Reversibility of Organotin Radical Attack on Terminal Olefins and 2-Butenes[1]

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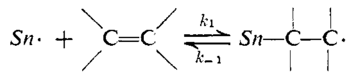
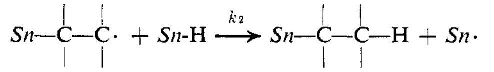
Abstract: *trans*-1-Deuterio-1-hexene has been prepared in high purity by hydroboration of 1-hexyne with disiamylborane, followed by acid cleavage of the resulting borane with deuterioacetic acid. The *cis* isomer has been prepared by hydroboration of 1-deuterio-1-hexyne in the same manner, followed by hydrolysis with acetic acid The *cis*- and *trans*-β-deuteriostyrenes were prepared similarly from phenylacetylene and β-deuteriophenylacetylene, respectively. Reaction of these with insufficient amounts of organotin hydrides, recovery of unreacted olefin, and examination by infrared spectroscopy has shown that attack by organotin radicals on 1-hexene is highly reversible, but attack on styrene is only slightly so under the conditions used. *cis*- and *trans*-2-butenes are isomerized to an equilibrium mixture upon irradiation with organotin hydrides, indicating readily reversible attack on the olefins by organotin radicals. It is shown that trimethyltin hydride forms an adduct with 2-butenes, albeit slowly, contrary to expectations from earlier reports.

The addition of organotin hydrides to terminal olefins (hydrostannation), first reported in 1957,[2] has been shown[3] to proceed in most cases by a free-radical chain mechanism for which the following chain carrying steps have been suggested[2b,3] (*Sn* is a trisubstituted tin group).



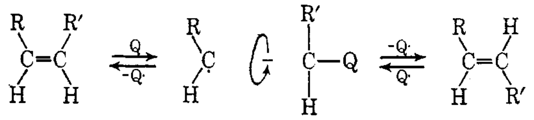
$$Sn\cdot + \gt C{=}C\lt \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Sn{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot \quad (1)$$



$$Sn{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}\cdot + Sn\text{-}H \xrightarrow{k_2} Sn{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H + Sn\cdot \quad (2)$$

Evidence for the free-radical nature of the reaction includes catalysis by free-radical sources such as azobisisobutyronitrile,[3] among others, and ultraviolet irradiation,[4,5] and retardation by the efficient scavenger, galvinoxyl.[3] Among the aspects of the mechanism which remain to be ascertained is whether or not reaction 1 is reversible.

The occurrence of reversibility in free-radical attack on a double bond is usually determined by kinetic studies or by examining unreacted olefin for conversion to its geometrical isomer.[6]



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Internal olefins have been reported[2b,7] not to add organotin hydrides except if the double bond is strained[8] or activated by a conjugated electron-attracting group.[3,7,9] These cases seemed unsuitable for a test of the reversibility of reaction 1. It is known, however, that replacement of a hydrogen by deuterium in terminal olefins is manifested in the infrared spectrum in the same way as replacement of hydrogen by an alkyl or aryl group.[10a] This provides the possibility of applying the isomerization test to terminal olefins, as has been done for thiyl radical attack on 1,2-dideuterioethylene.[10b]

***cis*- and *trans*-1-Deuterio-1-hexene.** The stereospecifically deuterated 1-hexenes were prepared by hydroboration of 1-alkynes with disiamylborane. Starting with 1-hexyne and cleavage of the resulting vinylborane with deuterioacetic acid yielded the *trans* isomer. To prepare the *cis* isomer, we started with 1-deuterio-1-hexyne and cleaved the vinylborane with acetic acid. In neither case could contamination by the other isomer be detected. Thus, these procedures are convenient and, perhaps, more readily carried out than that developed by Wilke and Muller.[11] A fourfold excess of each of the 1-hexenes was irradiated individually with tri-*n*-butyltin hydride for 2.5 hr at 10°. The infrared spectra of the recovered olefins were superimposable whether the starting olefin was the *cis* or *trans* isomer. The spectra contained bands due to each of the isomers indicating complete isomerization as shown in Figure 1. Since only a small amount of the organotin hydride had been consumed when the reaction was interrupted, it is clear that k_{-1} is much larger than $k_2[\text{SnH}]$.

