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Intramolecular Interaction of Free Radicals with Peroxides. Reactivity of Di-*tert*-butyl *p*-Benzenediperacetate and *tert*-Butyl *p*-Vinylphenylperacetate

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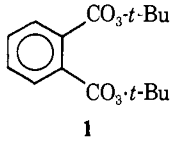
Abstract: Di-*tert*-butyl 1,4-benzenediperacetate (**15**) reacts in cumene with rates and activation parameters ($k_1 = 8.83 \times 10^{-4}$ s^{-1} at 100.3 °C, $\Delta H^* = 26.9$ kcal/mol, $\Delta S^* = -1.0$ eu) that require a mechanism involving rate-determining two-bond scission to form the *tert*-butyl *p*-benzylperacetate radical (**12**). The observed products are consistent with a scheme whereby **12** undergoes couplings and further reactions without the intervention of *p*-xylylene as an intermediate, but the formation of this latter species cannot be rigorously excluded. *tert*-Butyl *p*-vinylphenylperacetate (**17**) reacts in cumene with rates and activation parameters ($k_1 = 1.48 \times 10^{-3}$ s^{-1} at 100.3 °C, $\Delta H^* = 27.8$ kcal/mol, $\Delta S^* = 2.5$ eu) also requiring initial two-bond scission. The products from **17** are derived from radical couplings of the *p*-vinylbenzyl radical. The reaction of **17** with styrene and a free-radical initiator leads to a peroxide-containing polymer whose rate of reaction and activation parameters ($k_1 = 1.98 \times 10^{-3}$ s^{-1} at 100.3 °C, $\Delta H^* = 27.2$ kcal/mol, $\Delta S^* = 1.7$ eu) indicate rate-determining two-bond scission of a polystyrene with pendent phenylperacetate groups.

The study of the reactivity of organic peroxides substituted in the molecule with centers that may promote scission of the peroxide function is of critical importance for the understanding of the chemistry of this family of materials. In previous work we have studied the reactivity of the bisperesters di-*tert*-butyl perphthalate (**1**)[1] and di-*tert*-butyl *p*-percarboxyphenylperacetate (**2**).[2] It was concluded[1,2] that cleavage of one of the peroxy functions in these molecules to generate a free-radical intermediate with a peroxidic group remaining in the molecule did not lead to radical induced decomposition of the second peroxide.



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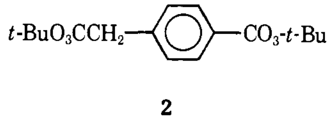

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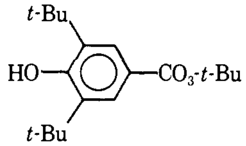
Related work has been reported recently from many laboratories. Examples include the phenolic peresters **3** and **4**. In the case of **3** radical or base removal of the hydroxy hydrogen leads to induced decomposition of the perester whereas the unimolecular reactivity of **3** is affected only by the normal substituent effect of the *p*-hydroxyl.[3] On the other hand, **4** is insensitive to base or radical induced decomposition, but undergoes rapid first-order reaction due to specific interactions with the *o*-hydroxyl.[4]



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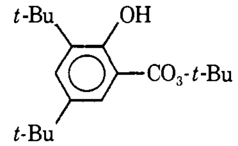

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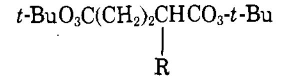
A variety of compounds have been studied which have two functional groups present which are potential sources of free radicals. These include bisperesters and bisdiacyl peroxides of the type **5**,[5] azo hydroperoxides and azo peresters of the type **6**,[6] diacyl peroxides of dicarboxylic acids of type **7** and **8**,[7a] and 2-substituted-1,3-perphthalates.[7b] Cyclic peroxides of diverse structural types have also been recently prepared and studied including compounds **9**,[8] **10**,[9] and **11**.[10]

Free-radical intramolecular induced decomposition routes

Table I. Kinetics of Decomposition of Peresters in Cumene[a]

	T, °C	k, s^{-1}	k_{rel}	ΔH^*, kcal/mol	ΔS^*, eu
p-t-$BuO_3CCH_2PhCH_2CO_3$-t-Bu (**15**)	100.3	8.83×10^{-4}			
	85.4	2.08×10^{-4}	1.3	26.9	−1.0
	70.9	3.69×10^{-5}			
p-$CH_2{=}CHPhCH_2CO_3$-t-Bu (**17**)	100.3	1.48×10^{-3}			
	85.4	3.00×10^{-4}	1.9	27.8	2.5
	70.9	5.54×10^{-5}			
$PhCH_2CO_3$-t-Bu (**29**)	100.3	6.90×10^{-4}			
	85.4	1.61×10^{-4}	1.0	27.7	0.9
	70.9[b]	2.70×10^{-5}			
Copolymer of **17** and styrene (**27**)	100.3	1.98×10^{-3}			
	85.4	4.58×10^{-4}	2.8	27.2	1.7
	70.9	7.92×10^{-5}			

