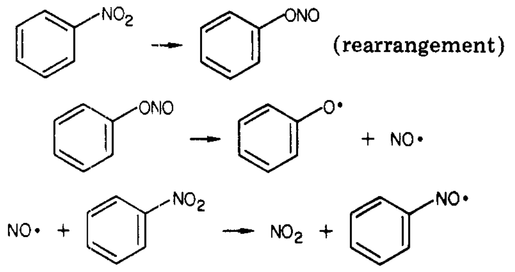
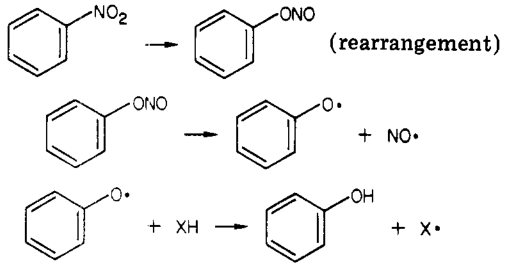
processes of nitrobenzene pyrolysis is the breaking of the arene–nitro bond to produce NO_2 and phenyl radical. This appearance of NO_2 is not, however, conclusive proof that NO_2 is a primary product. NO_2 could be a secondary product, formed via the following set of reactions:[5]



The liquid product distribution of our 600 °C nitrobenzene pyrolysis is presented in Table II. As expected, this distribution resembles that obtained earlier. In both studies, phenol and benzene are found to be major products. This contrasts with the stainless-steel-tube experiments where no phenol was detected.[6] The presence of phenol would indicate that some rearrangement of nitrobenzene to phenyl nitrite does precede decomposition.



Also, the presence of benzofuran and diphenyl ether could be due to an intermediate phenoxy radical. The presence of benzene and the di- and triphenyls may result from the direct decomposition of the nitro–arene bond to produce a phenyl radical which can subsequently combine with other phenyl radicals. In contrast to the result of Fields, we find a significantly higher ratio of benzene to biphenyl (2.7 vs. 0.3). The most obvious difference in experimental conditions which might cause such a change would be the contact times, 10 vs. 20 s. Another parameter affecting the liquid product distribution could be the total amount of nitrobenzene added during the course of a single experiment. We would expect conditions at the helical surfaces to be continually varying as liquid is added at 600 °C. If so, then the final product distribution should reflect the total amount of liquid added. In our experiments, 25 mL was added. The amount added by Fields was not mentioned in their paper. Aniline, the major product of the steel-tube reactor, here accounts for about 1% of the liquid products.

Conclusions

We believe that our finding of nitrogen dioxide in the pyrolysis off-gases, in conjunction with liquid products from phenyl radical reactions, requires that consideration be still given to the possibility for direct arene–nitro bond cleavage in the pyrolysis of nitrobenzene.

Registry No. Nitrobenzene, 98-95-3.

Supplementary Material Available: Figure 1, infrared spectrum for 2.4% NO_2 level; Figure 2, infrared spectrum for 20% NO_2 level (2 pages). Ordering information is given on any current masthead page.

Autoxidation of Ethyl Phosphinite, Phosphonite, and Phosphite Esters[1]

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Received December 7, 1979

The AIBN-initiated autoxidations in benzene of triethyl phosphite, $P(OEt)_3$, diethyl ethylphosphonite, $EtP(OEt)_2$, and ethyl diethylphosphinite, Et_2POEt, were studied at 50 °C. The quantitative conversion of $P(OEt)_3$ to triethyl phosphate obeys the rate law rate = $(2.0 \times 10^{-4}\ \mathrm{atm}^{-1}\ \mathrm{s}^{-1})[\mathrm{AIBN}]P_{O_2}$ and is zero order in phosphite. Autoxidation of $EtP(OEt)_2$ and Et_2POEt gives the complete mixture of intermediates and products predicted by Buckler's mechanism for the autoxidation of trialkylphosphines. At 1 atm of oxygen pressure and 0.02 M AIBN the pseudo-first-order rate law is rate = k'[organophosphorus ester], ester], with $k' = 7.49 \times 10^{-4}\ \mathrm{s}^{-1}$ for $EtP(OEt)_2$ and $2.37 \times 10^{-4}\ \mathrm{s}^{-1}$ for Et_2POEt.

