TEAP was recrystallized three times from triply distilled water and dried at 100°.

The tetra-*n*-butylammonium salt of the enolate of dibenzoylmethane was prepared as described[16] by the reaction of tetra-*n*-butylammonium hydroxide (Matheson Coleman and Bell) and dibenzoylmethane.

1,1,2,2-Tetrabenzoylethane (4) was prepared as described[19] by the addition of 2-bromo-1,3-diphenyl-1,3-propanedione (Eastman) to a solution of sodium iodide in acetone. The crystals that formed were washed with water and methanol. The white crystals (yield: 20%) had mp 208–211° (lit.[19] 204–208°). High-resolution mass spectrometry gave m/e 446.152 for the parent peak (calcd for $C_{30}H_{22}O_4$, 446.152).

Though 4 is quite insoluble, a suitable nmr spectrum was obtained from a 2 m*M* solution in DMSO-d_6. The spectrum showed two broad multiplets at δ 7.95 and 7.69 ppm corresponding to the phenyl protons. A singlet for the central methine protons was found at δ 6.70. Integration gave a value of 0.081 for the ratio of the area of the singlet to the total area for all the protons. For 4 in the keto form the ratio should be 2:22 or 0.091. The region of 14–17 ppm was searched for a possible enol proton resonance[9, 20] but none was found. On this basis, it is quite certain that the dimer is predominantly (> 80%) in the keto form.

Qualitative interpretation of the uv spectrum of 4 (in acetonitrile) in comparison to the uv spectrum of dibenzoylmethane and 2,2-dimethyl-1,3-diphenyl-1,3-propanedione also supported the above conclusion. Dibenzoylmethane is known[9] to be predominantly in

the enol form while the dimethyl derivative can only exist in the keto form. Dibenzoylmethane has a relatively strong uv absorption band centered at 340 nm while the dimethyl derivative has a band at 247 nm and none at 340 nm. The spectrum of 4 shows a band at 250 nm but none at 340 nm supporting the conclusion that 4 exists in the keto form.

Tetrabenzoylethylene (7) was prepared by the oxidation of 4 with chlorine.[21] Chlorine gas was bubbled for approximately 2 hr through a solution of 0.2 g of 4 in 10–15 ml of chloroform containing an equivalent amount of tetra-*n*-butylammonium hydroxide. The solution was then washed with aqueous solutions of Na_2CO_3, Na_2SO_4, and finally with water, and then dried over $MgSO_4$. Most of the chloroform was removed by evaporation and white crystals of 7 formed overnight, mp 183–185° (lit.[21] 184°). The infrared spectrum corresponded to that reported.[22] Tetrabenzoylethylene is fluorescent and light sensitive, turning yellow in 1–2 days time.[21, 22] The 2,2-dimethyl-1,3-diphenyl-1,3-propanedione was prepared earlier.[23]

Solutions were deaerated with nitrogen. The solution temperature was 24 ± 1° for all electrochemical experiments.

(19) Von Leopold Wolf and C. Tröltzsch, *J. Prakt. Chem.*, [4] 17, 69 (1962).
(20) J. L. Burdett and M. T. Rogers, *J. Amer. Chem. Soc.*, 86, 2105 (1964).

(21) H. von Halban and H. Geigel, *Z. Physik. Chem.*, 96, 233 (1920).
(22) H. Schmid, M. Hochweber, and H. von Halban, *Helv. Chim. Acta*, 31, 1899 (1948).
(23) R. C. Buchta and D. H. Evans, *J. Org. Chem.*, 35, 2844 (1970).

o- and *p*-Semibenzene Dimers of Benzylic Radicals. Autoxidation of Quinoid Dimers[1]

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Abstract: Dimerization of benzyl radicals substituted at the α position with (a) two methyl groups, (b) two ethyl groups, or (c) one methyl and one isopropyl group gave the following distribution of isomers: α–α (1,2-diphenylethane):α–ortho (*o*-semibenzene):α–para (*p*-semibenzene) = (a) 1:0.1:0.2, (b) 1:0.04:0.6, (c) 1:0.02:0.6. The radicals were generated by photolysis or thermolysis of the related azoalkanes. The order of increasing stability to homolysis is *o*-semibenzene < *p*-semibenzene ≃ azoalkane. The *o*-semibenzenes were identified by uv (λ_{max} ~315 nm), the *p*-semibenzenes by uv (λ_{max} ~265) and pmr and by autoxidation to an aromatized hydroperoxide. The proposed radical chain mechanism explains high hydroperoxide yield from autoxidation of triphenylmethyl dimer when termination is slow. In ether solution the triphenylmethyl dimer has λ_{max} 318.

W ithin 5 years of Gomberg's discovery of organic free radicals Flürscheim suggested that benzylic radicals should show "free affinity" at the ortho and para positions of the phenyl ring as well as at the α position.[3] His proposal of an equilibrium between triphenylmethyl and its α–α coupling product hexaphenylethane was, however, accepted for Gomberg's hydrocarbon until 1968.[4] Jacobson's quinoid or *p*-semibenzene structure (1), an α–para coupling product,

1
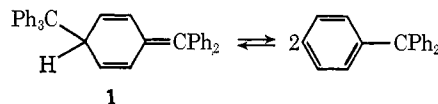
has now been established for the triphenylmethyl dimer,[5] and analogous structures have been proposed or demonstrated for coupling products of other radicals with triphenylmethyl radicals.[6] There is fragmentary

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(3) B. Flürscheim, *J. Prakt. Chem.*, [2] 71, 497 (1905).
(4) For references and discussion, see J. M. McBride, *Tetrahedron*, in press.