[a] Measured by the infrared method on 0.06 M solutions. Two runs were made at each temperature unless noted otherwise. [b] One run only at this temperature. Activation parameters derived including using two rate constants in the literature.[2]

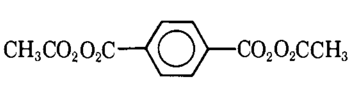


t-$BuO_3C(CH_2)_2\underset{R}{CH}CO_3$-$t$-Bu

5

$Me_2C(CN)N_2CMe_2CH_2CO_3$-$t$-Bu

6



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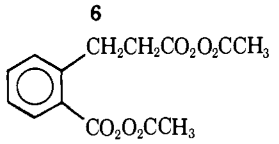

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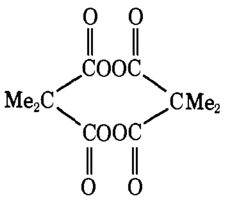

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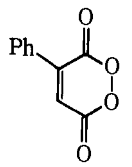

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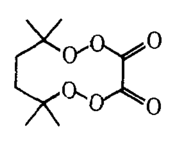

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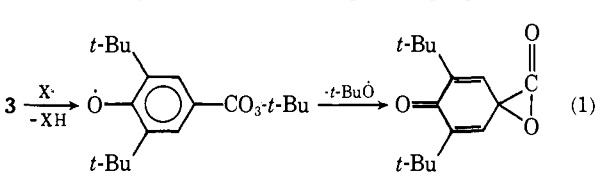
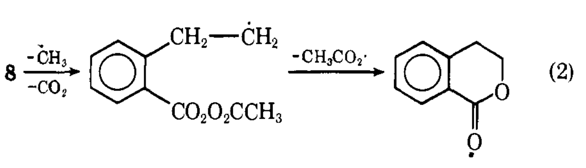
have been proposed for several of the derivatives mentioned. In the case of **3** this has been proposed to occur as shown in eq 1.[3] The induced pathway shown in eq 2 was proposed for **8**.[7]



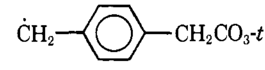


In **6** decomposition at the azo group and at the perester function was proposed[6c] to proceed independently but with similar rates. An intramolecular decomposition of the azo grouping following reaction at the perester group was proposed as shown in eq 3.

$$\mathbf{6} \xrightarrow{-t\text{-BuO}\cdot} Me_2C(CN)N_2CMe_2CH_2CO_2\cdot$$

$$\xrightarrow{-CO_2} Me_2C(CN)N_2CMe_2\dot{C}H_2 \xrightarrow{-N_2} Me_2\dot{C}CN + Me_2C{=}CH_2 \qquad (3)$$

In view of this widespread interest in intramolecular induced decomposition processes, we have studied the radical **12** and the substituted analogue **13** in order to determine if a benzylic radical can induce decomposition of the reactive phenylperacetate system. Phenylperacetates are about 60–100 times



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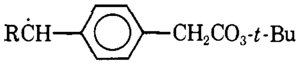

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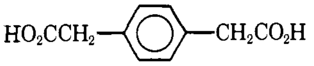
more reactive than perbenzoates, so intramolecular induced decomposition should also be much more favorable in **12** and **13** than in the radical intermediates derived from **1** and **2**.

Results

p-Benzenediacetic acid (**14**) was prepared by a known[11] method and converted into di-*tert*-butyl p-benzenediperacetate (**15**) by reaction of the diacyl chloride with *tert*-butyl hydroperoxide and pyridine (eq 4). The kinetics of decomposition



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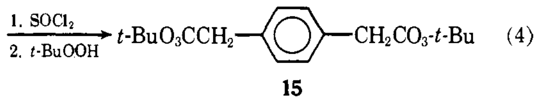

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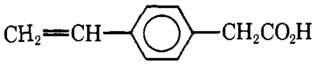
of **14** in cumene were followed by monitoring the disappearance of the perester carbonyl in the infrared[12] for 75% reaction and gave good first-order kinetics. The rate constants are listed in Table I.

p-Vinylphenylacetic acid (**16**) was prepared by modification of a reported method[13] and was converted to *tert*-butyl p-vinylphenylperacetate (**17**) by reaction of the acid chloride with *tert*-butyl hydroperoxide and pyridine (eq 5). Thermal decomposition of **17** in cumene solution was also followed by observation of the decrease of the carbonyl absorption in the infrared[12] and gave good first-order kinetics over 75% reaction. The rate constants are listed in Table I.