The autoxidation of low molecular weight aliphatic tertiary phosphites (eq I) requires heat and catalysis, e.g.,

$$2P(OR)_3 + O_2 \rightarrow 2P(O)(OR)_3 \qquad \text{(I)}$$

aluminum oxide at 120 °C[2] or radical [3-5] or photoinitiation.[6,7] At room temperature, in the absence of initiation, triethyl phosphite gives no reaction with air[8] or oxygen.[5] Only very limited rate studies of phosphite autoxidation have been reported. The rate of air autoxidation of triisopropyl phosphite was independent of phosphite concentration over much of the range with γ-ray initiation and enough water to give initiating radicals on radiolysis but not enough to cause extensive hydrolysis.[9] Under UV photoinitiation, tri-*n*-butyl phosphite underwent more rapid oxidation in pure oxygen than in air,[6] and the rate

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[1] Taken from a portion of the Dissertation submitted by W.S.H. to the Graduate School of Oregon State University in partial fulfillment of the requirements for the Ph.D. degree. Supported in part by NSF Grant MPS75-05782, which is acknowledged with thanks.

[2] Hooker Chemical Corp., British Patent 937 560 (1963); *Chem. Abstr.*, **60**, 15733 (1964).

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[5] I. B. Joedicke, Dissertation, Oregon State University, 1976.

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Scheme I. Mechanism of Autoxidation of Free Trialkylphosphines

$$\text{initiation (spontaneous or initiator added)} \rightarrow R\cdot + RO\cdot + RO_2\cdot \tag{1}$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \tag{2}$$

R_3P Reactions

$$R_3P + RO_2\cdot \rightarrow R_3\dot{P}OOR \rightarrow R_3PO + RO\cdot \tag{3}$$

$$R_3P + RO\cdot \rightarrow R_3\dot{P}OR \begin{cases} \rightarrow R_3PO + R\cdot & (4a) \\ \rightarrow R_2POR + R\cdot & (4b) \end{cases}$$

R_2POR Reactions

$$R_2POR + RO_2\cdot \rightarrow R_2(OR)\dot{P}OOR \rightarrow R_2P(O)(OR) + RO\cdot \tag{5}$$

$$R_2POR + RO\cdot \rightarrow R_2\dot{P}(OR)_2 \begin{cases} \rightarrow R_2P(O)(OR) + R\cdot & (6a) \\ \rightarrow RP(OR)_2 + R\cdot & (6b) \end{cases}$$

$RP(OR)_2$ Reactions

$$RP(OR)_2 + RO_2\cdot \rightarrow R(OR)_2\dot{P}OOR \rightarrow RP(O)(OR)_2 + RO\cdot \tag{7}$$

$$RP(OR)_2 + RO\cdot \rightarrow R\dot{P}(OR)_3 \begin{cases} \rightarrow RP(O)(OR)_2 + R\cdot & (8a) \\ \rightarrow P(OR)_3 + R\cdot & (8b) \end{cases}$$

$P(OR)_3$ Reactions

$$P(OR)_3 + RO_2\cdot \rightarrow ROO\dot{P}(OR)_3 \rightarrow P(O)(OR)_3 + RO\cdot \tag{9}$$

$$P(OR)_3 + RO\cdot \rightarrow RO\dot{P}(OR)_3 \rightarrow R(O)(OR)_3 + R\cdot \tag{10}$$

of phosphate formation was constant up to nearly 100% conversion, though there was a thermal excursion during the experiment. In contrast, Floyd and Boozer[4] found the AIBN-initiated autoxidation of tri-*n*-butyl phosphite at 70 °C and 740 torr of oxygen pressure to be first order in phosphite as well as in AIBN. They did not study the oxygen dependence of the rate, but in a simultaneous study of tri-*n*-butylphosphine autoxidation, they gave a surprising report of *inverse* first-order dependence on oxygen pressure.

