J. Org. Chem. **1983**, *48*, 955–963 955

pentadiendioate, 84695-27-2; phenyl bromide, 108-86-1; (*E*,*E*)-3-methyl-1,4-diphenyl-1,3-butadiene, 23637-43-6; methyl (*Z*)-3-bromo-2-methylpropenoate, 84695-28-3; (*E*)-1,3-dibromo-2-methylpropene, 28357-78-0; (*Z*)-1,3-dibromo-2-methylpropene, 28357-77-9; (*E*)-3-bromo-2-methylprop-2-en-1-ol, 84695-29-4; (*Z*)-3-bromo-2-methylprop-2-en-1-ol, 84695-30-7; (*Z*)-3-bromo-2-methylpropenal, 84695-31-8; ethene, 74-85-1; 1,3-butadiene, 106-99-0; (*Z*)-1,3-pentadiene, 1574-41-0; (*E*)-1,3-pentadiene, 2004-70-8; dimethyl (2*E*,4*E*,6*E*)-2,7-dimethyl-2,4,6-octatrienoate, 84695-32-9; dimethyl (2*E*,4*E*,6*E*,8*E*)-2,9-dimethyl-2,4,6,8-decatetraendioate, 84695-33-0; methyl (2*E*,4*E*,6*E*)-2-methyl-2,4,6-octatrienoate, 81714-88-7; methyl (2*E*,4*E*,6*Z*)-2-methyl-2,4,6-octatrienoate, 81714-89-8; dimethyl (2*E*,4*E*,6*E*,8*E*)-2,4,9-trimethyl-2,4,6,8-decatetraenedioate, 81715-00-6; 2-methyl-1,3-butadiene, 78-79-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; methyl (2*Z*,4*E*,6*E*)-2-methyl-2,4,6-octatrienoate, 84695-34-1; dimethyl (2*E*,4*E*,6*E*,8*E*)-2,5,9-trimethyl-2,4,6,8-decatetraenedioate, 81714-98-9; dimethyl (2*E*,4*E*,6*Z*,8*E*)-2,5,9-trimethyl-2,4,6,8-decatetraenedioate, 84773-41-1; methyl (2*E*,4*E*)-2,5,6-trimethyl-2,4,6-heptatrienoate, 81714-92-3; dimethyl (2*E*,4*E*,6*E*,8*E*)-2,5,6,9-tetramethyl-2,4,6,8-decatetraenedioate, 81724-46-1; (*E*,*Z*)-2,4-hexadiene, 5194-50-3; methyl (*E*)-2,4-pentadienoate, 2409-87-2; methyl (2*E*,4*E*,6*E*,8*E*)-2,4,7,9-tetramethyl-2,4,6,8-decatetraenedioate, 84695-35-2; methyl 2,4-dimethyl-2,4,6-octatrienoate, 81714-91-2; methyl (2*E*,4*Z*,6*Z*,8*E*)-2,4,7,9-tetramethyl-2,4,6,8-decatetraenedioate, 84695-36-3; dimethyl (2*E*,4*E*,6*E*)-2-methyl-2,4,6-octatrienedioate, 81714-83-2; (*Z*)-3-methyl-2,4-pentadienoic acid, 30288-18-7; (*E*)-1,3,5-hexatriene, 821-07-8; 1-methyl (2*E*,4*E*,6*Z*)-2,6-dimethyl-2,4,6-octatrienedioate, 84695-37-4; 1-methyl (2*E*,4*E*,6*E*)-2,6-dimethyl-2,4,6-octatrienedioate, 84695-38-5; dimethyl (2*E*,4*E*,6*E*,8*E*,10*E*)-2,11-dimethyl-2,4,6,8,10-dodecapentaenedioate, 84695-39-6.

Supplementary Material Available: Table II containing the physical properties, NMR spectra, and molecular weights of the products prepared and crystallographic data for (*E*,*E*,*E*,*E*)-dimethyl 2,4,7,9-tetramethyl-2,4,6,8-decatetraenedioate (Tables III and IV) and (*E*,*E*,*E*,*E*)-dimethyl 2,5,9-trimethyl-2,4,6,8-decatetraenedioate (Tables V and VI) (7 pages). Ordering information is given on any current masthead page.

Structure of ω-Arylalkyl Radicals: A ^{13}C CIDNP Investigation

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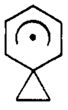
Received July 26, 1982

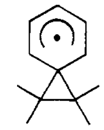
Thermolysis of a series of ω-arylalkanoyl *m*-chlorobenzoyl (and acetyl) peroxides at ~100 °C in cyclohexanone and in hexachloroacetone was studied by using ^{13}C chemically induced dynamic nuclear polarization. Analysis of the observed ^{13}C polarizations indicate that all the three radicals (β-arylethyl, γ-arylpropyl and δ-arylbutyl) have open-chain structures with no evidence for aryl participation resulting in spirocycloalkylcyclohexadienyl radicals.

Introduction

The 1,2-migration of phenyl groups in phenylethyl cations involving bridged species is well-known. For example, ionization of β-phenylethyl chloride under superacid conditions leads to the bridged ethylenebenzenium ion, which has been well characterized by spectroscopic means.[1] Analogous aryl migrations in β-arylethyl radicals are also of interest in reference to the structure of the intermediates. Such 1,2-aryl migrations have been shown to proceed best when a tertiary or a benzylic radical is formed or when steric compression at the β-carbon is relieved.[2–5]

An ESR spectroscopic study of the β-phenylethyl and neophyl radicals at low temperature[6] showed no resolvable hyperfine interaction with the aromatic hydrogens, indicating the absence of the spirocyclic radicals 1 and 2.


1


2

Recently, Ingold et al.[7] have estimated that the ring opening of radical 1 to the open-chain β-phenylethyl radical would be endothermic by ca. 17 kcal/mol. Radical 1 generated by hydrogen atom abstraction from spiro[2.5]-octa-4,6-diene could not be detected[7] by means of ESR spectroscopy even at temperature as low as 100 K. Instead, the ESR spectrum of the cyclopropyl ring-opened radical was obtained. However, 1 was identified by using optical detection methods by means of its absorption and fluorescence at ca. 560 nm, which is characteristic of cyclohexadienyl moiety.

In a recent study of the rearrangements of β-arylated nitroparaffins in the presence of sodium methylmercaptide, Kornblum et al.[8,9] proposed the intermediacy of spirocyclic free radicals such as 2.

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(1) (a) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1976**, *98*, 6284. (b) Olah, G. A.; Spear, R. J.; Forsyth, D. A. *J. Am. Chem. Soc.* **1977**, *99*, 2615.

(2) For a detailed discussion on radical rearrangements see: Wilt, J. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 333.

(3) Walling, C. In "Molecular Rearrangements"; de Mayo, P., Ed.; Interscience: New York, 1963; Vol. 1, p 409.

(4) Freidlina, R. Kh. In "Advances in Free Radical Chemistry"; Williams, A. H., Ed.; Academic Press: New York, 1965; Vol. 1, p 249.

(5) Pryor, W. A. "Free Radicals"; McGraw-Hill: New York, 1966; p 266.

(6) Kochi, J. K.; Krusic, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 3940.

(7) Effio, A.; Griller, D.; Ingold, K. U.; Scaino, J. C.; Sheng, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 6063.

(8) Kornblum, N.; Carlson, S. C.; Smith, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 647.

(9) Kornblum, N.; Widmer, J.; Carlson, S. C. *J. Am. Chem. Soc.* **1979**, *101*, 658.

