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Hydrogen Atom Abstraction from Hexamethyl(Dewar benzene), Hexamethylprismane, and a 1,3-Hydrogen-Shifted Isomer of Hexamethylbenzvalene. A Study by Electron Paramagnetic Resonance Spectroscopy[1]

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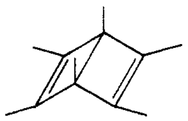
Photochemically generated *tert*-butoxyls abstract an allylic hydrogen atom from hexamethyl(Dewar benzene). The resultant allylic radical [$g = 2.0026_4$, a^{H}(2 H) = 12.40 G, a^{H}(3 H) = 15.48 G] can be observed from 150 to 375 K. The same radical is formed by hydrogen abstraction from hexamethylprismane even at 140 K. In this case it is presumed to arise by two successive cyclopropylcarbinyl ring-opening rearrangements. Hydrogen abstraction from 1,2,4,5,6-pentamethyl-3-methylenetricyclo[3.1.0.0^{2,6}]hexane (the hexamethylbenzvalene isomer) also gave an allylic radical [$g = 2.0025_9$, a^{H}(2 H) = 10.28 G, a^{H}(3 H) = 16.98 G] which could be observed from 150 to 225 K. At higher temperatures this radical probably undergoes a rearrangement to a substituted cyclopropyl radical. The latter could not be detected, probably because of its high reactivity.

Hexamethyl(Dewar benzene) (1) is a remarkable molecule that is readily available.[3] It contains one of the longest C–C single bonds on record (1.63 Å)[4] and has a strain energy of 45 kcal/mol[5] which makes it 60 kcal/mol less stable than hexamethylbenzene[5] (2). Nevertheless, the thermal conversion of 1 into 2 requires an activation energy of ca. 37 kcal/mol[5,6] which has been attributed to orbital symmetry imposed barriers.[7] On the other hand, treatment of 1 with HCl and related electrophiles causes a rapid rearrangement to α-substituted ethylpentamethylcyclopentadienes, e.g., 4, probably via an intermediate bicyclo[3.1.0]hexenyl cation,[8] e.g., 3. The protonation of 1 in "super-acid" medium at low temperatures yields rapidly interconverting isomeric *endo*- and *exo*-bicyclo[2.1.1]hexenyl cations[9,10] 5.



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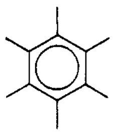

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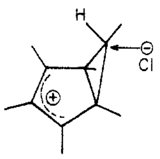

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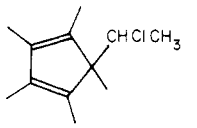

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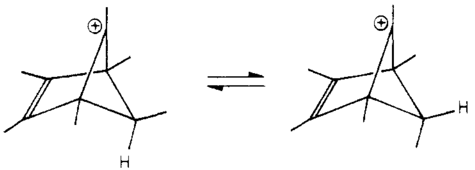

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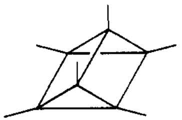
In addition to the above, 1 also serves as the precursor for the interesting valence isomers[11] hexamethylprismane[12] (6) and 1,2,4,5,6-pentamethyl-3-methylenetricyclo[3.1.0.0^{2,6}]hexane[13,14] (7), which is a 1,3-hydrogen-shifted isomer of the so-far unknown hexamethylbenzvalene (8). The prismane 6 is much less stable than 1, with an estimated strain energy of 116 kcal/mol.[5] The stability of 7 relative to 1 and 2 has not been measured. It has been suggested that 8 is more stable than 1.[5]



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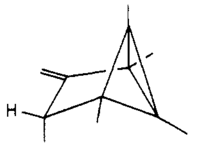

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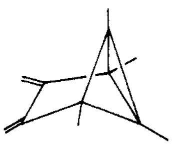
In contrast to the rather extensive work on the heterolytic chemistry of 1, 6, and 7, there does not appear to have been any study of their homolytic chemistry, particularly their reactions with free radicals. The only related work is a study by Elzinga and Hogeveen[16] of the products formed by reaction of CCl_4 and CCl_3Br with the diene 9 and enone 10 under free-radical conditions.



