Di-*tert*-butylvinylidenecarbene, Tetra-*tert*-butylbutatriene, Tetra-*tert*-butylhexapentaene, and Tetrakis(di-*tert*-butylvinylidene)cyclobutane[1]

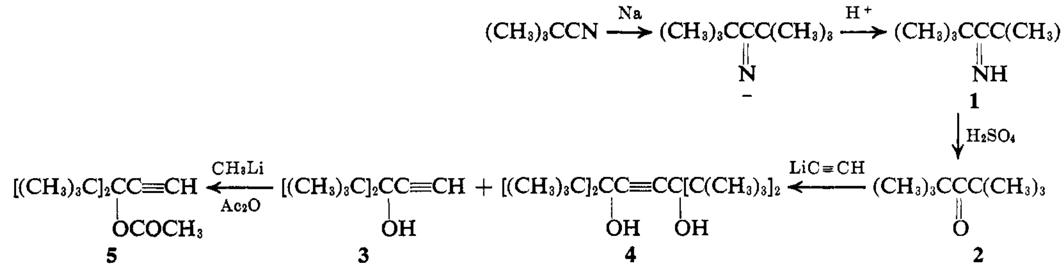
H. D. Hartzler

Contribution No. 1769 from the Central Research Department,
Experimental Station, E. I. Du Pont de Nemours and Company,
Wilmington, Delaware 19898. *Received December 14, 1970*

Abstract: The reaction of 3-ethynyl-2,2,4,4-tetramethyl-3-pentyl acetate (**5**) with potassium *tert*-butoxide and olefins gave di-*tert*-butylvinylidenecyclopropanes. The relative rates of reaction of the intermediate di-*tert*-butylvinylidenecarbene with olefins were determined and compared with previously obtained rates of reaction of the dimethylvinylidenecarbene. Arguments are presented which suggest that the carbenes are uncomplexed in the transition state of addition to olefins. Tetra-*tert*-butylbutatriene and -hexapentaene were synthesized. Cycloadditions to the latter occurred across the central double bond—probably by way of a thermally accessible diradical of the cumulene. Dimerization of the hexapentaene gave tetrakis(di-*tert*-butylvinylidene)cyclobutane—a stable cyclobutane derivative in which all four ring atoms are sp^2 hybridized.

Many highly reactive types of molecules have been stabilized by a shielding of reactivity with inert, bulky substituents. The *tert*-butyl substituent has been widely used for this purpose. Di-*tert*-butylketene could be isolated as a stable monomer.[2] Two *tert*-butyl substituents permitted the synthesis and isolation of a cyclopentadienone.[3] Recently many reactive strained small ring compounds have been found to be capable of isolation when suitably substituted with *tert*-butyl substituents. These include aziridinones,[4] cyclopropanones,[5] diaziridinones,[6] an allene oxide,[7] and oxadiaziridinones.[8] In the latter case the use of the *tert*-butyl substituent did not increase the stability of the ring system.

Scheme I. Synthesis of 3-Ethynyl-2,2,4,4-tetramethyl-3-pentyl acetate



We have previously investigated reactions of the dimethylvinylidenecarbene[9] and compared the relative rates of reaction with olefins of the carbene when generated by γ-elimination from 3-chloro-3-methyl-1-butyne[10] with those when the carbene was generated by α-elimination from 1-chloro-3-methyl-1,2-butadiene.[11] The intermediates in the two reactions had identical reactivities. This suggested that either the carbenes were not complexed (*e.g.*, as γ- or α-chloroorganometallics) in the transition state with olefins or that they were complexed in an identical manner. We thought that a similar study of the di-*tert*-butylvinylidenecarbene would be pertinent because the large perturbation at the γ-carbon of the carbene should change the manner in which the intermediate is complexed or solvated. From changes or lack of changes in the reactivity of the carbene we could then make inferences concerning its nature. This paper reports such a study as well as the synthesis and some chemistry of aliphatic cumulenes.

Results and Discussion

The starting point for the generation of di-*tert*-butylvinylidenecarbene was 3-ethynyl-2,2,4,4-tetramethyl-3-pentyl acetate (**5**). The synthesis of **5** is outlined in Scheme I. Pivalonitrile reacted smoothly with a sodium dispersion to give the imine of hexamethylacetone (**1**).[12] This interesting reaction probably proceeds by way of the anion radical of pivalonitrile, cleavage of the anion radical to *tert*-butyl radical and cyanide ion, and capture of the *tert*-butyl radical by the anion radical to give the anion of the imine. This scheme is very similar to that suggested for the formation of the di-*tert*-butyl nitroxide radical.[13]

Acid hydrolysis of **1** gave hexamethylacetone **2** in high yield. This is probably the most convenient

---

(1) Preliminary communication: H. D. Hartzler, *J. Amer. Chem. Soc.*, **88**, 3155 (1966).

(2) M. S. Newman, A. Arkell, and T. Fukunaga, *ibid.*, **82**, 2498 (1960).

(3) E. W. Garbish and R. F. Sprecher, *ibid.*, **88**, 3433 (1966); **91**, 6785 (1969).

