

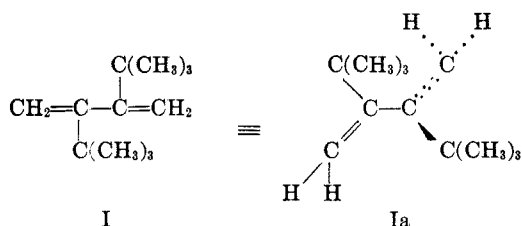
Free-Radical Reactions of 2-*t*-Butyl-1,3-butadiene and 2,3-Di-*t*-butyl-1,3-butadieneEARL S. HUYSER,¹ FREDERICK W. SIEGERT, HANS J. W. SINNIGE, AND HANS WYNBERG

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2,3-Di-*t*-butyl-1,3-butadiene (I) failed to yield free-radical addition products when allowed to react in peroxide- and light-induced reactions with either bromotrichloromethane or with *n*-butyl mercaptan. Under similar conditions, a mixture of the 1,4-addition products, 1-bromo-5,5,5-trichloro-2-*t*-butyl-2-pentene and 1-bromo-5,5,5-trichloro-3-*t*-butyl-2-pentene, were obtained in the reaction of 2-*t*-butyl-1,3-butadiene (II) with bromotrichloromethane. Only a single addition product, *n*-butyl-2-*t*-butyl-2-butenyl sulfide, was obtained in the reaction of II with *n*-butyl mercaptan. Competition reactions of II with 1-octene toward addition of both bromotrichloromethane and *n*-butyl mercaptan showed the expected high reactivity of the conjugated diene II toward free-radical addition. Competition reactions of I with 1-octene indicated that the reactivity of this diene toward free-radical addition was less than that of the alkene. Furthermore, I failed to copolymerize with styrene whereas II formed a copolymer with styrene. These results are discussed in terms of the nonconjugated nature of the 1,3-diene system in I.

The steric effects exerted by the large alkyl groups on the 2 and 3 positions of 2,3-di-*t*-butylbutadiene (I) have been reported to influence both its chemical

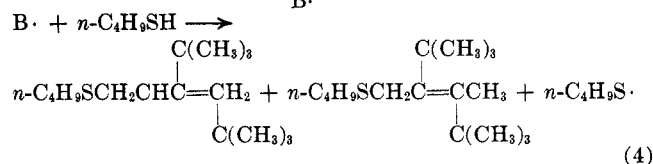
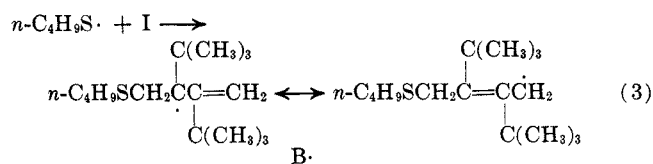
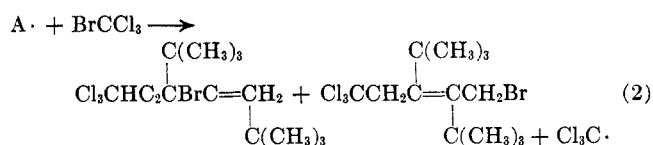
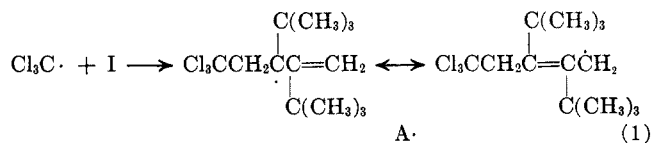


and physical properties causing it to behave as if it were a nonconjugated diene. Backer² found that I did not participate in diene reactions with either sulfur dioxide or maleic anhydride. More recently, the ultraviolet spectra of I was shown not only to lack the typical dialkyldiene absorption maximum at 220 m μ but to have an absorption maximum at 180 m μ and a shoulder at 209 m μ , absorptions which are consistent with MO calculations for a nonplanar 1,3-diene system³ such as is shown in Ia. In a preliminary communication we reported that I failed to participate in free-radical reactions with bromotrichloromethane and styrene in a manner expected for a conjugated 1,3-diene.⁴ The present report relates the results of a more detailed study of I in free-radical reactions and a comparison of its behavior with that of 2-*t*-butyl-1,3-butadiene.