0022-3263/83/1948-0955$01.50/0 © 1983 American Chemical Society

Table I. ^{13}C NMR Chemical Shifts[a] of Polarized Signals during the Thermolysis of β-Arylpropionyl *m*-Chlorobenzoyl Peroxide at ~100 °C

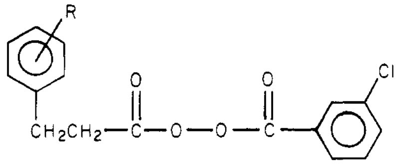
peroxide	4 >C=O	CO_2	4 α-CH_2	5 α-CH_2	6 α-CH_3	7 C_{ipso}	8 C_m	6 β-CH_2	4 γ-C_1	6 γ-C_1
				Solvent: Cyclohexanone						
3a	163.9	124.2	64.8	112.4	14.1	143.3	129.1	27.8	137.9	b
3b	164.0	124.3	65.1	111.4	14.2	143.8	129.2	27.5	134.4	140.4
3c	163.9	124.1	65.1	110.1	14.3	143.6	129.3	26.9	129.0	135.5
3d	163.9	124.3	64.8	112.4[c]	14.2	143.3	129.1	27.0	133.4[d]	139.3[d]
3e	164.8	125.2	65.4	115.0	14.7	144.1	130.0	28.5	141.3[e]	147.2[f]
3f	163.9	124.2	64.5	113.4	14.8	143.2	129.0	27.1	136.3	142.2
3g	164.0	124.2	63.2	117.3	12.2	144.0	130.2	21.1	134.1	136.9
peroxide	4 >C=O	CO_2	4 α-CH_2	5 α-CH_2	9 α-CH_2	7 C_{ipso}	10 C-Cl	9 β-CH_2	4 γ-C_1	9 γ-C_1
				Solvent: Hexachloroacetone						
3a	164.0	124.5	65.0	113.0	43.5	143.3	134.9	38.8	137.3	137.8
3b	163.9	124.4	65.1	112.0	43.7	143.3	134.0	38.4	134.8	134.6
3c	163.8	124.3	65.1	110.9	43.7	143.3	134.7	37.9	129.2	129.8
3d	163.8	124.4	64.8	113.0[g]	43.5	142.9	134.9	37.9	133.0[h]	133.4[h]
3e	164.9	124.9	65.5	115.6	44.0	143.9	134.9	37.4	140.8[e]	139.8[c]
3f	163.7	124.3	64.5	113.7	43.1	142.6	134.8	37.9	136.7	136.1
3g	164.0	124.4	63.4	117.9	41.7	143.8	134.8	34.9	130.1	131.1
sign of polarization[j]	A	E	A	A	E	E	A	A	A	E

[a] All chemical shifts are in ppm with respect to external Me_4Si. [b] Not observed. [c] $^6J_{C-F} = 2.2$ Hz. [d] $^4J_{C-F} = 2.0$ Hz. [e] $^3J_{C-F} = 7.7$ Hz. [f] $^3J_{C-F} = 7.3$ Hz. [g] $^6J_{C-F} = 1.9$ Hz. [h] $^4J_{C-F} = 2.4$ Hz. [i] $^3J_{C-F} = 7.5$ Hz. [j] A, absorption; E, emission.

Extending our interest in ω-arylalkyl cations,[1] the objective of our present work was to examine the nature of ω-arylalkyl radicals, generated by the thermolysis of aroyl(acyl) ω-arylalkanoyl peroxides, through ^{13}C CIDNP investigation.

Results and Discussion

(a) Thermolysis of β-Arylpropionyl *m*-Chlorobenzoyl Peroxides. Thermolyses of the β-arylpropionyl *m*-chlorobenzoyl peroxides (**3a–g**) were carried out at 100 °C in cyclohexanone or hexachloroacetone inside the probe of a Varian FT-80 NMR spectrometer. The resulting ^{13}C CIDNP spectra showed polarizations in the carbons indicated by an asterisk in Scheme I.

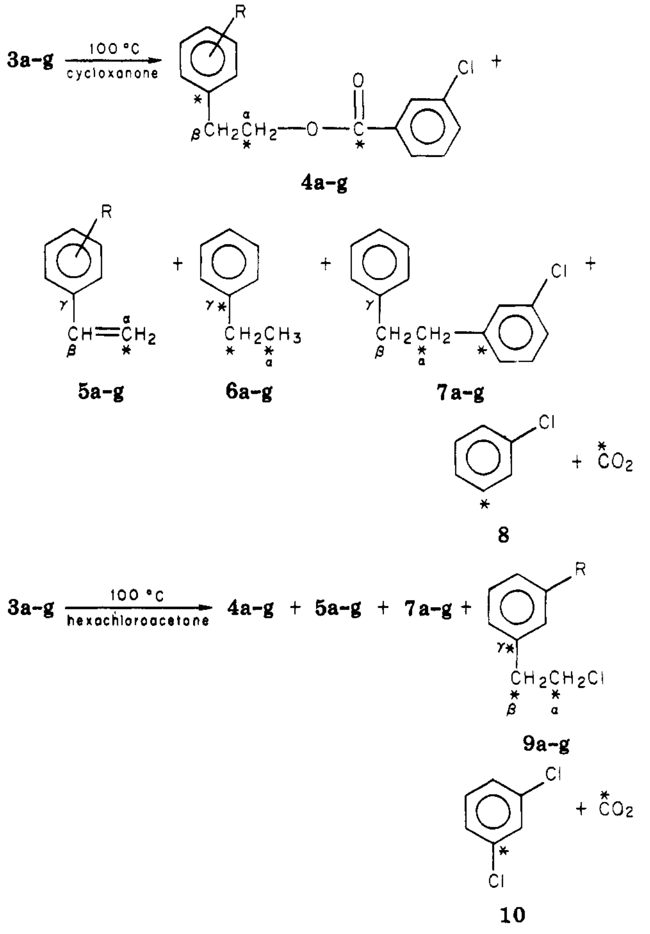


3a, R = H
b, R = *p*-CH_3
c, R = *p*-OCH_3
d, R = *p*-F
e, R = *m*-F
f, R = *p*-Cl
g, R = 2,4,6-$(CH_3)_3$

All the signals were identified by comparison with the ^{13}C spectra of authentic samples[10] or with literature data.[11] The signs of these polarized signals are as predicted by Kaptein's rules.[12] The chemical shifts and signs of these polarized signals are listed in Table I.

All the polarized signals identified in these thermolyses could be explained through the intermediacy of the radical pairs **12** + **13** and **12** + **14** as shown in Scheme II.

Scheme I



The radical pair **12** + **13** (Scheme II) recombines to form the ester **4** with enhanced polarization of the alkoxyl carbon and the carbonyl carbon. Substituted styrenes (**5**) with enhanced polarization of the CH_2 carbon are also produced in the solvent cage. Complementary polarizations are observed in the methyl carbon of arylethanes (**6**, in cyclohexanone) and in the α-methylene carbon of β-arylethyl chlorides (**9**, in hexachloroacetone). A polarized

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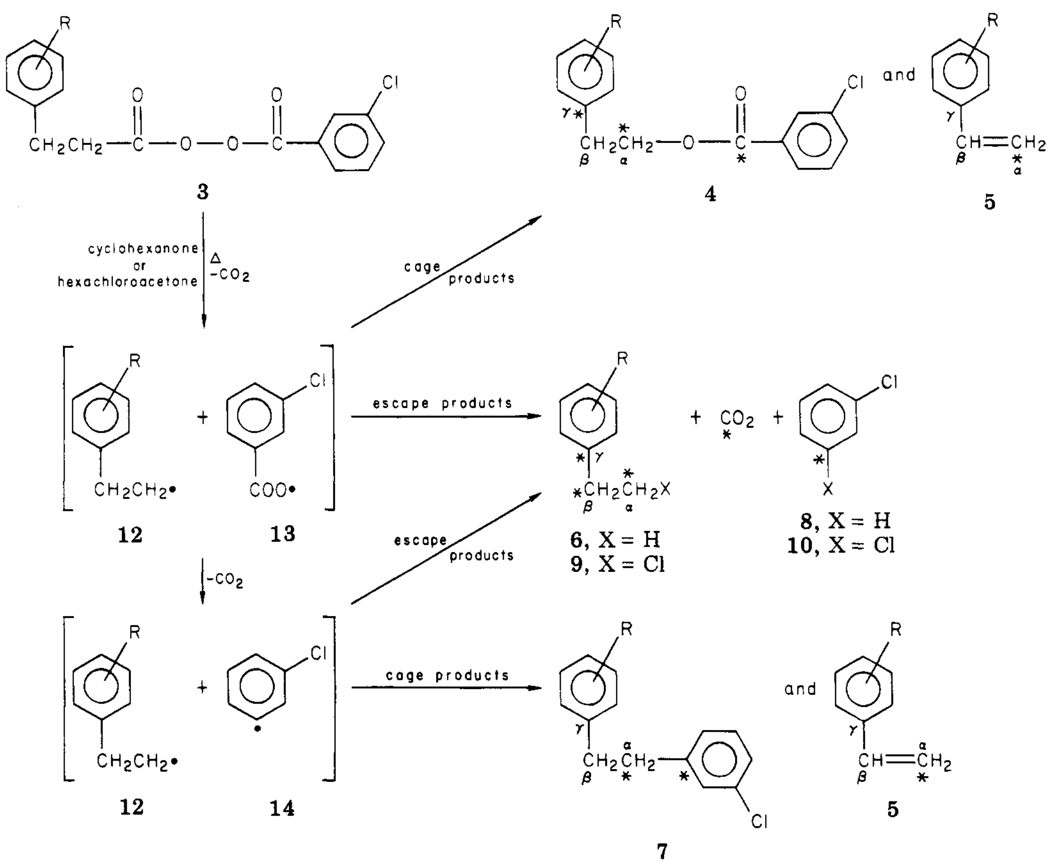
[10] The chemical shifts of the polarized signals agree with the chemical shifts of the corresponding carbons in the authentic samples within 1 ppm.