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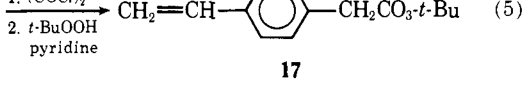

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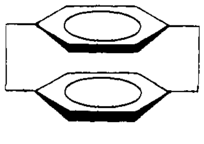
The products from thermal reaction of **15** were determined in toluene solution as it was felt that the product identification might be more reliable in this solvent. The results are listed in Table II. Authentic samples of [2.2]p-cyclophane (**22**) and tris[2.2.2]p-cyclophane (**23**)[14] were compared with the reaction product but no peaks were visible in the gas chromatogram of the product with the retention times of these compounds.

Table II. Products from Thermal Decomposition of Di-*tert*-butyl *p*-Benzenediperacetate (**15**) at 100 °C in Toluene

Product	Mol/mol of perester
CO_2	1.94
Acetone	0.16
t-BuOH	1.24
Bibenzyl	0.79
p-$MePhCH_2CH_2Ph$ (**18**)	0.02
p-*t*-$BuOCH_2PhCH_2O$-*t*-Bu (**19**)	0.10
p-*t*-$BuOCH_2PhCH_2CH_2Ph$ (**20**)	0.37
p-$PhCH_2CH_2PhCH_2CH_2Ph$ (**21**)	0.32



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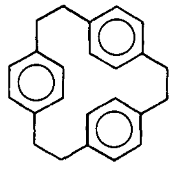

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The total yield of products derived from the aryl ring of **15** (**18**–**21**) was 81%. The products from the decomposition of **17** in toluene are listed in Table III. The total yield of products derived from the aryl ring of **17** (**24**–**26**) was 42%.

Copolymerization of **17** with styrene was also carried out by treatment in benzene at 25 °C with di-*tert*-butyl peroxyoxalate (DBPO). A molar ratio of reactants **17**:styrene:DBPO of 1:30:0.01 gave a solid polymer with an average molecular weight (viscometry) of 6000. This polymer was found to be soluble in cumene so the kinetics of its thermal decomposition were monitored by infrared observation of the decrease of the peroxy carbonyl as in the case of **15** and **17**. The rates are presented in Table I.

The elemental analysis of the polymer and its molecular weight were consistent with a ratio of styrene/**17** of 4/1 with *tert*-butoxy end groups. This elemental analysis is probably only approximate, as peresters of this type are rather unstable, and the analysis for **15** and **17** were not highly accurate.

Both **15** and **17** were decomposed thermally and photochemically in the probe of the NMR spectrometer but no CIDNP signals were observed in either. Emission was observed from the products of *tert*-butyl phenylperacetate under these conditions, as has been reported for phenylacetyl peroxide,[15] but apparently low resolution obscured the signals expected for the products of **15** and **17**. Efforts to observe the ESR spectra of the intermediate radicals from **15** and **17** were also futile.

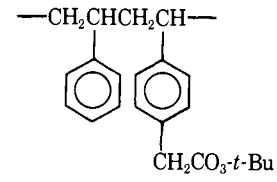
Discussion

The rates of decomposition of para-substituted phenylperacetates have been correlated[16] with the σ^+ parameters of the para substituents in chlorobenzene at 91 °C with a ρ^+ value of −1.09. In order to include **15** in the correlation, the relative rate of 1.3 of this compound (Table I) need not be statistically corrected for the equivalent groups inasmuch as the perester groupings appear to react independently (vide infra) and the observed absorption intensities are proportional to the sum of the absorption of the separate groups. The σ^+ value for the *p*-carboethoxymethyl group is −0.16,[17] which gives a predicted k_{rel} of 1.5 for **15**.

The σ^+ value for *p*-vinyl has recently been reported[18] as −0.16; the relative rate calculated for **17** using this value is 1.5. The copolymer of **2** with styrene presumably has the partial structure **27**, in which the para substituent would be electronically approximately equivalent to an ethyl group with $\sigma^+ = -0.30$ and the corresponding k_{rel} would be 2.1.

Table III. Products from Thermal Decomposition of *tert*-Butyl *p*-Vinylphenylperacetate (**17**) at 100 °C in Toluene

Product	Mol/mol of perester
CO_2	0.95
Acetone	0.10
t-BuOH	0.65
Bibenzyl	0.34
p-*t*-$BuOCH_2PhCH{=}CH_2$ (**24**)	0.24
p-$PhCH_2CH_2PhCH{=}CH_2$ (**25**)	0.17
p-$MePhCH{=}CH_2$ (**26**)	0.01



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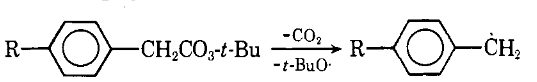
Thus the relative rates of reaction of **15**, **17**, and **27** fit very well with what is expected for para-substituted phenylperacetates reacting by the normal two-bond scission (eq 6). There are no special effects that can be attributed to the polymer backbone in **27**, and a conceivable concerted four-bond scission for **15** (eq 7) appears to be excluded. The activation energies for **15**, **17**, and the copolymer are very similar to those of *tert*-butyl phenylperacetate (**29**, Table I), and this is a further argument that the rate-determining step of all four is the same, namely simultaneous breaking of the peroxidic bond and decarboxylation with formation of a benzylic radical.