Dialkyltin hydride chlorides are known to add to olefins faster than trialkyltin hydrides.[12] Di-*n*-butyltin hydride chloride was irradiated with the isomeric deuteriohexenes under the same conditions as described above and complete consumption of the hydride chlo-

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[1] Supported by the National Science Foundation under Grant GP-5285.

[2] (a) G. J. M. van der Kerk, J. G. A. Luijten, and J. G. Noltes, *Chem. Ind.* (London), 352 (1956). For recent reviews see: (b) H. G. Kuivila in "Advances in Organometallic Chemistry," Vol. 1, F. G. A. Stone and R. West, Ed., Academic Press Inc., New York, N. Y., 1964, p 47; (c) W. P. Neumann, *Angew. Chem.*, **76**, 849 (1964).

[3] W. P. Neumann and R. Sommer, *Ann.*, **675**, 10 (1964).

[4] H. C. Clark, S. G. Furnival, and J. T. Kwon, *Can. J. Chem.*, **41**, 2889 (1963); C. Barnetson, H. C. Clark, and J. T. Kwon, *Chem. Ind.*, (London), 458 (1964); H. C. Clark and J. T. Kwon, *Can. J. Chem.*, **42**, 1288 (1964).

[5] J. C. Pommier and J. Valade, *Bull. Soc. Chim. France*, 951 (1963); J. Valade and J. C. Pommier, *ibid.*, 199 (1963).

[6] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957.

[7] W. P. Neumann, H. Niermann, and R. Sommer, *Ann.*, **659**, 27 (1963).

[8] Unpublished observations by O. R. Kahn, I. J. Tyminski, and F. L. Pelczar in these laboratories.

[9] J. G. Noltes and G. J. M. van der Kerk, "Functionally Substituted Organotin Compounds," Tin Research Institute, Greenford, England, 1958.

[10] (a) E. G. Hoffmann, *Ann.*, **618**, 276 (1958); H. W. Schroetter and E. G. Hoffmann, *ibid.*, **672**, 44 (1964); (b) D. M. Graham, R. L. Mieville, and C. Sivertz, *Can. J. Chem.*, **42**, 2239 (1964).

[11] G. Wilke and H. Muller, *ibid.*, **618**, 267 (1958).

[12] W. P. Neumann and J. Pedain, *Tetrahedron Letters*, 2461 (1964).

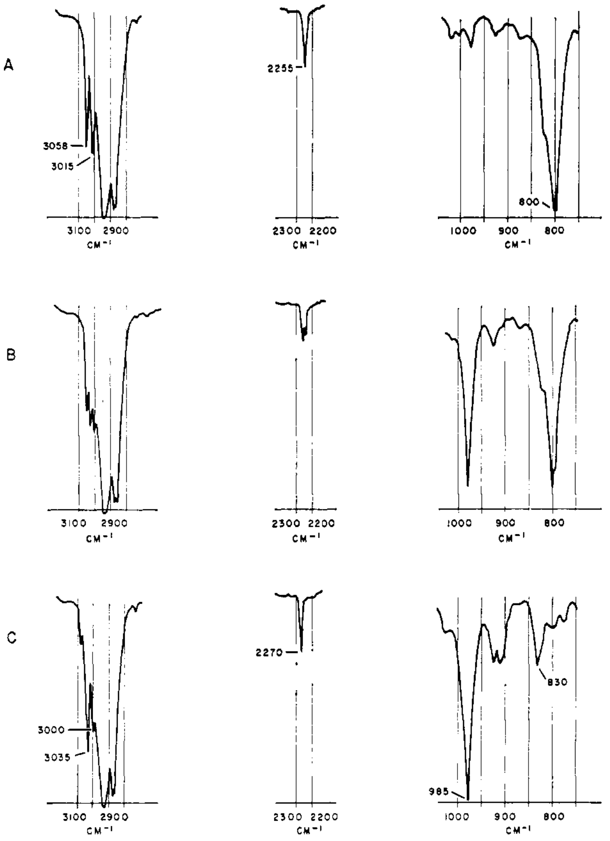

Figure 1. Infrared characteristics of 1-deuterio-1-hexenes: A, pure *cis* isomer; B, recovered after irradiation of either isomer in the presence of organotin hydride; C, pure *trans* isomer.

ride had occurred, yet the excess olefin was completely isomerized. This reveals that the rapid over-all reaction is not due to k_2[SnH] being much larger than k_{-1}; the reverse is, in fact, the case. Similarly, the *thermal* addition of triphenyltin hydride at 70° in diffuse daylight resulted, after 3.5 hr, in complete isomerization of the deuteriohexenes. Addition was not complete indicating qualitatively the same relationship between the steps governed by k_{-1} and k_2 as in the other examples.

