attacking carbon) on the reaction is also in accord with this postulate.

Triphenylphosphinebenzoylmethylene[10] (IId) and triphenylphosphinecarbethoxymethylene[9b,11] (IIe) have recently been prepared and their reactions with carbonyl compounds examined. Both reacted with benzaldehyde but failed to react with cyclohexanone in the usual manner. In both examples there is an available "electron sink" to compete with the $3d$-orbital of phosphorus for the electron pair on carbon, thereby increasing the stability and decreasing the reactivity of these reagents in a manner analogous to that operating in I.

An examination of the mechanism of the reaction of phosphinemethylenes with carbonyl compounds reveals that the more reactive and less stable reagent should possess the largest double bond character (*i.e.*, the largest concentration of negative charge on the carbon next to phosphorus). It is of interest to note that the measured electric dipole moments of I and IIa indicated that the P—C bond in both possessed roughly 50% double bond character, whereas they differed considerably in their reactivity.

EXPERIMENTAL[12]

Triphenylphosphoniumfluorenylide. Triphenylfluorenylphosphonium bromide, m.p. 289–291°, was prepared in 94% yield according to the procedure of Pinck and Hilbert.[2] It was then converted to I, m.p. 258–260, $\lambda_{\max}^{CHCl_3}$ 250 mμ(log ϵ 4.6), 258 (4.6), 284 (4.3), and 382 (3.6), in 88% yield.

Anal. Calcd. for $C_{31}H_{23}P$: C, 87.3; H, 5.4; P, 7.3. Found: C, 87.6; H, 5.4; P, 7.3.

Reaction of I with carbonyl compounds. The general procedure used in all reactions is described below. To a solution of 1.0 g. (2.35 mmoles) of I in 30 ml. of chloroform was added 2.35 mmoles of the carbonyl compound. After heating the orange solution under reflux for 3 hr. the solvent was evaporated on the steam bath. To the residual oil or solid was added 25 ml. of absolute ethanol and any unchanged I which precipitated was removed by filtration. The filtrate was diluted with water and the precipitated dibenzofulvene derivative was filtered and dried.

A. Benzaldehyde (0.3 g., 2.35 mmoles) and I were reacted as described above. No unchanged I precipitated upon the addition of absolute ethanol. The addition of a few ml. of water precipitated 0.5 g. (84%) of benzalfluorene (IIId), m.p. 71–74°. Recrystallization from ethanol-water afforded colorless leaflets, m.p. 74.5–76.0,° $\lambda_{\max}^{EtOH}$ 227 mμ(log ϵ 4.6), 248 (4.3), 256 (4.4), and 325 (4.1). (Lit.,[13] m.p. 76°.)

Anal. Calcd. for $C_{20}H_{14}$: C, 94.5; H, 5.5. Found: C, 94.9; H, 5.4.

The filtrate remaining after the removal of the benzalfluorene was quenched with water and exhaustively extracted with ether. The ethereal layer was dried and evaporated to a colorless solid. Hexane was added and the residual precipitate of triphenylphosphine oxide (0.5 g., 77%) was filtered and dried to m.p. 152–154°.

B. Anisaldehyde (0.32 g., 2.35 mmoles) and I were allowed to react as described here. The addition of absolute ethanol to the evaporation residue afforded 0.6 g. of unchanged I as a yellow precipitate. The filtrate remaining after the removal of I was treated with a few ml. of water resulting in the precipitation of 0.25 g. (93%) of *p*-methoxybenzalfluorene (IIIe), m.p. 129.5–131°, which was recrystallized from 95% ethanol as pale yellow plates, m.p. 130–131°, $\lambda_{\max}^{EtOH}$ 232 mμ(log ϵ 4.5), 247 (4.4), 257 (4.4), and 342 (4.2). (Lit.,[14] m.p. 128–129°.)

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.7; H, 5.7. Found: C, 88.9; H, 5.6.