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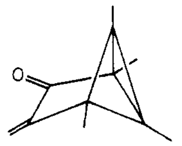

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In the present paper, we report on the radicals which can be observed directly in the cavity of a Varian E-104

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[1] Issued as NRCC No. 18861.

[2] NRCC Research Associate, 1978–1980.

[3] Schäfer, W. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 669.

[4] Cardillo, M. J.; Bauer, S. H. *J. Am. Chem. Soc.* **1970**, *92*, 2399.

[5] Oth, J. F. M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 646; *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 1185.

[6] See also: Volger, H. C.; Hogeveen, H. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 830.

[7] Woodward, R. B.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 781.

[8] Paquette, L. A.; Krow, G. R. *Tetrahedron Lett.* **1968**, 2139.

[9] Hogeveen, H.; Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 353.

[10] Paquette, L. A.; Krow, G. R.; Bollinger, J. M.; Olah, G. A. *J. Am. Chem. Soc.* **1968**, *90*, 7147.

[11] For an interesting discussion of benzene valence isomers, see: Greenberg, A.; Liebman, J. F. "Strained Organic Molecules"; Academic Press: New York, 1978; pp 232–245.

[12] Lemal, D. M.; Lokensgard, J. P. *J. Am. Chem. Soc.* **1966**, *88*, 5934.

[13] When first prepared this compound was given the tricyclic [2.2.0.0^{2,6}] structure.[15]

[14] Hogeveen, H.; Zwart, L. *J. Org. Chem.* **1979**, *44*, 1365.

[15] Hogeveen, H.; Kwant, P. W. *Tetrahedron Lett.* **1972**, 5357; *J. Org. Chem.* **1974**, *39*, 2624, 2626.

[16] Elzinga, J.; Hogeveen, H. *J. Org. Chem.* **1979**, *44*, 2381.

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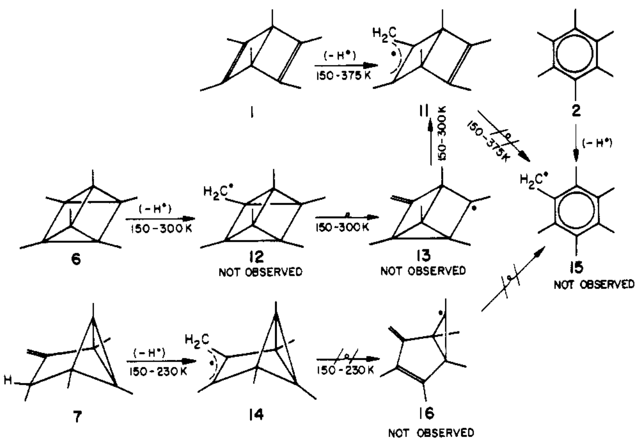
Scheme I



EPR spectrometer upon UV photolysis of di-*tert*-butyl peroxide and **1**, **2**, **6**, and **7** in either the neat peroxide or in suitable hydrocarbon solvents.