[11] Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972.

[12] Kaptein, R. *J. Chem. Soc., Chem. Commun.* 1971, 732.

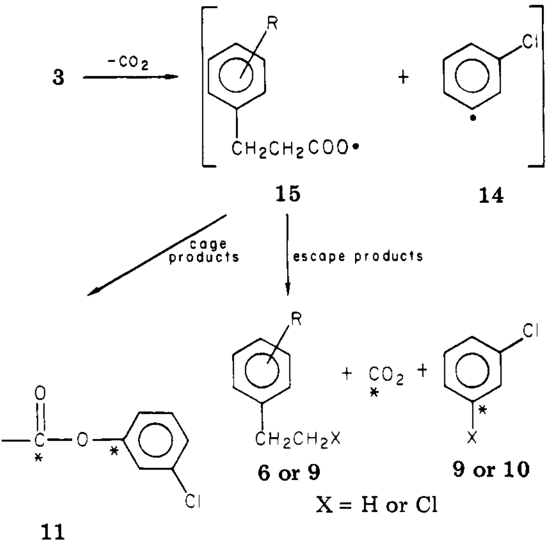
Scheme II



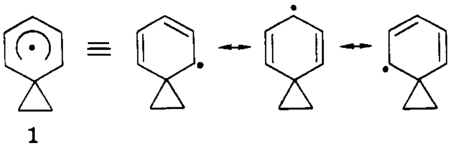
CO_2 signal is also observed at ~124 ppm complementary to the ester carbonyl polarization. The enhanced emission observed in the ipso carbon of 7 and the complementary enhanced absorption observed in the meta carbon of chlorobenzene (in cyclohexanone) and the ipso carbon of *m*-dichlorobenzene (in hexachloroacetone) is indicative of the "cooperative effect"[13-17] of the primary radical pair, **12** + **13**, and the secondary radical pair, **12** + **14** (formed by the loss of CO_2 from the primary radical pair, **12** + **13**). A small degree of polarization is also observed in the methylene carbon of **7** due to the cooperative effect of **12** + **13** and **12** + **14**. The sign of this polarization is complementary to that observed in arylethyl chlorides and in arylethanes (Table I).

During the thermolysis of **3c** and **3f** in hexachloroacetone, we observed a small degree of polarization on the carbon atoms indicated in **11**. This could be explained through the intermediacy of the radical pair **15** + **14** (Scheme III). However, the polarization factors induced on the carbon atoms in **11** are extremely low in comparison to the other signals. This may be due to very low concentration of this radical pair (**14** + **15**) even in these two cases. Moreover, these polarizations were not observed in any other thermolysis we studied. The absence of this radical pair (**14** + **15**) in all these thermolyses (except in that of **3c** and **3f** in hexachloroacetone) is not surprising, as one expects the acyloxy radical **15** to decarboxylate much faster than the aroyloxy radical **13**.[18] Thus the concentration of the radical pair **14** + **15** (if at all present) should be very low.

Scheme III



A spirocyclopropylcyclohexadienyl radical of the type **1** would have produced polarization at the ortho and/or para carbon atoms (eq 1). However, no such polarization is observed in our study. Moreover, such a symmetrical intermediate in equilibrium with the open-chain structure would scramble the polarization between the two methy-



(1)

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(14) Schwerzel, R. E.; Lawler, R. G.; Evans, G. T. *Chem. Phys. Lett.* **1974**, *29*, 106.

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(16) Den Hollander, J. A. *Chem. Phys.* **1975**, *10*, 167.

(17) Den Hollander, J. A.; Kaptein, R. *Chem. Phys. Lett.* **1976**, *41*, 257.

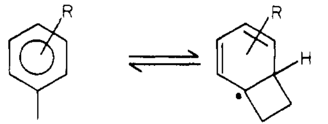
(18) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 102.

lene carbon atoms in **4**–**7** and **9**. But we observed that the benzylic carbon polarization in **6** and **9** is opposite in sign and much less in magnitude when compared to that of the other methylene carbon. This observation is also in accord with the polarization predicted by Kaptein's rule[12] for a carbon atom β to a radical center. Thus, the absence of any scrambling in the methylene polarization in addition to the failure to observe any polarization in the ortho and para carbons rules out the intermediacy of spirocyclopropylcyclohexadienyl radical of the type **1**.

Apart from the polarizations discussed above, we also observed substantial polarization in the ipso carbon of **4** and **6** (or **9**) formed from the radical pair **12** + **13** (Scheme II). The assignment of these polarized signals is based on the comparison with the ^{13}C spectra of authentic samples[10] and on the basis of the magnitude of $J_{\text{C-F}}$ observed in these signals during the thermolysis of **3d** and **3e** (cf. Table I).

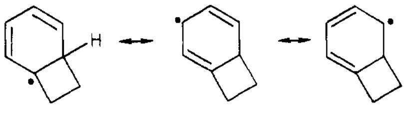
The polarization on the ipso carbon could be explained as arising due to a direct hyperfine coupling between the γ-carbon and the radical center. The hyperfine coupling constant between a γ-carbon and an unpaired electron varies to a large extent depending on the angle between the C_γ–C_β–C_α plane and the orbital carrying the unpaired electron.[19] However, no such data are available for β-phenylethyl radicals.

Alternatively, one could account for this polarization on the ipso carbon by proposing that the β-arylethyl radical is in fast equilibrium with the cyclized dihydrobenzocyclobuten-7-yl radical, **16**. This would explain the substantial polarization observed in the ipso carbon atom. The corresponding dihydrobenzocyclobuten-7-yl cation has been identified in the unimolecular decomposition of β-phenylethyl chloride and *n*-propylbenzene under mass spectral conditions.[20]



12 16

We did not observe any polarized signals due to the products derived directly from **16**, nor did we observe any polarization on the meta carbons as would be expected from the resonance hybrids **16b** and **16c**. It could be argued that even if the equilibrium **12** ⇄ **16** is fast under the NMR experimental conditions, at any instance the relative population of **16** is very low compared to that of **12**, and thus the product observed is essentially through **12** and not from **16**. The absence of polarization in the meta carbon might be due to very limited (if any) contribution of the resonance hybrids **16b** and **16c** to the overall structure of **16**. The resonance hybrid **16a** would be much preferred as the cyclobutane ring is not in the same plane as the six-membered ring, thus avoiding substantial strain. In structures **16b** and **16c** the two rings are forced more toward a single plane due to the sp^2 nature of one of the bridge carbons. Thus **16a** could be the major (if not the only) contributing structure. This explanation for ipso polarization would assume that the conversion of **12** to **16** at this temperature (~100 °C) is much faster than the polarization rate (<10^{-9} s). However, the known rates of cyclization of alkenyl radicals are much slower than this.[21]



16a 16b 16c

A third explanation would be a through-space interaction between the electron at the radical center and the aromatic π system, thus generating a hyperfine coupling between the ring carbon and the unpaired electron.[22] Although the greatest effect would be expected on the ipso carbon due to such an interaction, this would also produce polarization on all the carbon atoms throughout the ring. However, we did not observe polarization on any other ring carbons in our studies.