***cis*- and *trans*-β-Deuteriostyrenes.** The isomeric β-deuteriostyrenes were prepared by the reactions used in the preparation of the deuteriohexenes using phenylacetylene and β-deuteriophenylacetylene as starting materials.

The rate of attack of butanethiyl radicals on styrene is about 100 times their rate of attack on 1-pentene.[13] The rate of hydrogen transfer from the thiol to the resulting radicals is about 500 times greater with 2-pentyl radical than for the resonance-stabilized benzylic radical. Thus, if k_{-1} is of the same magnitude for the two species, reversibility of free-radical addition would be more facile in the styrene than in 1-pentene reaction.

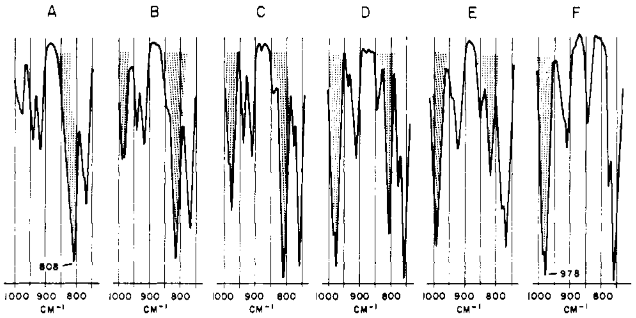

Figure 2. Infrared characteristics of β-deuteriostyrenes: A, *cis* isomer; F, *trans* isomer; B and C, styrene recovered after irradiation of *cis* isomer with tributyltin hydride for 3 and 6.5 hr, respectively; D and E, styrene recovered after irradiation of *trans* isomer for 6.5 and 3 hr, respectively.

When *cis*- or *trans*-β-deuteriostyrene was irradiated in the presence of tri-*n*-butyltin hydride for 3 hr at 10°, it was found that the unreacted olefin contained only minor amounts of the other isomer, as can be seen by inspection of Figure 2. Even after 6.5 hr, when all of the hydride had been consumed in the addition reaction, only partial isomerization was observed. Similarly, after irradiation of a fourfold excess of styrene with *n*-dibutyltin hydride chloride for 1.5 hr or dibutyltin dihydride for 3 hr (both at 10°), only partially isomerized styrenes were recovered. In the *thermal* addition of triphenyltin hydride to *cis*- or *trans*-styrene, which at 70° in the diffuse daylight is completed in less than 1.5 hr, the excess of the olefin shows only a minor amount of the other isomer.

On the basis of the considerations given above, it must be concluded that the lower degree of reversibility in the reactions with styrene than with 1-hexene is due to a smaller value of k_{-1} for styrene. In other words, the activation energy for trialkyltin radical loss from the resonance-stabilized benzylic radical is higher than that for the same reaction of a simple *sec*-alkyl radical.

***cis*- and *trans*-2-Butene.** The reported failure of the hydrostannation of internal olefins could be due to nonoccurrence of reaction 1 or to a high value of k_{-1} relative to k_2[SnH]. From the results with the deuterated olefins, the latter seemed to be probable. This could be shown by irradiation of several organotin hydrides with 2-butenes. The equilibrium mixture of recovered 2-butenes consisted of 25% *cis* and 75% *trans* (±2%). Results are given in Table I. Even in the diffuse daylight a slow isomerization takes place. With tributyltin hydride in several experiments significant amounts of *n*-butane were formed. One could suggest that the isomerization is due to an attack by butyl radicals rather than by organotin radicals. However, there is no doubt that organotin radicals do indeed attack the double bond, for we were able to isolate the addition product in the case of trimethyltin hydride and show it to have infrared and nmr spectra identical with an authentic sample of trimethyl-*sec*-butyltin.[14a]

Control Experiment. Pure *cis*- and *trans*-2-butenes were irradiated separately for 24 hr at 15° with the 100-w lamp and no isomerization was observed. After irradiation of *cis*- and *trans*-β-deuteriostyrene for 3.5 hr under the same conditions, some isomerization to the other isomers had occurred as indicated by small new bands at 978 and 808 cm^{-1}, respectively. Yet this amounted to 30% at most of the isomerization occurring in the presence of tributyltin hydride.

