

(5, M<sup>+</sup>), 167 (23, C<sub>10</sub>H<sub>19</sub>C≡O<sup>+</sup>), 124 [100, (C<sub>5</sub>H<sub>11</sub>CH=CHCH=CH<sub>2</sub>)<sup>+</sup>].

**Acknowledgments.** We would like to express our gratitude to the SUNY Research Foundation for financial support and to Dr. Bruce Norcross and Mr. Jon Stickles for technical assistance. We would also like to acknowledge the assistance of Mr. Michael Kushner in the preparation of some intermediates.

**Registry No.**—1, 59434-06-9; 2, 59434-07-0; 3, 59434-08-1; 4, 54844-69-8; 5, 54844-65-4; *n*-decyl bromide, 112-29-8.

### References and Notes

- (1) Part 2 of a series on pheromone synthesis. For part 1 see P. J. Kocienski and R. W. Ostrow, *J. Org. Chem.*, **41**, 398 (1976).
- (2) R. G. Smith, G. E. Daterman, and G. D. Daves, *Science*, **188**, 63 (1975).
- (3) K. Eiter, *Fortschr. Chem. Org. Naturst.*, **28**, 204 (1970); M. Jacobson, "Insect Sex Pheromones", Academic Press, New York, N.Y., 1972; J. G. McConnell and R. M. Silverstein, *Angew. Chem., Int. Ed. Engl.*, **12**, 644 (1973); D. A. Evans and C. L. Green, *Chem. Soc. Rev.*, **2**, 75 (1973).
- (4) R. G. Smith, G. D. Daves, and G. E. Daterman, *J. Org. Chem.*, **40**, 1593 (1975).
- (5) A more practical reason for choosing 4 as a key intermediate is the fact that reduction to the *E* olefin using Na/NH<sub>3</sub> is more amenable to large scale synthesis than alternative procedures for effecting reduction to the *Z* olefin. Smith and co-workers (see ref 2) have shown that the *E* isomer is also highly attractive.
- (6) R. K. Miller, D. Felix, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, **53**, 1479 (1970), and references cited therein.
- (7) The enol ether 1 was prepared by reaction of 2-*n*-pentylcyclohexane-1,3-dione [K. W. Rosenmund and H. Bach, *Chem. Ber.*, **94**, 2394 (1961)] with MeOH-H<sub>2</sub>SO<sub>4</sub>: *ir* (CCl<sub>4</sub>) 1655, 1620 cm<sup>-1</sup>; *NMR* (CCl<sub>4</sub>) δ 3.8 (s, 3 H), 2.55 (t, 2 H), 1.7–2.3 (m, 6 H), 1.25 (br, 6 H), 0.9 (distorted t, 3 H).

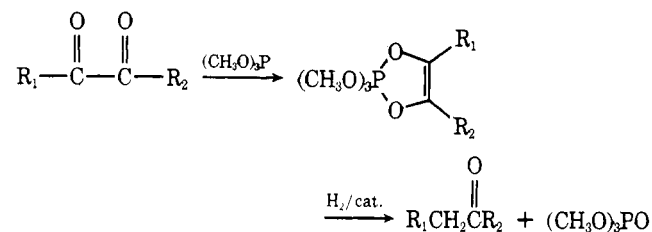
### Hydrogenation of Cyclic Unsaturated Oxyphosphoranes. A Novel Method for Reduction of α Diketones to Ketones

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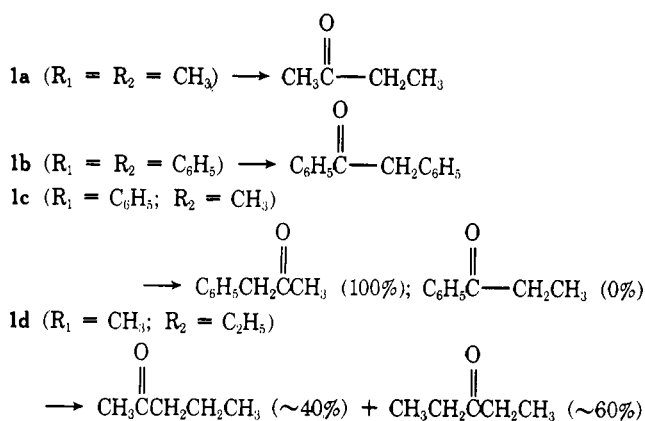
We wish to report that catalytic hydrogenation of unsaturated oxyphosphoranes such as 1 leads directly to high yields of phosphate and monoketone. Cycloadducts are obtained conveniently from diketones and phosphites.<sup>1</sup> Since diketones