Kinetic studies of autoxidations using simple phosphonite and phosphinite starting materials have not been reported, but such compounds are postulated intermediates in the radical chain mechanism of trialkylphosphine autoxidation put forward by Buckler[10] (Scheme I). They arise because the intermediate phosphoranyl radicals[3] can decompose either to give phosphoryl final products (eq 4a, 6a, and 8a) or to give new trivalent phosphorus intermediates (eq 4b, 6b, and 8b). Evidence for these processes and factors affecting them have been discussed by many workers.[11,12]

The autoxidation of triethylphosphine in its cobalt(II) complex $CoCl_2(Et_3P)_2$ goes by a completely different mechanism and gives triethylphosphine oxide quantitatively.[13] We have conducted[14] a study of the cobalt(II) chloride catalyzed autoxidation of the ligands L = $Et_nP(OEt)_{3-n}$ (n = 0–2) in benzene solution. The components are present as an equilibrium mixture[15] of three potentially oxidizable substrates (eq II). Therefore, in addition to

$$CoCl_2L_3 \rightleftharpoons CoCl_2L_2 + L \tag{II}$$

studying the autoxidation of the cobalt complexes, we investigated the autoxidation of the free organophosphorus esters themselves. The results of those product and rate studies are now reported.

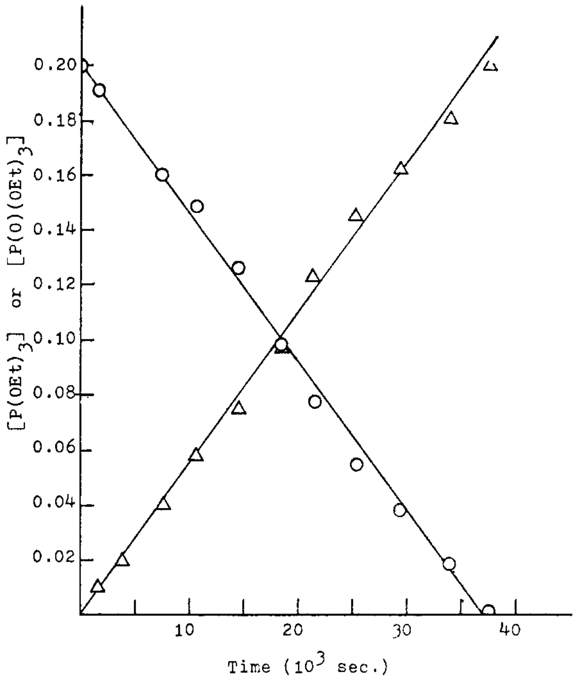

Figure 1. AIBN-initiated autoxidation of triethyl phosphite at 50 °C under 1.00 atm of oxygen: ○, $[P(OEt)_3]$; △, $[P(O)(OEt)_3]$.

Table I. Kinetic Data for Triethyl Phosphite Autoxidation in Benzene at 50 °C

P_{O_2}, atm	[AIBN], M	rate,[b] mol L^{-1} s^{-1}	k,[c] atm^{-1} s^{-1}
1.00	0.010 5	2.07×10^{-6} [a]	1.97×10^{-4}
1.00	0.029 13	5.44×10^{-6}	1.87×10^{-4}
0.209	0.064 14	2.88×10^{-6}	2.15×10^{-4}

[a] Average of identical duplicate runs with ±13% variation. [b] Rate = $k[\text{AIBN}]P_{O_2}$. [c] Mean value 2.0×10^{-4} atm^{-1} s^{-1}.