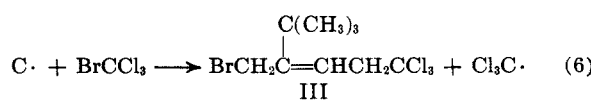
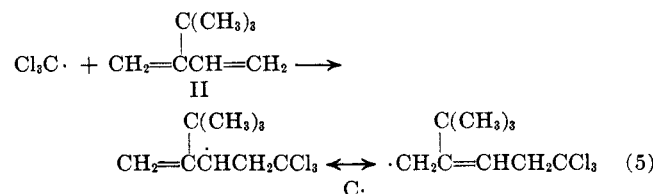
Results

The free-radical additions of bromotrichloromethane⁵ and of mercaptans⁶ to conjugated dienes yield mixtures of addition products in which the 1,4-addition products predominate over the 1,2-addition products. The light-induced reactions of I with *n*-butyl mercaptan and with bromotrichloromethane failed to yield isolable amounts of any reaction products. The peroxide-induced reaction of bromotrichloromethane with I yielded small amounts of high-boiling material but we were unable to detect any identifiable quantities of either of the

expected 1,2- or 1,4-addition products in this mixture. The inability of I to participate in these normally facile free-radical addition reactions suggests that either the addition of the Cl₃C· and *n*-C₄H₉S· radicals to the unsaturated system (reactions 1 and 3) or reaction of the expected hybrid adduct radicals A· and B· with the adding reagent (reactions 2 and 4) were retarded in some manner by the *t*-butyl groups on the 2 and 3 carbons of I.



Bromotrichloromethane added readily to 2-*t*-butyl-1,3-butadiene (II) in a light-induced reaction. A mixture of very nearly equal amounts of the 1:1 addition products, 1-bromo-5,5,5-trichloro-2-*t*-butyl-2-pentene (III), *via* reactions 5 and 6, and 1-bromo-5,5,5-trichloro-3-*t*-butyl-2-pentene (IV), *via* reactions 7 and 8, was obtained. Evidence that the composition of the



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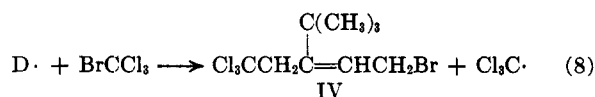
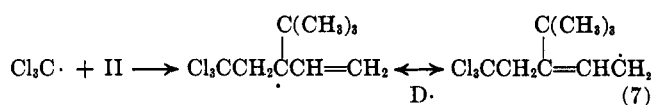
(2) H. J. Backer, *Rec. Trav. Chim.*, **58**, 643 (1939).

(3) H. Wynberg, A. De Groot, and D. W. Davis, *Tetrahedron Letters*, **No. 17**, 1083 (1963).

(4) E. S. Huyser, F. W. Siegert, and H. Wynberg, *ibid.*, **No. 30**, 2569 (1965).

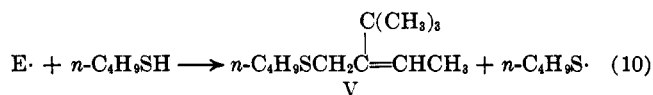
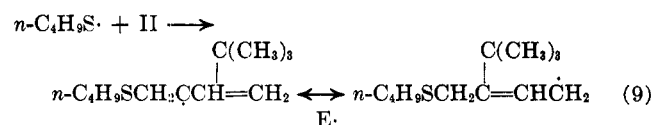
(5) For discussion of these reactions, see C. Walling and E. S. Huyser, *Org. Reactions*, **13**, 91 (1963).

(6) For discussion of these reactions, see F. W. Stacey and J. F. Harris, Jr., *ibid.*, **13**, 150 (1963).

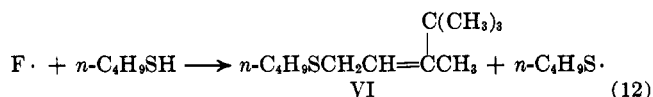
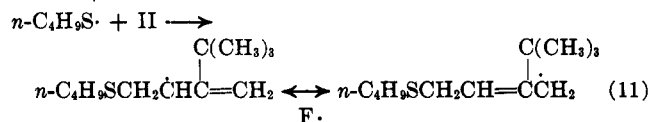