are, in turn, available from simple monoketones, the reaction sequence shown above represents a potential solution of a difficult synthetic problem, that of ketone transposition. The procedure also offers an alternative to standard procedures for converting acyloin condensation products to monoketones.

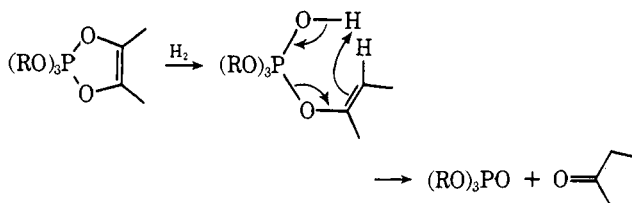
Uptake of hydrogen and yields of ketone are essentially quantitative in this reaction. Where both electronic and steric factors are contributing (example 1c) high selectivity toward a single product is shown. In example 1d where much lower discrimination would be expected, only a slight preference for reduction at the less hindered site is found.

This reaction appears to have little precedence in the literature. Indeed, we initiated the study with the intention of designing a method for producing stereochemically pure



erythro 1,2-diols. Alternate syntheses of the cyclic saturated oxyphosphoranes<sup>3</sup> expected from 1a confirmed that these compounds were stable at room temperature, and, further, could be recovered unchanged after prolonged treatment under catalytic hydrogenation conditions. Therefore the saturated compound evidently does not intervene in the process to produce ketone. In earlier work it had been demonstrated by Denney<sup>4</sup> et al. that these cyclic saturated compounds decompose (above 100 °C) and generally yield epoxides as predominant products.

Several mechanistic rationalizations of this reaction which do not involve double bond hydrogenation may be envisaged, but they are highly speculative at this time. A simple possibility involves hydrogenolysis of the vinyl carbon-oxygen



bond, followed by the 1,5 hydrogen shift shown above. Such hydrogenolysis is documented for vinyl<sup>5</sup> and phenyl<sup>6</sup> phosphates, and provides precedence for the present proposal.

### Experimental Section

**Diketones.** All diketones were available from Aldrich Chemical Co. and were purified by distillation or crystallization. Selenium dioxide oxidation of propiophenone was also employed to obtain 1-phenyl-1,2-propanedione in 60% yield.<sup>7</sup>

**Trimethyl phosphite** was distilled before each use.

**Cyclic unsaturated oxyphosphoranes (1a–d)** were prepared by mixing molar equivalents of trimethyl phosphite and diketone at room temperature as described by Ramirez and Desai.<sup>1</sup> These products were distilled or crystallized before use: 1a, bp 36 °C (0.5 mm); 1b, mp 48–50 °C; 1c, bp 116–119 °C (0.9 mm); 1d, bp 85–88 °C (10 mm).

**Hydrogenations** were accomplished at 1 atm H<sub>2</sub> over reduced PtO<sub>2</sub>. Cyclohexane, ethyl acetate, or benzene, 5–10% in oxyphosphorane, were used as solvents. The samples typically absorb 1 molar equiv of H<sub>2</sub> within 2–6 h,<sup>8</sup> at which time H<sub>2</sub> uptake had slowed substantially. Hydrogenation was terminated at this point. The reaction mixtures were filtered to remove catalyst. In the case of 1a NMR examination showed only 2-butanone and trimethyl phosphate from 1a; 1d showed 2- and 3-pentanone plus trimethyl phosphate. These products and product ratios were further quantified by VPC analysis. The yields were quantitative with no other products detectable. Similar analyses were performed for the products from 1b and 1c. The products could also be isolated by column chromatography over silica gel with ether eluent.