(5) H. Lankamp, W. Th. Nauta, and C. MacLean, *Tetrahedron Lett.*, 249 (1968); H. A. Staab, H. Brettschneider, and H. Brunner, *Chem. Ber.*, 103, 1101 (1970); R. D. Guthrie and G. R. Weisman, *Tetrahedron Lett.*, 1316 (1969).
(6) For references, see (a) J. A. Kampmeier, R. R. Geer, A. J. Meskin, and R. M. D'Silva, *J. Amer. Chem. Soc.*, 88, 1257 (1966); (b) J. P. Lorand and P. D. Bartlett, *ibid.*, 88, 3294 (1966); (c) W. A. Pryor, K. Smith, J. T. Echols, Jr., and D. L. Fuller, *J. Org. Chem.*, 37, 1753 (1972); (d) J.-J. L. Fu and W. G. Bentrude, *J. Amer. Chem. Soc.*, 94, 7710 (1972).

pmr evidence to support similar α–para structures for coupling products from benzhydryl radicals[7] and, in one case, from benzyl radicals.[8]

Although α–ortho coupling products are common for phenoxy radicals,[9] they have been suggested for hydrocarbon radical dimers only in the case of α-fluorobenzyl, and only on the basis of CIDNP evidence for two diastereomers of a transient intermediate.[10] Evidence presented below suggests that *both* α–ortho and α–para dimerizations of benzylic hydrocarbon radicals are more prevalent than has often been supposed, and that a dimer previously assigned the α–para structure[11] has instead the α–ortho structure.

Periodically since 1901 anomalies have been observed in the kinetics of triphenylmethyl autoxidation and in the yield of bis(triphenylmethyl) peroxide from this reaction.[4] In 1971 Lewis and Butler noted that such anomalies might be understood in terms of structure 1 for the dimer.[12] As shown below, product studies of the autoxidation of 1 and of its tetraethyl analog 4b confirm this suggestion.

Results

Pmr Spectra of α–Para Dimers. The pmr spectrum of Lankamp, Nauta, and MacLean was their most convincing evidence for the quinoid structure (1) for the triphenylmethyl dimer.[5] It consisted of a phenyl multiplet (δ 6.8–7.4), an olefinic quartet (5.8–6.4), and an unresolved multiplet (5.0) for the doubly allylic methine proton.

Photolysis at 366 nm of azoalkanes 2 in degassed

4a, $R_1 = R_2 = CH_3$
b, $R_1 = R_2 = C_2H_5$
c, $R_1 = CH_3$; $R_2 = i\text{-}C_3H_7$

disproportionation products
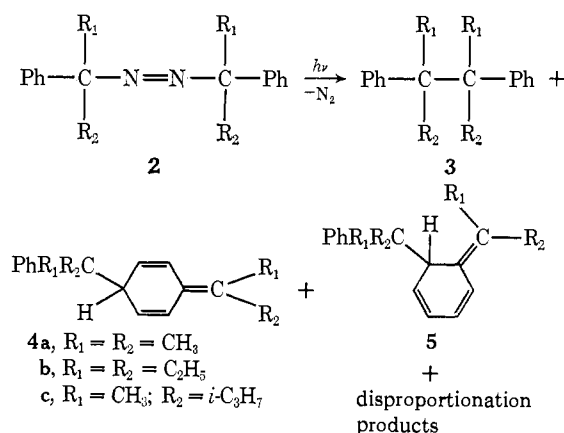
benzene or carbon tetrachloride solutions gives the symmetrical α–α dimers 3 as the major product,[11,13] but the pmr spectra also indicate the presence of α–para dimers 4.[13a] In the case of α–para dicumyl (4a) every predicted spectral peak can be observed, although the yield of this dimer is only 10–20%. The most remark-

able feature of the spectrum is the large (2.3 Hz) coupling across seven bonds between the methine hydrogen and the isopropylidene hydrogens. For the tetraethyl analog, 4b, the methylene proton resonances are obscured by those of the α–α dimer, but all its other absorptions stand out clearly, especially since the yield is about 40% in this case. In the methyl–isopropyl series the spectrum of the diastereomers of 4c in the δ 1–3 region is confused by those of the 3c diastereomers and of the disproportionation products, but absorptions of the methine and vinyl protons stand out clearly in the δ 3–7 region. Yields of 3c and 4c are 51 and 33%, respectively.

Signals for cumene and α-methylstyrene are observed from the sample of photolyzed 2a, but the yield is only about half that of the α–para coupling product. Signals for disproportionation products are not obvious in the spectra of photolyzed or thermolyzed 2b. No other peaks are observed for either sample. The vinyl proton signal of α-isopropylstyrene from photolysis of 2c indicates that in this case disproportionation occurs in about 13% yield.

When an evacuated sample tube containing 3b and 4b in benzene is heated at 70–71°, the peaks assigned to 4b disappear with a half-life of about 23 min, while those of 3b grow in proportion. Compound 4a reacts analogously with a half-life of about 80 min at 80–81°.