Experimental Section

The phosphorus esters, solvents, and other chemicals were prepared and purified as described previously.[13,15] All preparations of solutions, transfers, etc. were done in a steel drybox with an evacuable lock under an atmosphere of prepurified grade nitrogen. Each benzene solution, equimolar (ca. 0.2 M) in phosphorus substrate and in *o*-dichlorobenzene as the GC internal standard, with AIBN added was placed in a pear-shaped flask immersed in a water bath at 50.0 ± 0.5 °C. Nitrogen, oxygen, or dry air could be admitted by turning stopcocks in a gas manifold. The gas-inlet tube terminated in a frit for dispersion of fine bubbles. Unconsumed gas exited through an efficient reflux condenser system and a bubbler. Variation in the rate of gas flow within the range used had no effect on reaction rates. Samples could be removed by syringe through a side neck for analysis with an F&M Model 700 gas chromatograph with a thermal conductivity detector and a helium flow rate of 40 mL/min. The first injection of sample, on a UC-W98 column at 100 °C, gave a well-resolved separation of the solvent, the $Et_nP(OEt)_{3-n}$ compounds, and the internal standard. After the second injection, on a Reoplex 400 column at 170 °C, the unresolved, more volatile components were quickly eluted, followed by the internal standard and the $Et_nP(O)(OEt)_{3-n}$ phosphoryl compounds in the order n = 1, 0, and 2.

Results

Triethyl phosphite autoxidation to triethyl phosphate is quantitative and zero order in phosphite, as illustrated

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[10] S. A. Buckler, *J. Am. Chem. Soc.*, **84**, 3093 (1962).

[11] J. K. Kochi and P. J. Krusic, *J. Am. Chem. Soc.*, **91**, 3944 (1969).

[12] W. G. Bentrude, E. R. Hansen, W. A. Khan, T. B. Min, and P. E. Rogers, *J. Am. Chem. Soc.*, **95**, 2286 (1973), and references therein.

[13] D. D. Schmidt and J. T. Yoke, *J. Am. Chem. Soc.*, **93**, 637 (1971).

[14] W. S. Hwang, I. B. Joedicke, and J. T. Yoke, to be submitted for publication.

[15] I. B. Joedicke, H. V. Studer, and J. T. Yoke, *Inorg. Chem.*, **15**, 1352 (1976).

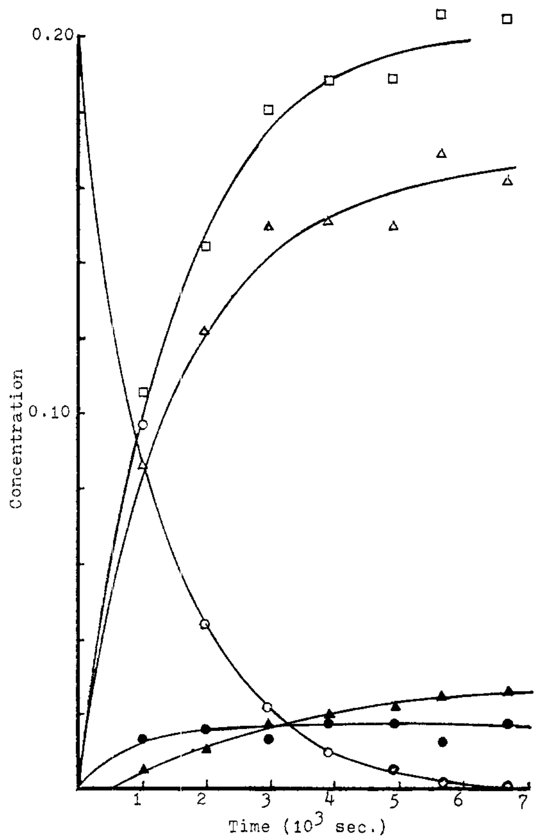

Figure 2. AIBN-initiated autoxidation of diethyl ethylphosphonite at 50 °C under 1.00 atm of oxygen: ○, $[EtP(OEt)_2]$; ▲, $[P(O)(OEt)_3]$; ●, $[P(OEt)_3]$; △, $[EtP(O)(OEt)_2]$; □, sum of the concentrations (moles per liter) of all oxidation products.

