. Only traces of carboxylic acid *t*-butyl ester, RC(O)O-*t*-Bu, are found. In addition, the mixed anhydride, $Ph_2P(O)O(O)CR$ (**3a**, R = Ph; **3b**, R = Me), is detected by ir spectroscopy. Catalytic amounts of cupric bromide accelerate the reaction. Mixed anhydride (**3**) and *t*-butyl diphenylphosphinate, *t*-BuO(O)PPh_2 (**7**), seem to be primary products of the reaction.

The reactions of diphenylphosphinous chloride,[2,3] Ph_2PCl (**1**), and triphenylphosphine[4,5] with benzoyl peroxide show interesting differences. The reaction of triphenylphosphine[4,5] yields triphenylphosphine oxide and benzoic anhydride, while reaction of **1** is more complex. The products are benzoyl chloride, benzoic anhydride, and diphenylphosphinic anhydride, $Ph_2P(O)O(O)PPh_2$ (**2**); also, a mixed anhydride, PhC(O)-O(O)PPh_2 (**3a**), is detected but not isolated. It has been shown[3] that the initial reaction of **1** with benzoyl peroxide is similar to that of triphenylphosphine, *i.e.*, an oxygen transfer (eq 1). The final products result

$$\underset{\mathbf{1}}{Ph_2PCl} + PhC(O)OO(O)CPh \longrightarrow Ph_2P(O)Cl + \underset{\mathbf{4}}{PhC(O)O(O)CPh} \quad (1)$$

from further reaction of the primary products, benzoic anhydride and diphenylphosphinyl chloride, $Ph_2P(O)Cl$

$$\underset{\mathbf{4}}{Ph_2P(O)Cl} + PhC(O)O(O)CPh \longrightarrow PhC(O)Cl + {}^1/_2PhC(O)O(O)CPh + {}^1/_2\underset{\mathbf{2}}{Ph_2P(O)O(O)PPh_2} \quad (2)$$

(**4**) (eq 2). **3a** is not a primary product, but is formed at a later stage.

Since the mechanism of the reaction of triphenylphosphine with another class of organic peroxide, the peresters,[6,7] is different from that with benzoyl peroxide, it was anticipated that further interesting results would result from a study of the reaction of **1** with *t*-butyl perbenzoate and *t*-butyl peracetate, *t*-BuOO(O)CR (**5a**, R = Ph; **5b**, R = Me).

Results

Preparative-scale reactions between **1** and **5a,b** were carried out at 1 *M* concentration in refluxing benzene. The products from the reaction of **5a** with **1** were *t*-butyl chloride, isobutylene, benzoyl chloride, benzoic anhydride, benzoic acid, compound **2**, and diphenylphosphinic acid, $Ph_2P(O)OH$ (**6**) (eq 3, R = Ph). In

$$\underset{\mathbf{1}}{Ph_2PCl} + \underset{\mathbf{5a,b}}{t\text{-}BuOO(O)CR} \longrightarrow CH_2{=}CMe_2 + t\text{-}BuCl + RC(O)Cl + RC(O)O(O)CR + \underset{\mathbf{2}}{Ph_2P(O)O(O)PPh_2} + RC(O)Cl + \underset{\mathbf{6}}{Ph_2P(O)OH} \quad (3)$$

addition, **3a** was detected, but could not be isolated. The reaction of **5b** with **1** yielded a similar product mixture (eq 3, R = Me); MeC(O)O(O)PPh_2 (**3b**) also was detected but not isolated. During the reactions of **1** with **5**, no gas (CO_2, HCl) was evolved, and neither chlorobenzene nor biphenyl was observed in the reaction products. The presence of catalytic amounts of cupric bromide did not alter the product composition. There was, however, an acceleration of the rate of disappearance of the peroxide.

The complex range of products, obtained from the reaction of peresters, indicated that secondary reactions had occurred. Various possible mixtures of primary products were, therefore, allowed to react under the same conditions, *i.e.*, in refluxing benzene at molar concentration.