Uv Spectra of α–Para Dimers. The other evidence of Lankamp, *et al.*, for the quinoid structure of 1 was a broad uv absorption at 315 nm, which they could measure in a KBr pellet despite interference from the monomer. The spectrum of 1 in solution has not been reported, presumably because of difficulty with the intense absorption of the monomer and sluggishness of equilibration as the solution is cooled to enhance the fraction of dimer.[14] We have measured the spectrum in diethyl ether solution using a sealed, degassed cell with a side arm to allow recrystallization and washing. The colorless crystals were dissolved below −70°, and the spectrum was measured at −64°, where the half-life for dissociation should be about 1 year.[14] The spectrum shows a broad featureless peak λ_{max} 318 nm which falls to the base line by 395 nm. The extinction coefficient cannot be determined in this experiment, because it is not clear what fraction of the sample dissolves at the low temperature. A lower limit (ϵ >500) can be established from the intensity of the 513-nm absorption of the monomer,[15] which grows in as the sample warms to 21°. This is almost certainly a gross underestimate, since the extinction coefficient at the 281-nm absorption maximum of 3-benzhydrylidenecyclohexane is 22,000.[16]

The α–para dimers 4, lacking conjugated phenyl groups, should absorb at much lower wavelengths by analogy with other 3-methylene-1,4-cyclohexadienes, which have absorption maxima at 240–260 nm depending on substitution.[17] When degassed 0.00015 *M* solutions of 2a–c in cyclohexane are exposed to 366-nm irradiation at 5–15°, a strong absorption grows in the region expected for 4: λ_{max} 262, 267, and 262 nm, re-

(7) N. Filipescu, L. M. Kindley, and F. L. Minn, *J. Org. Chem.*, **36**, 861 (1971).

(8) J. B. Levy and E. J. Lehmann, *J. Amer. Chem. Soc.*, **93**, 5790 (1971). *Cf.* C. F. Hobbs and H. Weingarten, *J. Org. Chem.*, **36**, 2881 (1971), which proposes α-para coupling of an α,α-diaminobenzyl radical.

(9) E. R. Altwicker, *Chem. Rev.*, **67**, 475 (1967).

(10) D. Bethell, M. R. Brinkman, and J. Hayes, *J. Chem. Soc., Chem. Commun.*, 1324 (1972). This observation seems as consistent with the α-para dimer which would have two diastereomers, as with the α-ortho, which would have four.

(11) S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, **88**, 137 (1966).

(12) E. S. Lewis and M. M. Butler, *J. Org. Chem.*, **36**, 2582 (1971).

(13) (a) K. J. Skinner, R. J. Blaskiewicz, and J. M. McBride, *Isr. J. Chem.*, **10**, 457 (1972); (b) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).

(14) $t_{1/2}$ = 110.5 min at −20° in toluene: K. Ziegler, P. Orth, and K. Weber, *Justus Liebigs Ann. Chem.*, **504**, 131 (1933).

(15) L. C. Anderson, *J. Amer. Chem. Soc.*, **57**, 1673 (1935).

(16) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2014 (1950).

(17) For example, see W. E. Doering, *et al.*, *Tetrahedron*, **4**, 178 (1958); H. Plieninger and W. Maier-Borst, *Chem. Ber.*, **98**, 2504 (1965); T. Tabata and H. Hart, *Tetrahedron Lett.*, 4929 (1969).
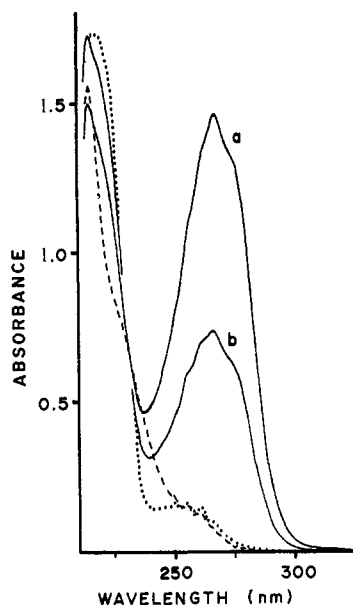
Figure 1. Sequential uv spectra of 1.58×10^{-4} M **2b** in cyclohexane: (- - - - -) before photolysis; (—) (a) after 87-min photolysis, (b) after 25 min at 70°; ($\cdots$) after 110 min at 82°.
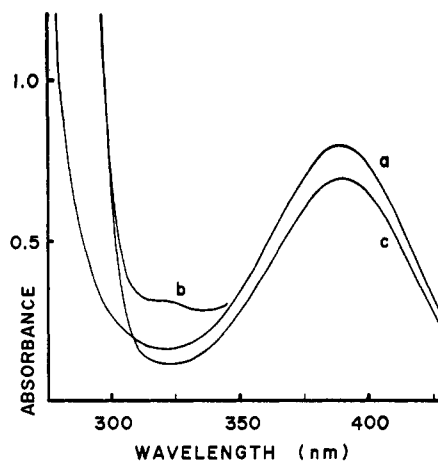

Figure 2. Sequential uv spectra of 2.05×10^{-2} M **2b** in cyclohexane: (a) before photolysis; (b) immediately after 4-min photolysis; scan of cold sample begins at 345 nm; (c) after 11 min in spectrometer cell compartment.

spectively, for **a**, **b**, and **c** (Figure 1). The peaks do not decay during continued exposure to the photolysis conditions, but disappear on heating. The thermolysis rates were not measured carefully, but the half-times for decay are approximately 90 min at 80° for **4a**, 23 min at 70° for **4b**, and 50 min at 70° for **4c**.