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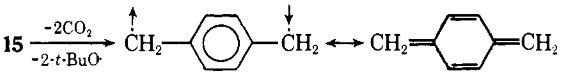

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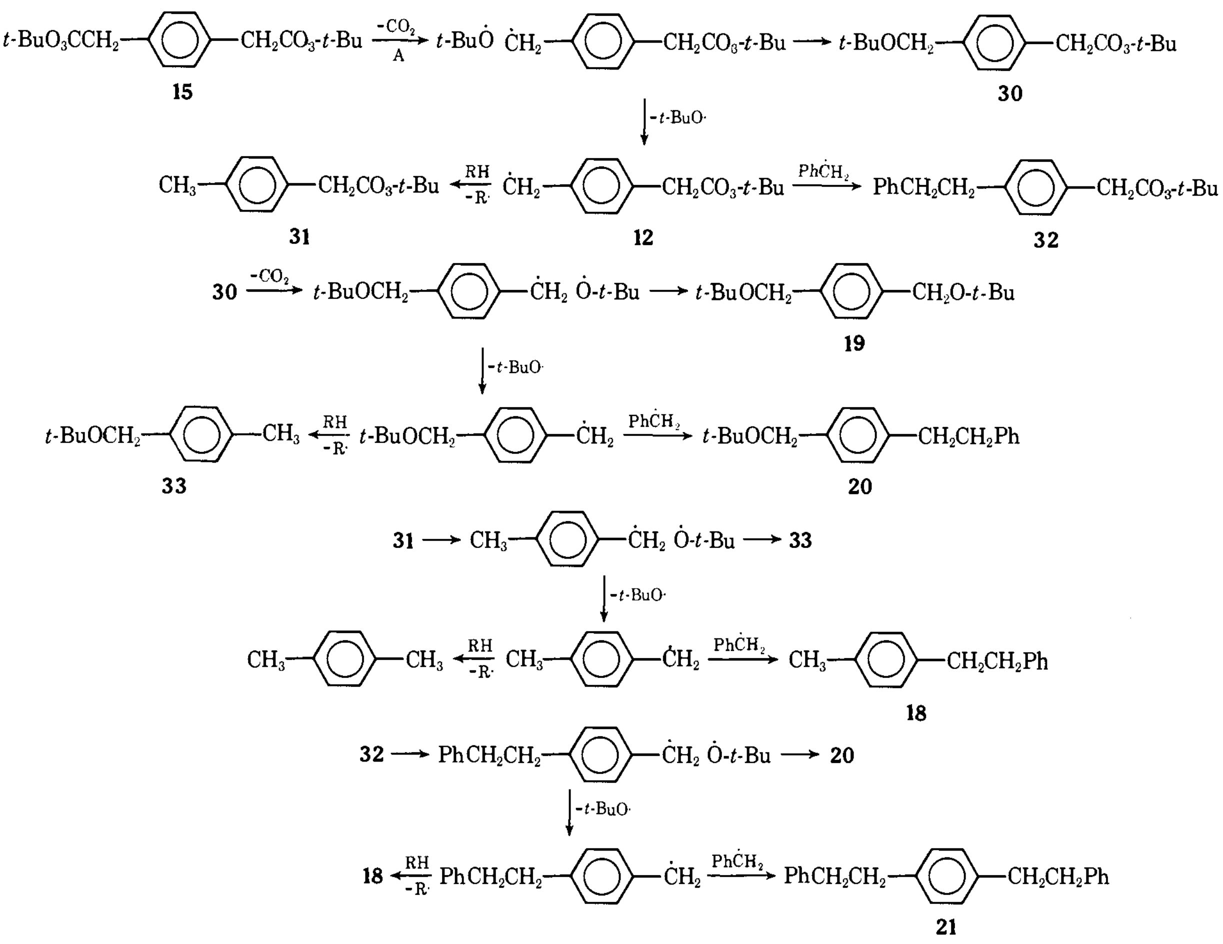
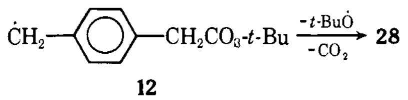
A mechanism for the reaction of **15** is formulated in Chart I which is consistent with the kinetic data and the observed products. Following the initial two-bond scission (step A), a caged-radical pair is formed. The amount of cage return of benzyl and *tert*-butoxy radicals in toluene at 95 °C has been estimated as 23–40%,[16a] and our product data can be accounted for by making the reasonable assumption that the efficiency of cage recombination of any of the radical pairs composed of *tert*-butoxy and a substituted benzyl is 33%. To account for the formation of **18** it may be assumed that the free benzyl radicals in Chart I abstract hydrogen with an efficiency of 2%. Application of these partitioning factors to all the reactions in Chart I predicts total yields of 2% of **18**, 11% of **19**, 44% of **20**, and 43% of **21**, as compared with the observed yields of 2, 10, 37, and 32%, respectively. The predicted yields of the unobserved products **33** and *p*-xylene are 0.9 and 0.02%, respectively. Thus the observed product distribution is in agreement with the scheme in Chart I and plausible assumptions regarding cage recombination and hydrogen atom abstraction. The intermediacy of **30** and **32** ought not to affect the kinetics significantly, as they would react further at rates comparable with **15**.