(4) H. E. Baumgarten, *ibid.*, **84**, 4975 (1962); H. E. Baumgarten, J. F. Fuerholzer, R. D. Clark, and R. D. Thompson, *ibid.*, **85**, 3303 (1963); J. C. Sheehan and I. Lengyel, *ibid.*, **86**, 746, 1356 (1964).

(5) J. F. Pazos and F. D. Greene, *ibid.*, **89**, 1030 (1967).

(6) F. D. Greene, J. C. Stowell, and W. R. Bergmark, *J. Org. Chem.*, **34**, 2254 (1969); F. D. Greene, W. R. Bergmark, and J. F. Pazos, *ibid.*, **35**, 2813 (1970).

(7) R. L. Camp and F. D. Greene, *J. Amer. Chem. Soc.*, **90**, 7349 (1968).

(8) F. D. Greene and S. S. Hecht, *J. Org. Chem.*, **35**, 2482 (1970).

(9) H. D. Hartzler, *J. Amer. Chem. Soc.*, **83**, 4990 (1961).

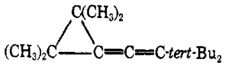
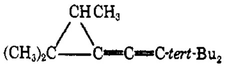
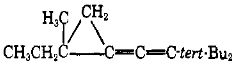
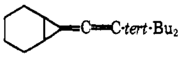
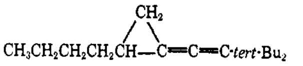
(10) H. D. Hartzler, *ibid.*, **83**, 4997 (1961).

(11) H. D. Hartzler, *J. Org. Chem.*, **29**, 1311 (1964).

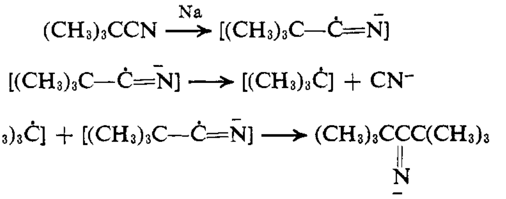
(12) V. L. Hansley, U. S. Patent 2,742,503 (1956).

(13) A. K. Hoffmann, W. G. Hodgson, and W. H. Jura, *J. Amer. Chem. Soc.*, **83**, 4675 (1961).

Table I. Di-*tert*-butylvinylidenecyclopropanes

Olefin	Product	Mp or bp (mm), °C	% yield	n^{25}D	Calcd, % C	Calcd, % H	Found, % C	Found, % H
$(CH_3)_2C=C(CH_3)_2$		69–70	52		87.1	12.9	87.4	12.8
$(CH_3)_2C=CHCH_3$		48 (0.4)	10		87.2	12.8	86.9	12.7
$CH_3CH_2C(CH_3)=CH_2$		54 (0.5)	10[a]	1.4789	87.2	12.8	87.0	12.8
		89 (0.35)	22	1.5095	87.8	12.2	87.3	11.9
$CH_3CH_2CH_2CH_2CH=CH_2$		75 (0.5)	22	1.4785	87.1	12.9	86.8	12.7

[a] Tetra-*tert*-butylhexapentaene formed in 20% yield.

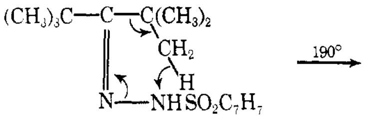


$$(CH_3)_3CCN \xrightarrow{Na} [(CH_3)_3C-\dot{C}=\bar{N}]$$

$$[(CH_3)_3C-\dot{C}=\bar{N}] \longrightarrow [(CH_3)_3\dot{C}] + CN^-$$

$$[(CH_3)_3\dot{C}] + [(CH_3)_3C-\dot{C}=\bar{N}] \longrightarrow (CH_3)_3C\underset{\underset{\bar{N}}{\|}}{C}C(CH_3)_3$$

method of synthesis of **2**. The imine **1** is also useful in the preparation of simple ketone derivatives of **2**. The only simple derivative of **2** previously prepared was the oxime and this was obtained under high pressure.[14] The hydrazone and *p*-toluenesulfonylhydrazone of hexamethylacetone were readily prepared. Attempts to prepare the diazo compound from either the hydrazone or the *p*-toluenesulfonylhydrazone have been unsuccessful to date. The *p*-toluenesulfonylhydrazone gave an interesting thermal fragmentation. At 190° it was converted to pivalonitrile, *p*-toluenesulfonamide, and isobutylene, probably by a concerted process.



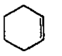
$$(CH_3)_3CCN + (CH_3)_2C=CH_2 + C_7H_7SO_2NH_2$$

Lithium acetylide added readily to **2** to give the acetylenic alcohol **3** in 80% yield. Small amounts of the substituted acetylenic diol **4** were also formed. The hindered alcohol **3** did not react with sodium hydride in dimethoxyethane at reflux. Acetylation of **3** was accomplished by preparing the lithium salt by reaction with methyllithium and acetylating it with acetic anhydride.