mixture was that of positional isomers rather than a mixture of *cis* and *trans* isomers of a single positional isomer was found in examination of the nmr spectrum of the product mixture which showed two singlets (1.09 and 1.11 ppm) that can be ascribed to the *t*-butyl groups, two singlets (3.85 and 4.05 ppm) due to the 1-methylene and 4-methylene hydrogens of III and IV, respectively, a triplet centered at 5.88 ppm ($J = 7.2$ cps) due to a vinyl hydrogen of either III or IV which was coupled with a doublet centered at 3.56 ppm ($J = 7.2$ cps) due to either the 4-methylene of III or the 1-methylene of IV, and another triplet centered at 6.20 ppm ($J = 9.0$ cps) which was coupled with a doublet centered at 4.12 ppm ($J = 9.0$ cps). The different coupling constants is evidence against a pair of *cis-trans* isomers of a single 1,4-addition product which would have the same coupling constant.

A single addition product, *n*-butyl-2-*t*-butyl-2-butenyl sulfide (V), was formed in the reaction of II with *n*-butyl mercaptan by the chain sequence 9 and 10. Its nmr spectrum showed only one singlet (1.09 ppm)



which was ascribed to the *t*-butyl group, a quartet centered at 5.58 ppm ($J = 6.8$ cps) due to the vinyl hydrogen which was coupled with a doublet due to the proton on the 4 carbon centered at 1.72 ppm ($J = 6.8$ cps), a singlet at 3.24 ppm ascribed to the 1-carbon methylene protons of the butenyl moiety, a quartet centered at 2.48 ppm ($J = 7.1$ cps) ascribed to the 1-carbon methylene of the *n*-butyl moiety and resonance absorption in the region 0.9–1.9 ppm due to the remaining protons of the *n*-butyl group. The failure of any of the isomeric sulfide VI to form by the sequence 11 and 12 is discussed later.



Competition reactions show that II reacts very much faster than 1-octene, as would be expected for a conjugated system, in addition reactions with both bromotrichloromethane and *n*-butyl mercaptan. The results of the competition reaction of I and 1-octene toward addition of these adding reagents are quite anomalous in that 1-octene is more reactive than the

diene toward addition of both reagents. However, I is far more reactive in the bromotrichloromethane reactions than it is in the *n*-butyl mercaptan reactions (Table I).

TABLE I
COMPETITION REACTIONS OF I AND II WITH RESPECT TO 1-OCTENE TOWARD FREE-RADICAL ADDITION

Adding reagent	Diene	\bar{P}^a	Av dev	No. of runs
BrCCl ₃	I	0.26	0.03	3
BrCCl ₃	II	62	11	4
<i>n</i> -C ₄ H ₉ SH	I	0.01	0.003	3
<i>n</i> -C ₄ H ₉ SH	II	115	15	2

^a \bar{P} equals the rate of addition to diene divided by the rate of addition to 1-octene.

It was observed that the presence of I markedly retarded the rate of reaction of bromotrichloromethane with 1-octene. In a light-induced reaction at 56°, 20 mole % of 1-octene in bromotrichloromethane was completely consumed in 15 min. The presence of 10 mole % of I in a similar reaction mixture increased the half-life of 1-octene to 80 min under similar conditions. Interestingly, the presence of I had no inhibiting effect on the rate of addition of *n*-butyl mercaptan to 1-octene. The half-life of 1-octene in a reaction mixture consisting of 15 mole % of this alkene in *n*-butyl mercaptan illuminated at 56° was about 8–10 min both in the presence and absence of I.

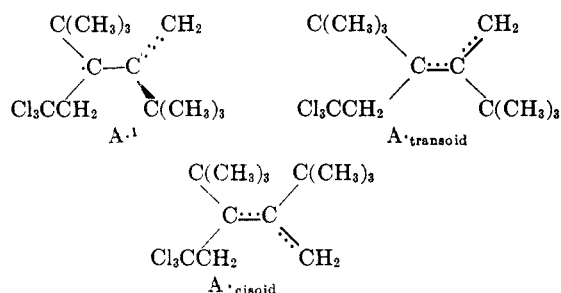
Attempts to form a copolymer of I and styrene by heating styrene with I at 80° in the presence of benzoyl peroxide yielded a polymer having nmr and infrared spectra that were indistinguishable from those of pure polystyrene. On the other hand, II did copolymerize readily with styrene. The composition of the copolymer (1.5:1.0 styrene-II) from an initial composition of 1:1 styrene-II indicated that II has the same order of reactivity as styrene toward radical addition.