Equimolar concentrations of *t*-butyl benzoate and **4** did not react. When varying proportions of the ester were replaced by benzoic acid, *t*-butyl benzoate was still unreactive; however, benzoic acid and **4** reacted in the mixture to form **2** and benzoyl chloride.

t-Butyl chloride reacted only slightly with **3a**; traces of *t*-butyl benzoate were detectable, but not benzoyl chloride or *t*-butyl diphenylphosphinate, $Ph_2P(O)O$-*t*-Bu (**7**). Compound **3a** in the reaction mixture decomposed to a mixture containing **3a** together with the two symmetrical anhydrides.

Ester **7** decomposed completely in the presence of equimolar benzoyl chloride. The products were the three anhydrides, the two corresponding acids, benzoyl chloride, *t*-butyl chloride, and isobutylene. A similar range of products resulted when a proportion of **7** was replaced by **6**.

Similar blank experiments were carried out with compounds containing the acetyl group, with results in general comparable to those with the benzoyl compounds.

Thus, *t*-butyl acetate did not react with equimolar **4**, both in the presence and absence of catalytic amounts of cupric bromide. When varying amounts of the *t*-butyl acetate were replaced by acetic acid, only a small part of the ester reacted; acetic acid and **4** reacted in the

---

(1) (a) Part VIII: G. Sosnovsky and E. H. Zaret, *J. Org. Chem.*, **34**, 968 (1969). (b) This investigation was supported by a grant from the Public Health Service, U. S. Department of Health, Education, and Welfare (GM 14932-01). (c) The preliminary results were presented in part in a talk at the International Symposium on the Chemistry of Organic Peroxides in Berlin, DDR, Sept 1967.

(2) G. Sosnovsky and D. J. Rawlinson, *Chem. Ind.* (London), 120 (1967).

(3) G. Sosnovsky and D. J. Rawlinson, *J. Org. Chem.*, **33**, 2325 (1968).

(4) F. Challenger and V. K. Wilson, *J. Chem. Soc.*, 213 (1927).

(5) L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

(6) D. B. Denney, W. F. Goodyear, and B. Goldstein, *J. Amer. Chem. Soc.*, **83**, 1727 (1961).

(7) R. F. Hudson, "Structure and Mechanism in Organo-Phosphorus Chemistry," Academic Press, New York, N. Y., 1965, p 170.

mixture with formation of **2**, acetyl chloride, and traces of acetic anhydride. *t*-Butyl chloride did not react with **3b**; no *t*-butyl acetate, acetyl chloride, or **7** was detected. The major reaction was the decomposition of **3b** to a mixture containing **3b** together with the two symmetrical anhydrides. Compound **7** decomposed in the presence of equimolar acetyl chloride. The initial product was an unidentified insoluble white solid, presumably **6**, which later redissolved. The final products identified by ir were the two symmetrical anhydrides and traces of *t*-butyl chloride and isobutylene.

In view of the complexity of the reaction products at 1 *M* concentration, conditions were sought where secondary reactions could be minimized, so as to follow the formation of initial products from the reactions of **1** with **5**. At room temperature, the reaction was too slow. However, in refluxing benzene solutions of 0.1 *M* concentration, the disappearance of products could be followed by ir spectroscopy. Unlike the reaction[3] of benzoyl peroxide with **1**, though, no clear-cut separation between primary and secondary interactions was attainable.

In the absence of copper salt catalyst, the first products to be seen, after disappearance of **5**, were **3** and **7**. As the reaction proceeded further, the concentrations of both **3** and **7** steadily decreased. The final ir spectra of these reaction mixtures were in general identical with those of the preparative-scale experiments, except that with **5b** a small amount of **7** survived undecomposed. With **5a**, **7** had completely decomposed in the later stages.

In the presence of catalytic amounts of cupric bromide, **3** was the first product to be seen after disappearance of **5**, and its concentration diminished in the later stages. However, with copper salt catalysis, **7** was not observed. The final product composition again appeared from ir spectra to be identical with that obtained in the preparative-scale experiments. At 0.1 *M* concentration of **1** and **5**, the cupric bromide catalyzed reaction was much more rapid than the uncatalyzed reaction.