C. *p*-Nitrobenzaldehyde (0.36 g., 2.35 mmoles) and I were mixed in 30 ml. of chloroform as described here. Almost immediately the characteristic orange color of I was replaced by a very pale yellow color. Heating under reflux for 3 hr. effected no visible color change. Evaporation of the solvent left a pale yellow oil. The addition of ethanol afforded 0.64 g. (96%) of *p*-nitrobenzalfluorene (IIIg), m.p. 167–168°, which was recrystallized from absolute ethanol as fine yellow needles, m.p. 167–168°, $\lambda_{\max}^{EtOH}$ 224 mμ(log ϵ 4.5), 258 (4.5), and 354 (4.1).

Anal. Calcd. for $C_{20}H_{13}NO_2$: C, 80.3; H, 4.4; N, 4.7. Found: C, 80.3; H, 4.3; N, 4.6.

D. 2,4,7-Trinitrofluorenone (0.74 g., 2.35 mmoles) and I were mixed in chloroform solution as described above resulting in the immediate formation of a deep red coloration. Heating for 3 hr. under reflux effected no visible change. The solution was cooled and a deep red-brown precipitate (1.1 g.) was removed by filtration and dried to m.p. 272–276°. All attempts at recrystallization failed. No unchanged I could be recovered upon evaporation of the chloroform filtrate and the addition of ethanol.

Hydrolysis of I. A slurry of 0.7 g. (1.6 mmoles) of I in 60 ml. of 30% aqueous ethanol was heated under reflux for 24 hr. The fluorenylide was initially insoluble in the solvent but dissolved with apparent reaction only after 18 hr. of reflux. Water, 200 ml., was added and the resulting solution was extracted with ether. Removal of the ether afforded 1.2 g. of a pale yellow solid which was in turn extracted with hexane. Evaporation of this extract left 0.20 g. (73%) of a colorless solid which crystallized from ethanol as colorless plates, m.p. 113–115°, undepressed on admixture with authentic fluorene.

To 100 ml. of a 70% ethanolic sodium hydroxide solution was added 0.93 g. (2.2 mmoles) of I and the mixture was heated under reflux for 18 hr. The solution was worked up as above to afford 0.32 g. (90%) of fluorene, m.p. 113–114.5°.

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[10] F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

[11] M. Vilkas and N. A. Abraham, *Compt. rend.*, **246**, 1434 (1958).

[12] Melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside 77, New York. Ultraviolet spectra were recorded in 95% ethanol with a Cary model 11 spectrophotometer by W. B. White.

[13] J. Thiele, *Ber.*, **33**, 851 (1900).

[14] J. Thiele and F. Henle, *Ann.*, **347**, 290 (1906).

Reaction of Mesityl Oxide with Peroxyacetic Acid

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The principal product usually obtained from the reaction of an α,β-unsaturated ketone with a peracid is an enol ester.[1] The ketones used, how-

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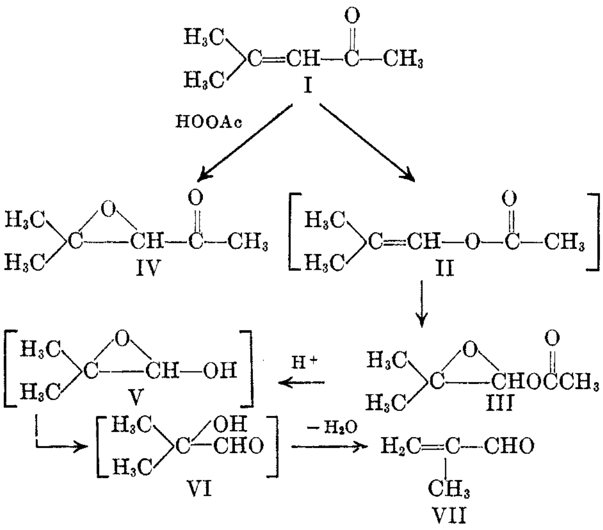
[1] See H. M. Walton, *J. Org. Chem.*, **22**, 1161 (1957) for a recent discussion of the possible products which might be expected from this reaction.

ever, have generally been those having a phenyl group in the β-position.[1,2]

We have observed that mesityl oxide, 4-methyl-3-pentene-2-one (I), having two alkyl groups in the β-position, on treatment with peroxyacetic acid afforded *no* enol ester, II. Instead, there was obtained in 53% yield (based on peroxyacetic acid) crude 3,3-dimethyl-2-acetoxyoxirane (III), contaminated with about 20% of what appeared to be the epoxy ketone, IV. The latter material has the same boiling point as III[3] and could not be separated by distillation. Gas chromatography also failed to give a separation. The presence of IV was indicated (a) by carbon and hydrogen analysis, (b) by ketone carbonyl absorption in the infrared, and (c) by virtue of its removal through water-washing of the mixture.[4] The latter procedure afforded III, in analytical purity, although in reduced yield due to loss to the water.



