2,5-dimethyl-2,4-hexadiene (n^{25}_{D} 1.4743, lit.[24] n^{23}_{D} 1.4752) in 100 ml of methylene chloride was added dropwise a solution of 13.5 g (0.026 mole) of lead tetraacetate in methylene chloride. The mixture was stirred and cooled to 0–5° in an ice–water bath during the addition. No red color appeared indicating rapid addition was occurring. Stirring as continued for 30 min. The mixture was filtered to remove a small amount of suspended solid and quickly washed twice with 75-ml portions of cold water. Drying was accomplished by swirling for 2 min over anhydrous sodium sulfate. The solvent was removed and the remaining solid was recrystallized twice from ether with the aid of a Dry Ice–acetone bath to give 1.4 g (18%) of white, crystalline XII, mp 107–108°. The infrared spectrum of XII contained an N-H band at 3.1 C=O bands at 5.75 and 5.85, and a C—O band at 8.0 μ. The nmr showed singlets at 1.48, 1.66, 2.02, 5.77, and 5.86 (6:6:3:1:1) and a multiplet at 7.44 ppm (5 H).

Anal. Calcd for $C_{18}H_{23}N_3O_4$: C, 62.58; H, 6.71; N, 12.17. Found: C, 62.44; H, 7.05; N, 12.04.

Attempted Reaction of Other Dienes with II.—The reaction of nopadiene (n^{25}_{D} 1.5020, lit.[25] n^{25}_{D} 1.5044) with II by the same procedure resulted in an oil that reverted to starting materials upon purification attempts. The infrared spectrum showed no N—H bands but C=O bands at 5.65 and 5.85 μ were present. The nmr contained complex multiplets in the C—H region, an olefinic peak at 5.5, and a phenyl peak at 7.45 ppm.

When an attempt was made to treat cyclooctatetraene (n^{25}_{D} 1.5360, lit.[25] n^{20}_{D} 1.5290), hexachlorobutadiene (n^{25}_{D} 1.5530, lit.[26] n^{20}_{D} 1.5542), and hexachlorocyclopentadiene (n^{25}_{D} 1.5602, lit.[27] n^{25}_{D} 1.5629) with II, no adduct formed. Rather, when the lead tetraacetate solution was added to a slurry of 4-phenylurazole in methylene chloride and in the presence of these compounds, the red color of II persisted. Continued treatment or warming ultimately resulted in the complete decomposition of the dienophile.

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[24] E. Braude and J. Coles, *J. Chem. Soc.*, 1425 (1952).

[25] W. Reppe, *Ann.*, **560**, 1 (1948).

[26] L. Kogan, N. Burmakin, and N. Chernyak, *Izv. Vysshikh Ucheb Zavedenii, Khim. i Khim. Tekhnol.*, 126 (1958).

[27] J. Krynitsky and R. Bost, *J. Am. Chem. Soc.*, **69**, 1919 (1947).

The Reaction of Triphenylphosphine with Peroxycyclohexadienones[1]

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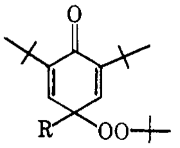
Triphenylphosphine reacts with 4-*t*-butylperoxy-4-methyl-2,6-di-*t*-butyl-2,5-cyclohexadien-1-one (**1a**) in *n*-heptane or chlorobenzene solution at 100° to form 2,6-di-*t*-butyl-*p*-cresol (**2**), 2,6-di-*t*-butyl-4-neopentylphenol (**3**), isobutene, and triphenylphosphine oxide, together with lesser amounts of 2,6-di-*t*-butyl-*p*-benzoquinone (**4**), 2,4,6-tri-*t*-butyl-4-methyl-2,5-cyclohexadien-1-one (**5**), and isobutane. A homolytic mechanism is proposed for this reaction and supported by further experiments. Reaction of 4-*t*-butylperoxy-2,4,6-tri-*t*-butyl-2,5-cyclohexadien-1-one (**1b**) with triphenylphosphine in *n*-heptane at 100° gives 2,4,6-tri-*t*-butylphenol (**11**), quinone **4**, 2,6-di-*t*-butyl-4-*t*-butoxyphenol (**12**), isobutene, triphenylphosphine oxide, and a trace of isobutane. This reaction also appears to occur largely *via* a homolytic mechanism, but incursion of a competing process which does not involve free radicals is indicated.

Mixtures of hindered phenols with compounds containing phosphorus or sulfur are widely used as inhibitors of hydrocarbon autoxidation.[4] Many inhibitor systems of this type owe their special effectiveness to the phenomenon of synergism; *i.e.*, their inhibitory power is greater than would be expected if the effects of the individual components were simply additive. An attractive rationalization for many of the observed synergistic effects is that the components function in different ways which are mutually reinforcing.[4a–c] Thus, the phenolic compound (primary stabilizer) can act as a trap for peroxy radicals, while the compound of phosphorus or sulfur (costabilizer) may function as a decomposer of the hydroperoxides which are responsible for chain initiation.[4a–c] However, in many cases it is quite clear that other reactions involving the inhibitors are likely to occur, and, in general, the complexity of these systems has precluded their description in terms of complete reaction mechanisms. One possible complicating factor, which to our knowledge has received attention in only one previous study,[4c] is that certain costabilizers may react with the peroxycyclohexadienones formed *in situ* from peroxy radicals and hindered phenols. Since reactions of peroxycyclohexadienones with phosphorus-containing costabilizers had not previously been investigated, we therefore thought it would be of interest to examine the interaction of two representative peroxides of this type (**1a** and **1b**) with triphenylphosphine. Although this phosphine is not particularly useful as a costabilizer itself, it was felt that its action upon peroxycyclohexadienones should parallel that of certain other compounds of trivalent phosphorus (*e.g.*, phosphites) which are more commonly used in multicomponent inhibitor systems. However, it should be remarked at the outset that this parallelism was not expected to be completely general, since reaction modes of phosphines and phosphites with certain oxygenated species were known to be strongly dependent upon structural and environmental factors.[5]



1a, R = Me
b, R = *t*-Bu

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[1] Part IV of a series on oxidation inhibitors. Part III: W. H. Starnes, Jr., *J. Org. Chem.*, **31**, 3164 (1966).

[2] Author to whom requests for reprints should be addressed.

[3] American Embassy, Bonn/Bad Godesberg, Germany.

[4] See, *inter alia*, (a) K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961), and references therein; (b) "Aging and Stabilization of Polymers," M. B. Neiman, Ed., Consultants Bureau, New York, N. Y., 1965, pp 29–33, 114–118, and references therein; (c) N. P. Neureiter and D. E. Bown, *Ind. Eng. Chem., Prod. Res. Develop.*, **1**, 236 (1962); (d) L. Friedman, U. S. Patent 3,039,993 (1962).

[5] (a) W. G. Bentrude, *Tetrahedron Letters*, 3543 (1965); (b) S. A. Buckler, *J. Am. Chem. Soc.*, **84**, 3093 (1962); (c) C. Walling and M. S. Pearson, *ibid.*, **86**, 2262 (1964).