by the data for a typical experiment shown in Figure 1. Rate measurements obtained by using several different reaction conditions are given in Table I, and show that the rate law is as shown in eq III. The solubility of oxygen

$$-d[P(OEt)_3]/dt = k[AIBN]P_{O_2} \qquad (III)$$

at 1 atm pressure in benzene at 50 °C is 0.00936 M;[16] thus, the second-order rate constant in Table I may also be expressed as 2.1×10^{-2} L mol^{-1} s^{-1}.

In contrast, autoxidation of diethyl ethylphosphonite or ethyl diethylphosphinite gives a mixture of products, as shown in Figures 2 and 3. At constant oxygen pressure, consumption of the phosphonite or phosphinite is pseudo first order in substrate, as shown in Figure 4. The dependence of the rate on AIBN concentration was not investigated in the case of the phosphonite. With the phosphinite, no effect of the variation of AIBN concentration on the rate is seen in Figures 3 and 4, but the range studied was not sufficient to permit a definite conclusion. The rate law for L = $EtP(OEt)_2$ or Et_2POEt at a fixed AIBN concentration is of the pseudo-first-order form of eq IV at constant oxygen pressure. At 50 °C with 1 atm

$$-d[L]/dt = k'[L] \qquad (IV)$$

of oxygen and 0.02 M AIBN, k' is 7.49×10^{-4} s^{-1} for diethyl ethylphosphonite and 2.37×10^{-4} s^{-1} for ethyl diethylphosphinite.

Discussion

The kinetic behavior for phosphite autoxidation is different in kind than that for phosphonite and phosphinite autoxidation. The rate is zero order in phosphite con-

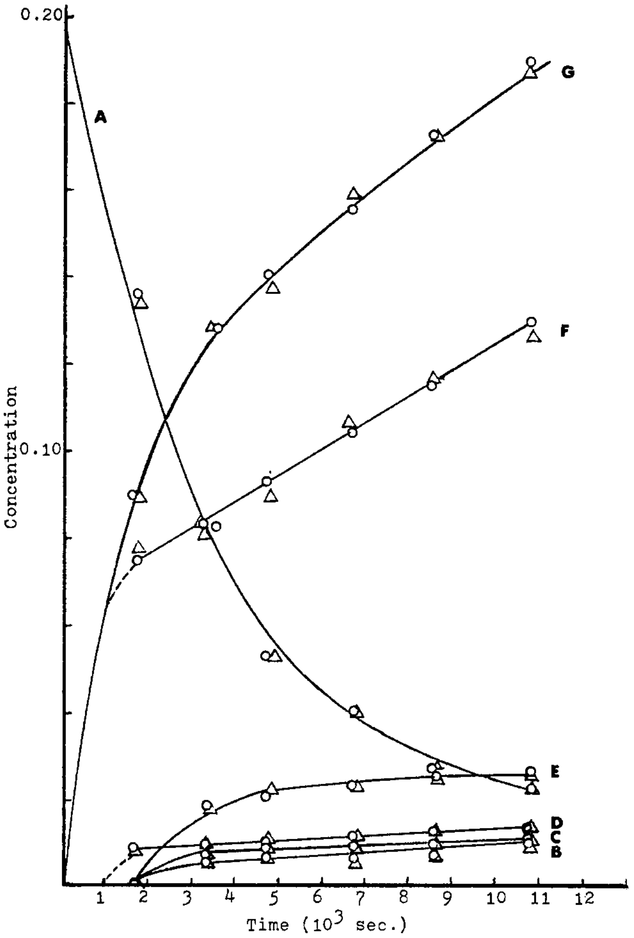

Figure 3. AIBN-initiated autoxidation of ethyl diethylphosphinite at 50 °C under 1.00 atm of oxygen: ○, 0.01783 M AIBN; △, 0.02022 M AIBN; A, $[Et_2POEt]$; B, $[P(O)(OEt)_3]$; C, $[P(OEt)_3]$; D, $[EtP(O)(OEt)_2]$; E, $[EtP(OEt)_2]$; F, $[Et_2P(O)OEt]$; G, the sum of the concentrations (moles per liter) of all oxidation products.