In order to test these alternate possibilities, we studied thermolysis of γ-arylbutanoyl and δ-arylpentanoyl peroxides. If the ipso polarization in the thermolysis of β-arylpropionyl peroxides is due to the fast equilibrium between the open chain radical **12** and the cyclized radical **16**, one would also expect similar polarization of the ipso carbons in the case of γ-arylpropyl and δ-arylbutyl radicals. Moreover, such cyclizations (although only to a small extent) of γ-arylpropyl radicals to indane and δ-arylbutyl radicals to Tetralin have been observed earlier.[23-25]

(b) Thermolysis of γ-Arylbutanoyl *m*-Chlorobenzoyl and δ-Arylpentanoyl *m*-Chlorobenzoyl Peroxides. We carried out thermolysis of five γ-arylbutanoyl *m*-chlorobenzoyl peroxides (**17a–e**) at ~100 °C in cyclohexanone and hexachloroacetone. All the ^{13}C polarizations observed can be explained through the intermediacy of the radical pairs **18** + **13** and **18** + **14** (Scheme IV). The chemical shifts and signs of the polarized signals are listed in Table II.

Strong polarizations were observed on the α-methylene carbons of γ-arylpropyl m-chlorobenzoates (**19a-e**) and 3-arylpropenes (**20a-e**; both of them being formed inside the cage). Complementary polarizations were observed in the α-carbon of arylpropanes (**21a-e**; in cyclohexanone) and of γ-arylpropyl chlorides (**22a-e**); in hexachloroacetone).

Enhanced absorption was also observed for the carbonyl carbon in **19a-e** with complementary emission in CO_2 signal. Small degrees of β and γ polarizations were also observed. However, no significant polarization was observed in the aromatic carbons. Moreover, we did not observe any polarization corresponding to indane in the aliphatic region.[26] The enhanced emission observed in the ipso carbon of 1-aryl-3-(*m*-chlorophenyl)propanes (**23a–e**, Scheme IV) and the complementary enhanced absorption in the ipso carbon signal of *m*-dichlorobenzene (**10** in hexachloroacetone) and the meta carbon of chlorobenzene (**8**, in cyclohexanone) are again indicative of the cooperative effect[13-17] of the primary radical pair, **18** + **13**, and the secondary radical pair, **18** + **14** (formed by the loss of CO_2 from the primary radical pair, **18** + **13**).

The ^{13}C polarizations observed during the thermolysis of four δ-arylpentanoyl *m*-chlorobenzoyl peroxides (**24a–d**)

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(20) Mclafferty, F. W.; Koppel, C. *J. Am. Chem. Soc.* **1976**, *98*, 8293.

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(22) This was suggested by one of the referees in the earlier version of this paper as a possible alternative.

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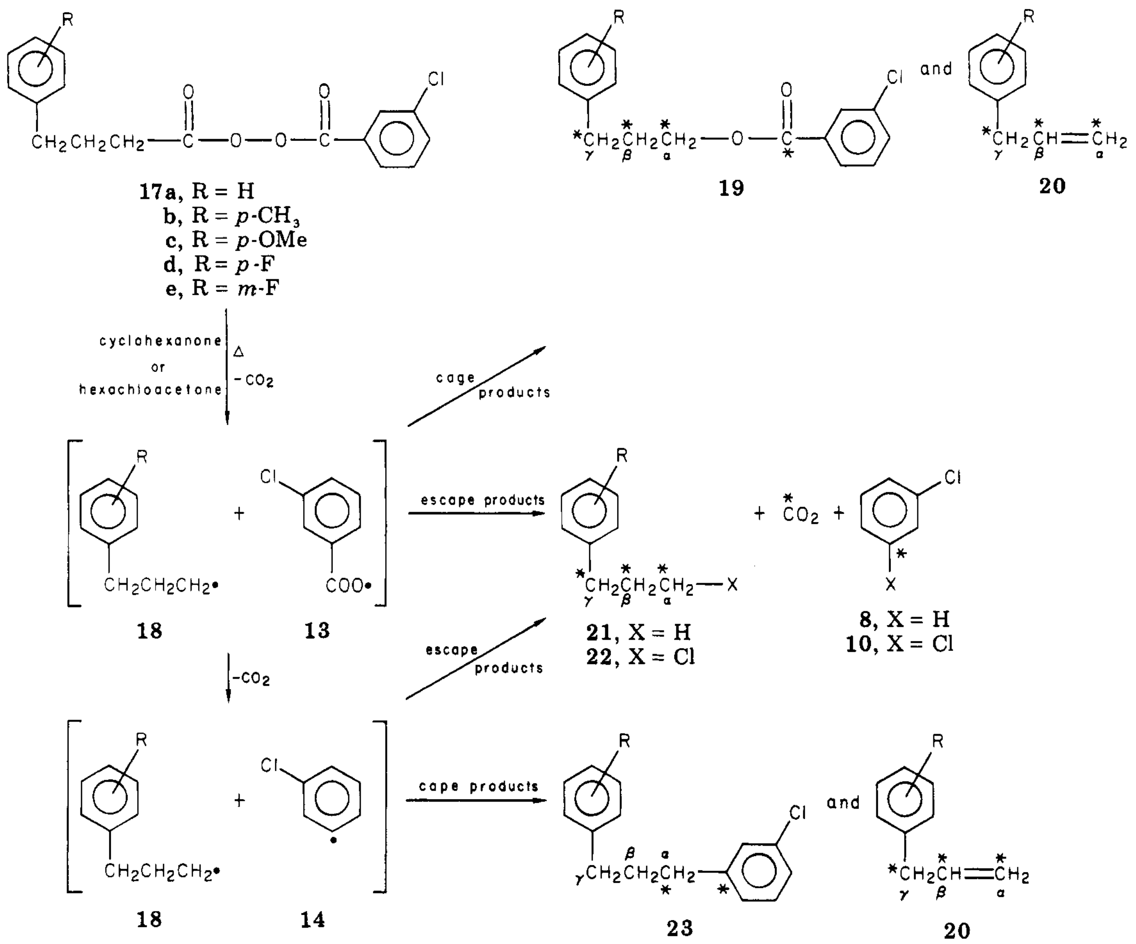
(24) Bunyan, P. J.; Hey, D. H. *J. Chem. Soc.* **1962**, 1360. However, no such cyclization to Tetralin was observed by Evans and Whally (Evans, E. A.; Whally, M. *Ibid.* **1954**, 3642) under the same conditions.

(25) Pines, H.; Sih, N. C.; Rosenfield, D. B. *J. Org. Chem.* **1966**, *31*, 2255.

(26) The α-carbon in indane resonates at 33.6 ppm.[11] Although we observed a signal ~33 ppm in hexachloroacetone solvent, it cannot be attributed to indane, as we do not observe any polarized signals around 33 ppm in cyclohexanone solvent at the same temperature.