Since this manuscript was submitted for publication, evidence for reversibility of attack by trimethyltin and

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(13) R. Back, G. Trick, C. McDonald, and C. Sivertz, *Can. J. Chem.*, **32**, 1078 (1954); M. Onyszchuk and C. Sivertz, *ibid.*, **33**, 1034 (1955).

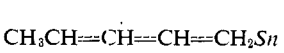
(14) (a) Meanwhile we have shown that organotin hydrides add to other internal olefins also. (b) W. P. Neumann, H. J. Albert, and W. Kaiser, *Tetrahedron Letters*, 2041 (1967).

Table I. Isomerization of 2-Butenes by Organotin Compounds

Entry	Organotin compd, mmoles	2-Butene isomer, mmoles	Conditions[a] Time, hr	Temp, °C[b]	Composition of recovered 2-butene in % trans[c,d,g]	
1	$(n\text{-}C_4H_9)_3SnH$, 4	*cis* ~14	24	20[e]	74.2	(6.5)
2	$(n\text{-}C_4H_9)_3SnH$, 4	*cis* ~6	24	15	75.0	(3.8)
3	$(n\text{-}C_4H_9)_3SnH$, 4	*cis* ~6	8.5	15	67.5	(2.7)
4	$(n\text{-}C_4H_9)_3SnH$, 4	*cis* ~14	10	−78	0.2	
5	$(n\text{-}C_4H_9)_3SnH$, 4	*cis* ~6	20	25[f]	3.2	
6	$(n\text{-}C_4H_9)_3SnH$, 4	*trans* ~6	24	15	76.1	(3.1)
7	$(n\text{-}C_4H_9)_3SnH$, 4	*trans* ~6	8	15	76.7	(1.4)
8	$(CH_3)_3SnH$, 5	*cis* ~6	8	15	73.8	
9	$(CH_3)_3SnH$, 5	*trans* ~6	8	15	75.9	
10	$(C_6H_5)_3SnH$, 4	*cis* ~14	24	20[e]	73.2	
11	$(n\text{-}C_4H_9)_4Sn$, 3	*cis* ~6	24	17	57.1	

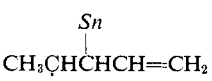
[a] Unless otherwise indicated, irradiation was carried out with a 100-w, medium-pressure mercury vapor lamp and no solvent was used. [b] ±1°. [c] Per cent *cis* = 100 − *trans*. [d] Figures in parentheses indicate per cent of recovered gas with same retention time (glpc) as butane. If no figure is given in parentheses, no butane was detected. [e] 250-w lamp. [f] Diffuse daylight. [g] In the gas phase at 25°, the thermodynamic equilibrium mixture contains 2% 1-butene, 23% *cis*-2-butene, and 75% *trans*-2-butene: A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **79**, 2888 (1957).

triphenyltin radicals to piperylenes has been reported.[14b] It was assumed that the organotin radical attacked the



$CH_3CH{=}\dot{C}H{=}CH{=}CH_2Sn$

3



$CH_3\underset{\cdot}{C}H\overset{Sn}{\overset{|}{C}}HCH{=}CH_2$

4

terminal carbon only, forming the allylic radical, **3**, which then could undergo rotation about the C_3–C_4 bond. Our results demonstrate that attack could also occur at one of the other vinylic carbons as well, although this would occur less frequently. If attack occurs at C_3, the product is **4** in which the C_3–C_4 bond has become a single bond, about which rotation would occur much more rapidly than it would about the approximately 1.5 bond in **3**.