Assignment of these absorptions to molecules of structure **4** is based on their positions and intensities and on the similarity of the thermal decay rates to those of the pmr peaks assigned to molecules of this structure. Any other product which could give such intense absorption should be detected by pmr. The cis isomer of **2** would not be stable under these conditions.[18] The related styrenes have uv absorption maxima much too weak and more than 20 nm too short in wavelength to account for the observation.[13a]

To check that the 267-nm absorption is not due to a product derived from cyclohexane solvent a degassed benzene solution containing 86 mg of **2b** was irradiated with 366-nm light for 3 hr and shown by pmr to contain about 35% of **4b**. The sealed nmr tube was then placed in a larger tube connected by a breakseal with a side-arm uv cell containing degassed cyclohexane. The larger tube was attached to the vacuum line and the nmr tube was broken so that benzene could be removed at 10^{-4} Torr without exposing the sample to the air. The breakseal was then broken and the residue dissolved in cyclohexane and sealed in the uv cell. Successive dilution in the cell allowed measurement of the OD at the 267-nm absorption maximum. From this value and the yield of **4b** measured by pmr an extinction coefficient of about 30,000–40,000 can be estimated for **4b**. A second pmr spectrum after exposing the sample to air momentarily during replacement of cyclohexane by carbon tetrachloride shows that **4b** survives, although diminished by about one-third. Assuming the same yield of **4a** in the dilute uv experiment as in the nmr experiment, one can calculate an extinction coefficient of about 25,000–40,000 at 262 nm for this compound.

(18) P. S. Engel and C. Steel, Accounts Chem. Res., 6, 275 (1973).

A similar calculation gives **4c** an extinction coefficient of 31,000.

When a degassed cyclohexane solution of **2b** is heated at 70–71°, the 267-nm peak grows over an hour to about one-fourth of the intensity generated by complete photolysis and then declines. This suggests that the thermolysis of **4b** is twice as fast at that of **2b**.[19]

Uv Spectra of α–Ortho Dimers. In their original study of the photolysis of azocumene (**2a**) Nelsen and Bartlett observed a transient uv absorption at 315 nm.[11] They assigned this absorption to α–para dicumyl (**4a**) because of the occurrence of similar absorptions in other systems which had contained hindered benzylic radicals,[20] and because at 25–40° decay of the absorption paralleled disappearance of an added stable free radical. These scavenging results allowed estimation of an extinction coefficient for **4a**, if a reasonable cage coupling to **3a** were assumed. The calculated extinction coefficient at that wavelength (10,000) seems high for a cross-conjugated triene, and our spectra of **4a**, **b**, and **c** show no such long-wavelength absorption. Moreover, the 315-nm transient they observed decayed with a half-life of 7.5 min at 40°, while the 262-nm absorption we assign to **4a** has a half-life of 90 min at 80°.

The conjugated triene 5-methylene-1,3-cyclohexadiene shows an absorption maximum at 303 nm (ϵ 4400).[21] The alkylation of this chromophore in α–ortho dicumyl (**5a**) would suggest a 10-nm bathochromic shift to 313 nm, in good agreement with the maximum observed for the transient. If the extinction coefficient of **5a** is 4400, its yield from photolysis of **2a** at 4° is 7%. If the 2.2% yield estimated by Nelsen and Bartlett from their scavenging study is accepted, the extinction coefficient would be about 15,000.

Photolysis of degassed 0.01 M cyclohexane solutions of **2b** and **2c** shows analogous transient absorptions at 318 and 320 nm, respectively (Figure 2). While these weak absorptions persist for some time at the 5–10° temperature of the photolysis bath, they decay with

(19) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 166.

(20) Their failure to observe such an absorption when azoisobutane was decomposed in p-cymene is more difficult to rationalize with our scheme than with theirs.

(21) W. J. Bailey and R. A. Baylouny, J. Org. Chem., 27, 3476 (1962).

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half-times of about 3 min as the uv cell warms from 10° to the temperature of the spectrometer cell compartment (30°). Intensities of the transients can be determined by differences between spectra of cold solutions and spectra measured after warming for 15 min. If the extinction coefficient of these absorptions is 4400, the yields, based on 2 destroyed, are 2.5 and 0.7% for 5b and 5c, respectively.

Autoxidation of 4b. Attempts to isolate 4b from low-temperature photolysis mixtures by preparative layer chromatography lead to a new product, which can also be obtained by bubbling oxygen for 5 min through solutions containing 4b. The pmr spectrum (CDCl₃) of the material, isolated chromatographically, lacks the vinyl and methine absorptions of 4b and shows only a narrow aromatic signal (δ 7.2, 9 H), two overlapping quartets (2.18, $J = 7$ Hz; 1.95, $J \simeq 7$ Hz and further split; total 8 H), and two equivalent triplets (0.62, 0.82; $J = 7$ Hz; total 12 H). In some samples a small, broad singlet can be observed at δ 8.1. This spectrum is consistent with expectations for the aromatized hydroperoxide 6a, which would be formed by the chain reaction of Scheme I. Diastereotopy of the methylene