Di-*tert*-butylvinylidenecyclopropanes were prepared in modest yield by the reaction of **5** with potassium *tert*-butoxide in the presence of olefins. The products that have been obtained are summarized in Table I. As was found previously with dimethylvinylidenecyclopropanes,[9] yields increased with increasing substitution on the double bond of the olefin.

Relative rates of addition of the carbene to olefins were determined by competition experiments in which a large excess of a mixture of cyclohexene and another olefin was allowed to react with a small amount of **5** and potassium *tert*-butoxide. Product analysis was by gas chromatography. The logarithms of the relative rates are given in Table II and compared with those previously obtained by the two modes of generation of the dimethylvinylidenecarbene. With the exception of the values obtained from 2-methyl-1-butene the results are in excellent agreement with the previous work. A possible explanation of the disparity with 2-methyl-1-butene would be that an unknown material had an identical retention time as the adduct of the dimethylvinylidenecarbene and 2-methyl-1-butene. The rate for this olefin had always appeared anomalously high.

Table II. Relative Rates of Reaction of Vinylidene carbenes with Olefins

Olefin	Log k/k_0 $(CH_3)_2$-$C=C=C:$[a]	$(CH_3)_2$-$C=C=C:$[b]	*tert*-Bu_2-$C=C=C:$[c]
$(CH_3)_2C=C(CH_3)_2$	1.2	1.3	1.2
$(CH_3)_2C=CHCH_3$	0.69	0.67	0.69
$CH_3CH_2(CH_3)C=CH_2$	0.62	0.70	0.31
	0.00	0.00	0.00
$CH_3CH_2CH_2CH_2CH=CH_2$	−0.64	−0.60	−0.70

[a] Carbene generated from $(CH_3)_2C=C=CHCl$ and KO-*tert*-Bu at −10°; ref 11. [b] Carbene generated from $(CH_3)_2CClC\equiv CH$ and KO-*tert*-Bu at −10°; ref 10. [c] Carbene generated from *tert*-$Bu_2C(OCOCH_3)C\equiv CH$ and KO-*tert*-Bu at 30°.

It follows that the rates of reaction of the two carbenes with olefins are very similar. The effect of the bulky *tert*-butyl substituents appears to be negligible. From the following three facts it appears that vinylidenecarbenes are essentially uncomplexed in the transition state of addition to olefins. (1) Identical reaction rates are obtained whether the carbene is generated from 3-chloro-3-methyl-1-butyne or from 1-chloro-3-methyl-1,2-butadiene. (2) There is no steric effect for substituents on the γ-carbon of the carbene. (3) There is no steric effect with respect to the number of substituents on the olefinic double bond. The absence of steric effects in olefin addition reactions of vinylidene-

---

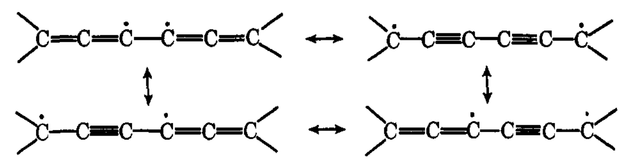
(14) W. H. Jones and E. W. Tristram, U. S. Patent 3,256,331 (1966).

carbenes is very different from addition reactions of methylenecarbenes where appreciable steric hindrance has been observed.[15,16]

Reaction of the acetylenic acetate **5** with potassium *tert*-butoxide in the absence of olefins gave the alkoxyallene **6** and the stable tetra-*tert*-butylhexapentaene (**7**). The formation of **7** probably occurs by a process similar to that previously suggested for the formation of tetraphenylhexapentaene.[9] The alkoxyallene **6** could result from an SN2′ reaction of *tert*-butoxide ion on **5** or a reaction of the *tert*-butoxide ion with the di-*tert*-butylvinylidenecarbene at the α-carbon atom. The latter course seems preferable, even though vinylidenecarbenes normally react with alcohols or alkoxide ions at the γ-carbon atom.[17] In this case reaction of *tert*-butoxide ion at the γ-carbon atom of the carbene would be sterically unfavorable. Reactions of vinylidenecarbenes at the α-carbon atom with anions have been previously described,[18] and this type of reaction is known to be very subject to steric effects.[19]

The synthesis of **7** represents only the third successful synthesis of an aliphatic substituted hexapentaene,[20,21] and allowed for the first time a study of some of the thermal chemical reactions of hexapentaenes. The melt of **7** (189°) resolidifies with the formation of a new white solid. This solid has been identified as the symmetrical dimer, tetrakis(di-*tert*-butylvinylidene)cyclobutane (**8**). The symmetry of **8** follows from the fact that the nmr spectrum of **8** shows all 72 hydrogen atoms as a sharp singlet at δ 1.20. The electronic absorption spectrum of **8** is similar in many respects to that reported for tetramethylenecyclobutane.[22] The thermal stability of **8** is remarkable. It melts at 361° with no decomposition giving a water white melt. No tendency to revert thermally to **7** was observed. Dimer **8** represents a system in which all cyclobutane carbon atoms are sp^2 hybridized and is a molecule in which the central 12 carbon atoms are bonded only to carbon.