Dimerization of **12** would lead to a group of still higher molecular weight products. Although these were not observed, it appears likely that they were also formed but were not detected and identified.

The possibility exists that radical **12** might undergo intramolecular induced decomposition to give *p*-xylylene (**28**, eq 8). *p*-Xylylene is a well-characterized species[19] that is diamagnetic[19] and whose UV,[19b] vibrational,[19b] and NMR[19c]

Chart I. Decomposition of Di-*tert*-butyl *p*-Benzenediperacetate (**15**) in Toluene at 100 °C





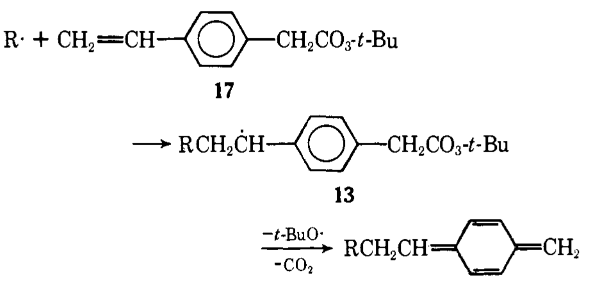
12 (8)

spectra can be measured. Solutions of *p*-xylylene are relatively stable at −78 °C,[19c,d] but polymerization occurs slowly at that temperature and very rapidly at room temperature. The polymerization results in a highly insoluble polymer as well as lower molecular weight products, including tris[2.2.2]*p*-cyclophane (**23**).[19] The absence of the polymer and **23** is evidence that **28** is not formed from the thermal decomposition of **12**. However, **28** might well have been intercepted by coupling with other radicals or by hydrogen abstraction. The fact that **17** could be polymerized to give a peroxide-containing polymer is evidence that radicals of the type **13** do not undergo induced decomposition to an appreciable extent in the time for chain propagation.

We have previously[2] given a method for calculation of the lifetime of intermediate radicals under these conditions. Application of this technique to the conditions of the product study in this case leads to an average lifetime for **12** of 8×10^{-4} s at 50% reaction.

In summary, **15** decomposes thermally by two-bond scission. Intramolecular decomposition of the radical intermediate to give *p*-xylylene is unlikely but cannot be excluded. All of the evidence is consistent with the path in Chart I which omits *p*-xylylene.

Decomposition of the *p*-vinyl perester **17** can be accounted for by the similar mechanism in Chart II. Formation of *p*-vinyltoluene is a very minor route due to the poor ability of toluene to donate a hydrogen atom to the intermediate *p*-vinylbenzyl radical. The overall yield of volatile products is much lower than from **15**, indicating that polymerization of some of the reactant or products has occurred. The fact that **17** can be copolymerized at 25 °C to give a peroxide-containing polymer[20] indicates that the intermediate **13** is stable to intramolecular induced decomposition of the type shown in eq 9, at

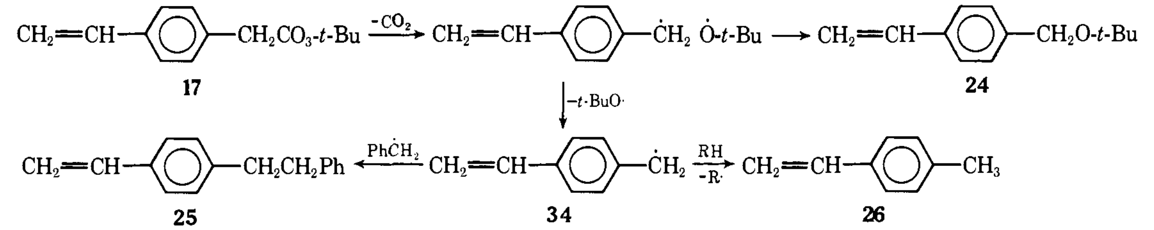


(9)

least at 25 °C. If any of **13** was formed during the course of the reaction of **12**, the products from coupling or further polymerization would not be expected to have significantly different thermal reactivity from **17**. The failure to detect the ESR spectrum of *p*-vinylbenzyl (**34**) or CIDNP spectra of its products precludes further discussion of the electronic structure of this species, a topic which has attracted some theoretical attention.[21] Some dimer of **34** was probably formed during the reaction, but either was consumed in further reactions or escaped detection.