TABLE I

REACTIONS OF PEROXYDIENONES WITH TRIPHENYLPHOSPHINE[a]

Peroxy-dienone	Solvent	Reacn time, hr	Products,[b] moles/mole of peroxydienone 2	3	4	5	11	12	(Ph)$_3$PO	Isobutene	Isobutane
1a	*n*-Heptane	22	0.62 ± 0.01	0.31 ± 0.02	0.02 ± 0.01	0.05 ± 0.02	...	...	1.86 ± 0.04	0.49 ± 0.03	0.001 ± 0.000
1a	PhCl	20[c]	0.67 ± 0.03	0.16 ± 0.02	0.12 ± 0.01	0.05 ± 0.02	...	...	1.89 ± 0.07	0.52 ± 0.06	0.01 ± 0.00
1b	*n*-Heptane	22	...	...	0.21	...	0.67	0.12	1.42	0.52	0.001
1b	*n*-Heptane	66	...	...	0.18	...	0.77	0.05	1.43	0.60	0.001

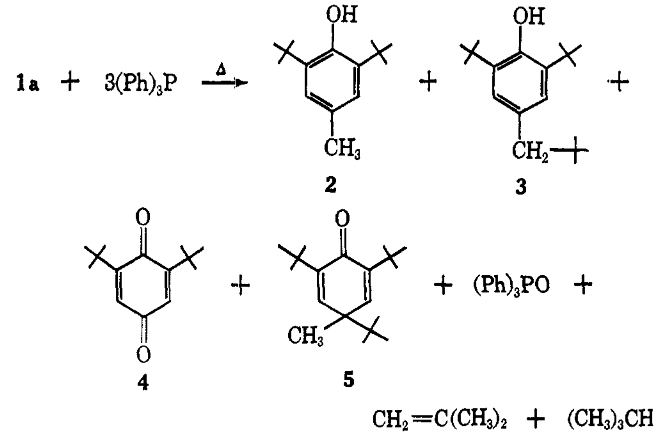
[a] Peroxydienone, 2.00 mmoles; (Ph)$_3$P, 6.00 mmoles; solvent, 25 ml; temperature, 100 ± 1°. [b] Deviations refer to duplicate runs. Traces of gaseous products tentatively identified (by gc retention times) as carbon dioxide, ethane, and propane (?) were also detected in various experiments. [c] Does not include 1–2 hr of refluxing to remove dissolved gases after completion of reaction.

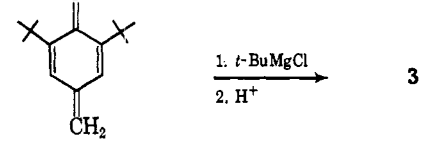
Results and Discussion

Reaction of Triphenylphosphine with Peroxydienone 1a.

Reaction of Triphenylphosphine with Peroxydienone 1a.—These experiments were carried out in *n*-heptane or chlorobenzene solution under helium at 100°. The identified products are shown in Scheme I; yields are recorded in Table I. Phenol **3**, a previously unreported compound, was shown to be identical with an authentic sample prepared by reaction of quinone methide **6** with the *t*-butyl Grignard reagent. Identification of dienone **5** was based on the correspondence of its gc retention time to that of a product formed from phenol **2** and *t*-butyl radicals (*vide infra*).

SCHEME I





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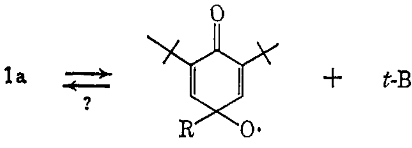
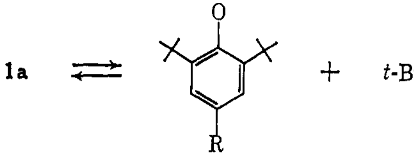
The small dependence of the product distribution upon solvent composition (Table I) is hardly compatible with the occurrence of competing radical and ionic mechanisms[6] and is not inconsistent with exclusive operation of the former type of process. Indeed, we see no way of accounting for all of the products (in particular, the formation of **3** and the production of nearly 2 molar equiv of triphenylphosphine oxide) in terms of any reasonable heterolytic scheme and, therefore, propose a mechanism for the reaction of **1a** with triphenylphosphine which is entirely homolytic in character (eq 1–11). Further justification of this mechanism is offered in the discussion which is given below.



7 (1)



8 (2)

$$7 \longrightarrow 4 + R\cdot \quad (3)$$

$$7 + (Ph)_3P \longrightarrow 8 + (Ph)_3PO \quad (4)$$

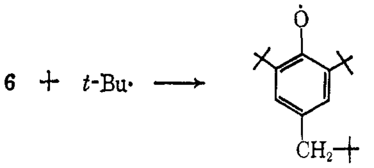
$$t\text{-BuO}_2\cdot + (Ph)_3P \longrightarrow t\text{-BuO}\cdot + (Ph)_3PO \quad (5)$$

$$t\text{-BuO}\cdot + (Ph)_3P \longrightarrow t\text{-Bu}\cdot + (Ph)_3PO \quad (6)$$

$$t\text{-Bu}\cdot + 8 \longrightarrow 5 \quad (7)$$

$$t\text{-Bu}\cdot + 8 \longrightarrow 2 + CH_2{=}C(CH_3)_2 \quad (8)$$

$$2(8) \longrightarrow 2 + 6 \quad (9)$$



9 (10)

$$9 + t\text{-Bu}\cdot \longrightarrow 3 + CH_2{=}C(CH_3)_2 \quad (11)$$

R = Me

Rough kinetic experiments, carried out in *n*-heptane solution, showed that the rate of decomposition of peroxydienone **1a** was strongly enhanced by triphenylphosphine. This observation is consistent with either a one-step bimolecular decomposition process, or with a two-step sequence involving rapid, reversible cleavage of the peroxide into radicals (eq 1 and/or 2) which are efficiently scavenged by the phosphorus compound (eq 4–6). While the former possibility cannot be rigorously excluded, we consider it unlikely in view of the failure of triphenylphosphine to accelerate the

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[6] Compare the large solvent effects reported by P. D. Bartlett and G. Meguerian, *J. Am. Chem. Soc.*, **78**, 3710 (1956).