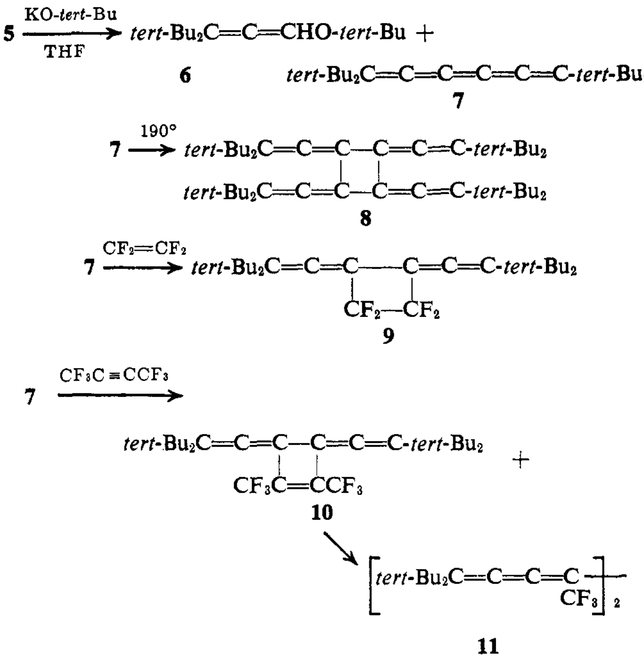
If the thermal decomposition of **7** is performed in solution in decahydronaphthalene instead of the melt, very little **8** (<3%) is obtained. The cumulene was not recovered. The products appeared to have been materials resulting from hydrogen abstraction from the solvent, but a pure product was not obtained. These results suggested that the thermal reactions of **7** might be occurring from a diradical form of **7**. Calculations have indicated that the perpendicular diradical forms of cumulenes become closer in energy to the planar forms as the length of the cumulated chain increases.[23] The diradical form of a hexapentaene, **7a**, might be expected to give clean cycloaddition reactions at the central double bond, especially if the terminal carbon atoms are sterically hindered by substituents such as *tert*-butyl.



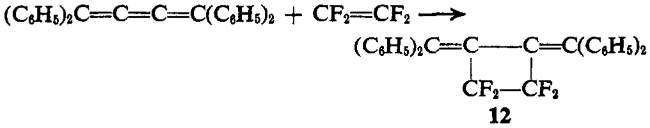
7a

Several other cycloadditions to **7** have been found (Scheme II). In all cases only addition to the central double bond was observed. Tetrafluoroethylene and **7** gave the cyclobutane **9** in 70% yield at 200°. Hexafluoro-2-butyne reacted similarly with **7** at 200°. In addition to the expected cyclobutene **10** there was obtained a yellow isomeric product **11**. Heating **10** alone produced **11**, indicating that **11** is the valence bond isomer bisbutatriene.

Scheme II. Synthesis and Reactions of 7



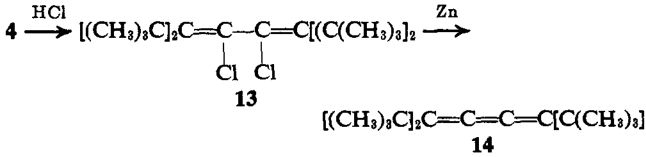
Cycloaddition of tetrafluoroethylene to tetraphenylbutatriene also occurred at 200°, although in low yield. The cyclobutane **12** was obtained. Cycloaddition reactions appeared to occur more readily with the hexapentaene than with the butatriene.



$$(C_6H_5)_2C{=}C{=}C{=}C(C_6H_5)_2 + CF_2{=}CF_2 \longrightarrow (C_6H_5)_2C{=}C{-}C{=}C(C_6H_5)_2 \text{ (ring: } CF_2{-}CF_2)$$

12

The synthesis of tetra-*tert*-butylbutatriene was sought as a possible route to another radialene, a derivative of trimethylenecyclopropane. Reaction of the acetylenic diol **4** with hydrochloric acid in acetic acid–dioxane gave the diene **13** in 96% yield. Although a diene, **13** showed no ultraviolet absorption maximum. The bulky *tert*-butyl groups twist the diene system out of planarity. The absence of diene absorption has previously been noted for dienes substituted with bulky alkyl



$$4 \xrightarrow{HCl} [(CH_3)_3C]_2C{=}C(Cl){-}C(Cl){=}C[(C(CH_3)_3]_2 \xrightarrow{Zn} [(CH_3)_3C]_2C{=}C{=}C{=}C[C(CH_3)_3]_2$$

13 **14**

---

[15] H. D. Hartzler, *J. Amer. Chem. Soc.*, **86**, 526 (1964).

[16] M. S. Newman and T. B. Patrick, *ibid.*, **92**, 4312 (1970).

[17] G. F. Hennion and D. E. Maloney, *ibid.*, **73**, 4735 (1951); G. F. Hennion and J. F. Motier, *J. Org. Chem.*, **34**, 1319 (1969).

[18] V. J. Shiner, Jr., and J. W. Wilson, *J. Amer. Chem. Soc.*, **84**, 2402 (1962).