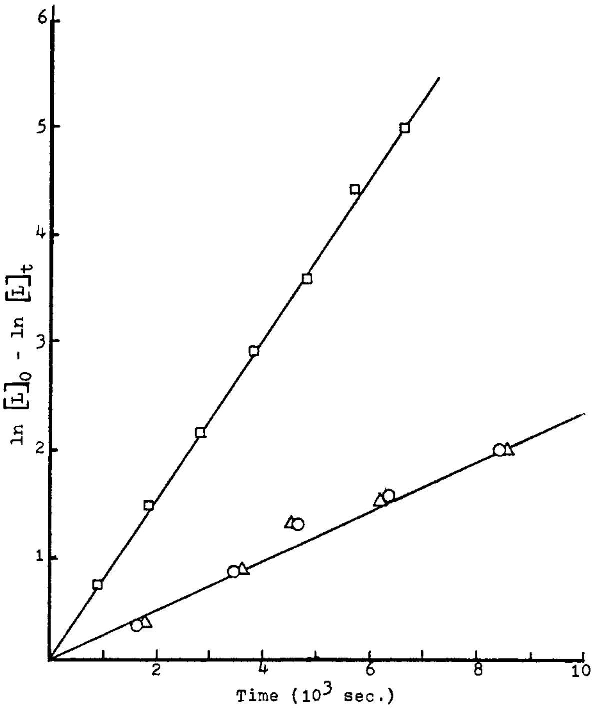

Figure 4. Pseudo-first-order kinetic plot for the autoxidation of $EtP(OEt)_2$ and Et_2POEt: □, $EtP(OEt)_2$, 0.0200 M AIBN; ○, Et_2POEt, 0.0178 M AIBN; △, Et_2POEt, 0.0202 M AIBN.

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[16] J. Horiuti, *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)*, 17, 125 (1931).

Table II. Comparison of Rates[a] of Initiation and Autoxidation in Benzene at 50 °C and 1.0 Atm of O_2

compd	rate of autoxidation	[AIBN], M	rate of initiation	ratio of rates
$P(OEt)_3$	2.07×10^{-6}	0.010 5	2.9×10^{-8}	7.1×10
$P(OEt)_3$	5.44×10^{-6}	0.029 13	8.1×10^{-8}	6.7×10
$EtP(OEt)_2$	1.50×10^{-4} [b]	0.020 0	5.6×10^{-8}	2.7×10^3
Et_2POEt	4.74×10^{-5} [b]	0.017 83	5.0×10^{-8}	9.5×10^2
Et_2POEt	4.74×10^{-5} [b]	0.020 22	5.6×10^{-8}	8.5×10^2

[a] Units of mol L^{-1} s^{-1}. [b] Initial rates.

centration but first order in the concentration of the other two esters. Phosphite autoxidation is found to be first order in oxygen pressure, and this is presumed to be true for the other two esters as well.

Triethyl phosphite autoxidation is first order in AIBN concentration, and there is no reaction in the absence of added initiator. In contrast, both of the other two esters do undergo autoxidation in solution in the absence of added AIBN, the phosphinite very slowly (5 days at 60 °C and 1 atm of oxygen) and the phosphonite more rapidly.[5] Since this result might depend on adventitous traces of impurities, the kinetic studies of their autoxidations were conducted with added AIBN to provide much more rapid and equal initiation.