thermal decomposition of di-*t*-butyl peroxide.[7] This same failure also argues against reversal of eq 1 as the source of the rate enhancement observed with **1a**.[8] On the other hand, reversibility of eq 2 provides an attractive explanation for the increase in rate. Esr measurements[9a] and product studies[9b] clearly show that the forward reaction of eq 2 is involved in the thermal decomposition of **1a**, while studies of the kinetics[10a] and products[10b] of autoxidations inhibited by **2** are in good accord with an inhibition mechanism involving the reverse process of eq 2 as the chain-terminating step.[11] In any event, regardless of the relative extents to which eq 1 and 2 occur, subsequent fast reactions with triphenylphosphine would be expected to convert a major fraction of the radicals formed in these steps into a mixture of **8** and *t*-butyl radicals. The ability of triphenylphosphine to deoxygenate the *t*-butoxy radical (eq 6) has been amply demonstrated,[7] and this process has been shown to be rapid.[5c] Deoxygenation of radical **7** to produce the resonance-stabilized species **8** (eq 4) might reasonably be expected to be even more facile, although in this case the thermodynamic stability of the incipient quinone should facilitate the occurrence of the competitive β-scission process (eq 3).[12] Evidence for deoxygenation of peroxy radicals by phosphites and phosphines (eq 5) also appears in the literature.[5a,b,13] Although the rate of eq 5 is not known, it should be at least as rapid as the rate of eq 6; indeed, it might be even faster owing to a more favorable polar effect, decreased steric repulsion, and the relative weakness of the oxygen–oxygen bond. On the other hand, the failure of triphenylphosphine to deoxygenate phenoxy radicals **8** and **9** is not surprising in view of the high carbon–oxygen bond strengths of these resonance-stabilized species and the steric hindrance exerted by the bulky *ortho* substituents (*cf.* the low yields of benzene obtained from phosphites and benzenethiyl radicals[5c,7a] and the apparent inability of triphenyl phosphite to deoxygenate phenoxy radicals[5a]).

On the assumption that all of the unrecovered peroxy oxygen can be accounted for by abstraction of hydrogen from *n*-heptane by *t*-butoxy radicals, the data of Table I can be used to calculate the relative reactivity of these radicals toward triphenylphosphine and solvent. The calculations[14] show that the rate of the deoxygenation reaction is *at least* some 400 ± 200 times faster than hydrogen abstraction, a value which is anomalously high in comparison with the reactivity ratios of *ca.* 7–10 determined at 130° by Walling and Pearson[5c] for competing reactions of this type using several hydrocarbons as substrates. While these divergent results might be due partly to the difference in temperature and partly to a relatively low reactivity of *n*-heptane, both of these factors taken together hardly seem capable of explaining the discrepancy. Since the two competing reactions involved are rapid processes requiring low energies of activation, the ratio of their rates should not be greatly influenced by a temperature change of only 30°. A change in the ratio of only 20-fold upon going from 100 to 130° requires that the activation energy for abstraction be higher than that for deoxygenation by about 30 kcal/mole; this is obviously impossible. Moreover, an examination of published data[15] suggestst hat the reactivity of *n*-heptane toward *t*-butoxy radicals at 100° should not differ from that of the saturated hydrocarbons studied by Walling and Pearson[5c] by more than a factor of 2–3, at most. In order to resolve the discrepancy in question, we have determined the relative reactivity of triphenylphosphine and *n*-heptane toward *t*-butoxy radicals (from di-*t*-butyl peroxide) at 100° by direct competition experiments, employing quantities of phosphine and solvent identical with those used for the peroxydienone experiments. Since the value for k_D/k_A found in this way[14] was 260 ± 60,[16] we do not believe that the high yields of triphenylphosphine oxide obtained in the peroxydienone experiments are

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[7] (a) C. Walling, O. H. Basedow, and E. S. Savas, *J. Am. Chem. Soc.*, **82**, 2181 (1960). (b) They[7a] obtained "much unreacted peroxide" in a reaction which had been allowed to run for 92 hr at 114° and inferred the absence of a direct interaction between triphenylphosphine and di-*t*-butyl peroxide on this basis. Their conclusion has been confirmed in this laboratory by a brief kinetic study carried out in *o*-dichlorobenzene solution at 130°: N. P. Neureiter, unpublished results.

[8] Decomposition *via* the forward reaction of eq 1 must occur to some extent (*cf.* the formation of **4** and ref 9b), but occurrence of the reverse reaction under our conditions is by no means certain. If reversibility does occur, it almost certainly involves "caged" radicals, which of course are inherently difficult to scavenge. Noncage recombination of the radicals produced in eq 1 seems highly improbable in view of recent work by R. Hiatt and T. G. Traylor, *J. Am. Chem. Soc.*, **87**, 3766 (1965).

[9] (a) Thermal decomposition of **1a** in xylene solution produces the spectrum of radical **8** [J. M. Turner, quoted in Varian Associates Advertisement No. 24, "EPR at work series," *ibid.*, **83**, No. 20, the outside rear cover (1961)]. (b) In a private communication, Dr. J. M. Turner has supplied us with information regarding the products formed upon thermal decomposition of **1a** in solution under a variety of conditions. His results show quite conclusively that the decomposition involves both C–O and O–O cleavage. Evidence for O–O cleavage was reported earlier by T. W. Campbell and G. M. Coppinger [*ibid.*, **74**, 1469 (1952)], who obtained acetone from thermal decomposition of the pure peroxide.

[10] (a) J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **42**, 2324 (1964), and references therein; (b) E. C. Horswill and K. U. Ingold, *ibid.*, **44**, 263 (1966).

[11] G. M. Coppinger [*J. Am. Chem. Soc.*, **86**, 4385 (1964)] has cited the failure of radical **8** to react with oxygen as evidence against the occurrence of the reverse reaction of eq 2. However, the assumption of comparable reactivities for oxygen and peroxy radicals in this reaction would appear to require further verification.

[12] The alternative mode of β scission is disfavored by the high energy of the resulting alkenyl radical. The fate of all of the methyl radicals produced in eq 3 was not determined; however, see Table I, footnote *b*.

[13] (a) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1243 (1959); (b) M. B. Floyd and C. E. Boozer, *ibid.*, **85**, 984 (1963); (c) J. I. G. Cadogan, M. Cameron-Wood, and W. R. Foster, *J. Chem. Soc.*, 2549 (1963); (d) P. I. Levin, *Russ. J. Phys. Chem.* (Engl. Transl.), **38**, 352 (1964).

[14] The equation used was

$$(k_D/k_A) \log \{([A] - [t\text{-BuOH}])/[A]\} = f \log \{([B] - [(Ph)_3PO])/[B]\}$$

where [A] and [B] are initial amounts of *n*-heptane and triphenylphosphine, respectively, *f* is the fraction of (Ph)$_3$PO formed from *t*-butoxy radicals, and k_D and k_A are second-order rate constants for deoxygenation and hydrogen abstraction, respectively [*cf.* T. S. Lee in "Technique of Organic Chemistry," Vol. VIII, S. L. Friess and A. Weissburger, Ed., Interscience Publishers, Inc., New York, N. Y., 1953, p 108]. For experiments with **1a**, $f = \{[(Ph)_3PO] - ([\mathbf{1a}] - [\mathbf{4}])\}/[(Ph)_3PO]$, and $t\text{-BuOH} = 2[\mathbf{1a}] - [(Ph)_3PO] - [\mathbf{4}]$, while for experiments with di-*t*-butyl peroxide, $f = 1$, and *t*-BuOH yields were measured directly. A sample calculation follows, using data from one of the runs averaged in line 1 of Table I.