The reactivities of the bisperester **15** and the *p*-vinyl perester **17** are explicable in terms of rate-determining two-bond scissions. The benzylic radicals **12** and **13** with *p*-peracetate substituents further appear to have considerable resistance to intramolecular induced decomposition of the peroxide linkages. This behavior is at variance with that of the *β*-*tert*-butyl per-

Chart II. Decomposition of *tert*-Butylperoxy *p*-Vinylphenylperacetate (17) in Toluene at 100 °C



carboxyethyl radical **35** (eq 10),[22] but parallels our experience with the bisperesters **1** and **2**.

$$\underset{\mathbf{35}}{t\text{-BuO}_3\text{CCHPh}\dot{\text{C}}\text{HPh}} \xrightarrow[-t\text{-BuO}\cdot]{-\text{CO}_2} \text{PhCH}{=}\text{CHPh} \qquad (10)$$

We are making use of this remarkable ability of the perester groupings to survive free-radical reactions at neighboring positions to develop routes to new types of polymeric materials.

Experimental Section

General. Elemental analyses were performed by A. B. Gygli Microanalysis, Ltd., Toronto. NMR spectra were measured using a Varian T-60 instrument with Me_4Si as an internal standard in CCl_4 solutions. Melting points (hot stage) and boiling points are not corrected. Cumeme, toluene, *tert*-butyl hydroperoxide, and pyridine were purified as before.[2] Quantitative vapor phase chromatographic analyses were performed using a Varian-Aerograph Model 1700 instrument with a flame ionization detector and a Varian recorder equipped with a disk integrator. Product isolations by VPC were done using a Varian-Aerograph Model 920 instrument.

Kinetics. Rate runs were carried out by the infrared method[12] using a Perkin-Elmer 180 spectrophotometer by our previous procedures.[2] The reactions were followed to 75% of completion and gave good first-order kinetics.

***p*-Benzenediacetic acid (14)**[11] was prepared by treating α,α'-dibromo-*p*-xylene (Aldrich) with KCN in H_2O-EtOH, followed by hydrolysis with hot concentrated HCl,[11] and the acid was converted to the acid chloride with thionyl chloride.[11]

Di-*tert*-butyl *p*-benzenediperacetate (15) was obtained by dropwise addition of *p*-benzenediacetyl chloride (2.05 g, 8.6 mmol) in 30 ml of pentane and 5 ml of ether over 20 min to a stirred solution of pyridine (0.68 g, 8.6 mmol) and purified *tert*-butyl hydroperoxide (0.78 g, 8.6 mmol) in 25 ml of pentane and 5 ml of ether at −25 °C. After stirring 4 h at −25 °C, the solution was filtered and washed successively with cold water, cold 5% H_2SO_4, cold 5% NaOH, and cold water and was then dried over magnesium sulfate at 0 °C and evaporated. Recrystallization from pentane gave **15** (1.56 g, 5.0 mmol, 57%): mp 84-85 °C; IR (CCl_4) 1776 cm^{-1} (C=O); NMR (CCl_4) δ 1.24 (s, 18, *t*-Bu), 3.54 (s, 4, $ArCH_2$), and 7.25 (s, 4, Ar).

Anal. Calcd for $C_{18}H_{26}O_6$ (338.38): C, 63.89; H, 7.75. Found: C, 63.13; H, 7.88.

Methyl *p*-acetylphenylacetate was prepared by the reported[13] procedure for acetylation of methyl phenylacetate. Contrary to the report,[13] the presence of both ortho and para isomers in the liquid product was shown by gas chromatography (Carbowax 20M on Chromsorb W column, 3 m × 3 mm, 200 °C). Crystallization from 95% ethanol at dry ice temperature gave the para isomer in 41% overall yield: mp 33-33.5 °C; IR (CCl_4) 1785 cm^{-1} (C=O); NMR (CCl_4) δ 2.50 (s, 3, Ac), 3.60 (s, 2, $ArCH_2$), 3.68 (s, 3, CH_3O), and 7.60 (q, 4, Ar). This was reduced with $NaBH_4$ to the liquid alcohol and dehydrated as reported[13] with potassium acid sulfate to give methyl *p*-vinylphenylacetate: bp 70-72 °C (0.6 Torr); IR (CCl_4) 1755 cm^{-1} (C=O); NMR (CCl_4) δ 3.50 (s, 2, $ArCH_2$), 3.62 (s, 3, CH_3), 5.40 (q, 2, $=CH_2$), 6.70 (q, 1, =CHAr), and 7.24 (s, 4, Ar). Hydrolysis of the ester with KOH and copper powder[13] gave the acid **16**: mp 90-91 °C (lit.[13] 101 °C); IR (CCl_4) 1702 cm^{-1} (C=O); NMR (CCl_4) δ 3.50 (s, 2, $ArCH_2$), 5.30 (q, 2, $=CH_2$), 6.60 (q, 1, =CHAr), 7.20 (s, 4, Ar), and 10.1 (s, 1, CO_2H).