Scheme I

6a, R = C₂H₅
b, R = C₆H₅
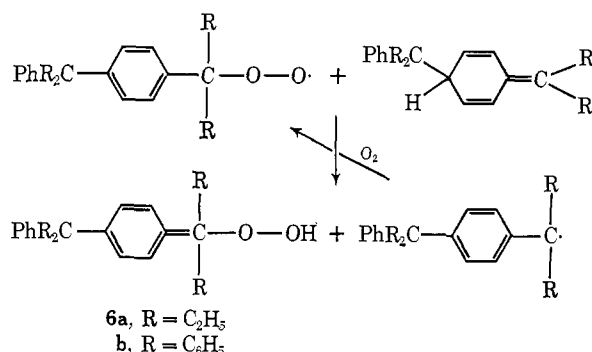
protons α to the hydroperoxy group accounts for the extra splitting in the 1.95 quartet. The chemical shift of the small singlet is consistent with that of hydroperoxy protons,[22] and an ir spectrum in CCl₄ shows the weak doublet at 3565 cm⁻¹ characteristic of OH stretching in aralkyl hydroperoxides for groups which are either free or internally hydrogen bonded to aromatic rings.[23]

The possibility that the substance might be the symmetrical dialkyl peroxide is further excluded by iodometric titration which gives an apparent hydroperoxide content of 90%. The dialkyl peroxide could give no more than 50% in this titration.

The product mixture obtained by treating a small sample of the hydroperoxide with acidic aqueous ethanol contains a substance with vpc retention time identical with that of 3-pentanone, and a base-soluble fraction which gives the ferric chloride test for a phenol. Such products would be expected from acid-catalyzed rearrangement of this aralkyl hydroperoxide.

Chain Autoxidation of "Triphenylmethyl" (1). Identification of the product from chain autoxidation of 4b led us to reinvestigate the induced chain component in the autoxidation of triphenylmethyl, which is often said to yield bis(triphenylmethyl) peroxide.[4,24] Since tri-

phenylmethyl radicals would inhibit such a chain process, we reduced their steady-state concentration by conducting the reaction in an atmosphere of pure oxygen at low temperature. The dimer:monomer ratio was maximized by using a saturated solution.

When a cloudy, orange toluene suspension of 1, prepared from 46 mmol of triphenylmethyl chloride, is stirred at −13° under 1 atm of oxygen, the color immediately fades to light yellow. Over 100 min 22.7 mmol of oxygen is absorbed, and the solid dissolves. Crystallization of the product mixture gives a colorless crystalline solid and an oil. The solid can be identified as hydroperoxide 6b by elemental analysis, ir spectros-

6b   7
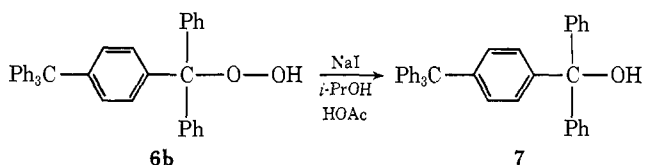
copy (intramolecular aromatic hydrogen bonded O–H stretch at 3525 cm⁻¹), and reduction by sodium iodide to the related carbinol 7. The yield of crystalline 6b from triphenylmethyl chloride is 41%. If one includes the oil, which by tlc and ir is predominantly 6b, the total yield of 6b is 96%. Oxidation at higher temperature gives more complicated product mixtures which include the symmetrical peroxide.

Discussion

It is likely that conjugation, steric, and polarity considerations are all necessary to rationalize the distribution of dimer isomers from the coupling of benzyl radicals. Thermodynamically the added aromatic stability of the α–α dimers is often overriding. Thus, although it is virtually certain that the α–para semibenzene structure 1 is favored among the dimers of triphenylmethyl, all of the semibenzenes observed in this work (4, 5) are unstable with respect to the α–α dimers (3).[25] Even as small a change as from triphenylmethyl to 9-phenylfluorenyl results in sufficient reduction of steric hindrance to make the α–α dimer the preferred isomer.[26]

Kinetically the balance among the effects is more delicate. A recent perturbational calculation of the interaction energy of two benzyl radicals in parallel planes separated by 2.5 Å suggests that the α–α geometry is most favorable, with the α–ortho and α–para geometries about equal in energy and lower than ortho–ortho and para–para.[27] A preference for small radicals to attack triphenylmethyl at the α position and for bulkier radicals to attack para has been noted previously.[6a,b,d] A similar trend is evident in our observation that the ratio of para to α coupling increases two- to sixfold on replacing two methyl hydrogens of the cumyl radical by methyl groups. This increase in

(22) D. Swern, A. H. Clements, and T. M. Luong, *Anal. Chem.*, 41, 412 (1969).

(23) D. Swern, Ed., "Organic Peroxides," Vol. 2, Wiley-Interscience, New York, N. Y., 1971, p 692.

(24) See, for example, C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 408.

(25) *Cf.* (a) H. Hart and J. D. DeVrieze, *Tetrahedron Lett.*, 4259 (1968); (b) B. Miller and K.-H. Lai, *J. Amer. Chem. Soc.*, 94, 3472 (1972); (c) P. Gilgen, J. Zsindely, and H. Schmid, *Helv. Chim. Acta*, 56, 681 (1973).

(26) H. A. Staab, K. S. Rao, and H. Brunner, *Chem. Ber.*, 104, 2634 (1971). We have recently found that a sample of pentaphenylethane, provided by Dr. F. Y. Wiselogle, shows no vinylic resonances in pmr: W. E. Bachmann and F. Y. Wiselogle, *J. Org. Chem.*, 1, 354 (1936).

(27) R. Zahradník and P. Čársky, *Progr. Phys. Org. Chem.*, 10, 375 (1973).

steric hindrance also decreases the ratio of ortho to para coupling by about an order of magnitude.