Discussion

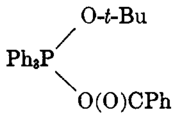
The reaction of triphenylphosphine with peresters[5,6,8] produces triphenylphosphine oxide and the corresponding carboxylic ester, together with varying amounts of the carboxylic acid (eq 4).

$$\mathrm{PPh_3 + RC(O)OO\text{-}\mathit{t}\text{-}Bu \longrightarrow PPh_3(O) + RC(O)O\text{-}\mathit{t}\text{-}Bu + RC(O)OH} \quad (4)$$

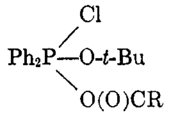
When one of the phenyl groups of triphenylphosphine is replaced by a chlorine atom, an interesting change in the composition of the products is observed. Thus, the reaction of **1** with perester produces an unexpectedly complex mixture. This consists of carboxylic anhydride, **2**, the corresponding carboxylic acid, carboxylic acid chloride, *t*-butyl chloride, and isobutylene; in addition, **3** is detected (eq 3). In contrast to the reaction of triphenylphosphine, the carboxylic *t*-butyl esters are formed only in minor amounts.

The complexity of products indicates that secondary reactions occurred either during the reaction period or during work-up. Evidence concerning the primary products and pathway was obtained indirectly, from studies of synthetic mixtures of possible primary products, and directly, from the ir studies of incomplete reactions at lower concentrations.

The mechanism of the reaction of triphenylphosphine with **5a** (eq 4) has not been firmly established. A suggestion[6] proposing a pentavalent intermediate (**8**) has more recently been elaborated.[7] The participation of an analogous pentacovalent intermediate (**9**) in the reaction of **1** with peresters would lead one to expect three possible sets (1, 2, 3) of primary products according to the mode of decomposition of **9**. The mechanism



8



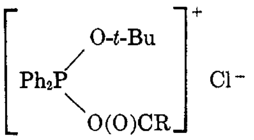
9

1. $\underset{\mathbf{4}}{\mathrm{Ph_2P(O)Cl}} + \mathrm{RC(O)O\text{-}\mathit{t}\text{-}Bu + RC(O)OH + CH_2{=}CMe_2}$

2. $\underset{\mathbf{3}}{\mathrm{Ph_2P(O)O(O)CR}} + \mathrm{\mathit{t}\text{-}BuCl}$

3. $\underset{\mathbf{7}}{\mathrm{Ph_2P(O)O\mathit{t}\text{-}Bu}} + \underset{\mathbf{6}}{\mathrm{Ph_2P(O)OH}} + \mathrm{CH_2{=}CMe_2 + RC(O)Cl}$

of formation of the products in set 1 would be strictly analogous to that of reaction of triphenylphosphine with peresters.[6,7] Either of the sets of products 2 and 3 could be visualized as resulting from an ion pair (**10**), followed by attack of chloride ion either at alkyl carbon or at acyl carbon.



10

Set 1, which is analogous to the pathway of triphenylphosphine, is in fact excluded by the experimental data. Separate experiments establish that carboxylic acid *t*-butyl ester is stable in the presence of the other components of set 1. Hence, if formed by the reaction of **5** according to set 1, it should survive under the experimental conditions. However, carboxylic ester is not detected as an initial product in the experiments at 0.1 *M* concentration, and was only isolated in small quantity in the preparative experiments at 1 *M* concentration. On this basis, it is concluded that carboxylic ester cannot be a primary product, and that the small quantities isolated in the preparative-scale experiments are secondary products.