Experimental Section

Boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer and a Beckmann IR 12 spectrophotometer. For glpc separations, an F & M Model 720 temperature-programmed gas chromatograph was used with a flow rate of 60 cc/min of helium.

Materials. *cis*- and *trans*-2-butene of 99.9% purity (Matheson Co.) were used directly from a cylinder. Organotin hydrides were prepared by reduction of organotin chlorides with $LiAlH_4$ in ether.[2b,c]

***trans*-1-Deuterio-1-hexene.** Disiamylborane was prepared according to the procedure of Brown and Zweifel[15] from 100.8 g (1.44 moles) of 2-methyl-2-butene, 20.4 g (0.54 mole) of sodium borohydride, and 102.2 g (0.72 mole) of boron fluoride etherate in 300 ml of diglyme. The suspension of disiamylborane in diglyme was added to 49.2 g (0.6 mole) of 1-hexyne with stirring and cooling to 0°. After 3 hr of stirring at 20°, the vinylborane was cleaved with 250 ml of deuterioacetic acid (prepared from 99.8% D_2O and acetic anhydride). The hexene was separated as described by Brown. Distillation of the hexene–ether mixture through a 100 cm × 6 mm Todd column, with a stainless steel spiral, gave 26.4 g of *trans*-1-deuterio-1-hexene (52% yield), bp 63–64° (760 mm), $n^{20}D$ 1.3872. Glpc analysis (6-ft diisodecyl phthalate 10% on Diatoport W 60–80, 40° isothermal) showed that it consisted to 99.7% of 1-hexenes. The infrared spectrum was in agreement with the reported one[10] (C–H stretching frequencies of the vinyl hydrogens at 3035, 3000, and 2980 cm^{-1}, C–D stretching frequency at 2270 cm^{-1}, C=C stretching frequency at 1620 cm^{-1}, and out-of-plane deformation frequencies at 985 and 830 cm^{-1}). Small absorptions at 3080, 1640, and 910 cm^{-1} indicated a very small amount of undeuterated 1-hexene. The absence of an absorption, especially at 800 cm^{-1}, showed that it was free of detectable amounts of *cis*-1-deuterio-1-hexene.

***cis*-1-Deuterio-1-hexene** was prepared as described above from 49.2 g (0.6 mole) of 1-deuterio-1-hexyne[16] instead of 1-hexyne and cleavage with 300 ml of glacial acetic acid instead of deuterioacetic acid. The *cis*-1-deuterio-1-hexene was obtained after distillation of the crude hexene–ether mixture through the Todd column in 57% yield, bp 63–64° (760 mm), $n^{20}D$ 1.3873. Glpc analysis (as above) showed a purity of 99.9% 1-hexenes. The infrared spectrum was consistent with the reported one[16] (C–H stretching frequencies of the vinyl hydrogens at 3058, 3015, and 2980 cm^{-1}, C–D stretching frequency at 2255 cm^{-1}, C=C stretching frequency at 1620 cm^{-1}, and out-of-plane deformation frequency at 800 cm^{-1}). Absorptions at 1640, 910, and 995 cm^{-1} characteristic of undeuterated 1-hexene were absent. The content of *trans*-1-deuterio-1-hexene was less than 1% (estimated from the out-of-plane deformation frequency at 985 cm^{-1}).

***cis*-β-Deuteriostyrene** was prepared by hydroboration of 61.3 g (0.6 mole) of 1-deuteriophenylacetylene[17] with disiamylborane as described above for *trans*-1-deuterio-1-hexene. After cleavage of the vinylborane with 300 ml of glacial acetic acid at 0° and stirring for 3 hr at 20°, the mixture was poured into a separatory funnel with ice water; the organic layer was separated and shaken with dilute sodium hydroxide solution, saturated sodium chloride solution, and several times with water. The styrene was separated from the boron compounds by distillation (10 mm) and collected in a trap cooled with liquid nitrogen. The distillation flask was heated slowly to 75° and maintained at that temperature for 1 hr. The crude styrene was shaken several times with an alkaline solution of mannitol, then with water, and dried over anhydrous magnesium sulfate. Fractional distillation yielded 23.9 g of styrene (38%), bp 62–63° (40 mm), and 2.5 g of polystyrene. Glpc analysis of the styrene (6-ft Lac 10% on Diatoport W 60–80, 70–170°, 10°/min) showed that it consisted of 96.5% styrenes and 1.0% ethylbenzene. The infrared spectrum showed the expected C–D stretching frequency at 2258 cm^{-1} and the strong out-of-plane deformation absorption at 808 cm^{-1}. Small bands at 1630, 910, and 992 cm^{-1} were due to undeuterated styrene since the D_2O used in this preparation contained about 4% hydrogen. The presence of a small amount of *trans*-β-deuteriostyrene could not be excluded since the characteristic absorption of this compound at 978 cm^{-1} would be partially superimposed on the absorption of undeuterated styrene at 992 cm^{-1}.