From the data given by Huyser,[17] one may calculate for AIBN a half-life of 85.6 h at 50 °C and a rate of formation of initiating radicals as in eq V, where k_1 is 2.25×10^{-6} s^{-1}

$$d[(CH_3)_2(CN)C\cdot]/dt = 2ak_1[AIBN] \qquad (V)$$

and a, the efficiency of radical generation,[18] is 0.62. Under the conditions of each of the present experiments, the AIBN concentration changes by 2% or less, i.e., is effectively constant. It is of interest to compare the (initial) rates of autoxidation of the organophosphorus substrates with the rate of formation of initiating radicals; this is done in Table II. Assuming comparable efficiencies of initiation, the ratio of these rates should be an approximate relative measure of the chain length. The result is 1–2 orders of magnitude smaller for the phosphite than for the phosphonite or phosphinite. Presumably this is the reason for the diffferent dependence of the rate of phosphite autoxidation on substrate concentration. The zero-order dependence is not in agreement with the previous report of Floyd and Boozer[4] but agrees with previous more qualitative observations.[6,9]

The autoxidation of the phosphonite and the phosphinite to mixtures of products, e.g., in the latter case to phosphinate, phosphonite, phosphonate, phosphite, and phosphate, is in complete agreement with and provides experimental proof of the postulate of Buckler[10] for the mechanism of autoxidation of tertiary phosphines (Scheme I). Under conditions of comparable initiation, the phosphonite reacts more rapidly than the phosphinite, showing that the reactivity order $R_3P > R_2POR > RP(OR)_2 > P(OR)_3$ postulated by Razumov et al.[19] is incorrect.

Registry No. $P(OEt)_3$, 122-52-1; $EtP(OEt)_2$, 2651-85-6; Et_2POEt, 2303-77-7.

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[18] G. S. Hammond, J. N. Sen, and C. E. Boozer, *J. Am. Chem. Soc.*, 77, 3244 (1955).

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Photorearrangements of Epoxy Ketones. Epoxides of Hexamethylbicyclo[3.2.0]hepta-2,5-dienone, a Valence Tautomer of Hexamethyltropone

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The double bond in the four-membered ring of hexamethylbicyclo[3.2.0]hepta-3,6-dien-2-one (1) is selectively oxidized by *m*-chloroperbenzoic acid, whereas the enone double bond is selectively epoxidized by alkaline hydrogen peroxide to give **2** and **3**, respectively. In each case, a single stereoisomer is formed. The exo stereochemistry of the epoxides was deduced from X-ray structures on diepoxides **4** and **5** obtained by further epoxidation of **2** and **3**. Irradiation of **2** gives pentamethylphenol (**6**) and ketene; if **2** is labeled at the C_4 methyl with deuterium, the resulting **6** is labeled para to the hydroxyl group. A novel rearrangement of the four-membered ring to give a 7-norbornenyl-type intermediate is suggested to rationalize the labeling result. Irradiation of **3** gives, in addition to minor amounts of pentamethylphenol and its acetate, a tetracyclic product formulated as **10**, which rearranges thermally to 1-acetylpentamethylcyclopentadiene (**12**). A mechanism involving photochemical C–C bond cleavage of the epoxide ring in **3** is suggested to account for the results.

Although the photochemistry of ketones, alkenes, and epoxides has been extensively studied,[1] it is still not easy to predict with a high degree of accuracy what will happen when a particular molecule containing these three functions is irradiated. This is because the arrangement of these groups with respect to one another and the substituents which they carry affect the reaction outcome. Although some generalizations can be made,[2] empiricism is still a very prevalent feature of this area of photochemistry. The extent to which this is so is apparent in the

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[1] The extent to which this is so each year is evident by the large fraction of each volume of *Photochemistry* (published annually by the Chemical Society) that is devoted to these three functional groups.

[2] Hart, H.; Peng, C.-T.; Shih, E.-M. *J. Org. Chem.* 1977, *42*, 3635.

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