$$[(Ph)_3PO] = 1.82[\mathbf{1a}] = 1.82(2) = 3.64 \text{ mmoles}$$

$$[\mathbf{4}] = 0.01[\mathbf{1a}] = 0.01(2) = 0.02 \text{ mmole}$$

$$(k_D/k_A) \log ([169.66 - 2(2) + 3.64 + 0.02]/169.66) = [(3.64 - 2 + 0.02)/3.64] \log [(6 - 3.64)/6]$$

$$k_D/k_A = 213$$

[15] A. L. Williams, E. A. Oberright, and J. W. Brooks, *J. Am. Chem. Soc.*, **78**, 1190 (1956); J. H. T. Brook, *Trans. Faraday Soc.*, **53**, 327 (1957); C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

[16] Owing to experimental uncertainties in analyzing for very low yields of *t*-butyl alcohol, the absolute accuracy of this value probably leaves something to be desired. However, we have no reason to doubt the correctness of its order of magnitude.

anomalous. However, we have no explanation for the low reactivity ratios reported by the earlier workers.[5c]

Turning now to the remaining steps in the peroxydienone reaction, we next consider the rather surprising formation of phenol **3**. While it might be argued that this phenol results from coupling of *t*-butyl and benzyl-type radicals, there is, in fact, no basis for this supposition. *A priori*, there are only three possible ways in which the requisite benzyl radicals might be formed, *viz.* (1) abstraction of hydrogen from the 4-methyl group of **2** by radicals derived from the *t*-butylperoxy moiety or from solvent, (2) abstraction of hydrogen from this group by aryloxy radicals, and (3) rearrangement of radical **8**.[17] The first alternative does not fit the stoichiometry in *n*-heptane (in this case the maximum number of unaccounted-for radicals available for abstraction is less than half the yield of **3**), requires the (undoubtedly incorrect) assumption that the 4-methyl hydrogens be several hundred times more reactive than *n*-heptane hydrogens, and is not in accord with excellent published evidence indicating that abstraction of hydrogen from **2** by peroxy[10b] and *t*-butoxy[18] radicals occurs preferentially from the hydroxyl function. The second and third alternatives are rigorously excluded by the work of Bauer and Coppinger,[19] who showed that radical **8** undergoes quantitative conversion into phenol **2** and quinone methide **6** in dilute solution (eq 9). In view of these considerations, we strongly disfavor the formation of appreciable amounts of benzyl-type radicals in our reaction and believe, therefore, that addition of *t*-butyl radicals to **6** (eq 10) provides the only reasonable explanation for the generation of the neopentyl substituent. The final disproportionation step (eq 11) is demanded by stoichiometry, and a similar reaction of radical **8** occurring earlier in the sequence (eq 8) accounts for the rest of the isobutene and the higher yield of **2** compared with **3**. However, the mechanism requires that the yields of **2** and isobutene be equal, and, since this condition is not quite fulfilled experimentally (*cf.* Table I), it appears that radicals other than *t*-butyl undergo disproportionation with **8** and **9** to a minor extent. In *n*-heptane these are apparently heptyl radicals (resulting primarily from *t*-butoxy abstraction), while in chlorobenzene they are presumably substituted cyclohexadienyl radicals formed by addition of *t*-butyl radicals to the solvent. This addition probably also accounts for the relatively low *t*-butyl recovery in chlorobenzene.[20]

Equation 7 clearly provides the most attractive route to dienone **5**, although stoichiometric considerations do not exclude an alternate sequence involving addition of the *t*-butyl radical to phenol **2**, followed by abstraction of hydrogen by **8** and/or **9** from the adduct. The low yield of **5** may simply reflect its instability under the reaction conditions,[21] and it is possible that some of the recovered isobutene and **2** resulted from decomposition of this compound.

Further support for the proposed mechanism was forthcoming from model experiments. Since interaction of di-*t*-butyl peroxide, triphenylphosphine, and phenol **2** should produce a mixture of *t*-butyl radicals and radical **8**, it was anticipated that the products of this reaction would closely resemble those formed from the phosphine and **1a**. This proved to be the case, and in a typical experiment the products were found to be phenol **3** (13%), dienone **5** (15%), and triphenylphosphine oxide, together with much unreacted **2** and small amounts of materials tentatively identified as dimeric products derived therefrom (gaseous products

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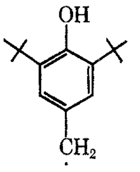
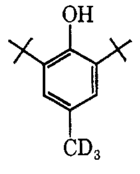
(17) As postulated by C. D. Cook, N. G. Nash, and H. R. Flanagan, *J. Am. Chem. Soc.*, **77**, 1783 (1955).

(18) K. U. Ingold, *Can. J. Chem.*, **41**, 2807 (1963).

(19) (a) R. H. Bauer and G. M. Coppinger, *Tetrahedron*, **19**, 1201 (1963); also H.-D. Becker, *J. Org. Chem.*, **30**, 982 (1965). Although the results of these workers constitute excellent evidence for the occurrence of eq 9 under conditions similar to ours (*i.e.*, in the absence of added oxidizing agents), the literature contains a number of confusing and contradictory observations regarding the fate of radical **8** which seem worth mentioning here. One area of disagreement is the kinetics of the disappearance of **8**, both first- and second-order kinetics having been reported [J. E. Bennett, *Nature*, **186**, 385 (1960); E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2016 (1963); A. L. Buchachenko, "Stable Radicals," Consultants Bureau, New York, N. Y., 1965, p 93]. Moreover, the postulated rearrangement of **8** to i[17] has recently been revived by A. I. Brodskii, V. D. Pokhodenko, and L. N. Ganyuk [*Roczniki Chem.*, **38**, 105 (1964); see also V. D. Pokhodenko, L. N. Ganyuk, and A. I. Brodskii, *Proc. Acad. Sci. USSR, Chem. Sect.*, **145**, 676 (1962); V. D. Pokhodenko, L. N. Ganyuk, E. A. Yakovleva, A. I. Shatenshtein, and A. I. Brodskii, *ibid.*, **148**, 165 (1963); V. D. Pokhodenko and V. A. Bidzilya, *Teor. i Eksperim. Khim., Akad. Nauk Ukr. SSR*, **1**, 801 (1965); *Chem. Abstr.*, **64**, 9557 (1966); and, for related work on a similar system, V. D. Pokhodenko and L. N. Ganyuk, *Dopovidi Akad. Nauk Ukr. RSR*, 73 (1963); *Chem. Abstr.*, **59**, 6232 (1963)] on the basis of deuterium labeling and esr studies of the oxidation of **2**. However, the migration of hydrogen from the 4-methyl group to oxygen, demonstrated by Brodskii, *et al.*, is readily accounted for by the mechanism of Bauer and Coppinger [*vide supra;* see also L. Filar and S. Winstein, *Tetrahedron Letters*, No. 25, 9 (1960)], and the esr spectrum assigned to i (1:2:1 triplet with splitting = 1.9 oe) by the Russian workers seems unlikely on theoretical grounds. Brodskii, *et al.*, ascribe the small splitting reported for i to the two *meta* hydrogens but then proceed to demolish the internal consistency of this argument by reporting that oxidation of ii gives a benzyl radical whose spectrum is a broad singlet resulting from incompletely resolved splitting by deuterium. In this connection, it should be noted that J. K. Becconsall, S. Clough, and G. Scott [*Proc. Chem. Soc.*, 308 (1959); *Trans. Faraday Soc.*, **56**, 459 (1960)] oxidized **2** under conditions comparable with those used by the Russian group and observed (as a secondary product) a species producing a 1:2:1 triplet (splitting, 1.3 gauss) which appeared to be identical with the 2,6-di-*t*-butyl-4-formylphenoxy radical. However, the formation of such a species does not account for the singlet observed by Brodskii, *et al.*, upon oxidation of ii, and further investigations of the problem are clearly in order. For a recent study in this area, see B. R. Loy, *J. Org. Chem.*, **31**, 2386 (1966). (b) NOTE ADDED IN PROOF.—A. I. Brodskii, V. D. Pokhodenko, V. A. Khizhnyi, and N. N. Kalibabchuk [*Dokl. Akad. Nauk SSSR*, **169**, 339 (1966)] have recently reported first-order kinetics for the disappearance of radical **8** (R = Me), as determined by esr spectroscopy. However, it is not clear from their report whether or not the kinetics were run under conditions which would have prevented interference by secondary radical species such as those resulting from spontaneous dimerization of **6**.