Discussion

The difference in behavior of the 1,3-dienes I and II in these free-radical reactions can be explained in terms of the nonconjugative nature of the diene system of I which renders it relatively unreactive toward radical addition whereas II displays chemical characteristics of conjugated 1,3-dienes. The difference in the reactions of bromotrichloromethane and *n*-butyl mercaptan with these dienes is largely due to a reversible addition of thiyl radicals and a nonreversible addition of trichloromethyl radicals to the unsaturated systems.

Competition reactions of II with 1-octene toward free-radical addition, as well as the reactivity of this diene in copolymerization reactions with styrene, is not unexpected for a 1,3-diene since additions of radicals to II yield resonance-stabilized allyl radicals. The competition reactions of I with 1-octene toward addition of the trichloromethyl radical show that the sum of the reactivities of the two double bonds of this diene is only about one-fourth that of 1-octene. The formation of about equal amounts of the two addition products III and IV in the reaction of bromotrichloromethane with II argues against steric hindrance caused by either of the *t*-butyl groups being solely responsible for the low reactivity of I toward addition of the

trichloromethyl radical. Generally, the stability of the adduct radical formed plays an important role in determining the rate of addition of a radical to an unsaturated linkage (*i.e.*, the rapid rate of addition to a truly conjugated diene because of formation of the resonance-stabilized allyl radical). The low rate of addition of the trichloromethyl radical to I is indicative of little or no contribution of the resonance-stabilized hybrid radical $A\cdot$ in lowering the transition state energy requirement for this reaction. It may well be that the steric problems encountered in the hybrid radical are great enough to preclude the formation of the hybrid radical $A\cdot$ and only the adduct radical $A\cdot$ is formed in the addition of the trichloromethyl radical to I. Examination of the steric factors that would be encountered in the hybrid radical $A\cdot$ suggests that such a species might well be quite unstable relative to the allylic radical obtained from addition to a conjugated diene such as 1,3-butadiene. If the adduct radical $A\cdot$ existed in the cisoid conformation, the positioning of the two *t*-butyl groups would be similar to that found in *o*-di-*t*-butylbenzene. The steric strain resulting from interactions of the *t*-butyl groups in *o*-di-*t*-butylbenzene has been estimated to be about 17 kcal/mole.⁷ Steric strain might also be expected if the hybrid adduct radical existed in the transoid conformation. There would be an interaction of the hydrogens of the *t*-butyl group bonded to the 3 carbon of the radical with one of the vinyl hydrogens of the 5 carbon. Indeed, it is two such interactions that are



most likely responsible for the fact that I itself does not assume the transoid conformation. Another steric interaction in the radical would be that between the hydrogens of the *t*-butyl group bonded to the 4 carbon with the methylene hydrogens of the 2 carbon. Assuming that only the adduct radical $A\cdot$ is formed in the addition of the trichloromethyl radical to I, the strain in the hybrid adduct radical can be crudely approximated, from the difference in the resonance energies of a *t*-alkyl radical and allyl radical,⁸ to exceed 15–20 kcal/mole.

It is not too surprising, in light of its low reactivity toward radical addition, that I does not copolymerize to any observable extent with styrene. The conjugated diene II, having a considerably higher reactivity toward radical addition, would be expected to participate in a copolymerization reaction with styrene.

Although the reactivity of I toward addition of the trichloromethyl radical is low, it is not small enough to preclude the formation of an addition product with bromotrichloromethane provided that abstraction of

a bromine atom from the polyhalomethane by the adduct radical proceeds at a reasonable rate. Finding no isolable amounts of an addition product suggests that the reaction of the adduct radical $A\cdot$ with bromotrichloromethane is sterically hindered. Also, the fact that no 1,4-addition product is formed supports the earlier suggestion that the adduct radical is not the hybrid allylic radical $A\cdot$ since it is not obvious why transfer leading to a 1,4 adduct should be sterically hindered if addition of the trichloromethyl radical is not precluded at the terminal carbons of I because of steric effects due to either of the *t*-butyl groups. The 1,4-addition product would, of course, be subjected to the same steric interactions cited for the hybrid adduct radical. The residue formed in the benzoyl peroxide induced reaction of I with bromotrichloromethane may be a mixture of products resulting from coupling or disproportionation reactions of the adduct radicals.