The early detection of **3a** and **7** together indicates that both are primary intermediates. This is confirmed by the blank experiments with possible primary products. The range of products obtained from **1** and perester is similar to that isolated from **7** and benzoyl chloride. However, the ratios of products differ for the two reactions. This is also confirmed by differences in the infrared spectra of the reaction mixtures before work-up. Thus, neither of the sets of products obtained from set 2 or 3 alone seems to explain the products obtained from the reaction of **1** with peroxide. A combination of the two is, however, satisfactory. Participation at an even earlier stage of the reaction by intermediate **9**, which decomposes simultaneously according to sets 2 and 3 (but *not* according to set 1),

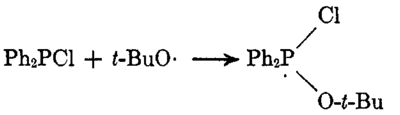
---

(8) D. B. Denney, W. F. Goodyear, and B. Goldstein, *J. Amer. Chem. Soc.*, **82**, 1393 (1960).

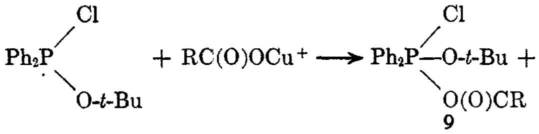
seems to afford the best rationalization of the observations. The reaction thus differs, on the one hand, from the reaction of triphenylphosphine with peresters,[5-8] and, on the other hand, from that of **1** with benzoyl peroxide,[2,3] where **3** is formed at a later stage of the reaction.

For the reaction of triphenylphosphine with peresters, a homolytic reaction has in general been discounted.[6,7] In the reaction of **1**, the absence of carbon dioxide in the products and the inertness of the solvent seem also to exclude a radical reaction. However, traces of copper ion accelerate the reaction, and since copper ions are known to accelerate homolytic processes of peresters,[9] it seems possible that at least the copper ion catalyzed part of the reaction between **1** and **5** might be proceeding by a radical route. By an adaptation of our mechanism of the perester reaction,[9] the following steps are proposed for the formation of intermediate **9** (eq 5–7).

$$\mathrm{RC(O)OO}\text{-}t\text{-Bu} + \mathrm{Cu^+} \longrightarrow \mathrm{RC(O)OCu^+} + t\text{-BuO}\cdot \quad (5)$$



$$\mathrm{Ph_2PCl} + t\text{-BuO}\cdot \longrightarrow \mathrm{Ph_2\dot{P}}\begin{matrix}\mathrm{Cl}\\ \mathrm{O}\text{-}t\text{-Bu}\end{matrix} \quad (6)$$



$$\mathrm{Ph_2\dot{P}}\begin{matrix}\mathrm{Cl}\\ \mathrm{O}\text{-}t\text{-Bu}\end{matrix} + \mathrm{RC(O)OCu^+} \longrightarrow \mathrm{Ph_2P}\begin{matrix}\mathrm{Cl}\\ \text{—O-}t\text{-Bu}\\ \mathrm{O(O)CR}\end{matrix} + \mathrm{Cu^+} \quad (7)$$

Experimental Section

Compounds **1** (Stauffer Chemical Company), **5a**, and **5b** (75% solution in benzene) (Lucidol Division, Wallace and Tiernan, Inc.) were gifts. *t*-Butyl benzoate,[10] **7**,[11] **4**,[12] **6**,[13] and **2**[14] were made by literature methods. Compound **3b** was prepared by a method analogous to that used previously to make **3a**, which is more convenient than the literature method.[15] All other chemicals were purchased.

The experimental approach was similar[16] to that described in a previous paper.[3] In preparative-scale experiments, the products were either isolated by distillation and recrystallization, *or*, in some cases, detected by ir spectroscopy without isolation. Ir spectra were used to follow the progress of the reactions and isolation procedures, and to confirm the characterization of isolated materials.

Registry No.—**1**, 1079-66-9; **5a**, 614-45-9; **5b**, 107-71-1.

Acknowledgment.—The authors wish to thank Mr. W. J. Mertz for technical assistance.

---

[9] G. Sosnovsky and O. S. Lawesson, *Angew. Chem. Intern. Ed. Engl.*, **3**, 269 (1964).

[10] J. F. Norris and G. W. Rigby, *J. Amer. Chem. Soc.*, **54**, 2098 (1932).

[11] R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc.*, 722 (1966).

[12] P. Hauke and G. Hurst, *J. Amer. Chem. Soc.*, **88**, 2544 (1966).