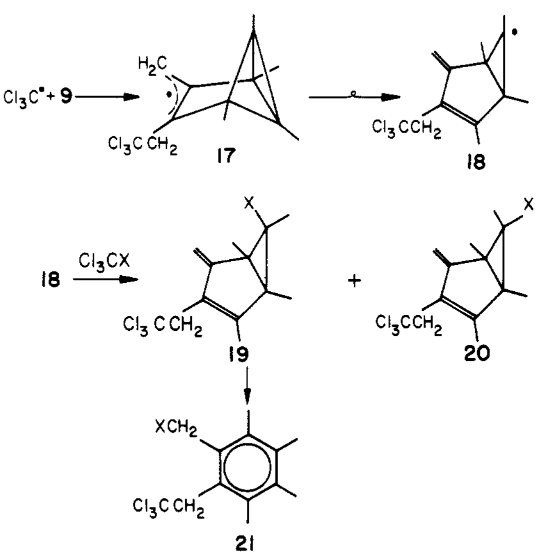
Results and Discussion

The principal results obtained in this work are indicated in Scheme I. At temperatures from 150 (in cyclopropane) to 375 K (in neat peroxide) hexamethyl(Dewar benzene) gave a radical having fairly broad lines ($\Delta H_{pp} = 2.0$ G) with $g = 2.0026_4$, $a^{\mathrm{H}}(2\ \mathrm{H}) = 12.40$ G, and $a^{\mathrm{H}}(3\ \mathrm{H}) = 15.48$ G. This we identify as **11** formed by abstraction of one of the allylic hydrogen atoms by *tert*-butoxyl radical. Hexamethylprismane gave the same spectrum even at temperatures as low as 140 K (in cyclopropane; no spectrum could be obtained in ethylene at still lower temperatures). The formation of **11** from **6** can be readily understood because **12**, which must be formed initially, is a cyclopropylcarbinyl radical and, as such, will undergo a rapid ring opening to give **13**. This, in turn, will suffer a second cyclopropylcarbinyl radical ring opening and so form **11**. The fact that **11**, rather than **12** or **13**, was observed by EPR implies that the rate constants for both of these rearrangements must be greater than 10^3 s^{-1} at the temperature of the experiment.[17]

Hydrogen atom abstraction from **7** at temperatures from 150 to 225 K gives a spectrum similar to but not identical with that of **11**. The radical formed, which we identify as **14**, has $g = 2.0025_9$, $a^{\mathrm{H}}(2\ \mathrm{H}) = 10.28$ G, and $a^{\mathrm{H}}(3\ \mathrm{H}) = 16.98$ G, and each line in its spectrum can be further resolved into a multiplet consisting of not less than 13 lines with an average spacing of ca. 0.3 G.[20] This additional hyperfine splitting can be attributed to the four methyl groups on the bicyclobutane moiety which should appear as two equivalent and two inequivalent groups (which could give up to 112 lines). No radical could be detected from **7** at temperatures between 230 and 390 K.

Attempts to observe the pentamethylbenzyl radical (**15**) by reaction of photochemically generated *tert*-butoxyl radicals with hexamethylbenzene at temperatures from 290 (limited by the solubility of hexamethylbenzene in inert hydrocarbon solvents) to 390 K were uniformly unsuccessful. It seems unlikely that hydrogen atom abstraction would be slow. However, **15** will certainly be a transient species,[21] and since its spectrum is expected to have a great many lines (3 × 7 × 7 × 4 = 588) its steady-state concentration could well be below the level needed for detection. This appears to be the case since **15** could be observed by a chlorine atom abstraction from pentamethylbenzyl chloride using photochemically generated tri-*n*-butyltin radicals in toluene at 180 to ca. 240 K. At higher temperatures the EPR spectrum (which was not analyzed because of its complexity) became lost in the spectrometer noise.

Scheme II



Although **15** could not be observed, we can be certain that **11** does not rearrange to **15** at temperatures below 375 K[23] because the EPR signal due to **11** was still visible at this temperature. Furthermore, **11** decayed with *second*-order kinetics and at a rate equal to or near the diffusion-controlled limit. This means that the rate constant for the **11** → **15** rearrangement must be less than 10^3 s^{-1} at 375 K. On the assumption that the Arrhenius preexponential factor for this radical rearrangement is the same as that found for the **1** → **2** molecular rearrangement, viz.,[5] 10^{15} s^{-1}, the activation energy must be ≥20.5 kcal/mol. This can be compared with an activation energy of 37 kcal/mol for the molecular rearrangement.[5] If, therefore, the barrier to the disrotary opening of the central bond of **1** *is* reduced in the radical, the reduction is less than a factor of 2.

