the *meta*/*para* absorbance ratio obtained by trapping the unresolved vpc peak, the ratio of these isomers could be determined.

Since no separation of cyclohexyltoluenes was possible on the $^1/_4$-in. columns listed, Beer's law plots were constructed for all three isomers, employing bands at 755 (*ortho*), 778 (*meta*), and 809 cm^{-1} (*para*). Such plots were linear over the concentration range studied (<0.05 *M* in CS_2). Fortunately column C separated the cyclohexyltoluenes from phenylcyclohexylmethane and bibenzyl; hence this peak was trapped in its entirety, and from the absorbances at the wave numbers previously mentioned, actual amounts of each isomer could be calculated. The isomer distribution so determined agreed with a partial isomer distribution obtained from column D which separated *o*- and *m*-cyclohexyltoluene as a combined peak from the *para* isomer in the ratio 75:25.

Preparation of Anisole Derivatives. 1,2-Diphenoxyethane was obtained as a white solid (mp 96–97°; lit.[30] 97–98°) from the condensation of phenol with ethylene bromide under basic conditions. Phenyl cyclohexylmethyl ether (bp 139–141° at 10 mm) was prepared by a similar condensation of phenol with cyclohexylmethyl bromide.

Preparation of Toluene Derivatives. Phenylcyclohexylmethane (bp 71–73° at 0.5 mm) was formed in very low yield ($\sim$1%) by the action of benzyl chloride upon an ethereal solution of cyclohexyl Grignard reagent. A benzyltoluene mixture (bp 107–110° at 0.3 mm) was produced in 50% yield by the reaction of toluene with benzyl chloride and $AlCl_3$. Bibenzyl was commercially available.

Thermal Decomposition of DTBP in Cyclohexane–Benzonitrile Solution. DTBP (7.3 g, 0.05 mole), cyclohexane (21.0 g, 0.25 mole), and benzonitrile (103.0 g, 1.00 mole) were placed in a three-neck 300-ml flask equipped with thermometer, magnetic stirring bar, nitrogen inlet, condenser, and bubbler. The system was flushed with N_2 for 30 min and then refluxed for 70 hr. The reaction mixture was analyzed as in the photolytic case. Duplicate experiments gave *ortho*:*meta*:*para* ratios of 49:3:48 and 49:4:47.

Synthesis and Photolysis of 1-Phenyl-1-cyclohexylmethylenimine. To an ethereal solution of 0.40 mole of cyclohexylmagnesium chloride was added an equimolar amount of benzonitrile dropwise. Following this addition the reaction was hydrolyzed with ice and HCl while keeping the mixture near pH 7 to avoid hydrolysis and/or hydrochloride formation of the imine. The ether layer was removed, washed with water, dried with Na_2SO_4, and filtered. Distillation gave a 35% yield of the imine (bp 114–119° at 0.4 mm) which gradually crystallized to a pale yellow solid (mp 52–53°). The infrared spectrum showed a strong absorption at 1670 cm^{-1} in the region where a C=N stretching vibration should appear, and the ultraviolet spectrum (in cyclohexane) showed maxima at 240 mμ (ϵ 11,800), 275 (660), 288 (410), and 325 (60). A solution of 9.3 g of the imine (0.05 mole) in cyclohexane was photolyzed for 24 hr. Only 3.9 g of the imine (42%) was recovered by distillation. No attempts were made to identify the products of this photolysis. That this imine, and not N-benzylidenecyclohexylamine, was indeed formed in the thermal decomposition of DTBP in the cyclohexane–benzonitrile system was demonstrated by vpc peak enrichment and comparison of infrared spectra.

Decomposition of Benzoyl Peroxide in Benzonitrile. A solution of 12.1 g of benzoyl peroxide (0.05 mole) in 103.0 g of benzonitrile (1.00 mole) was heated at 90–110° for 3 hr, during which time CO_2 evolution was observed. Analysis of the reaction mixture on column D showed an appreciable amount of 1,1-diphenylmethylenimine but no N-benzylideneaniline. The imine was synthesized as previously described (bp 123–125° at 1 mm) (lit.[31] 127° at 3.5 mm) while the Schiff base was formed from benzaldehyde and aniline. The expected cyanobiphenyls were also present and the *ortho* isomer appeared as a shoulder on the *larger* imine peak.

Decomposition of *t*-Butyl Peroxypivalate in Chlorobenzene. The perester is supplied as a 75% solution in mineral spirits and known as Lupersol 11. An amount of this solution containing 0.10 mole of perester was thermally decomposed at 60° in 200 ml of chlorobenzene for 25 hr (5 half-lives) under an inert atmosphere. No *t*-butylchlorobenzenes were detected from this reaction.