We have previously reported that restriction on the motion of the radical pair formed by photolysis of crystalline **2b** precludes para coupling.[13a] We find an analogous effect when **2c** is photolyzed as a solid or in viscous solution.[28]

Although the earlier steric rationalization for exclusive α–para dimerization of hexafluorocumyl radicals seems plausible,[8] the observation of apparent quinoid coupling for α-fluorobenzyl radicals suggests that polar complementarity may be another important factor in determining the coupling path.

The stability of semibenzenes **4** and **5** is pertinent to recent discussions of the mechanism of semibenzene–benzene rearrangements.[25] The migration of methyl, allyl, allenyl, propargyl, and benzyl from the para to the α position is nonconcerted and appears to involve free radical chains with propagation by radical attack at the exocyclic carbon of the semibenzene.[25] The stability we observe for compounds **4** suggests that the 15-min half-life reported for compound **8** at 39° was due to

PhCH₂ / H / 8 / =CH₂
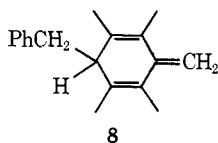
reactions involving other substances in the solution.[25b] Schmid has shown that rearrangement of allenyl and propargyl from the ortho to the α position is a concerted sigmatropic reaction, but was unable to prepare an o-semibenzene with a benzyl group in position to rearrange.[25c] Nelsen and Bartlett's demonstration that radicals can be trapped during thermolysis of the intermediate which we now believe to be **5a**, and that the rates of scavenging and of unscavenged thermolysis are identical shows that this benzyl-substituted o-semibenzene does rearrange by unimolecular homolysis. The variation in thermal stability among azo compounds **2** and the corresponding dimers **3**, **4**, and **5** provides for thermal generation of given hydrocarbon radical pairs over a wide range of temperatures. We have not yet studied the photochemistry of dimers **4** and **5**, but it seems likely that they could be useful as precursors for radical pairs in geometries different from those formed by azoalkane photolysis.

The chain process we suggest for autoxidation of **4** propagates by abstraction of the doubly allylic hydrogen atom to generate a benzylic radical. Compounds of similar structure are often invoked as hydrogen donors, and Lewis has observed aromatization of **1** catalyzed by phenylthiyl radical.[12] Two previous instances of semibenzene autoxidation to give hydroperoxide or phenolic products, which were interpreted in terms of rearrangement or oxidation of radical to carbonium ion,[29] may well be further examples of the autoxidation mechanism proposed above. The intractable oils which are always found together with the symmetrical peroxide when the autoxidation of **1** is conducted under nonlimiting conditions,[30] probably

contain the various coupling and hydrogen abstraction products derived from reaction of triphenylmethyl and triphenylmethylperoxy radicals with the molecules involved in the induced chain of Scheme I.

Experimental Section

Pmr spectra were measured using a Jeolco Minimar-100 spectrometer, uv spectra with a Bausch and Lomb-Shimadzu UV-200, and ir spectra with a Perkin-Elmer 337. Photolysis was by 366-nm light from a 450-W Hanovia L lamp isolated by Corning 7-54 and 0-52 filters. During photolysis samples were held in an unsilvered Pyrex dewar flask containing water at 5–10°. Microanalyses were by Atlantic Microlab, Inc.

Azoalkanes 2a–c were prepared by reaction of phenylmagnesium bromide with the appropriate dichloroazoalkane and recrystallized three to five times at low temperature from acetone or ether.[31] Samples which had been stored in the refrigerator for more than a year gave melting point (Fischer-Johns, uncorr.): **2a**, cracking 85.5°, melting 90.5–92° (lit.[11] 86.9–88.7°); **2b**, 29–30.5° (lit.[13a] 30–31°); meso-**2c**, 35–37.5° (lit.[32] 40.0–40.3°). Pmr spectra of the compounds showed no impurities except for a small (<0.5% of total integral) unidentified singlet just upfield of the δ 1.4 singlet of **2c**.

Pmr of α–Para Dimers (4). Solutions of 70–95 mg of azoalkanes **2a–c** in about 1 ml of benzene or CCl₄/TMS were sealed into 5-mm pmr tubes after degassing by four or five freeze–pump–thaw cycles. The compounds photolyzed at similar rates, 3–6 hr being required for 99% destruction of the starting material. The pmr spectra were unaffected by continued photolysis of the samples.

The photolysate of **2a** in CCl₄/TMS showed the methyl (δ 1.28, s) and phenyl (7.00, m) signals of **3a** and the following peaks for **4a**: methyl (1.25, s), vinylic methyl (1.77, d, $J = 2.3$ Hz), methine (3.23, m), vinyl double doublets (5.40, $J = 11$ and 4 Hz; 6.42, $J = 11$ and 2 Hz). The δ 1.77 doublet collapsed to a singlet when the 3.23 methine signal was decoupled. One member of the cumene methyl doublet was visible as a small peak 6 Hz upfield of the 1.25 singlet. No other signals were evident. A similar experiment with benzene solvent showed both peaks of the cumene doublet. By peak heights the distribution **3a**:**4a**:cumene was estimated as 78:16:6. When the benzene sample was heated in an 80–81° oil bath, spectra at 60-min intervals showed disappearance of the high-field signals assigned to **4a** with a half-time of about 80 min.