The inhibitory effect I has on the rate of reaction of bromotrichloromethane with 1-octene supports the suggestion that addition of a trichloromethyl radical to I results in formation of an unreactive adduct radical. Since an appreciable number of chain-carrying trichloromethyl radicals add to I forming unreactive radical intermediates, the normally long kinetic chain length of the reaction of 1-octene with bromotrichloromethane would be shortened.

Both the very low reactivity of I with respect to 1-octene toward addition of *n*-butyl mercaptan and the fact that I does not inhibit the rate of addition of this thiol to 1-octene are indicative of the reversibility of the addition of thiol radicals to I. Previously reported investigations have shown that, although the relative reactivities of many unsaturates toward addition of trichloromethyl and thiol radicals are similar,⁹ alkenes having methyl substituents on the 4 carbon are less reactive toward addition of thiol radicals than toward addition of trichloromethyl radicals.¹⁰ An explanation given for this observation was that the adduct radicals can have conformations which result in crowding about the site of addition caused by atoms in the 6 position.¹¹ Relief of this crowding can be attained by elimination of the adding radical, a reaction which thiol radicals undergo,¹² but the trichloromethyl radicals do not.¹³ Addition of the *n*-butane thiol radical to I yields such an adduct radical. Elimination of the thiol radical from the adduct radical $B\cdot$ at a faster rate than reaction with the mercaptan giving the addition product would account for the very low reactivity of I in the competition reactions with 1-octene toward addition of *n*-butyl mercaptan. Furthermore, the rate of addition of *n*-butyl mercaptan to 1-octene should not be retarded by the presence of I since there would be no trapping of chain-carrying radicals similar to that encountered in the polyhalomethane reactions.

Addition of an alkane thiol radical to II at the 4 carbon yields the adduct radical $F\cdot$ which has the same

(9) C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).

(10) E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 1676 (1963).

(11) M. S. Newman, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 206.

(12) C. Sivertz, W. Andrews, W. Eldsen, and K. Graham, *J. Polymer Sci.*, **19**, 587 (1956).

(13) P. S. Skell and R. C. Woodworth, *J. Am. Chem. Soc.*, **77**, 4638 (1955).

(7) U. Kruerke, C. Hoogzand, and W. Hübel, *Chem. Ber.*, **94**, 2817 (1961).

(8) For discussion on the resonance energies of radical, see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp 50–53.

steric problem encountered in the addition of a thiyl radical to either terminal carbon of I. Elimination of the thiyl radical from F· very likely is faster than reaction of it with *n*-butyl mercaptan as is evidenced by the observation that the 1,4-addition product VI is not formed in the reaction of II with *n*-butyl mercaptan. On the other hand, radical E·, which is formed by addition of the thiyl radical to II at the 1 carbon, does not possess the same sort of steric problems encountered in either B· or F·. Although the addition of the thiyl radical at the 1 carbon of II is undoubtedly a reversible reaction, the rate of elimination of the thiyl radical from E· is not so fast as to exclude any reaction of E· with *n*-butyl mercaptan yielding the addition product V. Addition of the trichloromethyl radical at the 1 carbon and the 4 carbon of II yields adduct radicals C· and D·, respectively. Since the addition of the trichloromethyl radical is essentially nonreversible,¹³ both C· and D· are available to react with bromotrichloromethane yielding the observed addition products III and IV, respectively.

Experimental Section

Materials.—2,3-Di-*t*-butyl-1,3-butadiene was prepared in a previously described method which consisted of dehydration of 2,3-di-*t*-butyl-2,3-butanediol. This diol was obtained by reduction of pinacolone with sodium in moist ether. All samples of this material used in this work gave a single peak on gas chromatographic analysis. 2-*t*-Butyl-1,3-butadiene (bp 104–106°, *n*_D²⁰ 1.4250) was prepared by dehydrohalogenation with collidine of the allylic bromide mixture obtained from the reaction of *N*-bromosuccinimide with the olefin mixture resulting from dehydration of 2,2,3-trimethyl-3-pentanol. The alcohol was prepared by reaction of ethylmagnesium bromide with pinacolone. Bromotrichloromethane was supplied by the Dow Chemical Co. All other reagents were commercial materials purified, when necessary, by standard techniques.