***trans*-β-Deuteriostyrene.** The procedure followed that given for the *cis* isomer with the exception that phenylacetylene was used and the cleavage was carried out with 200 ml of deuterioacetic acid (prepared from acetic anhydride and ~96% D_2O). *trans*-β-Deuteriostyrene was obtained in 47% yield (29.5 g). The C=C stretching frequency was at 1613 cm^{-1}, the C–D stretching frequency at 2278 cm^{-1}, and the strong out-of-plane deformation absorptions at 978 and 845 cm^{-1}. Bands at 1630, 992, and 910 cm^{-1} belonged to undeuterated styrene. Very weak bands in the C–D region and in the region of the out-of-plane deformation absorp-

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(15) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **83**, 3834 (1961).

(16) P. S. Skell and P. K. Freeman, *J. Org. Chem.*, **29**, 2524 (1964).

(17) R. West and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **83**, 765 (1961).

tions indicated the presence of small amounts of other styrenes, one of them due to a reversed addition of the disiamylborane to phenylacetylene. Bands due to the *cis* isomer were not evident.

Trimethyl-*sec*-butyltin. *sec*-Butylmagnesium bromide was prepared from 54.9 g (0.4 mole) of *sec*-butyl bromide and 14.6 g (0.6 g-atom) of magnesium in 400 ml of dry ether. The Grignard reagent was separated from excess magnesium by forcing it with argon pressure through a glass tubing with a glass wool filter into another flask. Trimethyltin chloride (39.9 g, 0.2 mole) in 50 ml of ether was added at 20° and the mixture heated to reflux for 2 hr and hydrolyzed after cooling by pouring onto ice and ammonium chloride. The organic layer was separated, dried over calcium chloride, and fractionated over a 20-cm column packed with glass helices to yield 28.5 g (64%) of product, bp 145.5–146° (760 mm), $n^{20}\text{D}$ 1.4614. Glpc analysis indicated a purity of 99% (6-ft silicone rubber SE 30 10% on Diatoport W 60–80, 70° isothermal). *Anal.* Calcd for $C_7H_{18}Sn$: Sn, 53.73. Found: Sn, 53.38.

Addition of Organotin Hydrides to Olefins. Ampoules of Pyrex glass were evacuated, heated, and filled with argon. Organotin hydride (1.5 mmoles) and styrene or hexene (6 mmoles) were placed in the ampoule under a steady stream of argon and sealed after cooling to −78°. The ampoules were then heated or irradiated with a 100-w, medium-pressure mercury vapor lamp. The excess olefin was recovered by distillation (10 mm) into a trap cooled to −78°, and analyzed by infrared spectroscopy. In the reactions with *cis*- and *trans*-2-butenes 0.3–0.4 g (about 6 mmoles) of the olefin was condensed from the tank into the air-free ampoule at −78°, and 1.0 ml of an organotin hydride was added. The ampoules were sealed and irradiated with a 100- or 250-w lamp as described above. The recovered 2-butenes were analyzed by glpc (15-ft dimethylsulfolane 28% on crushed Firebrick, 0°, isothermal). After the trapping of butenes, the remaining liquids were analyzed by glpc. When tri-*n*-butyltin hydride was used, small amounts of tetrabutyltin and hexa-*n*-butylditin were found (4-ft silicone rubber SE 30 20% on Chromosorb W 60–80, 240° isothermal). When trimethyltin hydride was used, trimethyl-*sec*-butyltin was formed along with small amounts of tetramethyltin and hexamethylditin. It was separated by distillation [bp 146–148° (760 mm)]. Its infrared and nmr spectra were found to be identical with those of an authentic sample.