**Saturated oxyphosphoranes** were prepared from both *meso*- and *dl*-2,3-butanediol by exchange of these diols with pentaethoxyphosphorane. These procedures are described by Denney and Jones.<sup>3</sup> These saturated compounds could be recovered unchanged after prolonged exposure to H<sub>2</sub>/Pt in ethyl acetate or cyclohexane.

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**Registry No.**—1a, 1665-79-8; 1b, 4850-55-9; 1c, 1566-72-9; 1d, 52938-47-3; 2,3-butanedione, 431-03-8; diphenylethanedione, 134-81-6; 1-phenyl-1,2-propanedione, 579-07-7; 2,3-pentanedione, 600-14-6; trimethyl phosphite, 121-45-9; 2-butanone, 78-93-3; 1,2-diphenylethanone, 451-40-1; 1-phenyl-2-propanone, 103-79-7; 2-pentanone, 107-87-9; 3-pentanone, 96-22-0.

### References and Notes

- (1) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2652 (1960).
- (2) H. L. Riley, *J. Chem. Soc.*, 1875 (1932).
- (3) For synthetic details see D. B. Denney and D. Jones, *J. Am. Chem. Soc.*, **91**, 5825 (1969).
- (4) D. B. Denney et al., *J. Am. Chem. Soc.*, **93**, 4004 (1971).
- (5) A. Jung and R. Engel, *J. Org. Chem.*, **40**, 3652 (1975).
- (6) A. Jung and R. Engel, *J. Org. Chem.*, **40**, 244 (1975).
- (7) N. Rabjohn, *Org. React.*, **5**, 331 (1949).
- (8) If the diketone-phosphite adduct is not purified, hydrogenation frequently fails. We believe that this is due to contamination by phosphite which poisons the catalyst surface.
- (9) Camille and Henry Dreyfus Teacher-Scholar, Alfred P. Sloan Foundation Fellow. Case Western Reserve University.

### Chemiluminescent Oxidations of 4- and 7-Aminophthalide

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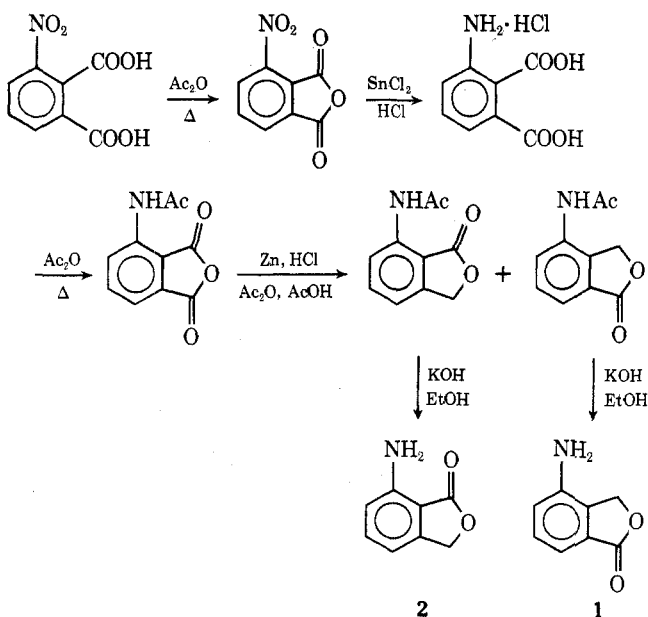
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A large variety of organic compounds undergo oxidation with chemiluminescence. Acyl hydrazides are one important class of chemiluminescent substrates, with luminol (5-amino-2,3-dihydrophthalazine-1,4-dione) probably the most notable example.<sup>2</sup> Radical autoxidation of hydrocarbons can also lead to chemiluminescence, by disproportionation of peroxy radicals via a tetroxide intermediate.<sup>3,4</sup> Recently, it has been proposed that a tetroxide intermediate could play a significant role in the chemiluminescent oxidation of luminol.<sup>5</sup>