[19] G. F. Hennion and C. V. DiGiovanna, *J. Org. Chem.*, **30**, 3696 (1965).

[20] F. Bohlmann and K. Kieslick, *Chem. Ber.*, **87**, 1363 (1954).

[21] L. Skattbøl, *Tetrahedron*, **21**, 1357 (1965).

[22] G. W. Griffin and L. I. Peterson, *J. Amer. Chem. Soc.*, **85**, 2268 (1963).

[23] H. Fischer, "Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 1137.

groups.[24] The isomeric acetylenic dichloride structure is thought to be unlikely for **13** because of the lack of solvolytic reactivity of the chlorine substituents. Reaction of **13** with zinc dust in acetonitrile gave the butatriene **14** in 45% yield. The ultraviolet spectrum of **14** was very similar to that of a previously prepared aliphatic butatriene.[20]

The reaction of 1,1-dibromo-2-methylpropene, methyllithium, and **14**[15] gave no detectable trimethylenecyclopropane. This reaction had been successfully applied to tetramethylbutatriene to prepare tris(isopropylidene)cyclopropane.[25] The bulky *tert*-butyl groups of **14** blocked reaction at the terminal double bonds as expected, but also prevented addition of the carbene to the central double bond.

Experimental Section

Spectral measurements were determined with the following instruments: ir, Perkin-Elmer Model 21; uv, Cary Model 14; nmr Varian A-60 and A-56/60. ^{19}F nmr chemical shifts are given in parts per million from fluorotrichloromethane. Melting points and boiling points are uncorrected.

2,2,4,4-Tetramethyl-3-pentanonimine (1).[12] A suspension of 59 g of finely divided sodium in 650 ml of petroleum ether was stirred under nitrogen while 166.2 g of trimethylacetonitrile was added over 1.5 hr. The temperature was kept between 25 and 32° by intermittent cooling. Stirring was continued for 15 min after addition. Water (200 ml) was added, cautiously at first. The layers were separated. The organic layer was dried over magnesium sulfate, filtered, and distilled to give the imine (60.2 g, 43%): bp 78.5–80° (50 mm); $n^{25}\mathrm{D}$ 1.4363; nmr (CS$_2$) δ 1.24 (s, 18), 9.39 (broad s, 1). The *tert*-butyl groups remained split down to $-106°$.

2,2,4,4-Tetramethyl-3-pentanone (2). The imine (60.2 g) was added to a mixture of 43 g of sulfuric acid and 390 ml of water. The resultant mixture was steam distilled. The organic layer of the distillate was separated and redistilled to give the ketone (56.3 g, 93%): bp 151°; $n^{25}\mathrm{D}$ 1.4190 (lit.[26] bp 145–151°; $n^{23}\mathrm{D}$ 1.4215).

3-Ethynyl-2,2,4,4-tetramethyl-3-pentanol (3). Lithium amide was prepared from 2 g of lithium wire in 300 ml of anhydrous ammonia containing a trace of ferric chloride. Acetylene was passed through the solution for 1 hr. A solution of 28.4 g of hexamethylacetone in 100 ml of ether was added over a 2-hr period while acetylene was passed through the mixture. The ammonia was evaporated overnight. The ether soluble product was distilled to give the acetylenic alcohol (26.5 g, 80%): bp 68.5° (5 mm); $n^{25}\mathrm{D}$ 1.4569 (lit.[27] $n^{20}\mathrm{D}$ 1.4589).

From the distillation residue there was obtained 1.53 g of 3,6-di-*tert*-butyl-2,2,7,7-tetramethyl-4-octyne-3,6-diol (**4**): mp 157.2–158.6° (hexane) (lit.[27] mp 152–154°).

3-Ethynyl-2,2,4,4-tetramethyl-3-pentyl Acetate (5). A solution containing approximately 0.06 mol of methyllithium in ether was dropped into a solution of 10.14 g of the acetylenic alcohol in 50 ml of ether. After 30 min acetic anhydride (10 g) was added. After 1 more hr water and ether were added and the organic product was separated. The ester was crystallized from hexane to give 5.4 g of product, mp 102–104°. Recrystallization from hexane gave the pure acetate: mp 104.8–105.4°; ir max 3.09, 4.74, 5.75 μ; nmr (CDCl$_3$) δ 1.23 (s, 18) 2.09 (s, 3), 2.75 (s, 1).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.23; H, 10.55. Found: C, 74.36; H, 10.52.

2,2,4,4-Tetramethyl-3-pentanone Hydrazone. A mixture of 70.5 g of the imine of hexamethylacetone, 125 ml of hydrazine hydrate, and 65 g of hydrazine sulfate was heated at reflux for 4 days. The mixture was cooled and the organic product was extracted into ether solution. The ether was evaporated and the residual solid was filtered and rinsed with methanol to give 55.64 g (71%) of the hydrazone, mp 66–68°. A sample was recrystallized from hexane: mp 68–69°; ir max 2.97, 3.03, 3.09, 3.36, 3.48, 6.10, 6.34, 7.21, 7.34 μ; nmr (CDCl$_3$) δ 1.20 (s, 9), 1.39 (s, 9), 5.3 (broad, 2). The *tert*-butyl groups remained nonequivalent even at 136° in hexadeuteriodimethyl sulfoxide.