The photolyzed benzene solution of **2b** showed the methyl (0.63, t, $J = 7$ Hz) and methylene (1.92, q, $J = 7$ Hz) signals of **3b** and the following signals for **4b**: methyl (0.80, t, $J = 7$ Hz), methyl (0.91, t, $J = 7$ Hz), methylene (~1.9, m), methine (3.40, unresolved m). On the basis of methyl peak heights the ratio **3b**:**4b** was estimated as 60:40. In a CCl₄/TMS run the vinyl double doublets were observed (5.60, $J = 10$ and 2 Hz; 6.34, $J = 10$ and 1). Heating the benzene sample at 70–71° caused the peaks of **3b** to grow relative to TMS standard as the peaks assigned to **4b** disappeared with a half-time of about 23 min. No other absorptions as high as 1% of those of **3b** were observed.

The photolysate of **2c** in CCl₄/TMS had more than 27 peaks upfield of δ 2. The high-field isopropyl signals of **3c** were easily distinguished[13b] as were the following unresolved multiplets attributed to the diastereomers of **4c**: methine (3.73), vinyl (5.25, $J = 11$ Hz; 5.75, $J = 10$ Hz; 6.30, $J = 12$ Hz; 6.55, $J = 10$ Hz). The vinyl doublet of 3-methyl-2-phenyl-1-butene appeared at δ 4.95 and 5.03. Integration of these signals against the phenyl multiplet gave yields of 51, 33, and 13% for **3c**, **4c**, and the olefin, respectively.

Uv Spectra of α–Para Dimers (4). The solvent for uv work was Fisher Spectranalyzed cyclohexane which had been refluxed with a small amount of di-tert-butyl diperoxyoxalate to destroy radical scavengers and distilled. Degassed solutions of **2a**, **2b**, and **2c** had uv maxima at 368 nm (ε 50), 389 (39), and 376 (35), respectively [lit. for **2a**, 367 (44);[11] **2c**, 375 (37)[22]]. Dilute degassed solutions of all three azo compounds showed intense absorption maxima at 215 nm (ε 10,000) near the 207 nm solvent cut-off. Each had a 260-nm shoulder (ε 800) with barely resolved structure. During 90-min photolysis an intense peak grew in each spectrum with λ_max (OD/initial [2]) 262 (4800), 267 (10,400), and 262 (10,400) for **2a**, **b**, and **c**, respectively. For **2b** and **c** these absorptions were unaffected by exposure to another 100-min photolysis. For **2a** the absorption

(28) M. J. Tremelling, unpublished work.

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(30) N. N. Lichtin and G. R. Thomas, *J. Amer. Chem. Soc.*, **76**, 3020 (1954).

(31) We thank Dr. M. J. Tremelling and Mr. R. J. Blaskiewicz for preparing **2c** and **2a**.

(32) J. M. McBride, Ph.D. Thesis, Harvard University, 1967.

may have decayed by about 2%. The position and intensity of the 215-nm peak changed very little during photolysis of 2.

Extinction coefficients were assigned to compounds 4 on the basis of the observed intensities and of the yields measured by pmr. A confirmation that the product distributions were similar for dilute cyclohexane and for concentrated benzene solutions is described under Results.

When the cell containing photolyzed 2b was opened to the air, the 267-nm absorption decayed over several hours to a 255-nm shoulder with about one-sixth of the OD. When an undegassed solution of 2b was photolyzed, a new absorption grew at 237 nm instead of at 267. Its rate of growth and final intensity were comparable to those of the 267-nm peak from degassed solutions.

Approximate first-order rate constants were determined for the thermal decay of these new absorptions by monitoring the spectrum five or six times while the cell was heated in an oil bath. Results are presented above.

Uv spectra of α-ortho dimers (5) were measured in the same way as those of 4 except that the low yields required more concentrated solutions, and the thermal instability of 5b and 5c required measurement of the spectra before the sample warmed to the temperature of the cell chamber. Differences between absorption before and after warming were necessary to fix the position and intensity of the bands of 5b and 5c, and at irradiation times longer than 10 min the absorptions were lost in the tail from 4b and 4c.

Autoxidation of 4b. Samples of ~500 mg of 2b in 5 ml of benzene were degassed and photolyzed for 2 hr. After the tubes were opened and oxygen was bubbled through the solutions for 0.5 hr, about half the solvent was removed and the residue was chromatographed on Merck silica gel F-254 PLC plates. Elution with 3% ether in hexane gave four bands. The first two gave 3b and 2b, and the third gave an unidentified oil. The fourth (R_f 0.2) was removed from the silica gel with methanol and washed through a short silica gel column with ether. After pumping the eluent at 0.001 Torr for 1.5 hr the residue was shown by ir and pmr to be 6a (see Results) and to contain 26 mol % ether.

Titration of Hydroperoxide 6a. The oil containing 6a was dissolved in 25 ml of 2-propanol and two aliquots were refluxed gently with potassium iodide. Titrations of the iodine released with sodium thiosulfate and correction for residual ether in the oil gave apparent hydroperoxide content of 88 and 89.5%.