i



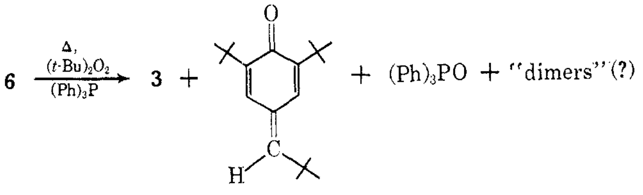
ii

(20) The occurrence of eq 7, 8, 10, and 11 in preference to the disproportionation or coupling of two *t*-butyl radicals is noteworthy. This behavior is explicable in terms of several factors: the relative slowness of reactions between two *t*-butyls [*cf.* E. L. Metcalfe, *J. Chem. Soc.*, 3560 (1963)], facilitation of reactions between unlike radicals by polar effects, and generation of a species highly stabilized by resonance in the case of eq 10. The alternative mode of disproportionation between *t*-butyl radicals and aryloxy radicals is disfavored by the relatively low resonance energies of quinone methides as compared to the corresponding phenols. Although it is not required to explain the products, the disproportionation reaction between radicals **8** and **9** to produce quinone methide **6** and phenol **3** probably occurs also, since its rate should be comparable with that of eq 9. The absence of quinone methide **10** is understandable, since disproportionation reactions leading to this species should be subject to considerable steric retardation. Reversible transfer of hydroxyl hydrogen between phenols and phenoxy radicals [*cf.* C. D. Cook, C. B. Depatie, and E. S. English, *J. Org. Chem.*, **24**, 1356 (1959); R. W. Kreilick and S. I. Weissman, *J. Am. Chem. Soc.*, **84**, 306 (1962)] may influence the product distribution.

(21) Loss of *t*-butyl from the quaternary ring carbon atom of cyclohexadienones is known to occur quite readily. See H. E. Albert and W. C. Sears, *ibid.*, **76**, 4979 (1954); T. Matsuura and H. J. Cahnmann, *ibid.*, **82**, 2055 (1960); A. Rieker, *Ber.*, **98**, 715 (1965); B. Miller and H. Margulies, *Tetrahedron Letters*, 1727 (1965).

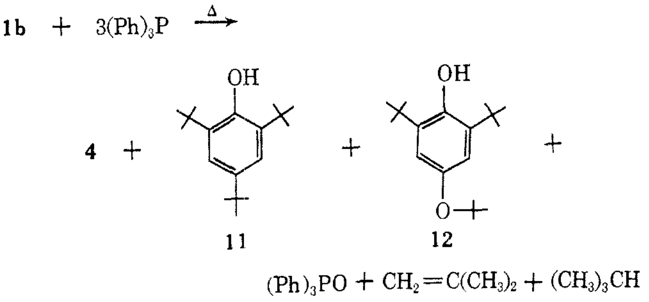
were not examined).[22] Yields of **5** obtained from this reaction were not reproducible, and the source of this difficulty was traced to a rather rapid decomposition of the compound in solution. Attempts to isolate a pure sample of **5** by gc usually gave complex mixtures; however, in one case we succeeded in isolating a fraction which was approximately 90% pure and gave infrared, mass, and nmr spectra that were consistent with the proposed structure. The formation of **5** is of some significance in view of the reported failure of phenol **2** to give the corresponding 4-methyl-4-*t*-butoxydienone upon interaction with *t*-butoxy radicals—a result which was rationalized in terms of unfavorable steric effects and susceptibility of the product to thermal homolysis.[18]

The feasibility of our suggested route to phenol **3** was demonstrated by carrying out a separate reaction of quinone methide **6** with *t*-butyl radicals generated from di-*t*-butyl peroxide and triphenylphosphine in refluxing chlorobenzene. The principal products were **3** (13%), quinone methide **10** (10%), triphenylphosphine oxide, and a mixture of heavier materials that were presumed to have resulted from the competing dimerization of **6**. Oxidation of **3** with alkaline ferricyanide provided a reference sample of the new substance (**10**).

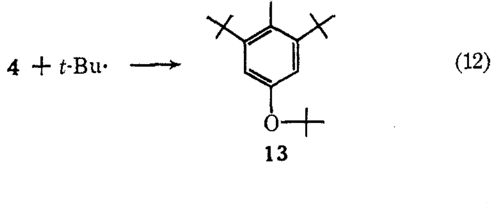


10

Reaction of Triphenylphosphine with Peroxydienone 1b.—The products formed from **1b** and excess triphenylphosphine are depicted below; Table I summarizes pertinent details. In line with our previous arguments,



a mechanism can be written for this reaction which includes eq 1–6, 8 (R = *t*-Bu in all cases), and the additional steps shown as eq 12 and 13. Here there is no evidence regarding the relative extents to which eq 1 and 2 occur. However, predominant (and perhaps exclusive) occurrence of the former process seems likely, since decomposition of the closely related substance, bis(1,3,5-tri-*t*-butyl-2,5-cyclohexadien-4-one) peroxide, is known to occur solely *via* O–O scission under a variety of conditions.[23] Formation of **4** and **12** is favored by this mode of cleavage, by steric retardation of eq 4, and by enhancement in the rate of eq 3 owing to the stability of the incipient *t*-butyl radical. On the other hand, heterolytic decomposition of **1b** would also give **4**,[1] and, in fact, the incursion of one or more decomposition mechanisms which do not involve free radicals is strongly suggested by the low yield of isobutene and the low recovery of products containing peroxy oxygen. Cage reaction of the radicals produced in eq 1 to form **4** and di-*t*-butyl ether also seems possible, and it is clear that detailed elaboration of the complete mechanism must await further investigation.