Scheme IV



Scheme V

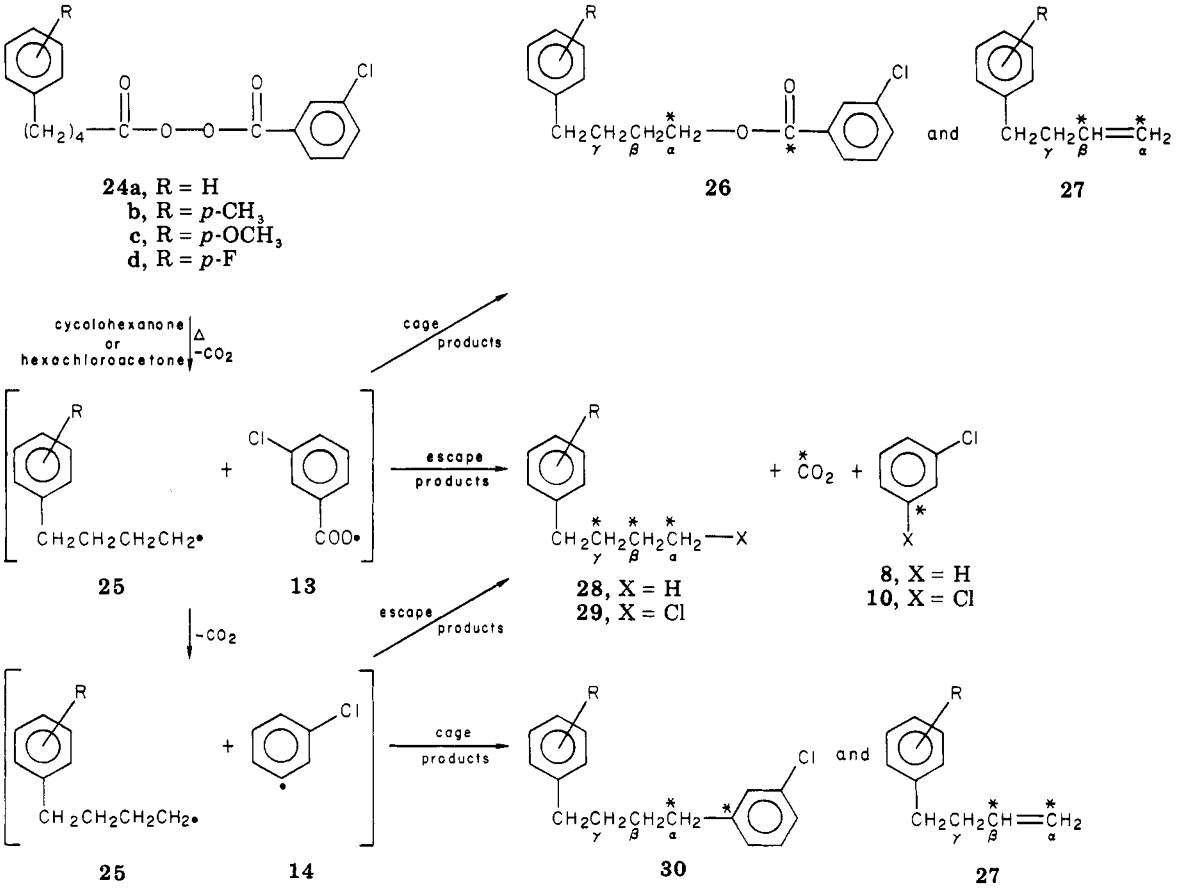


Table II. ^{13}C NMR Chemical Shifts[a] of Polarized Signals during the Thermolysis of γ-Arylbutanoyl *m*-Chlorobenzoyl Peroxide at ~100 °C

peroxide	19 >C=O	CO_2	19 α-CH_2	20 α-CH_2	21 α-CH_3	23 C_{ipso}	8 C_m	23 α-CH_2	19 β-CH_2	20 β-CH	21 β-CH_2	19 γ-CH_2	20 γ-CH_2	21 γ-CH_2
Solvent: Cyclohexanone														
17a	164.6	124.8	64.6	114.9	12.9	144.7	129.7	34.8	30.1	137.4	23.9	*b*	39.8	37.7
17b	164.9	125.1	64.9	114.8	13.2	145.0	130.0	35.0	*b*	*b*	24.1	*b*	39.0	37.5
17c	164.8	125.1	64.9	114.4	13.1	145.0	129.9	34.9	*b*	136.0	24.3	*b*	39.1	37.1
17d	165.0	125.3	64.9	115.4	13.2	144.9	130.0	35.1	30.5	137.6	24.3	31.7	39.2	37.2
17e	164.9	125.2	64.8	115.8	13.2	144.8	130.0	35.0	30.1	137.0	23.9	32.2	39.7	37.7
	19 >C=O	CO_2	19 α-CH_2	20 α-CH_2	22 α-CH_2	23 C_{ipso}	10 C-Cl	23 α-CH_2	19 β-CH_2	20 β-CH	22 β-CH_2	19 γ-CH_2	20 γ-CH_2	22 γ-CH_2
Solvent: Hexachloroacetone														
17a	164.5	125.1	64.7	115.7	43.6	144.7	135.4	35.2	*b*	137.4	34.1	*b*	40.1	33.1
17b	164.8	125.3	65.0	115.7	43.8	144.7	135.7	35.4	30.6	137.9	34.4	*b*	39.9	32.9
17c	164.8	125.3	65.1	115.7	44.0	144.8	135.8	35.5	*b*	138.2	34.7	*b*	39.0	32.5
17d	164.9	125.4	64.9	116.3	43.8	144.5	135.7	35.5	30.7	137.5	34.5	32.1	39.6	32.6
17e	164.9	125.4	64.9	116.7	43.7	144.4	135.8	35.5	30.4	136.8	34.1	31.7	40.1	33.2
sign of polarization[c]	A	E	A	A	E	E	A	A	E	E	A	A	A	E

[a] All chemical shifts are in ppm with respect to external Me_4Si. [b] Not observed. [c] A, absorption; E, emission.

Table III. ^{13}C NMR Chemical Shifts[a] of Polarized Signals during the Thermolysis of δ-Arylpentanoyl *m*-Chlorobenzoyl Peroxide at ~100 °C

peroxide	26 >C=O	CO_2	26 α-CH_2	27 α-CH_2	28 α-CH_3	30 C_{ipso}	8 C_m	30 α-CH_2	28 β-CH_2	28 γ-CH	27 β-CH
Solvent: Cyclohexanone											
24a	164.6	125.4	65.0	114.2	13.1	144.9	129.7	35.1	21.9	33.1	137.9
24b	164.9	125.2	65.3	114.4	13.4	145.3	130.0	35.2	22.2	33.6	138.4
24c	164.8	125.1	65.3	114.3	13.3	145.1	129.9	35.2	22.1	33.6	138.3
24d	164.8	125.2	65.3	114.8	13.5	145.2	130.1	35.4	22.2	33.5	138.1
	26 >C=O	CO_2	26 α-CH_2	27 α-CH_2	29 α-CH_2	30 C_{ipso}	10 C-Cl	30 α-CH_2	29 β-CH_2	29 γ-CH_2	27 β-CH
Solvent: Hexachloroacetone											
24a	164.6	125.0	65.1	114.1	44.2	144.5	135.4	35.3	32.3	28.4	137.9
24b	164.8	125.3	65.4	115.2	44.4	144.8	135.7	35.8	32.6	28.8	138.4
24c	164.8	125.3	65.3	115.1	44.3	144.8	135.7	35.7	32.5	28.8	138.3
24d	165.0	125.4	65.3	115.6	44.3	144.8	135.9	35.8	32.6	28.9	137.9
sign of polarization[b]	A	E	A	A	E	E	A	A	A	E	E

[a] All chemical shifts are in ppm with respect to external Me_4Si. [b] A, absorption; E, emission.

Table IV. ^{13}C NMR Chemical Shifts[a] of Polarized Signals during the Thermolysis of Acetyl β-Arylpropionyl Peroxide at ~100 °C

peroxide	21 Me	CH_4	21 α-CH_2	6 α-CH_3	21 β-CH_2	6 β-CH_2	21 γ-C_1	6 γ-C_1
Solvent: Cyclohexanone								
31a	13.5	−5.4	24.4	14.1	38.3	28.9	142.9	144.6
31f	13.4	−5.5	24.2	14.3	37.5	28.4	141.3	144.9
sign of polarization[b]	E	A	A	E	E	A	A	E

[a] All chemical shifts are in ppm with respect to external Me_4Si. [b] A, absorption; E, emission.

can be accounted for through the intermediacy of the radical pairs, **25** + **13** and **25** + **14** (Scheme V). Table III lists the chemical shifts and the signs of these plarized signals.

As in the previous cases major polarizations were those of the α-carbons of **26–30a–d**. Small degrees of β and γ polarizations were also observed. No significant polarizations in the aromatic carbons were observed as would be expected from a cyclized intermediate leading to Tetralin. Moreover, a polarized Tetralin signal (~30 ppm)[11] was not observed in any of these thermolyses. The absence of cyclization in δ-arylbutyl radical is also in line with the earlier ESR results.[6]

(c) Thermolysis of Acetyl ω-Arylalkanoyl Peroxides. We also carried out thermolysis (at ~100 °C) of the acetyl peroxides **31a,f** in cyclohexanone, of **32a,b,d,e** in hexachloroacetone and in cyclohexanone, and of **33a,b,d** in hexachloroacetone and in cyclohexanone. The results are summarized in Scheme VI and in Tables IV–VI. As in the case of *m*-chlorobenzoyl peroxide (**3**, **17**, and **24**) decompositions, the major polarizations were in the α-carbon atoms. Small degree of β and γ polarizations were also observed. The only aromatic polarization observed in the thermolysis of **31** is on the ipso carbon of **21** and **6**. All these polarizations could be explained by the intermediacy of the radical pair $Ar(CH_2)_nCH_2\cdot + \cdot CH_3$ (where n = 1–3).