Anal. Calcd for $C_9H_{20}N_2$: C, 69.18; H, 12.90; N, 17.93. Found: C, 69.20; H, 13.02; N, 17.83.

When the reaction was run for 18 hr, a 57% yield of the hydrazone was obtained.

***p*-Toluenesulfonylhydrazone of 2,2,4,4-Tetramethyl-3-pentanone.** A solution of 3.12 g of the hydrazone of hexamethylacetone in 15 ml of pyridine was stirred at $-5°$ while 4.0 g of *p*-toluenesulfonyl chloride was added. The temperature rose to 15° during addition and the solid separated. The system was stirred for 30 min and poured into 100 ml of ice water containing 15 ml of concentrated hydrochloric acid. The crude solid was collected and crystallized from benzene–hexane (3:1) to give 4.1 g (66%) of the tosylhydrazone, mp 174–176° dec. A sublimed sample had mp 177–179° dec; nmr (CDCl$_3$) δ 1.12 (s, 9), 1.27 (s, 9), 2.40 (s, 3), 7.48 (m, 4), 8.5 (broad, 1).

Anal. Calcd for $C_{16}H_{26}N_2O_2S$: C, 61.89; H, 8.44; N, 9.03; S, 10.33. Found: C, 62.09; H, 8.52; N, 9.01; S, 10.59.

Thermal Decomposition of the *p*-Toluenesulfonylhydrazene of 2,2,4,4-Tetramethyl-3-pentanone. A pot connected to a short still head and containing 1.9 g of hexamethylacetone tosylhydrazone was immersed in a bath at 190°. After 10 min gas evolution had ceased and all solid had melted. Liquid (bp 95–100°) distilled from the pot and was identified as trimethylacetonitrile ($n^{25}\mathrm{D}$ 1.3775). The pot residue solidified upon cooling. It was recrystallized from water to give 0.83 g (85%) of *p*-toluenesulfonamide, mp 134–136°.

Di-*tert*-butylvinylidenecyclopropanes. The properties of the compounds are given in Table I. A typical procedure is given for the preparation of 1-di-*tert*-butylvinylidene-2-ethyl-2-methylcyclopropane.

A slurry of 4.0 g of potassium *tert*-butoxide in 21 g of 2-methyl-1-butene was stirred at room temperature under nitrogen. A solution of 5.94 g of **7** in 29 ml of tetrahydrofuran was added dropwise. The temperature was allowed to rise to 35°. The mixture was filtered through Celite and the filter cake was rinsed with pentane. The filtrate was evaporated and the residue was chromatographed on a Florisil column with hexane as the eluent. Recrystallization from methanol gave 0.80 g of tetra-*tert*-butylhexapentaene. The filtrate was distilled through a microcolumn to give 0.52 g of the vinylidenecyclopropane which was collected at 54° (0.5 mm), $n^{25}\mathrm{D}$ 1.4789.

All of the di-*tert*-butylvinylidenecyclopropanes had the ir absorption of the allene between 4.99 and 5.03 μ with the exception of the adduct to cyclohexene which had a doublet at 4.97 and 5.04 μ.

Competition Experiments with 7, Potassium *tert*-butoxide, and Olefins. Mixtures containing cyclohexene and another olefin (*ca.* 0.2 mol of total olefin) and 1.13 g of potassium *tert*-butoxide were stirred under nitrogen at room temperature. A solution of 2.1 g (0.01 mol) of **7** in 14 ml of tetrahydrofuran was added dropwise. The average temperature during reaction was 30° (range 25–35°). Pentane (30 ml) was added and the mixtures were filtered through Celite. The filtrates were concentrated under nitrogen and the residues were chromatographed on Florisil with hexane as eluent. The material in hexane was concentrated under nitrogen and the solutions were analyzed by gas–liquid chromatography. The column was a 2-m tube packed with 20% tris(cyanoethyl)glyceryl ether on firebrick operated at 125° with a preheat of 170°. Retention times were determined with authentic samples and were between 3 and 19 min. The product ratios where divided by the mole fraction ratios of the starting olefins to give the relative rates of addition. The logarithms of the relative rates are given in Table II. Duplicate experiments agreed within 10%.

1,1,6,6-Tetra-*tert*-butylhexapentaene (7). A slurry of 6.65 g of potassium *tert*-butoxide and 10 ml of tetrahydrofuran was stirred at room temperature under nitrogen. A solution of 6.3 g of the acetylenic acetate in 25 ml of tetrahydrofuran was added dropwise. The temperature rose to 35°. The mixture was filtered through Celite and the filter cake was rinsed with pentane. The filtrate was evaporated under nitrogen to leave a partly solid residue. This was triturated with methanol and filtered to give 1.3 g of crude cumulene, mp 185°. Recrystallization from ethanol gave pure cumulene as pale yellow crystals: mp 188–189°; uv max (isooctane) 417, 336, 308, 237, 223 nm (ϵ 870, 33,000, 28,900, 185,000, 60,000); ir max 3.38, 3.44, 3.88, 4.95, 5.04 μ; nmr (CDCl$_3$) δ 1.28 (s).