Inhibition of Free-Radical Reactions. IV. The Synergistic Effect of 2,6-Di-*t*-butylphenols on Hydrocarbon Oxidation Retarded by 4-Methoxyphenol

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Dearborn, Michigan 48121. *Received April 7, 1967*

Abstract: By means of stop-flow studies it has been demonstrated that the rate of reaction of the 4-methoxyphenoxy radical with 2,4,6-tri-*t*-butylphenol is 425–850 times faster than interaction with 9,10-dihydroanthracenyl hydroperoxide and 7400–14,800 times faster than its reaction with 9,10-dihydroanthracene at 60° in chlorobenzene. The effects of the addition of 2,6-di-*t*-butylphenols on the rates of oxygen absorption of 9,10-dihydroanthracene retarded by 4-methoxyphenol have been determined over wide ranges of concentration. At low ratios of the concentrations of 4-methoxyphenol to hydrocarbon, the results for 2,6-di-*t*-butyl-4-methylphenol are quantitatively described by a kinetic scheme which involves the regeneration of 4-methoxyphenol by means of its radical reacting with the hindered phenol and the termination of the hindered phenoxy radical by reaction with peroxy radicals. In the case of 2,4,6-tri-*t*-butylphenol and 2,6-di-*t*-butylphenol the termination involves both peroxy and phenoxy radicals with the hindered phenoxy radical. As the ratio of the concentrations of 4-methoxyphenol to hydrocarbon is increased, the oxidation results obtained upon the addition of the three hindered phenols are described by a scheme which involves a fast equilibrium between the 4-methoxyphenoxy radical and the hindered phenoxy radical and termination by both dimerization of the 4-methoxyphenoxy radical and the reaction of the 4-methoxyphenoxy radical with the hindered phenoxy radical. The analysis of these kinetic results reveal that (1) the value of the rate constant for the reaction of 2,6-di-*t*-butyl-4-methylphenoxy with the peroxy radical is considerably larger than $8.7 \times 10^7\ M^{-1}\ \text{sec}^{-1}$, (2) the rate constant for the dimerization of the 4-methoxyphenoxy radical is smaller than $1 \times 10^7\ M^{-1}\ \text{sec}^{-1}$, (3) the rate constant for hydrogen abstraction by the 4-methoxyphenoxy radical from 9,10-dihydroanthracene is smaller than $115\ M^{-1}\ \text{sec}^{-1}$, and (4) the equilibrium constant for hydrogen transfer between peroxy radicals and 4-methoxyphenol is larger than 50. In agreement with the kinetic results, the addition of the hindered phenols have a dramatic synergistic effect on the length of the inhibition period produced by 4-methoxyphenol. The quinol ether produced by reaction of 4-methoxyphenoxy and 2,4,6-tri-*t*-butylphenoxy has been shown to function as an inhibitor at low concentrations and as an initiator at concentrations greater than $2 \times 10^{-3}\ M$. This observation and results of ancillary experiments suggest that this compound is in equilibrium with its precursors. In addition it has been demonstrated that 3,5,3′,5′-tetra-*t*-butylstilbene-4,4′-quinone is produced only upon evaporation of a solution of 2,6-di-*t*-butylquinone-4-methide, produced by the reaction of peroxy radicals with mixtures of 4-methoxyphenol and 2,6-di-*t*-butyl-4-methylphenol. The results of the kinetic, *inhibition period*, and product studies for this system have been related to the general phenomenon of antioxidant synergism manifested by mixtures of hindered and nonhindered phenols. A correlation has been demonstrated between the magnitude of synergism observed in practice and the competition between hydroperoxide and hindered phenoxy for the nonhindered phenoxy radical as measured in the laboratory.

The rates of oxygen absorption of solutions of 9,10-dihydroanthracene (DHA) and 2,2′,3,3′-tetraphenylbutane (TPB) containing hindered phenols or hydroquinones have been explained by a relatively simple rate equation.[1] The expression was derived from a scheme

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(1) L. R. Mahoney, *J. Am. Chem. Soc.*, **88**, 3035 (1966).