2,3-Di-*t*-butyl-1,3-butadiene and Bromotrichloromethane.—A mixture consisting of bromotrichloromethane (8.0 g, 0.04 mole) and 2,3-di-*t*-butyl-1,3-butadiene (1.66 g, 0.01 mole) was illuminated for 3.5 hr with a 275-w sunlamp (Phillips) at 56° (acetone vapor bath). Gas chromatographic analysis of the resulting mixture indicated that only 5% of the diene had reacted in this period. Another reaction mixture consisting of bromotrichloromethane (14.8 g, 0.075 mole), 2,3-di-*t*-butyl-1,3-butadiene (2.5 g, 0.015 mole), and benzoyl peroxide (0.51 g, 0.0021 mole, added in four equal portions during the heating period) was heated for 36 hr at 78°. Distillation of the resulting reaction mixture yielded 1.2 g of unreacted diene. A high-boiling residue remained after removal of the diene. All attempts to rectify this mixture failed to yield any identifiable products other than benzoic acid.

2,3-Di-*t*-butyl-1,3-butadiene and *n*-Butyl Mercaptan.—A reaction mixture consisting of *n*-butyl mercaptan (9.0 g, 0.10 mole) and 2,3-di-*t*-butyl-1,3-butadiene (3.3 g, 0.02 mole) was illuminated with a 275-w sunlamp for 3 hr. A low reaction temperature (15°) was maintained during the illumination in order to minimize the rate of the elimination of the thiyl radical from the adduct radical. However, an essentially quantitative recovery of the diene was effected on distillation of the resulting reaction mixture.

2-*t*-Butyl-1,3-butadiene and Bromotrichloromethane.—A mixture consisting of bromotrichloromethane (8.8 g, 0.044 mole) and 2-*t*-butyl-1,3-butadiene (2.5 g, 0.022 mole) was illuminated at 56° with a 275-w sunlamp for 2 hr. Distillation of the reaction mixture yielded 2.5 g (36% of theory) of a mixture of 1:1 addition products 1-bromo-5,5,5-trichloro-2-*t*-butyl-2-pentene and 1-bromo-5,5,5-trichloro-3-*t*-butyl-2-pentene [bp 60° (0.1 mm), *n*_D²⁰ 1.5203].

Anal. Calcd for C₉H₁₄BrCl₃: C, 35.04; H, 4.57; Br, 25.90; Cl, 34.48. Found: C, 35.31; H, 4.58; Br, 25.70; Cl, 34.22.

The nmr spectrum of this mixture was described earlier in this paper. After distillation of these addition products, a residue amounting to 0.5 g remained.

2-*t*-Butyl-1,3-butadiene and *n*-Butyl Mercaptan.—A reaction mixture consisting of *n*-butyl mercaptan (8.0 g, 0.10 mole) and 2-*t*-butyl-1,3-butadiene (6.0 g, 0.054 mole) was illuminated at 56° for 2 hr with a 275-w sunlamp. Distillation of the reaction mixture yielded 2.0 g (35% of theory) of the 1:1 addition product, *n*-butyl-2-*t*-butyl-2-butenyl sulfide (bp 98–100° (4 mm), *n*_D²⁰ 1.4758).

Anal. Calcd for C₁₂H₂₄S: C, 71.92; H, 12.08; S, 16.00. Found: C, 72.18; H, 11.94; S, 16.23.

The nmr spectrum of this material is described earlier in this paper.

Attempted Copolymerization of Styrene and 2,3-Di-*t*-butyl-1,3-butadiene.—Styrene (0.52 g, 0.005 mole), 2,3-di-*t*-butyl-1,3-butadiene (1.66 g, 0.01 mole), and benzoyl peroxide (1.2 mg, 0.05 mole) were placed in a sealed tube and heated for 4 hr at 78°. The partially polymerized mixture was dissolved in methyl ethyl ketone and this solution was dripped slowly with stirring into methanol. The precipitated polymer was collected, redissolved, reprecipitated, again collected, dried, and weighed. This process was repeated until the weight of polymer was constant. In this manner, 93.5 mg of polymer was obtained. The nmr spectrum of the polymer in carbon tetrachloride was indistinguishable from that of pure polystyrene.