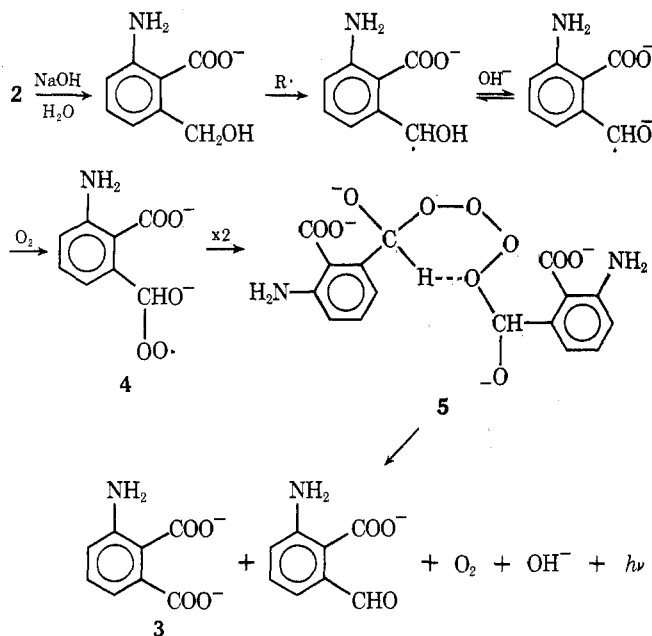
We have synthesized 4- and 7-aminophthalide (1 and 2, respectively; see Scheme I) and subjected them to free-radical

### Scheme I. Synthesis of the Aminophthalides



autoxidation and other oxidation conditions. The aminophthalides would be expected to be oxidized to 3-aminophthalate (3), which has been demonstrated to be the oxidation product and the emitting species in luminol chemiluminescence.<sup>6</sup> The expected oxidation mechanism for the aminophthalides would be that of radical autoxidation, consistent with the mechanism established for hydrocarbon oxidations<sup>3,4</sup> (Scheme II). Thus, we expected to generate an independent

### Scheme II. Oxidation of the Aminophthalides



route to the intermediates (4 and 5) which were suggested for the mechanism of luminol chemiluminescence.<sup>5</sup>

The 4- and 7-aminophthalides were dissolved in basic aqueous solution, which opens the lactone ring, and they were subjected to a variety of oxidants: (a) oxygen with peroxydisulfate as radical initiator; (b) hydrogen peroxide with a catalytic amount of hemin; (c) calcium hypochlorite; (d) sodium hypochlorite. In all cases, the red-brown product solution was shown by paper chromatography to be equivalent to the product mixture obtained by subjecting luminol or authentic 3-aminophthalic acid to the same conditions. We were unable to specifically isolate 3-aminophthalic acid from the reaction mixtures, however, or conclusively prove its presence. The very mild oxidation conditions necessary to isolate 3-aminophthalic acid from luminol oxidations in aqueous solution<sup>2</sup> were ineffective toward the aminophthalides; furthermore, the aminophthalides were unreactive in Me<sub>2</sub>SO toward simply O<sub>2</sub> and base (*n*-Bu<sub>4</sub>N<sup>+</sup>OH<sup>-</sup>), which is an effective procedure for isolation of aminophthalic acid in nonaqueous luminol oxidations.<sup>2</sup>

When either of the aminophthalides was oxidized by peroxydisulfate or H<sub>2</sub>O<sub>2</sub>-hemin (radical oxidants), weak chemiluminescence was observed, detected by photon counting. Treatment of either of the aminophthalides with sodium or calcium hypochlorite (ionic oxidants) led to oxidation but did not lead to any detectable chemiluminescence. Figure 1 shows the chemiluminescence yields from the aminophthalides as a function of their concentration. Steady-state analysis indicates that the chemiluminescence intensity should be proportional to concentration.<sup>7</sup> Maximum chemiluminescence efficiencies, which are proportional to concentration, are observed at low concentrations; these are indicated by the lines on the figure, the slopes of which are the quantum yields. Pronounced curvature was observed at higher concentrations, probably owing to absorption of some chemiluminescence by