The absence of any polarization in the aromatic carbons during the thermolysis of γ-arylbutanoyl and δ-arylpentanoyl peroxides strongly argues against the interme-

Table V. ^{13}C NMR Chemical Shifts[a] of Polarized Signals during the Thermolysis of Acetyl γ-Arylbutanoyl Peroxide at ~100 °C

peroxide	28 Me	CH_4	28 α-CH_2	21 α-CH_3	28 β-CH_2	21 β-CH_2	28 γ-CH_2	21 γ-CH_2
			Solvent: Cyclohexanone					
32a	13.3[c]	*b*	22.3	13.3[c]	33.5	24.2	35.7	38.2
32b	13.3[c]	−5.7	22.2	13.3[c]	33.6	26.6	35.1	37.7
32d	13.2[c]	−5.0	22.2	13.2[c]	33.6	24.3	34.7	37.2
32e	13.1[c]	*b*	22.2	13.1[c]	33.2	23.9	35.2	37.7
	28 Me	CH_3Cl	28 α-CH_2	22 α-CH_2	28 β-CH_2	22 β-CH_2	28 γ-CH_2	22 γ-CH_2
			Solvent: Hexachloroacetone					
32a	13.9	*b*	22.4	43.8	*b*	34.3	35.9	33.5
32b	14.1	25.1	22.5	44.0	33.0	34.5	35.5	33.7
32d	13.9	25.0	22.4	43.7	32.7	34.5	35.1	33.6
32e	13.9	25.0	22.5	43.7	*b*	34.1	35.7	33.3
sign of polarization[d]	E	A	A	E	E	A	A	E

[a] All chemical shifts are in ppm with respect to external Me_4Si. [b] Not observed. [c] Resolved only in two cases, **32a** and **32d**. [d] A, absorption; E, emission.

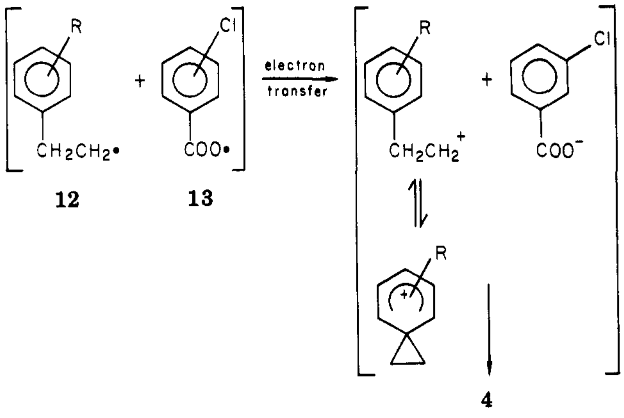
Table VI. ^{13}C NMR Chemical Shifts[a] of Polarized Signals during the Thermolysis of Acetyl δ-Arylpentanoyl Peroxides at ~100 °C

peroxide	34 Me	CH_4	34 α-CH_2	'28 α-CH_3	34 β-CH_2	28 β-CH_2	34 γ-CH_2	28 γ-CH_2
			Solvent: Cyclohexanone					
33a	13.5[c]	−5.6	22.4[c]	13.5[c]	31.6	22.4[c]	30.9	33.4
33b	13.4[c]	−5.6	22.4[c]	13.4[c]	31.5	22.4[c]	31.0	33.6
33d	13.4[c]	−5.6	22.4[c]	13.4[c]	31.5	22.4[c]	31.0	*b*
	34 Me	CH_3Cl	34 α-CH_2	29 α-CH_2	34 β-CH_2	29 β-CH_2	34 γ-CH_2	29 γ-CH_2
			Solvent: Hexachloroacetone					
33a	14.1	*b*	22.7	44.4	31.8	32.7	31.0	28.8
33b	14.1	25.1	22.7	44.4	31.9	32.7	31.1	28.8
33d	14.2	25.2	22.7	44.4	31.8	32.6	31.2	28.9
sign of polarization[d]	E	A	A	E	E	A	A	E

[a] All chemical shifts are in ppm with respect to external Me_4Si. [b] Not observed. [c] Not resolved. [d] A, absorption; E, emission.

diacy of cyclized dihydrobenzocyclobuten-7-yl radicals in β-arylpropionyl peroxide decomposition. Moreover, γ-polarizations were observed in γ-arylpropyl and δ-arylbutyl radicals, indicating that the ipso polarization in the β-arylethyl radical is due to direct hyperfine interaction of the γ-carbon with the unpaired electron.

The mechanism of diacyl peroxide decomposition itself has been extensively studied recently.[27-34] It has long been known that mixed diacyl peroxides decompose thermally by both polar and radical pathways. Walling et al.[28] recently proposed a mechanism that combines the radical and the polar routes. Lawler et al.[29] reported CIDNP evidence for an electron-transfer process between neopentyl and *m*-chlorobenzoyloxy radicals (generated by the thermolysis of *tert*-butylacetyl *m*-chlorobenzoyl peroxide), producing *m*-chlorobenzoate anion and an incipient neopentyl cation that subsequently rearranges to the *tert*-amyl cation. A similar electron-transfer process between **12** and **13** would produce a β-arylethyl cation and a *m*-chlorobenzoate anion. It is well established that the β-arylethyl cation has a symmetrical ethylenebenzenium ion structure.[1] If the ester **4** (cage recombination product in the thermolysis of **3**) is formed by rapid collapse of the ion pair produced after such an electron transfer, one would expect the polarization on the α-carbon atom in **12** to be scrambled between the two methylene carbons in the spiro cation and also in the product ester, **4**. However, as has been pointed out earlier, such scrambling of polarization is not



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[27] For a recent review, see: Hiatt, R. In "Organic Peroxides"; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Vol. 2, p 799.

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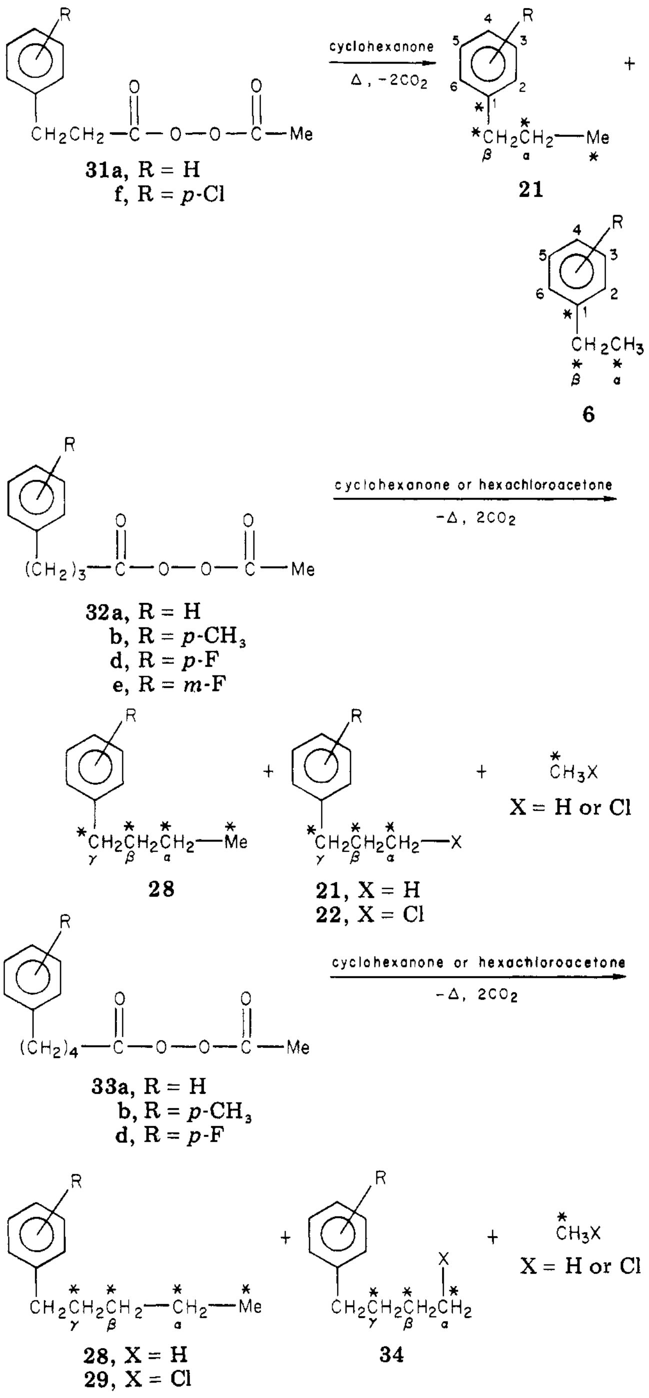
Scheme VI



observed in our study, indicating that there is no electron transfer between **12** and **13**.