***tert*-Butyl *p*-vinylphenylperacetate (17)** was obtained by treating **16** (1.6 g, 0.01 mol) with oxalyl chloride (3.5 g, 0.04 mol) in 15 ml of pentane for 10 h at 25 °C. Evaporation of the solvent gave *p*-vinylphenylacetyl chloride as a pale-yellow solid which was dissolved in 15 ml of dry pentane with purified *tert*-butyl hydroperoxide (1 g, 0.011 mol). Pyridine (5 ml) was added dropwise, and the solution was stirred 5 h at −20 °C, filtered, and washed successively with cold water, cold 5% H_2SO_4, cold 5% NaOH, and cold water. After drying over magnesium sulfate, the solvent was evaporated at 0 °C and the product recrystallized from pentane to give **17** (1.52 g, 0.0065 mol, 65%): mp 27.5-28.5 °C; IR (CCl_4) 1775 cm^{-1} (C=O); NMR (CCl_4) δ 1.14 (s, 9, *t*-Bu), 3.47 (s, 2, $ArCH_2$), 5.35 (q, 2, $=CH_2$), 6.59 (q, 1, =CHAr), and 7.24 (s, 4, Ar).

Anal. Calcd for $C_{14}H_{18}O_3$ (234.28): C, 71.77; H, 7.74. Found: C, 70.76; H, 7.89.

Product Analyses. Di-*tert*-butyl *p*-benzenediperacetate (15) (0.231 g, 0.683 mmol) dissolved in 3 ml of toluene to give a 0.23 M solution was degassed three times and heated at 100 °C for 24 h. The sample was opened on the vacuum line in a separate experiment and the CO_2 determined by absorption on Ascarite. Biphenyl was added to the solution as an internal standard, and the yields of volatile products were measured by gas chromatography using a Varian-Aerograph Model 1700 chromatograph with flame ionization detector and a 3 m × 4 mm 3% SE-30 on Chromosorb W column connected to a CEC 21-490 mass spectrometer. Acetone and *tert*-butyl alcohol were separated at 70 °C, and the remaining products were obtained using temperature programming to 200 °C. The yield of bibenzyl was taken relative to the biphenyl internal standard, and the yields of the other products were determined from their peak areas relative to that of bibenzyl. An authentic sample of *p*-di(*tert*-butoxymethyl)benzene (**19**) was prepared by reaction of potassium *tert*-butoxide with α,α'-dibromoxylene to confirm the identification of this reaction product. The identifications of *p*-methylbibenzyl (**18**), **19**, *p-tert*-butoxymethylbibenzyl (**20**), and *p*-di(2-phenylethyl)benzene (**21**) were based on their mass spectral molecular weights. These identifications were confirmed by the NMR spectra of materials isolated by gas chromatography (3 m × 12 mm 30% SE-30) for all but **18**, for which insufficient material was obtained: (**19**) δ 1.24 (s, 18, *t*-Bu), 4.36 (s, 4, $ArCH_2$), and 7.16 (s, 4, Ar); (**20**) δ 1.24 (s, 9, *t*-Bu), 2.85 (s, 4, $ArCH_2CH_2Ar'$), 4.34 (s, 2, CH_2O), and 7.08 (broad s, 9, Ar and Ar′); (**21**) δ 2.85 (s, 8, CH_2), 6.96 (s, 4, Ar), and 7.10 (s, 10, 2Ar′).

***tert*-Butyl *p*-vinylphenylperacetate (17)** (0.032 g, 0.137 mmol) dissolved in 2 ml of toluene to give a 0.068 M solution was degassed three times and heated at 100 °C for 24 h. The yields of the products were determined using gas chromatography, and CO_2 was determined using absorption on Ascarite as described above. The yield of bibenzyl was determined from a calibration curve of concentration vs. peak area, and the yields of the other products were taken from their peak areas relative to that of bibenzyl. *p-tert*-Butoxymethylstyrene (**24**) and *p*-2-phenylethylstyrene (**25**) were identified from their mass spectral molecular weights and the NMR spectra of the reaction products collected from gas chromatographic separation using a Varian-Aerograph Model 920 chromatograph and a 3 m × 12 mm SE-30 on Chromosorb W column: (**24**) δ 1.22 (s, 9, *t*-Bu), 4.31 (s, 2, $ArCH_2$), 5.1-6.8 (m, 3, vinyl), and 7.06 (s, 4, Ar); (**25**) δ 2.82 (s, 4, CH_2), 5.1-6.8 (m, 3, vinyl), and 7.02 (broad s, 9, Ar and Ar′). *p*-Methylstyrene was identified by its mass spectral molecular weight and comparison with the gas chromatographic retention time of an authentic sample (Aldrich Chemical Co.). An authentic sample of **24** was also prepared by reaction of potassium *tert*-butoxide with *p*-chloromethylstyrene for comparison. The product isolations were performed using 0.245 g (1.05 mmol) of **17** in 30 ml of toluene to give a 0.035 M solution. The bulk of the solvent was evaporated under vacuum before separation of products.