13

$$13 + t\text{-Bu}\cdot \longrightarrow 12 + CH_2{=}C(CH_3)_2 \qquad (13)$$

Direct rearrangement of **7** constitutes an alternative route to radical **13**, but to our knowledge there are no well-established precedents for alkyl shifts of this kind in alkoxy radical chemistry. Support for our suggested route to phenol **12** was obtained by carrying out a reaction of **4** with *t*-butyl radicals (from di-*t*-butyl peroxide and triphenylphosphine) under the conditions of the peroxydienone experiments. The identified products (moles/mole of starting quinone) were **12** (0.17), triphenylphosphine oxide (0.47), isobutene (0.17), and unreacted **4** (0.70).

Autoxidation Inhibition by Phosphorus Compounds and Phenols.—On the basis of the studies described in this paper, it would seem that the ability of trivalent phosphorus compounds to reduce peroxycyclohexadienones to phenoxy radicals and phenols may have important consequences with regard to the over-all mechanism of autoxidation inhibition. However, it is quite obvious that this reductive process is only one of the inhibitor functions which are operative in these highly complicated systems. Moreover, as was pointed out earlier, there is no guarantee that all costabilizers containing trivalent phosphorus will react with peroxycyclohexadienones in the way established here for triphenylphosphine. An intimation of the complexities which might be encountered in other cases comes from the work of Bentrude,[5a] who showed that *t*-butoxy radicals displace aryloxy radicals from aryl phosphites with particular ease. This displacement destroys a chain-propagating radical, produces an inhibitory species, and leaves the oxidizable phosphorus function intact; such reactions may be at least partly responsible for the relatively high antioxidant efficiencies of phosphites derived from phenols.[13d]

Experimental Section[24]

Materials.—*n*-Heptane (reagent grade) was dried by percolation through a silica gel column. Chlorobenzene (Eastman) was

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[22] Exact correspondence between these products and those formed from **1a** was not expected, of course, since the steady-state concentrations of the various reactive species were not necessarily the same in both cases.

[23] (a) C. D. Cook, R. C. Woodworth, and P. Fianu, *J. Am. Chem. Soc.*, **78**, 4159 (1956); (b) E. Müller, K. Ley, and W. Schmidhuber, *Ber.*, **89**, 1738 (1956); (c) V. D. Pokhodenko, L. N. Ganyuk, and A. I. Brodskii, *Proc. Acad. Sci. USSR, Chem. Sect.*, **149**, 214 (1963); (d) C. D. Cook and M. Fraser, *J. Org. Chem.*, **29**, 3716 (1964).

[24] Melting points and boiling points are uncorrected. The melting points were determined with a Fisher-Johns apparatus. Elemental microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Much of the instrumental analytical work was done by Mrs. M. B. Bonds, Miss T. Reid, and Messrs. T. J. Denson, J. Dzilsky, T. Hines, H. W. Kinsey, A. C. Raymer, V. H. Rushing, R. K. Saunders, G. R. Taylor, and J. L. Taylor.

distilled from calcium hydride in a nitrogen atmosphere. Literature methods were used to prepare reference samples of quinone 4[25] and phenol 12.[23a] All other chemicals used were commercial products, further purified (if necessary) by conventional means. Purities were checked by spectroscopic methods and by determinations of appropriate physical constants.

Instrumental Analyses.—Infrared, nmr, and mass spectra were obtained using instruments and techniques which have been described previously.[1] Programmed-temperature gc analyses were performed in a previously indicated manner[1] using the following columns: A, 6 ft × 0.25 in., stainless steel, 5% SE-30 on 42–60 mesh Chromosorb W; B, 6 ft × 0.25 in., stainless steel, 0.5% SE-30 on 42–60 mesh Chromosorb W. Except where noted differently, peaks were identified by comparing their retention times and the spectral properties of trapped fractions with those of authentic specimens. Gaseous mixtures were analyzed by gc according to rigorously controlled procedures developed by the analytical research section of these laboratories; pure reference compounds were used for calibration.

Preparation of Peroxycyclohexadienones (1a and 1b).—These compounds were synthesized *via* a published procedure[26] and purified by methods described in the preceding paper of this series.[1]

Reactions of Peroxycyclohexadienones with Triphenylphosphine.—These experiments were carried out in a thermostated flask equipped with a magnetic stirring bar and connected in series to a reflux condenser, two cold traps kept at −78°, a removable trap for collecting gas samples, and a gas buret filled with mercury. The reaction vessel and stirrer were soaked in concentrated ammonium hydroxide to ensure neutralization of acidic sites and then dried at 120° immediately before use. All reactions were performed under helium after thorough degassing of the system by cooling and evacuation (three cycles). For experiments in chlorobenzene solution, mixtures were refluxed gently for 1 hr at the end of the reaction period in order to transfer dissolved gases to the cold traps. In all experiments gas volumes were measured after allowing the contents of the cold traps to expand into the buret at ambient temperature and pressure. The measured volumes were corrected to STP, and the samples were analyzed by gc as described above. For experiments in *n*-heptane solution, most of the triphenylphosphine oxide was recovered by filtering the cooled reaction mixtures. The material thus obtained was washed several times with petroleum ether (bp 30–60°) and was shown to be pure by melting point determinations and infrared spectra. The filtrate and washings were combined, freed of solvent by evaporation *in vacuo* at room temperature, and analyzed by programmed temperature gc (column A) after adding a weighed amount of a suitable internal standard. Sensitivity factors were determined using known mixtures of pure reference compounds; dienone 5 was assumed to have the same sensitivity factor as the compound producing the nearest neighboring peak (phenol 2). Accurate analyses for unreacted triphenylphosphine could not be obtained by this method, since the sensitivity factor of this compound showed a wide, unexplained variation, even under carefully controlled conditions. Reaction mixtures containing chlorobenzene were evaporated to remove solvent, boiled with 25 ml of *n*-heptane, cooled, filtered to recover triphenylphosphine oxide, and then processed in the manner just described. A careful search, employing a variety of analytical techniques, gave no evidence for the formation of dimeric products derived from 6 in the experiments with peroxydienone 1a.

Rates of decomposition of 1a were followed by infrared spectroscopy using the 873-cm^{-1} band of the peroxide as the analytical wavelength. Times required for 50 and 100% reaction of a solution containing both peroxydienone (0.065 *M*) and triphenylphosphine (0.20 *M*) in *n*-heptane at 100° were 1.4 and 8 hr, respectively, whereas the corresponding times for a solution containing only the peroxydienone at about the same concentration were 13 and 32 hr (approximately). Decomposition rates of 1b were not determined; however, the failure of the product composition to change appreciably after 22 hr (*cf.* Table I) shows that the reaction of this peroxydienone with triphenylphosphine must have been essentially complete at the end of this time under our experimental conditions.