---

[24] H. Wynberg, Ae. de Groot, and D. W. Davies, *Tetrahedron Lett.*, 1083 (1963); Ae. de Groot, B. Evenhuis, and H. Wynberg, *J. Org. Chem.*, **33**, 2214 (1968).

[25] G. Köbrich and H. Heinemann, *Angew. Chem.*, **77**, 590 (1965).

[26] M. S. Newman, A. Arkell, and T. Fukunaga, *J. Amer. Chem. Soc.*, **82**, 2498 (1960).

[27] W. J. Hickenbottom, A. A. Hyatt, and M. B. Sparke, *J. Chem. Soc.*, 2529 (1954).

Anal. Calcd for $C_{22}H_{36}$: C, 87.92; H, 12.08. Found: C, 87.98; H, 12.10.

The cumulene was obtained in 18% yield using lithium piperidide as base but could not be obtained from the acetylenic ester with sodium hydride in glyme.

1-*tert*-Butoxy-3-*tert*-butyl-4,4-dimethyl-1,2-pentadiene (6). The methanol filtrate from the preparation of the hexapentaene was distilled through a microcolumn to give 1.29 g (19%) of the alkoxyallene: bp 57° (0.4 mm); n^{25}D 1.4624; ir max 3.39, 5.11, 5.17, 9.0 μ; nmr ($CDCl_3$) δ 1.20, 1.26 (s, s, 27), 6.25 (s, 1).

Anal. Calcd for $C_{15}H_{28}O$: C, 80.27; H, 12.58. Found: C, 80.31; H, 12.65.

Tetrakis(di-*tert*-butylvinylidene)cyclobutane (8). A sample of 0.30 g of tetra-*tert*-butylhexapentaene was immersed in an oil bath at 200° for 15 min. After cooling pentane was added and the suspension was filtered to give 0.27 g (90%) of the dimer, mp 350–360°. Recrystallization from xylene gave white crystals: mp 361°; uv max (tetrahydrofuran) 316, 298, 268, 258, 250 nm (ϵ 2040, 1720, 13,200, 16,300, 15,800); ir max 3.37, 3.43, 3.47, 5.12, 5.19 μ; nmr ($CDCl_3$) δ 1.20 (s).

Anal. Calcd for $C_{44}H_{72}$: C, 87.92; H, 12.08; mol wt, 601. Found: C, 88.05; H, 12.02; mol wt 595 (ebullient in benzene).

1,2-Bis(di-*tert*-butylvinylidene)-3,3,4,4-tetrafluorocyclobutane (9). A Carius tube containing 0.92 g of tetra-*tert*-butylhexapentaene, 7.5 g of tetrafluoroethylene, and 20 ml of benzene was sealed and heated at 200° for 6 hr. The solvent was removed and the residue was crystallized from methanol to give 0.93 g (70%) of the cycloadduct, mp 128–130°. An analytical sample was recrystallized from methanol: mp 129.5–130.5°; ir max 3.35, 3.46, 5.12, 7.17, 7.31, 7.5–9.0 μ; ^{1}H nmr ($CDCl_3$) δ 1.24 (s); ^{19}F nmr ($CDCl_3$) +112 ppm (s).

Anal. Calcd for $C_{24}H_{36}F_4$: C, 71.97; H, 9.06; F, 18.97. Found: C, 71.90; H, 8.98; F, 18.79.

1,2-Bis(trifluoromethyl)-3,4-bis(di-*tert*-butylvinylidene)cyclobutene (10). A mixture of 1.47 g of tetra-*tert*-butylhexapentaene, 12 g of hexafluoro-2-butyne, and 10 ml of benzene was heated at 190° in a Carius tube for 2 hr. The tube was cooled and opened, the solvent was evaporated, and the crude solid was sublimed at 100° (0.5 mm) to give 0.30 g of the cycloadduct: mp 135.5–137°; uv max (EtOH) 270 nm (ϵ 11,100); ir max 3.39, 3.40, 3.45, 5.05, 5.10, 6.07, 7.25, 8–9 μ.

Anal. Calcd for $C_{26}H_{36}F_6$: C, 67.50; H, 7.85; F, 24.65. Found: C, 67.16; H, 7.92; F, 25.07.

3,10-Di-*tert*-butyl-2,2,11,11-tetramethyl-6,6-bis(trifluoromethyl)-3,4,5,7,8,9-dodecahexaene (11). The sublimate bottom from the above reaction was recrystallized from ethanol to give the dodecahexene (0.30 g) as lemon yellow crystals: mp 158–159°; uv max (EtOH) 377, 355 sh, 330, 243 nm (ϵ 76,300, 46,700, 119,000, 3840); ir max 3.35, 3.41, 3.46, 4.84, 7.16, 7.31, 8–9 μ; ^{1}H nmr ($CDCl_3$) δ 1.30 (s); ^{19}F nmr ($CDCl_3$) +74.6 ppm (s).