Although hexamethyl(Dewar benzene) is very reactive toward electrophiles (with preferential endo attack),[24] it does not appear to be reactive toward radicals which normally add to double bonds. For example, photolysis of **1**, di-*tert*-butyl peroxide, and either trimethylsilane (as a source of $Me_3Si\cdot$) or diethyl phosphite (as a source of $(EtO)_2\dot{P}{=}O$) gave only **11**.

Perhaps our most surprising result is that the substituted cyclopropyl radical **16** was not observed on hydrogen atom abstraction from **7**. Elzinga and Hogeveen[16] found that UV irradiation of **9** in CCl_4 gave the two halides **19**

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[17] For comparison, the rate constant for the ring-opening of cyclopropylmethyl radical at 140 K is 1.6 × 10^3 s^{-1}.[18] Methyl-substituted cyclopropylmethyl radicals undergo a more rapid ring-opening.[19]

[18] Maillard, B.; Forrest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024.

[19] For a review see: Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, in press.

[20] This spectrum actually serves also to confirm the structure of **7** since it could not possibly arise if the structure of the starting hydrocarbon had been that originally proposed.[13,15] The compound with the originally proposed structure would, by loss of a hydrogen atom, have yielded **13** as its initial radical product. Hence, **11**, rather than **14**, would have been observed on hydrogen atom abstraction.

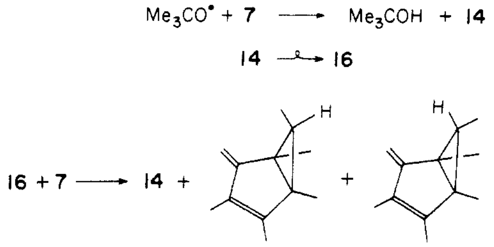
[21] Even 2,4,6-tri-*tert*-butylbenzyl radical is transient.[22]

[22] Griller, D.; Barclay, L. R. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1975**, *97*, 6151.

[23] Higher temperatures were not used because it is known[5] that **1** rearranges to **2** above 355 K.

[24] Paquette, L. A.; Krow, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 6107.

Scheme III



and **20** (in a ratio of 68:32, respectively; X = Cl) in a yield of 90% at 273 K. In refluxing CCl_4, **19** aromatized to **21** (X = Cl), but **20** did not. This addition reaction is presumably a free-radical process in which radical **17**, which is closely related to **14**, undergoes ring opening to form **18**, which then yields the observed products (see Scheme II). Similarly, treatment of **9** with CCl_3Br at room temperature yielded **20** and **21** (in a ratio of 73:27, respectively; X = Br) in a yield of 70%. Although the rate constants for halogen abstraction from CCl_4 and CCl_3Br by an allylic radical do not appear to have been measured, it would seem reasonable to assume that they will be of similar magnitude to those for abstraction by a benzylic radical. From the chain-transfer constants for CCl_4[25,26a] and CCl_3Br[27] and the known Arrhenius parameters for chain propagation in the polymerization of styrene,[26b,28] the rate constants for the reactions (eq 1) can be calculated to be

$$\sim\!\sim CH_2\dot{C}HC_6H_5 + CCl_3X \rightarrow \sim\!\sim CH_2CHXC_6H_5 + Cl_3C\cdot \qquad (1)$$

ca. 0.01 $M^{-1}\,s^{-1}$ at 273 K for X = Cl and ca. $2.4 \times 10^3\ M^{-1}\,s^{-1}$ at 298 K for X = Br. If the polystyryl radical is accepted as a reasonable model for **17**, then the fact that the **17** → **18** rearrangement is faster than bromine abstraction from neat, i.e., ca. 10 M, CCl_3Br implies that the rate constant for the ring opening of **17** must be considerably greater than $10 \times 2.4 \times 10^3 = 2.4 \times 10^4\ s^{-1}$ at room temperature.