Preparation of 2,6-Di-*t*-butyl-4-neopentylphenol (3).—A solution of quinone methide 6 (0.0327 mole, contaminated with an unknown amount of 2,6-di-*t*-butyphenol[27]) was added at ambient temperature under nitrogen to a stirred solution of *t*-butylmagnesium chloride (0.100 mole) in 150 ml of anhydrous ether. The temperature rose slightly during the addition, which required approximately 10 min, and a white precipitate appeared. After having been stirred for 1 additional hr, the mixture was poured into a solution of ammonium chloride (1 mole) in ice water. The organic moiety was separated, washed twice with water, dried over sodium sulfate, concentrated on a rotary evaporator, and then fractionated through a short Vigreux column at 0.65 mm. Following removal of a forerun which was mostly 2,6-di-*t*-butylphenol, two fractions were collected. The first fraction (1.70 g) boiled at 88–102° and was shown by nmr analysis to contain phenol 3 (78%), 2,6-di-*t*-butylphenol (21%), and traces of other materials. The second fraction, bp 102–103°, proved to be essentially pure 3 (4.10 g, 45% yield). This material solidified upon cooling and was recrystallized twice from methanol-water to give cream-colored platelets, mp 66–66.5°. The infrared spectrum (CS_2) showed a strong, sharp band at 3655 cm^{-1} (hindered hydroxyl), while the nmr spectrum (CCl_4) consisted of sharp singlets at τ 3.20 (2 H, ring protons), 5.17 (1 H, hydroxyl hydrogen), 7.63 (2 H, methylene group), 8.58 (18 H, ring *t*-butyls), and 9.12 (9 H, side-chain *t*-butyl).

Anal. Calcd for $C_{19}H_{32}O$: C, 82.54; H, 11.66. Found: C, 82.58; H, 11.76.

Relative Reactivity of Triphenylphosphine and *n*-Heptane toward *t*-Butoxy Radicals.—Carefully degassed solutions of di-*t*-butyl peroxide and triphenylphosphine in *n*-heptane were allowed to react under helium for 3–4 days at 100 ± 1° in the apparatus used for the peroxydienone experiments. All volatile materials were then transferred to the cold traps (−78°) by distillation under high vacuum at temperatures ranging up to 50°. These solutions were analyzed for *t*-butyl alcohol by gc at 75° on a Perkin-Elmer instrument, Model 154, equipped with a stainless steel column (50 ft × 0.25 in.) containing 40% of 3,3′-oxydipropionitrile on 30–45 mesh Chromosorb P. *n*-Propyl chloride was used as an internal standard; sensitivity factors were determined with synthetic mixtures of pure reference compounds. The solid residues were analyzed for triphenylphosphine oxide by programmed temperature gc (column A) in the manner described earlier, and k_D/k_A was then calculated in the usual way.[14] Values of 200 and 300 were obtained from two experiments starting with 0.2923 g (2.000 mmoles) of peroxide, 1.5737 g (6.000 mmoles) of the phosphine, and 25.00 ml (169.7 mmoles) of *n*-heptane. A similar experiment starting with 1.1696 g (8.000 mmoles) of peroxide gave a value of 320.

Reaction of 2,6-Di-*t*-butyl-*p*-cresol (2) with Di-*t*-butyl Peroxide and Triphenylphosphine.—A mixture of phenol 2 (5.51 g, 0.0250 mole), di-*t*-butyl peroxide (5.00 g, 0.0342 mole), and triphenylphosphine (6.56 g, 0.0250 mole) was stirred under reflux in a nitrogen atmosphere for 22 hr. Volatile constituents were removed at room temperature under vacuum, and the residue was then stirred with 50 ml of *n*-heptane and filtered to recover a considerable amount of triphenylphosphine oxide. Analysis of the heptane solution by programmed-temperature gc (column A) gave the following result (yields in moles/mole of starting 2): 2 (0.51), dienone 5 (0.15), phenol 3 (0.13), 4,4′-ethylenebis(2,6-di-*t*-butylphenol) (0.06, tentative identification based on mass spectrum of a trapped fraction), and triphenylphosphine oxide (1.04, including material isolated earlier). Several small, unidentified peaks were also noted. A trapped peak corresponding to 5 was shown to be approximately 90% pure by an additional gc run. The mass spectrum (70 ev) of this dienone showed a weak parent peak at *m/e* 276, another weak peak at *m/e* 261, strong peaks at *m/e* 220 and 219, and a very strong peak at *m/e* 205. At 7 ev the only peaks noted were at *m/e* 276 (weak) and 220 (strong). The nmr spectrum (CCl_4) exhibited sharp singlets at τ 9.08 (9 H, 4-*t*-butyl group), 8.86 (3 H, 4-methyl group), 8.79 (18 H, 2- and 6-*t*-butyls), and 3.48 (2 H, ring protons), together with a few small peaks in the *t*-butyl region that were presumed to have been caused by impurities. The infrared spectrum (neat sample) showed a pair of strong peaks, characteristic of the 2,5-cyclohexadienone structure,[28] at 1662 and 1644 cm^{-1}. Other experiments gave varying yields of 5, and repeated gc analyses, carried out over a period of several days, showed that the dienone

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[25] V. V. Ershov, G. N. Bogdanov, and A. A. Volod'kin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 138 (1963).

[26] A. F. Bickel, E. C. Kooyman, and C. la Lau, *J. Chem. Soc.*, 3211 (1953).

[27] *Cf.* N. P. Neureiter, *J. Org. Chem.*, **28**, 3486 (1963).

[28] G. M. Coppinger, *J. Am. Chem. Soc.*, **79**, 2758 (1957).

underwent decomposition upon standing in solution. The stability of the compound was also found to be strongly influenced by small variations in the composition of the gc column.

Reaction of Quinone Methide 6 with Di-*t*-butyl Peroxide and Triphenylphosphine.—Triphenylphosphine (13.64 g, 52.0 mmoles) and di-*t*-butyl peroxide (3.80 g, 26.0 mmoles) were added to a freshly prepared solution of quinone methide **6** (13.0 mmoles, generated by dehydrochlorination of 3.31 g of purified 2,6-di-*t*-butyl-4-chloromethylphenol with triethylamine[1]) in chlorobenzene (160 ml), and the mixture was refluxed with stirring under nitrogen for 24 hr. Solvent and other volatile constituents were then removed by evaporation *in vacuo*, and the residue was boiled with 200 ml of *n*-hexane. After cooling to room temperature, the mixture was filtered, and the recovered solid was washed several times with fresh *n*-hexane before drying. This solid (11.29 g) melted at 148–155° and was shown by infrared and nmr analysis to consist almost entirely of triphenylphosphine oxide. The filtrate and washings were combined, concentrated, and subjected to a rough analysis by programmed temperature gc (column B) without using pure reference compounds for calibration. This analysis showed the presence of phenol **3** (13% yield based on **6**), quinone methide **10** (10% yield based on **6**), triphenylphosphine oxide (82% total yield based on the starting phosphine, including material recovered by filtration), and triphenylphosphine (20% recovery). The remainder of the chromatogram consisted primarily of peaks whose long retention times suggested that they were due to compounds formed by dimerization of the starting quinone methide.