[13] L. R. Ocone, *et al.*, *U. S. Dept. Comm., Office Tech. Serv., P. B. Rept.*, AS262, 806 (1961); *Chem. Abstr.*, **59**, 2853*h* (1963).

[14] R. L. Dannley and K. R. Kabre, *J. Amer. Chem. Soc.*, **87**, 4805 (1965).

[15] D. L. Venesky and C. F. Poranski, Jr., *J. Org. Chem.*, **32**, 838 (1967).

[16] Full experimental details have been deposited as Document No. 00496 with the ASIS National Auxiliary Publications Service, % CCM Information Corp., 909 Third Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting $3.00 for photoprints, or $1.00 for microfiche. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Resin Acids. XVII. Synthesis of 7- and 11-Oxygenated Abietanes[1,2]

WERNER HERZ AND J. J. SCHMID[3]

Department of Chemistry, Florida State University, Tallahassee, Florida 32306

Received January 14, 1969

The oxidation of methyl 13β-abiet-8-(9)-en-18-oate (**4b**) with *t*-butyl chromate is described. The structure and stereochemistry of the oxidation products has been elucidated and the conversion of some of them to methyl 11-oxo-13β-abietan-18-oate (**17**) is described. **17** and its 9β epimer **25** were obtained also by transformations of the epoxide of **4b**. Hydroboration of **4b** provides a simple route to 7-oxygenated abietanes.

In earlier paper[4] we described results which led to the unambiguous specification of configuration for the abietanoic acids, **1**, **2**, and **3a**.[5,6] These substances were needed as reference compounds for other investigations. In the present communication we describe that part of our work which had as its goal the transformation of abietic acid to 11-oxygenated derivatives which were envisioned as intermediates for the partial synthesis of more highly functionalized naturally occurring diterpenoids. In the course of this effort a number of other interesting observations bearing on stereochemical aspects in the perhydrophenanthrene series were made and are reported herewith.

Although previous attempts at allylic oxidation of methyl 13β-abiet-8(9)-en-18-oate (**4b**) had resulted only in aromatization of ring C,[7] oxidation of **4b** with *t*-butyl chromate in refluxing carbon tetrachloride gave a mixture of five nonaromatic substances which were separated by column chromatography. In order of increasing polarity, these were three ketones, A (15%), B (15%), and C (35%), a hydroxy ketone D (10%), and a hydroxy ketone E (2%). The balance consisted of a very polar mixture of further oxidation products.

The least polar ketone, A, mp 108–109°, was α,β-unsaturated [ir band at 1650 cm^{-1}, $\lambda_{\max}$ 245 nm (ε

---

[1] Resin Acids. XVI: W. Herz and J. J. Schmid, *J. Org. Chem.*, **34**, 2775 (1969).

[2] Supported in part by National Science Foundation Grant GP-6362.

[3] National Science Foundation Fellow, 1967–1968.

[4] J. W. Huffman, T. Kamiya, L. H. Wright, J. J. Schmid, and W. Herz, *ibid.*, **31**, 4128 (1966).

[5] Similar conclusions have been reached by A. W. Burgstahler, J. N. Marx, and D. F. Zinkel, *ibid.*, **34**, 1550 (1969).

[6] The numbering and nomenclature employed by us follows a recent proposal (third revision, Oct 1968) by J. W. Rowe, Forest Products Laboratory, Madison, Wis., "The Common and Systematic Nomenclature of Cyclic Diterpenes," subscribed to by most workers in the field. The parent abietane skeleton as proposed by E. Fujita, T. Fujita, and H. Katayama, *Chem. Commun.*, 968 (1967), has the *trans-anti-trans* configuration with a 13α-isopropyl group. Thus **1** is referred to as abietan-18-oic acid. Inverted configurations are designated by the position number and the correct stereochemistry before the skeletal name.

[7] W. Herz and H. J. Wahlborg, *J. Org. Chem.*, **30**, 1881 (1965); H. J. Wahlborg, Ph.D. Dissertation, Florida State University, 1965.