Copolymerization of Styrene and 2-*t*-Butyl-1,3-butadiene.—A mixture of styrene (0.57 g, 0.0051 mole) and 2-*t*-butyl-1,3-butadiene (0.55 g, 0.0055 mole) was heated in the presence of benzoyl peroxide (1.2 mg, 0.05 mole) at 78° for 4 hr. The resulting mixture was dissolved in methyl ethyl ketone and the polymer was precipitated by slowly dripping the solution into methanol. The resulting polymer was purified by redissolving in methyl ethyl ketone, reprecipitating, collecting, and drying. This process was repeated until a constant weight (120 mg) of the polymer was attained. The nmr spectrum of this material taken in carbon tetrachloride showed broad absorption centered at 7.1 and 6.7 ppm which are attributed to the aromatic protons and a broad absorption centered at 1.7 ppm. These resonance absorptions are similar to those found in the spectrum of pure polystyrene. In addition to these, the copolymer showed a broad absorption centered at 1.01 ppm due to the *t*-butyl group and an absorption centered at 5.0 ppm caused by the vinyl proton. Calculations based on the integrated resonance absorptions indicated that the copolymer was composed by weight of 60% styrene units and 40% 2-*t*-butyl-1,3-butadiene units.

Competition Studies. 1-Octene and 2-*t*-Butyl-1,3-butadiene.—Samples of 1-octene and the diene were accurately weighed into a Pyrex tube containing the adding reagent (BrCCl₃ or *n*-C₄H₉SH) in about a twofold excess of the total number of moles of unsaturates and an accurately weighed amount of chlorobenzene. A sample of the mixture was subjected to gas chromatographic analysis and the areas of 1-octene, diene, and chlorobenzene peaks were measured. The reaction mixture was then illuminated at 56° until sufficient amounts of the unsaturates had reacted to allow for meaningful calculations (2.5 hr in the case of the bromotrichloromethane reaction and 10 min for the *n*-butyl mercaptan reactions). After illumination, another sample was chromatographed and from the peak areas, assuming no reaction of chlorobenzene which does not react under these conditions, the amounts of the 1-octene and diene were calculated. These values were used to calculate the relative reactivity ratio of 1-octene with respect to the diene, \bar{P} from the equation

$$\bar{P} = \frac{\log(O_0/O_t)}{\log(D_0/D_t)}$$

where O_0 and D_0 are the amounts of 1-octene and the diene, respectively, before reaction, and O_t and D_t are the amounts after reaction. Duplicate determinations of \bar{P} were made using different initial ratios of the diene to the alkene.

1-Octene and 2,3-Di-*t*-butyl-1,3-butadiene Reactions.—In these competition reactions, accurately weighed amounts of 1-octene and the diene were mixed with a twofold excess of the adding reagent and illuminated at 56°. Illumination periods of 10 min and 4.5 hr for the *n*-butyl mercaptan and bromotrichloromethane reactions, respectively, were required for sufficient reaction of the unsaturates to allow for meaningful calculations. Accurately weighed samples of the reaction mixture were mixed with a known amount of cyclooctane and subjected to gas chromatographic analysis. The amounts of 1-octene and the diene were determined from a comparison of their peak areas to that of the cyclooctane. The necessary correction factor relating peak area ratios to mole ratios was determined from known mixtures

of cyclooctane, 1-octene, and 2,3-di-*t*-butyl-1,3-butadiene. The data were treated in the manner described above and three or more runs with different initial ratios of 1-octene to diene were made in each case.

Inhibitory Effect of 2,3-Di-*t*-butyl-1,3-butadiene.—A solution consisting of 20 mole % 1-octene in bromotrichloromethane was illuminated at 56° with a 275-w sunlamp. Samples of the reaction mixture were withdrawn at 3-min intervals and the amount of 1-octene was determined by gas chromatographic analysis. Within 15 min, the 1-octene was completely consumed. A similar mixture containing 10 mole % 2,3-di-*t*-butyl-1,3-butadiene was subjected to the same treatment. During the first 15 min, very little of the 1-octene was consumed. After 80 min of illumination, approximately 50% of the 1-octene had undergone reaction with the bromotrichloromethane.

Following the rate of reaction of 1-octene (15 mole %) with *n*-butyl mercaptan in light-induced reactions at 56° by de-

termining the 1-octene remaining in samples withdrawn from the reaction mixture at 3–5-min intervals showed that the presence of I (15 mole %) has no appreciable effect on the rate of reaction of the alkene with the mercaptan. In both cases, the half-life of the 1-octene was about 8–10 min.