Preparation of Quinone Methide 10.—A rapidly stirred solution of phenol **3** (0.69 g, 2.5 mmoles) in benzene (25 ml) was freed of oxygen by bubbling with nitrogen for several minutes. A similarly degassed solution of potassium ferricyanide (4.0 g, 12 mmoles) and potassium hydroxide (2.0 g) in water (50 ml) was then added, and the mixture was stirred vigorously under nitrogen for 1.7 hr. The amber-colored benzene layer was separated, washed with water until a neutral aqueous phase was obtained, dried over Drierite, and evaporated to give 0.59 g of viscous, yellow oil that could not be induced to crystallize, but which was shown by gc analysis (column B) to consist primarily of a single species (85 area %). This species was identified as quinone methide **10** by a variety of spectroscopic measurements. The nmr spectrum ($CDCl_3$) of the crude mixture exhibited weak peaks of equal intensity at τ 3.82 (singlet, olefinic proton of side chain), 3.38 (doublet, $J \sim 2.5$ cps, ring proton *cis* to olefinic proton of side chain), and 2.57 (doublet, $J \sim 2.5$ cps, ring proton *trans* to olefinic proton of side chain), as well as three strong singlets in the *t*-butyl region at τ 8.76, 8.77, and 8.79. Olefinic proton assignments are based on comparisons with the spectra of several similar compounds that are currently under study in these laboratories. Accurate integration of the strong *t*-butyl peaks was not possible because of interference by a number of other small peaks; however, the intensities of the strong peaks were qualitatively in accord with the theoretical values. A purified sample of **10**, trapped after elution from the gas chromatograph, showed no infrared absorption (CS_2) for hydroxyl, but did exhibit a broad, strong band at 1625 cm^{-1} (exact position probably slightly in error owing to solvent interference), as well as a sharp band of medium intensity at 1705 cm^{-1}. The mass spectrum displayed a sizable parent peak at *m/e* 274.

Reaction of Quinone 4 with Di-*t*-butyl Peroxide and Triphenylphosphine.—This reaction was carried out under helium using the apparatus and procedure described for the peroxydienone experiments. After 48 hr at 100 ± 1°, a solution of 0.2203 g (1.00 mmole) of **4**, 0.2924 g (2.00 mmoles) of di-*t*-butyl peroxide, and 1.5738 g (6.00 mmoles) of triphenylphosphine in 25 ml of *n*-heptane gave 0.17 mmole of phenol **12**, 0.47 mmole of triphenylphosphine oxide, 0.70 mmole of unreacted quinone, and 0.17 mmole of isobutene. Product analyses were done by the usual gc methods. The cooled reaction mixture also contained a small amount of brownish solid which was not identified. The low conversion of **4** obtained in this experiment is not surprising in view of the rather slow rate of decomposition of di-*t*-butyl peroxide at 100°.[29]

Acknowledgments.—The authors wish to thank Drs. H. G. Schutze and F. H. Field for their interest and support during the course of this study, and to acknowledge helpful discussions of analytical problems with numerous colleagues in the analytical research section of these laboratories. We are particularly indebted to Mr. H. J. Tarski for his skillful performance of much of the experimental work.

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(29) *Cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 469.

A New Synthesis of 3-Methylcyclopent-2-en-2-ol-1-one

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The synthesis of 3-methylcyclopent-2-en-2-ol-1-one (I) was accomplished by the hydrolysis and decarboxylation of 5-carbethoxy-5-methylcyclopent-2-en-2-ol-1-one (IV) which was obtained by the nitrosation and hydrolysis of 2-carbethoxy-2-methylcyclopentanone (III). The selenium dioxide oxidation of the ketone III gave the previously unreported ketone, 5-carbethoxy-5-methylcyclopent-2-en-2-ol-1-one (IV), while the DMSO oxidation of 5-bromo-2-carbethoxy-2-methylcyclopentanone (V) gave the unexpected product, 3-bromo-5-carbethoxy-5-methylcyclopent-2-en-2-ol-1-one (VIIa), in good yield.

The potential use of 3-methylcyclopent-2-en-2-ol-1-one (I), cyclotene as a spice, has created a recent interest in new methods for its synthesis. A survey of the literature indicates that I has been obtained by several procedures from divinyl glycol,[1] 2,2-dichloro-5-methylcyclopentan-1-one,[2] 3-methyl-3,5-dicarbethoxy-1,2-cyclopentanedione,[3] and 3-methylcyclopent-2-en-1-one,[4,5] as well as from natural sources.[6] Recently, compound I was reported to be one of the important constituents of coffee aroma[7a] and has been utilized as an intermediate in the synthesis of dihydrojasmone.[7b] Investigations have shown that I[7b,8] rather than Ia[9]

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(1) (a) G. Dupont and E. Urion, *Compt. Rend.*, **197**, 158 (1933); (b) E. Urion, *Ann. Chim.* (Paris), [11] **1**, 5 (1934).

(2) H. Gault and J. Burkhard, *Compt. Rend.*, **205**, 1416 (1937).

(3) G. Hesse and K. W. F. Bockmann, *Ann.*, **563**, 37 (1949).

(4) H. O. House and R. L. Wasson, *J. Am. Chem. Soc.*, **79**, 1488 (1957).

(5) Preparations of I from other starting materials are described in the following references: (a) J. Lichtenberger and G. Gabriel, *Bull. Soc. Chim. France*, [5] **4**, 1978 (1937); (b) I. N. Nazarov and A. A. Ahrem, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1383 (1956); (c) L. I. Krimen, *et al.*, U. S. Patent 2,865,962 (1958); (d) G. B. Payne, *J. Am. Chem. Soc.*, **81**, 4901 (1959); (e) G. I. Fray, *Tetrahedron*, **14**, 161 (1961).

(6) (a) J. Meyerfeld, *Chem. Ztg.*, **36**, 549 (1912); (b) V. E. Tishchenko, M. I. Lishkevich, and L. A. Skulskaya, *Zhur. Priklad. Khim.*, **3**, 375 (1930); (c) A. W. Goos and A. A. Reiter, *Ind. Eng. Chem.*, **38**, 132 (1946); (d) A. A. Reiter and F. L. Beman, U. S. Patent 2,400,466 (1946); (e) N. Hellström, *Acta Polytech.*, **9**, 13 (1947); (f) D. Tishchenko, K. Bardysheva, and N. Nosova, *Zhur. Prikladnoi Khim.*, **21**, 976 (1948); (g) U. P. Sumarokov and M. G. Pershanova, *ibid.*, **27**, 656 (1954).

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