Rearrangement of 6a. A transient yellow color appeared when 8 drops of concentrated sulfuric acid and 5 drops water were added to 2 ml of ethanol containing 160 mg of 6a, prepared as above. After standing at room temperature for 6.5 hr, the sample was neutralized with sodium bicarbonate and extracted between ether and aqueous sodium hydroxide. The ether layer gave a vpc peak (10 ft × 0.25 in., 15% Carbowax 20M on Anakrom A, 80°) with the same retention time as authentic 3-pentanone. Ether, ethanol, and benzene had quite different retention times. The aqueous fraction was acidified with hydrochloric acid, extracted with ether, and dried. The organic residue had a phenolic odor and gave a green color when treated with ferric chloride dissolved in chloroform and pyridine.[33]

Autoxidation of "Triphenylmethyl" (1). A flask containing 12.91 g (46.3 mmol) of triphenylmethyl chloride, 125 ml of toluene, and 42.0 g (0.209 g-atom) of mercury was evacuated to 24 Torr at room temperature and closed. After 7.5 hr of magnetic stirring in the dark the mixture was filtered in a nitrogen-filled glove bag.

The filtrate became lighter orange and very cloudy when cooled to −13°. The cooled flask was transferred quickly to a gas manifold, and nitrogen was removed by an aspirator. When oxygen was admitted the mixture became light yellow. Oxygen consumption at atmospheric pressure was monitored by a water-filled gas buret for 100 min while the sample was maintained at −14 to −15° and stirred vigorously. During 80% of the oxygen absorption the rate was independent of time (0.45 mmol/min), but as the last of the

solid phase disappeared, the absorption rate decreased. In all 547 ml of oxygen (22.7 mmol, 98% of theoretical) was consumed.

Isolation of p-Trityl Triphenylmethyl Hydroperoxide (6b). After storage at 0° the yellow oxidation mixture was filtered through a fine frit to remove 295 mg of fine, white precipitate identified as ditrityl peroxide by ir. The filtrate was divided into two fractions. The larger (64.5%) was stored at 0° while a work-up procedure was developed with the smaller. After 1 week the stored solution had deposited 171 mg of a fine, white powder, which was removed by filtration. It had mp 199.7–201.4°, was insoluble in benzene or CCl₄, and gave an ir spectrum similar to, but readily distinguished from, that of ditrityl peroxide (lit.[34] mp 185–186°). Condensation of the filtrate left a yellow solid, which was recrystallized from benzene–petroleum ether to give 3.20 g of white solid and 4.28 g of brown oil. On tlc (Eastman Chromogram Sheet, benzene) the solid showed two very faint spots (R_f 0.97, 0.38) in addition to the principal one (R_f 0.74), while the oil showed four additional components (R_f 0.89, 0.85, 0.79, 0.63). Benzophenone and p-tritylphenol had R_f 0.79 and 0.63, respectively. In addition to the ir bands of the solid, the oil showed peaks or shoulders at 3615, 1660, 1317, 1276, and 939 cm⁻¹. The solid was apparently unstable to recrystallization, since, while subsequent recrystallizations gave solids of unchanged ir spectrum, an insoluble white powder invariably appeared (mp 201.5–203°, ir identical with the 171 mg of powder formed during storage. *Anal.* C, 89.31; H, 6.15; inorganic residue, 1.45), and the mother liquors contained the same impurities.

The solid (mp 165–166°) was identified as 6b on the basis of reduction to carbinol (7), a sharp ir peak for the internally H-bonded OH stretch at 3523 cm⁻¹ (CCl₄),[22] and elemental analysis. *Anal.* Calcd for $C_{38}H_{30}O_2$: C, 88.00; H, 5.83. Found: C, 88.35; H, 5.97. The high CH values suggest contamination by 8% hydrocarbon or 16% carbinol. The yield of purified 6b from triphenylmethyl chloride was 41%. If the oil also is taken as 6b and its decomposition products, the implied initial yield of 6b is 96%.

Reduction of 6b. The hydroperoxide (436 mg) was suspended in 60 ml of boiling 2-propanol. Addition of 673 mg of powdered sodium iodide gave immediate coloration. After 1 min 1.2 ml of acetic acid was added and the mixture was swirled and heated for another 2 min. Titration of the cooled solution with sodium thiosulfate gave titers less than 50% of theoretical, but removal of the solvent, dissolution in benzene, washing with water, drying, and removing solvent left 375 mg of an oil which by ir and tlc was nearly pure carbinol 7. Two recrystallizations from benzene–petroleum ether gave material identical by melting point (223.5–224.5°, lit.[35] 220–220.5°), mixture melting point, and ir with the authentic carbinol prepared by the method of Chichibabin.[35]

Uv Spectra of Triphenylmethyl Dimer (1). Hydrocarbon 1 was prepared as above and recrystallized several times from acetone under vacuum. A mixture of solid 1 and ether was degassed and filtered through a fine frit into a uv cell with a side arm of slightly larger volume. By distilling solvent back through the frit more 1 could be transferred to give a solid–ether mixture in the cell assembly which was sealed off and stored at 0°. Even on standing under vacuum in the solid state at this temperature the crystals became yellow. To measure the spectrum of 1, solution was poured into the cell from the side arm and solvent partially distilled back several times to give freshly crystallized, colorless 1 in the cell. The crystals were rinsed with several portions of ether distilled from the side arm and all solvent was distilled back to the side arm. Solvent was distilled during several hours into the cell cooled to −70° from the side arm, which was cooled to −15° to prevent warming of the cell by rapid condensation of ether. The cell was then quickly transferred to a copper housing, cooled by a stream of cold nitrogen gas, in the cell compartment of the spectrometer. The temperature was monitored by a thermocouple in contact with the cell.

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