In summary, our results indicate no cyclization of β-arylethyl radicals to spirocyclopropylcyclohexadienyl radicals. All the three arylalkyl radicals studied exist essentially in their open-chain form.

Experimental Section

All the peroxides used in this study were prepared from the corresponding arylalkanoic acids as described in the subsequent general procedures. β-Phenylpropionic acid (Pfaltz and Bauer Inc.), β-(p-tolyl)propionic acid (Pfaltz and Bauer Inc.), β-(p-chlorophenyl)propionic acid (Pfaltz and Bauer Inc.), γ-phenylbutanoic acid (Aldrich Chemical Co.), and δ-phenylpentanoic acid (Aldrich Chemical Co.) are commercially available and were used as such. Other β-arylpropionic acids were prepared by the sequence

$$\mathrm{ArCH_2CH_2OH} \xrightarrow{\mathrm{SOCl_2/py}} \mathrm{ArCH_2CH_2Cl} \xrightarrow[\mathrm{(2)\ CO_2}]{\mathrm{(1)\ Mg/THF}} \mathrm{ArCH_2CH_2COOH}$$

γ-Arylbutanoic acids[35] were prepared by the sequence

$$\mathrm{ArH} \xrightarrow{\overline{\mathrm{C(O)CH_2CH_2C(O)O}}/\mathrm{AlCl_3}} \mathrm{ArC(O)CH_2CH_2COOH} \xrightarrow[\mathrm{HCl}]{\mathrm{Zn/Hg}} \mathrm{ArCH_2CH_2CH_2COOH}$$

δ-Arylpentanoic acids were prepared by the sequence

$$\mathrm{ArCH_2CH_2Cl} \xrightarrow[\mathrm{(2)\ \underline{CH_2CH_2O}}]{\mathrm{(1)\ Mg/THF}} \mathrm{Ar(CH_2)_4OH} \rightarrow\ \rightarrow \mathrm{Ar(CH_2)_4COOH}$$

These syntheses involve standard literature procedure for individual steps. β-Arylethanols were in turn prepared from the reaction of the corresponding aryl Grignard reagents with ethylene oxide. m-Chloroperbenzoic acid (Aldrich Chemical Co.) and 70% peracetic acid (Pfaltz and Bauer Inc.) are commercially available and were used as such. All the compounds gave satisfactory ^{13}C and/or ^{1}H NMR spectral data. The NMR spectra were recorded by using a Varian XL-200 NMR spectrometer. All CIDNP studies were performed in the variable-temperature probe of a Varian FT-80 NMR spectrometer equipped with a Sykes Flexidisk accessory.

General Procedure for the Conversion of Arylalkanoic Acids to the Acid Chlorides. A solution of 5 g of arylalkanoic acid in 25 mL of dry ether was refluxed with 5 mL of thionyl chloride under N_2 atmosphere for 12 h with constant stirring. Ether and the excess thionyl chloride were then distilled off at atmospheric pressure, and the last traces were removed at low pressure. The product acid chloride was distilled at ~2 torr with a fractionating column. The yields of the acid chlorides were 70–80%. The products were then analyzed by ^{13}C NMR spectroscopy.

General Procedure for the Reaction of Arylalkanoyl Chloride with Peracids. To a stirred solution of 10 mmol of arylalkanoyl chloride in dry ether or in dry CH_2Cl_2 was added 12 mmol of the peracid (peracetic or m-chloroperbenzoic acid) under N_2 atmosphere. The solution was cooled in an ice bath, and 2 mL of pyridine in 10 mL of dry ether or CH_2Cl_2 was added dropwise at such a rate that the reaction temperature does not rise above 5 °C. The mixture was then stirred for 30 min at 0 °C followed by 2 h at 25 °C. The precipitated pyridinium chloride was dissolved in cold water and the organic layer separated from the aqueous layer. It was then washed consecutively with 10% HCl, saturated $NaHCO_3$, and brine solution and dried over anhydrous sodium sulfate. The solvent was removed under vacuum at room temperature and the product analyzed by ^{13}C NMR spectroscopy. The peroxides (obtained in 80–90% yield) were essentially pure and used as such in the thermolysis. The ^{13}C NMR chemical shift data (ppm with respect to Me_4Si) of all the peroxides prepared in this study are as follows. **3a**: 168.3, 161.8, 139.2, 135.0, 134.3, 130.2, 129.7, 128.7, 128.3, 127.8, 127.2, 126.7, 31.7, 30.7. **3b**: 168.3, 162.4, 136.2, 135.0, 134.3, 133.3, 130.2, 130.1, 129.6, 129.3, 128.1, 127.7, 31.7, 30.2, 21.0. **3c**: 168.3, 162.6, 158.3, 135.0, 134.3, 131.2, 130.1, 129.6, 129.2, 127.7, 127.2, 114.0, 55.2, 31.9, 29.8. **3d**:[36] 168.1, 162.8 (J = 245.0 Hz), 162.1, 135.0, 134.8 (J = 3.8 Hz), 134.3, 130.1, 129.7 (J = 7.4 Hz), 129.6, 127.7, 127.1, 115.4 (J = 20.9 Hz), 31.7, 29.8. **3e**:[36] 167.9, 162.7 (J = 246.0 Hz), 161.7, 141.5 (J = 7.2 Hz), 134.9, 134.2, 130.1 (J = 8.4 Hz), 130.0, 129.6, 127.7, 127.0, 123.8 (J = 3.0 Hz), 115.2 (J = 20.8 Hz), 113.5 (J = 20.7 Hz), 31.2, 30.2. **3f**: 168.0, 161.7, 137.6, 135.0, 134.3, 132.5, 130.1, 129.7, 129.6, 128.8, 127.7, 127.1, 31.4, 29.9. **3g**: 168.4, 161.9, 136.0, 135.0, 134.3, 132.8, 130.1, 129.7, 129.1, 127.8, 127.7, 127.2, 29.2, 24.6, 20.8, 19.6. **17a**: 168.9, 161.9, 140.6, 135.0, 134.3, 130.2, 129.7, 128.5, 128.5, 127.8, 127.2, 126.2, 34.7, 29.2, 26.4. **17b**: 168.8, 161.8, 137.5, 135.6, 134.9, 134.2, 130.1, 129.6, 129.1, 128.4, 127.7, 127.2, 34.2, 29.1, 26.5, 20.9. **17c**: 168.8, 161.7, 157.6, 134.8, 134.2, 132.5, 130.1, 129.5, 129.3, 127.6, 127.2, 113.8, 55.1, 33.7, 28.9, 26.6.

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[35] γ-(m-Fluorophenyl)butanoic acid was prepared by the sequence

$$\mathrm{ArCH_2CH_2COOH} \xrightarrow{\mathrm{LAH/Et_2O}} \mathrm{ArCH_2CH_2CH_2OH} \rightarrow\ \rightarrow \mathrm{Ar(CH_2)_3COOH}$$

[36] Values in parentheses are ^{13}C–^{19}F coupling constants in hertz.