Copolymerization of *tert*-butyl *p*-vinylphenylperacetate (17) (0.112 g, 0.5 mmol) with styrene (1.7 g, 16 mmol) was initiated by 4 mg

(0.004 mmol) of di-*tert*-butyl peroxyoxylate in 15 ml of benzene by stirring 10 h at 25 °C. The products were precipitated by the addition of methanol and dried in vacuo to give a solid that softened at about 85 °C and had appreciable solubility in benzene, chloroform, and acetone: IR (KBr) 1776 cm^{-1} (C=O); NMR ($CDCl_3$) δ 0.9–2.1 (broad, $CHCH_2$), 1.24 (s, *t*-Bu), and 6.1–7.2 (broad, Ar); mol wt (toluene) 6100.

Anal. Calcd for $(\text{styrene})_{36}(\mathbf{17})_9(\text{O-}t\text{-Bu})_2$ (mol wt 6004): C, 84.41; H, 7.86. Found: C, 84.00, 85.49; H, 7.43, 7.82.

Attempted CIDNP Experiments. *tert*-Butyl phenylperacetate in CCl_4 was heated to 116 °C in the probe of a Varian A-60 NMR spectrometer. CIDNP signals were noted at δ 2.9 (absorption, CH_3Cl), 3.1 (emission, unknown), 3.7 (absorption, unknown), 4.1 (absorption, $PhCH_2O$-*t*-Bu), 4.7 (emission, $PhCH_2Cl$), and 7.27 (emission, $CHCl_3$). The normal NMR spectrum of **15** was observed at 100 °C but CIDNP signals were absent, and for **17** at 100 °C no NMR signals at all were visible, perhaps because of polymerization.

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Organotellurium Chemistry. 1. Benzyl Tellurocyanate: a Stable Alkyl Tellurocyanate[1] †

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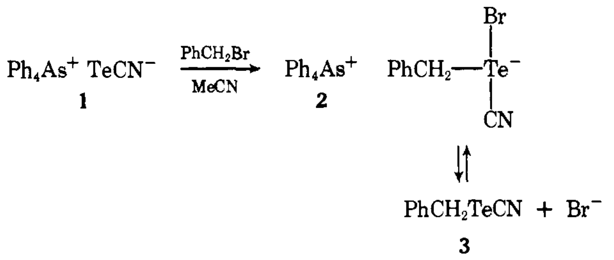
Abstract: Solutions of alkali-metal tellurocyanates were prepared for the first time and have been employed in the synthesis of benzyl tellurocyanate (**3**). Compound **3**, which represents the first isolable alkyl tellurocyanate, has been physically characterized, and its reactions with selected reagents (oxygen, bromine, hydroxide ion, hypophosphorous acid, and benzyl mercaptan) are reported.

Introduction

Despite the fact that salts of the thiocyanate and selenocyanate ions have been known for more than a century, unsuccessful attempts to prepare the analogous tellurocyanate ion were reported as late as 1964.[2] The first tellurocyanate salt, a dimethylformamide solvate of tetraethylammonium tellurocyanate, was reported by Downs in 1968.[3] Several years later, Austad et al. reported the isolation of solvent-free tetramethylammonium and tetraphenylarsonium tellurocyanates.[4] It appeared that the tellurocyanate anion was stable only adjacent to a large, nonpolarizing cation, at least in the absence of an interposed solvent molecule. In accord with this idea, it has long been known that tellurium dissolves slowly in a liquid ammonia solution of potassium cyanide, but is recovered as elemental tellurium upon evaporation of the solvent.[5] The known tellurocyanate salts are sensitive to air oxidation and are decomposed by water with the liberation of tellurium.[3,4]

The only report of the reaction of tellurocyanate ion with an alkyl halide appeared in 1973.[6] In this study, in which benzyl bromide was reacted with tetraphenylarsonium tellurocyanate (**1**) in acetonitrile, rate measurements showed tellurocyanate ion to be even more reactive as a nucleophile than selenocyanate ion. Product isolation afforded, in high yield, a crystalline substance which analyzed as a 1:1 adduct of benzyl tellurocyanate and tetraphenylarsonium bromide. This material was suggested to be tetraphenylarsonium bromocyanobenzyltellurate (**2**), an example of a four-electron three-



$$\underset{\mathbf{1}}{Ph_4As^+\ TeCN^-} \xrightarrow[\text{MeCN}]{PhCH_2Br} \underset{\mathbf{2}}{Ph_4As^+}\ PhCH_2{-}\overset{Br}{\underset{CN}{Te^-}} \rightleftharpoons \underset{\mathbf{3}}{PhCH_2TeCN} + Br^-$$

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† Dedicated to Professor R. B. Woodward on the occasion of his 60th birthday.