Anal. Calcd for $C_{26}H_{36}F_6$: C, 67.50; H, 7.85; F, 24.65. Found: C, 67.15; H, 7.91; F, 25.13.

Formation of 11 from 10. A solution of 0.20 g of **10** in 20 ml of diphenylmethane was heated at 220° under nitrogen for 4 hr. The mixture was cooled and filtered to give 0.13 g of yellow **11**, mp 156–158°. After recrystallization from ethanol the material melted at 158–159° and had an ir spectrum identical with that of **11**.

1,2-Bis(diphenylmethylene)-3,3,4,4-tetrafluorocyclobutane (12). A mixture of 3.0 g of tetraphenylbutatriene, 21 g of tetrafluoroethylene, and 40 ml of benzene was heated at 200° for 6 hr in a Carius tube. The mixture was cooled and filtered to return 0.22 g of unreacted butatriene. From the filtrate there was obtained 0.80 g of crude cycloadduct, mp 184–195°. Recrystallization from hexane gave yellow crystals: mp 195–196°; ir max 3.24, 6.25, 6.35, 6.67, 7.5–9 μ; ^{19}F nmr ($CDCl_3$) +109.6 ppm (s).

Anal. Calcd for $C_{30}H_{20}F_4$: C, 78.93; H, 4.42; F, 16.65. Found: C, 79.17; H, 4.31; F, 16.26.

3,6-Di-*tert*-butyl-4,5-dichloro-2,2,7,7-tetramethyl-3,5-octadiene (13). A solution of 40 g of 3,6-di-*tert*-butyl-2,2,7,7-tetramethyl-4-octyne-3,6-diol in 300 ml of dioxane was added dropwise to a stirred solution of 400 ml of concentrated hydrochloric acid and 200 ml of acetic acid. The mixture was stirred 4 hr at room temperature. The product precipitated and was filtered, washed with water, and dried to give 43 g (96%) of solid, mp 99–105°. Recrystallization from acetonitrile gave solid: mp 113–114°; uv no absorption maxima; ir max 3.36, 6.10, 7.17, 7.30, 12.9 μ; nmr ($CDCl_3$) δ 1.40 (s).

Anal. Calcd for $C_{20}H_{36}Cl_2$: C, 69.13; H, 10.45; Cl, 20.42. Found: C, 69.14; H, 10.52; Cl, 20.35.

3,6-Di-*tert*-butyl-2,2,7,7-tetramethyl-3,4,5-octatriene (Tetra-*tert*-butylbutatriene) (14). A mixture of 15.5 g of 3,6-di-*tert*-butyl-4,5-dichloro-2,2,7,7-tetramethyl-3,5-octadiene, 6 g of zinc dust, and 125 ml of acetonitrile was heated at reflux for 3 hr. The hot mixture was filtered, and the butatriene crystallized in the filtrate. Sublimation of the crude solid at 80° (0.5 mm) gave 5.58 g (45%) of the butatriene, mp 135°. Recrystallization from acetonitrile gave white crystals: mp 135–137°; uv max 300, 264, 228 nm (ϵ 3150, 32,400, 9050); ir max 3.38, 3.43, 7.20, 7.33 μ; nmr ($CDCl_3$) δ 1.32 (s).

Anal. Calcd for $C_{20}H_{36}$: C, 86.87; H, 13.13. Found: C, 86.68; H, 13.23.

Electrochemical Oxidation of Phenylethylenes. I. Conversion of Tetraphenylethylene to 9,10-Diphenylphenanthrene[1a]

James D. Stuart[1b] and William E. Ohnesorge*

Contribution from the Department of Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015. *Received October 30, 1970*

Abstract: Electrochemical oxidation of tetraphenylethylene in acetonitrile solution at *ca.* +1.3 V *vs.* (aqueous) sce produces high yields of 9,10-diphenylphenanthrene. Cyclic voltammetry indicates that the detailed mechanism is rather complicated and involves several electrode (E) and follow-up chemical (C) reactions.

The initial step in the electrochemical oxidation of many organic compounds is the loss of a π electron to form a (monovalent) carbonium ion radical. Follow-up chemical reactions often involve attack by a nucleophile; if approach to the reactive site(s) on the carbonium ion is relatively unhindered and the species is not stabilized, *e.g.*, by a high degree of charge delocalization, these reactions occur rapidly. Moreover, additional reactions may follow so that the overall electrochemical oxidation is a very complicated process involving a variety of electrode (E) and chemical (C) steps—sometimes occurring in parallel as well as in series.[2] Therefore, it is usually not possible to de-

---

[1] (a) Presented in part at the May 1969 meeting of The Electrochemical Society, New York, N. Y. (b) Based on the Ph.D. Thesis of J. D. S., Lehigh University, 1969.

[2] L. Jeftić and R. N. Adams, *J. Amer. Chem. Soc.*, **92**, 1332 (1970).