The epoxy ester III was undoubtedly formed *via* the enol ester II,[1] since, in a blank experiment, the epoxy ketone IV underwent less than 5% reaction with peroxyacetic acid. The fact that no enol ester II was isolated indicates that it must have reacted much more rapidly with the peracid than did the starting material. The failure of the reaction rate to decrease with time (as determined by a plot of *log* peracid concentration *vs.* time) over 90% of the reaction was evidence in support of this view.

The reaction of III with hot acidic ethanol afforded 2-methylpropenal (VII), presumably formed by way of intermediates V and VI; it was isolated as the 2,4-dinitrophenylhydrazone.

When methyl isopropenyl ketone and methyl vinyl ketone, compounds containing neither aryl nor alkyl substitution at the β-carbon, were treated with peroxyacetic acid, very slow reaction rates were encountered.[5] Whereas mesityl oxide was oxidized in 4.5 hr. at room temperature, methyl isopropenyl ketone required 5 days for 95% reaction and methyl vinyl ketone required 26 days for 92% reaction. The product isolated in 22% yield from the methyl isopropenyl ketone reaction was the epoxy ketone, 3-methyl-3,4-epoxy-2-butanone, apparently contaminated with about 10% of the corresponding epoxy ester, 2-methyl-2-acetoxyoxirane. The presence of the latter was inferred from carbon and hydrogen analysis, saponification value, and infrared analysis.

In view of the low recovery of epoxy derivatives obtained in the reaction of methyl isopropenyl ketone with peroxyacetic acid (undoubtedly due to the hydrolysis of primary products to water-soluble fragments during the 5-day reaction period), the reaction mixture from methyl vinyl ketone was not investigated.

EXPERIMENTAL

Reaction of mesityl oxide with peroxyacetic acid. To a stirred solution of 49 g. (0.50 mole) of mesityl oxide (n_D^{20} 1.4401) in 250 ml. of chloroform was added 0.50 mole of 45% peroxyacetic acid[6] (previously treated with sodium acetate to neutralize the sulfuric acid present). The mixture was stirred at 20–25° using a water bath held at 15–20° by the periodic addition of ice, and the rate of disappearance of peroxyacetic acid was followed iodometrically[7]:

Time (Hr.)	% Peroxyacetic Acid Consumed
1	53
2.5	89
3.5	93
4.5	96

The mixture was treated with 150 ml. of water followed by the portionwise addition of 125 g. of sodium bicarbonate. When carbon dioxide was no longer evolved, excess solid was removed by filtration and the organic layer was washed with 100 ml. of half-saturated ammonium sulfate solution. After drying over magnesium sulfate, the bulk of the chloroform was removed at atmospheric pressure using a 10-tray Oldershaw column. When the kettle temperature reached 120°, distillation was continued under vacuum through a 0.5 × 60 cm. glass spiral-packed column. The following fractions were obtained. Fraction 1: 54–70° (100 mm.), 1.8 g.; Fraction 2: 70–72° (100 mm.), 20.7 g., n_D^{20} 1.4402; Frac-

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(2) J. Boeseken and A. Kramer, *Rec. trav. chim.*, **50**, 827 (1931); J. Boeseken and A. L. Soesman, *Rec. trav. chim.*, **52**, 874 (1933); J. Boeseken and J. Jacobs, *Rec. trav. chim.*, **55**, 786 (1936).

(3) R. S. Wilder and A. A. Dolnick, U. S. Patent **2,431,718** (Dec. 2, 1947).

(4) Epoxy ketone IV, prepared by alkaline epoxidation of mesityl oxide (reference 3), is soluble in an equal volume of water while III is less water-soluble.