17d:[36] 168.7, 161.8, 161.4 (J = 245.0 Hz), 136.2, 134.9, 134.3, 130.1, 129.7 (J = 8.4 Hz), 129.6, 127.7, 127.1, 115.2 (J = 22.0 Hz), 33.8, 29.0, 26.5. **17e:**[36] 168.6, 162.7, (J = 245.0 Hz), 161.7, 143.0 (J = 7.5 Hz), 134.9, 134.2, 130.0, 129.7 (J = 8.6 Hz), 129.5, 127.6, 127.1, 124.0 (J = 2.4 Hz), 115.2 (J = 20.7 Hz), 113.0 (J = 20.7 Hz), 34.2 (J = 2.5 Hz), 28.9, 25.9. **24a**: 168.9, 161.9, 141.7, 135.0, 134.3, 130.2, 129.7, 128.4, 128.3, 127.8, 127.3, 125.9, 35.4, 30.6, 29.8, 24.4. **24b**: 168.8, 161.7, 138.4, 135.2, 134.9, 134.1, 130.1, 129.6, 128.9, 128.1, 127.7, 127.1, 34.7, 30.5, 29.8, 24.3, 20.8. **24c**: 168.8, 161.7, 157.6, 134.8, 134.1, 133.7, 130.0, 129.5, 129.1, 127.6, 127.1, 113.6, 55.1, 34.3, 30.7, 29.7, 24.2. **24d:**[36] 169.0, 161.9, 161.1 (J = 247.0 Hz), 137.2 (J = 2.4 Hz), 135.1, 134.4, 130.3, 129.5 (J = 7.5 Hz), 129.3, 127.7, 127.1, 115.8 (J = 22.0 Hz), 34.4, 30.4, 29.8, 24.2. **31a**: 168.3, 166.0, 139.2, 128.6, 128.2, 126.6, 31.5, 30.5, 16.4. **31f**: 168.2, 166.1, 137.7, 132.5, 129.6, 128.7, 31.4, 29.9, 16.5. **32a**: 168.8, 166.0, 140.5, 128.3, 128.3, 126.0, 34.7, 28.9, 26.2, 16.3. **32b**: 168.9, 166.0, 137.5, 135.6, 129.9, 128.3, 34.2, 29.1, 28.4, 20.9, 16.4. **32d:**[36] 168.8, 166.0, 161.3 (J = 242.8 Hz), 136.2, 129.8 (J = 7.4 Hz), 115.1 (J = 21.7 Hz), 33.7, 28.9, 26.4, 16.4. **32e:**[36] 168.6, 165.9, 162.7 (J = 237.3 Hz), 143.1 (J = 7.3 Hz) 129.7 (J = 7.4 Hz), 124.0 (J = 2.5 Hz), 115.1 (J = 20.8 Hz), 112.8 (J = 20.7 Hz), 34.1, 28.8, 25.9, 16.2. **33a**: 169.0, 165.9, 141.5, 128.1, 128.1, 125.7, 35.1, 30.4, 29.6, 24.2, 16.4. **33b**: 168.9, 166.0, 138.5, 135.1, 128.9, 128.0, 34.7, 30.5, 29.7, 24.2, 20.8, 16.4. **33d:**[36] 168.9, 166.1, 164.6 (J = 245.0 Hz), 137.2, 129.7 (J = 7.4 Hz), 114.9 (J = 20.8 Hz), 34.4, 30.5, 29.7, 24.2, 16.5.

General Procedure for ^{13}C CIDNP Studies. Neat cyclohexanone or hexachloroacetone ($\sim$1.0 mL) in an NMR tube was preheated to $\sim$100 °C inside the probe of a Varian FT-80 NMR spectrometer. A concentrated solution (or a slurry) of $\sim$250 mg of the peroxide in the same solvent was added *all at once* into the NMR tube. The lock was held externally and each FID was time averaged for 20 (90° flip angle) consecutive pulses with 0.8 s of acquisition time per pulse. Ten consecutive FID's were stored in a Sykes Flexidisk Accessory. The FID's were Fourier transformed at the end of the reaction and plotted. Each experiment was approximately 5 min in length. However, polarized signals were observed only for about 1–2 min. The identity of the signals were established by comparison with the spectra of authentic samples[10] or with literature data.[11]

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Registry No. **3a**, 84648-15-7; **3b**, 84648-16-8; **3c**, 84648-17-9; **3d**, 84648-18-0; **3e**, 84648-19-1; **3f**, 84648-20-4; **3g**, 84648-21-5; **4a**, 84648-22-6; **4b**, 84648-23-7; **4c**, 84648-24-8; **4d**, 84648-25-9; **4e**, 84648-26-0; **4f**, 84648-27-1; **4g**, 84648-28-2; **5a**, 100-42-5; **5b**, 622-97-9; **5c**, 637-69-4; **5d**, 405-99-2; **5e**, 350-51-6; **5f**, 1073-67-2; **5g**, 769-25-5; **6a**, 100-41-4; **6b**, 622-96-8; **6c**, 1515-95-3; **6d**, 459-47-2; **6e**, 696-39-9; **6f**, 622-98-0; **6g**, 3982-67-0; **7a**, 34176-92-6; **7b**, 84648-29-3; **7c**, 84648-30-6; **7d**, 24941-75-1; **7e**, 84648-31-7; **7f**, 84648-32-8; **7g**, 84648-33-9; 8, 108-90-7; **9a**, 622-24-2; **9b**, 32327-68-7; **9c**, 18217-00-0; **9d**, 332-43-4; **9e**, 41037-51-8; **9f**, 32327-70-1; **9g**, 25692-16-4; **10**, 541-73-1; **17a**, 84648-34-0; **17b**, 84648-35-1; **17c**, 84648-36-2; **17d**, 84648-37-3; **17e**, 84680-82-0; **19a**, 84648-38-4; **19b**, 84648-39-5; **19c**, 84648-40-8; **19d**, 84648-41-9; **19e**, 84648-42-0; **20a**, 300-57-2; **20b**, 3333-13-9; **20c**, 140-67-0; **20d**, 1737-16-2; **20e**, 30984-53-3; **21a**, 103-65-1; **21b**, 1074-55-1; **21c**, 104-45-0; **21d**, 405-64-1; **21e**, 28593-12-6; **22a**, 104-52-9; **22b**, 77975-31-6; **22c**, 59623-12-0; **22d**, 64747-82-6; **22e**, 84648-43-1; **23a**, 84648-44-2; **23b**, 84648-45-3; **23c**, 84648-46-4; **23d**, 84648-47-5; **23e**, 84648-48-6; **24a**, 84648-49-7; **24b**, 84648-50-0; **24c**, 84648-51-1; **24d**, 84648-52-2; **26a**, 84648-53-3; **26b**, 84648-54-4; **26c**, 84648-55-5; **26d**, 84648-56-6; **27a**, 768-56-9; **27b**, 20574-99-6; **27c**, 20574-98-5; **27d**, 2248-13-7; **28a**, 104-51-8; **28b**, 1595-05-7; **28c**, 18272-84-9; **28d**, 20651-65-4; **29a**, 4830-93-7; **29b**, 84648-57-7; **29c**, 23002-61-1; **29d**, 54540-58-8; **30a**, 84648-58-8; **30b**, 84648-59-9; **30c**, 84648-60-2; **30d**, 84648-61-3; **31a**, 84648-62-4; **31f**, 84648-63-5; **32a**, 84648-64-6; **32b**, 84648-65-7; **32d**, 84648-66-8; **32e**, 84648-67-9; **33a**, 84648-68-0; **33b**, 84648-69-1; **33d**, 84648-70-4; **34a**, 538-68-1; **34b**, 1595-09-1; **34d**, 28593-14-8.

Solid-State Chemistry, Kinetics, and Electron Spin Resonance Spectroscopy of 2-Biphenylmethylene

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The chemistry and kinetics of 2-biphenylmethylene have been examined in low-temperature glasses and polycrystals. Photolysis of 2-biphenyldiazomethane at 77 K produces a single set of triplet carbene resonance peaks. They have been assigned to the unresolved superposition of syn and anti rotamers of the carbene. The carbene kinetics are fastest in diethyl ether glass. The decay rates of 4T in diethyl-d_{10} ether and in a perfluorinated alkane polycrystal are comparable. This indicated that the main carbene reaction in diethyl ether is hydrogen atom abstraction. The reaction of 4T in diethyl-d_{10} ether is a mixture of reaction with solvent and cyclization to fluorene. These interpretations are consistent with the observed product distributions. Matrix effects on the observed chemistry are discussed.

Electron spin resonance spectroscopy has been used successfully to characterize carbenes which are ground-state triplets.[2] Through the analysis of the zero-field parameters and hyperfine splitting parameters of diphenylcarbene, fluorenylidene, and methylene it was determined that carbenes are substantially bent.[3] This value is in good agreement with more recently determined results

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