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Cycloadditions. IX. Mechanism of the Thermal Interconversion of *exo*- and *endo*-Dicyclopentadiene¹

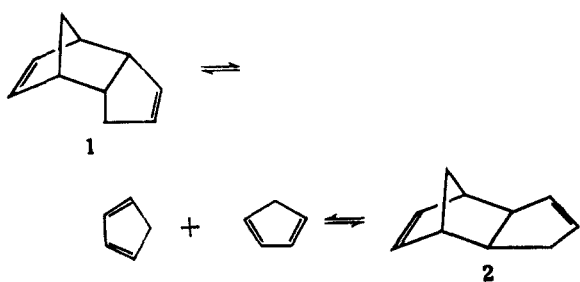
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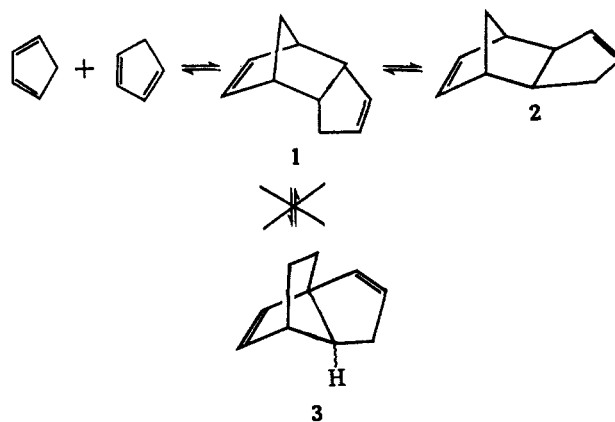
At 196°, *endo*-dicyclopentadiene specifically labeled with deuterium in one cyclopentadiene moiety rearranges by way of kinetically free cyclopentadiene to give *exo*-dicyclopentadiene having a scrambled deuterium distribution. Labeled *endo*-dicyclopentadiene recovered after short reaction times is only partially scrambled, while *exo*-dicyclopentadiene maintains its labeling integrity under the reaction conditions.

The thermal isomerization of *endo*-dicyclopentadiene (1) to *exo*-dicyclopentadiene (2) was observed and rationalized mechanistically by Alder and Stein in 1933.² They held² that at 170° an equilibrium between the *endo* dimer and cyclopentadiene affords a significant concentration of the monomer, and that redimerization of the cyclopentadiene could give either isomeric dicyclopentadiene.



At 180–240°, *endo*-dicyclopentadiene was converted to an isomer initially proposed³ to be a tricyclo-[4.2.2.0^{1,5}]deca-2,7-diene (3) but soon recognized⁴ as the *exo* dimer 2. This isomer (2) was found³ to be unable to dissociate at these temperatures directly to two molecules of cyclopentadiene. It was transformed intramolecularly to *endo*-dicyclopentadiene with an activation energy of 8 kcal/mole, and the *endo*-diene in turn suffered cycloelimination to give a monomer.³

The rationale of Alder and Stein and the reports of Schröder are incompatible; this disparity seemed to



call for fresh experimentation. An internal pathway for the interconversion of *endo*- and *exo*-dicyclopentadiene would constitute a rare example of an intramolecular *endo*-*exo* isomerization of a Diels-Alder adduct that might have far-reaching mechanistic significance.⁵

Experimental Design.—An experimental distinction between intramolecular and intermolecular mechanistic pathways for the interconversions of *endo*- and *exo*-dicyclopentadiene was sought through a study of the rearrangements of dienes appropriately labeled with deuterium.

The distinction depends, in principle, on the different predictions one would make for the thermal rearrangement of a dicyclopentadiene labeled with deuterium in only one ring. If neither isomer dissociated reversibly to cyclopentadiene during the rearrangement, an internal pathway for the interconversion would give the isomeric diene containing the same deuterium

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(2) K. Alder and G. Stein, *Ann.*, **504**, 216 (1933).

(3) W. Schröder, *Angew. Chem.*, **72**, 865 (1960).

(4) W. Schröder, *ibid.*, **73**, 241 (1961).

(5) C. Ganter, U. Scheidegger, and J. D. Roberts [*J. Am. Chem. Soc.*, **87**, 2771 (1965)] have given a rigorous test for an internal pathway in another *exo*-*endo* isomerization, and a summary of the pertinent literature.