(5) This would be expected on the basis of a mechanistic interpretation advanced for this general reaction by W. Wenkert and M. Rubin, *Nature*, **170**, 708 (1952).

(6) F. P. Greenspan, *Ind. Eng. Chem.*, **39**, 847 (1947).

(7) F. P. Greenspan and D. G. Mackellar, *Anal. Chem.*, **20**, 1061 (1948).

tion 3: 72–82° (100–50 mm.), 3.8 g.; Fraction 4: 82–83° (50 mm.), 17.3 g.; Residue, 3 g.

Fraction 2 was recovered mesityl oxide (0.21 mole); its refractive index indicated the absence of any enol ester (II).[8] Analysis of Fraction 4 indicated it to be a mixture composed of 78% w. 3,3-dimethyl-2-acetoxyoxirane and 22% w. 4-methyl-3,4-epoxy-2-pentanone.

Anal. Calcd. for 78% $C_6H_{10}O_3$ and 22% $C_6H_{10}O_2$: C, 57.1; H, 8.0. Found: C, 57.1; H, 8.0.

The infrared spectrum showed ester carbonyl absorption at 5.73μ with a shoulder at 5.84μ. A sample of 4-methyl-3,4-epoxy-2-pentanone[3] exhibited carbonyl absorption at 5.84μ.

Fraction 4 (15 g.) was washed with three 25-ml. portions of water, dried over magnesium sulfate and Claisen distilled to give 7 g. of 3,3-dimethyl-2-acetoxyoxirane, b.p. 60° (20 mm.), n_D^{20} 1.4128, which, by analysis, was substantially free of the ketone epoxide.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.4; H, 7.7. Found: C, 55.8; H, 7.9.

A 2,4-dinitrophenylhydrazone was prepared[9] from Fraction 4 and recrystallized from ethyl acetate, m.p. 199–200° (dec.). The same derivative was prepared from freshly distilled 2-methylpropenal, m.p. 200–201° (dec.). The mixed m.p. was 199–200° (dec.). The derivative from Fraction 4 was subjected to analysis.

Anal. Calcd. for $C_{10}H_{10}N_4O_4$: C, 48.0; H, 4.0; N, 22.4. Found: C, 47.8; H, 4.2; N, 22.3.

Reaction of methyl isopropenyl ketone with peroxyacetic acid. A solution of 84 g. (1.0 mole) of methyl isopropenyl ketone[10] (b.p. 98–99°; 98% purity by bromine number) and 1.0 mole of 45% peroxyacetic acid in 500 ml. of chloroform was allowed to stand at room temperature for 5 days. Iodometric titration at that time indicated that 96% of the theoretical amount of peracid had been consumed. The mixture was worked up as above and distilled through a 10-tray Oldershaw column to give, after removal of solvent and 10.0 g. of crude starting material, b.p. 50–54° (150 mm.), 22.2 g. (22% yield) of product, b.p. 58–59° (50 mm.); n_D^{20} 1.4171. Analysis of the product indicated it to be a mixture containing 89% of 3-methyl-3,4-epoxy-2-butanone[11] and 11% of 2-methyl-2-acetoxyoxirane.

Anal. Calcd. for 89% $C_5H_8O_2$ and 11% $C_5H_8O_3$: C, 59.2; H, 7.9. Found: C, 59.1; H, 8.0.

A 1.96 g. sample of the product was allowed to stand overnight with 50.0 ml. of 0.102*N* sodium hydroxide. Back titration with standard acid indicated the presence of 10.8% by weight of ester calculated as 2-methyl-2-acetoxyoxirane.

The infrared spectrum of the product was virtually identical with that of the epoxy ketone obtained from the alkaline epoxidation of methyl isopropenyl ketone[11]: maxima at 5.84, 7.35, 8.87, 9.92, 10.56, 10.88, and 11.92μ. The only significant difference was a shoulder at 5.71μ, consistent with the presence of small amount of ester impurity.