It seems reasonable to assume that the **14** → **16** rearrangement will occur at a rate similar to that of the **17** → **18** rearrangement, and, hence, **14** should be observable by EPR means only at subambient temperatures. Our failure to detect **14** at temperatures of 230 K and above can therefore be attributed to its rearrangement to **16**, and the rate constant for this reaction must be ca. $10^3\ s^{-1}$ at ca. 225 K.[29] Our failure to detect **16** above 230 K is not so easily explained. Clearly,[16] it cannot be due to a rearrangement to **15**. Furthermore, unsubstituted and methyl-substituted cyclopropyl radicals have been detected by EPR in solution[30,31] at low temperatures.[32] However, it must be remembered that cyclopropyl radicals are destabilized[33,34] and, hence, are highly reactive in intermolecular hydrogen atom abstractions. We therefore suggest that **16** is not detected by EPR because at the temperatures where it is formed it abstracts hydrogen from the surrounding medium. Compound **7** should be a particularly good hydrogen atom donor. Hydrogen atom abstraction from **7** at ambient temperatures by *tert*-butoxyl radicals might therefore be expected to lead to its chain decomposition via the reaction sequence shown in Scheme III. Experiments showed that **7** was rapidly consumed when cyclopropane solutions of **7** and di-*tert*-butyl peroxide were irradiated for a few minutes at ambient temperatures. The products were not, however, isolated.

Experimental Section

The hexamethyl(Dewar benzene) (**1**) was a gift from Dr. P. J. Garratt. Hexamethylbenzene (**2**, Aldrich) and pentamethylbenzyl chloride (Pfaltz and Bauer) were used without further purification. Hexamethylprismane (**6**) was synthesized by the method of Lemal and Lokensgard[12] and 1,2,4,5,6-pentamethyl-3-methylenetricyclo[3.1.0.0^{2,6}]hexane (**7**) by the method of Hogeveen and Kwant.[15] The latter compound was purified by preparative VPC at 373 K on a 10 ft × $^3/_8$ in. aluminum column packed with 20% OV-101 on Chromosorb P (AW-DMCS treated).

EPR spectra were recorded on a Varian E-104 EPR spectrometer.

Acknowledgment. We are most grateful to Dr. P. J. Garratt (University College London) for generously supplying the hexamethyl(Dewar benzene) used throughout this work.

Registry No. 1, 7641-77-2; **6**, 14551-30-5; **7**, 75101-75-6.

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(25) Gregg, R. A.; Mayo, F. R. *J. Am. Chem. Soc.* **1948**, *70*, 2373.

(26) (a) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; pp 152–153. (b) *Ibid.*, p 95.

(27) Harker, D. A. J.; Thomson, R. A. M.; Walters, I. R. *Trans. Faraday Soc.* **1971**, *67*, 3057.

(28) Matheson, M. S.; Auer, E. E.; Bevilacqua, E. B.; Hart, E. J. *J. Am. Chem. Soc.* **1951**, *73*, 1700.

(29) The suggestion of Elzinga and Hogeveen[16] that the rate constant for this ring-opening should be similar to that for the cyclopropylmethyl radical[18] (which would be very much faster than $10^3\ s^{-1}$ at 225 K) ignored the fact that **14** is actually a resonance-stabilized allyl radical. The thermodynamics for ring opening will therefore be much less favorable for **14** than for cyclopropylmethyl radical.

(30) Chen, K. S.; Edge, D. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 7036.

(31) Kawamura, T.; Tsumura, M.; Yonezawa, T. *J. Chem. Soc., Chem. Commun.* **1977**, 373. Kawamura, T.; Tsumura, M.; Yokomichi, Y.; Yonezawa, T. *J. Am. Chem. Soc.* **1977**, *99*, 8251.

(32) For example, cyclopropyl radical at ≤179 K,[30] 2,2,3,3-tetramethylcyclopropyl radical at ≤225 K,[30] and 2,2-dimethylcyclopropyl radical at 165 K.[31]

(33) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13.

(34) $D(c\text{-}C_3H_5\text{–}H)$ is ca. 105 kcal/mol.[35]

(35) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.