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[8] A. P. Terent'ev, A. N. Kost, A. M. Yurkevich, and E. E. Khaskina (Moscow State University) *Zhur. Obshchei Khim.* **23**, 746 (1953); *Chem. Abstr.* **48**, 4430 (1954) report b.p. 121–124°, n_D^{20} 1.4106 for isobutyraldehyde enol acetate (II).

[9] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley & Sons, Inc., New York 1948, p. 143.

[10] Prepared by liquid phase alkali-catalyzed condensation between methyl ethyl ketone and formaldehyde (Shell Development Co., unpublished results).

[11] Wilder and Dolnick (reference 3) report b.p. 130–138°; n_D^{20} 1.4192. We repeated their alkaline epoxidation and found b.p. 58–59° (50 mm.); n_D^{20} 1.4182.

7α-Hydroxy-Reichstein's Substance S

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During an extensive investigation of the microbiological transformation of Reichstein's substance S (I) with a variety of organisms, several monohydroxylated products were obtained.[1] The fermentation of this substrate with *Cephalosporium sp.* (Lederle No. Z-164) to form 7α-hydroxy-Reichstein's substance S (IIa)[2] and the tentative proof of its structure is elaborated in this paper.

The structure of IIa was assigned on the basis of the following considerations. Elemental analysis indicated the addition of one oxygen to the parent compound. Treatment of IIa in pyridine with acetic anhydride (one equivalent or an excess over two equivalents) at room temperature provided a monoacetate IIb or a diacetate IIc, respectively, which indicated the addition of an acylable hydroxyl group. Furthermore, reaction of IIa in methanol with 8% (v/v) sulfuric acid at reflux temperature gave in 79% yield 17α,21-dihydroxy-4,6-pregnadiene-3,20-dione (IIIa). An attempt to prepare the 3-monoketal of the monoacetate IIb by treatment with ethylene glycol (benzene reflux, *p*-toluenesulfonic acid) led only to the known 21-acetoxy-17α-hydroxy-4,6-pregnadiene-3,20-dione (IIIb).[3] It is interesting to note that the $\Delta^{4,6}$-3-one moiety is apparently unreactive under these conditions to ethylene glycol.

Since the physical constants of IIa did not agree with either 6α- or 6β-hydroxy-Reichstein's substance S,[4] it seemed obvious that the new group must be on the C7 carbon atom in order to permit

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[1] The microbiological synthesis of 15α- and 15β-hydroxy substance S has been announced by this laboratory: S. Bernstein, L. I. Feldman, W. S. Allen, R. H. Blank, and C. E. Linden, *Chem. & Ind.* (*London*), 111 (1956).

[2] Other observed microbiological hydroxylations at C7 of various steroids have been reported: (a) A. Krámli and J. Horváth, *Nature*, **162**, 619 (1948); **163**, 219 (1949); (b) F. W. Kahnt, Ch. Meystre, R. Neher, E. Vischer, and A. Wettstein, *Experientia*, **8**, 422 (1952); (c) Ch. Meystre, E. Vischer, and A. Wettstein, *Helv. Chim. Acta*, **38**, 381 (1955); (d) J. Fried, R. W. Thoma, D. Perlman, J. E. Herz, and A. Borman, *Recent Progress in Hormone Research*, **11**, 157 (1955); (e) H. C. Murray and D. H. Peterson, U. S. Patent **2,702,809** (Feb. 22, 1955); (f) W. J. McAleer, M. A. Kozlowski, T. H. Stoudt, and J. M. Chemerda, Meeting-in-Miniature of the American Chemical Society, New York Section, March 14, 1958; (g) W. J. McAleer, M. A. Kozlowski, T. H. Stoudt, and J. M. Chemerda, *J. Org. Chem.*, **23**, 958 (1958).

[3] F. Sondheimer, C. Amendola, and G. Rosenkranz, *J. Am. Chem. Soc.*, **75**, 5932 (1953).

[4] D. H. Peterson, S. H. Eppstein, P. D. Meister, B. J. Magerlein, H. C. Murray, H. Marian Leigh, A. Weintraub, and L. M. Reineke, *J. Am. Chem. Soc.*, **75**, 412 (1953); K. Florey and M. Ehrenstein, *J. Org. Chem.*, **19**, 1331 (1954).