Acknowledgment. This work is a part of a continuing study of the reaction of free radicals supported by the Goodyear Tire and Rubber Company, Akron, Ohio.

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[30] A. Mikaye, *J. Am. Chem. Soc.*, **82**, 3040 (1960).

[31] P. Bourbon and P. Puig, *Compt. Rend.*, **258**, 3323 (1964); *Chem. Abstr.*, **61**, 638*a* (1964).

Radical-Ionic Reaction Mechanisms. Homolysis of the Carbonium Ion *t*-Butyl Tropeniumperacetate[1,2]

G. R. Jurch, Jr., and T. G. Traylor

Contribution from the Department of Chemistry, Revelle College,
University of California, San Diego, La Jolla, California. *Received August 2, 1966*

Abstract: Calculations of delocalization energies of certain radical cations and their precursors indicate that such species should sometimes form under ordinary ionic reaction conditions. One such system has been studied. The carbonium ion *t*-butyl tropeniumperacetate fluoroborate decomposes in acetonitrile 2700 times faster than does *t*-butyl phenylperacetate in the same solvent. The ratio of *t*-butyl alcohol to acetone produced in this decomposition and the induced decomposition at high concentrations indicate homolytic decomposition. This rate comparison implies that a tropeniumyl group stabilizes the methyl radical much more than does a phenyl group. Such a finding is at variance with the predictions of polar effects on free-radical reactions but accords with our predictions based on molecular orbital calculations of the stabilities of benzyl and tropeniumylmethyl radicals.

Resonance stabilization of carbonium ions and free radicals is well known.[3a] Furthermore, free radicals are stabilized by delocalization into either electron-rich or electron-deficient π systems. For example, both the tri-*p*-anisylmethyl and tri-(*p*-nitrophenyl)methyl radicals are more stable than the triphenylmethyl radical.[3b] Calculations on methyl or benzyl radicals indicate that either CH_2^+ or CH_2^- should stabilize these radicals.[4] Thus substitution

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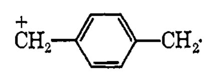
[1] This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR 514-64.

[2] (a) Abstracted from the Ph.D. Thesis of G. R. Jurch, Jr., University of California, San Diego, 1965; (b) National Defense and Education Act Predoctoral Fellow, 1961–1964.

[3] (a) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957; (b) p 531.

[4] A. Streitwieser, Jr., and C. Perrin, *J. Am. Chem. Soc.*, **86**, 4938 (1964).

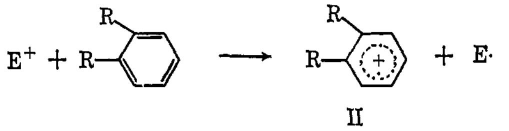
of CH_2^+ for H in benzyl radical is estimated to considerably stabilize the benzyl radical (I).



I

If this stabilization is sufficiently large, then we may expect these radical cations to be produced by ordinary chemical reactions and there will be a crossover from ionic to free-radical reactions in a single reaction sequence. Such radical cations might be produced by various free-radical reactions on carbonium ion intermediates or by ionic reactions on intermediate free radicals in addition to electron-transfer processes. For example, reactions of electrophiles with amines or certain aromatic systems might take any of three paths illustrated below.

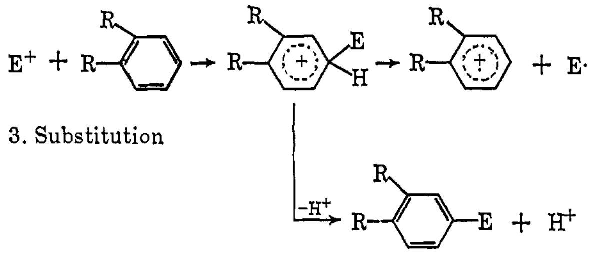
1. Electron Transfer



(1)

II

2. Heterohomolysis



3. Substitution

(2)

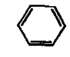
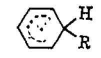
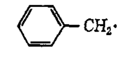
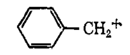
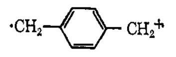
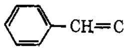
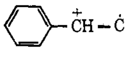
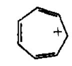
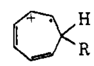
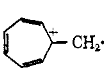
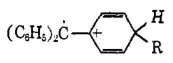
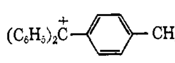
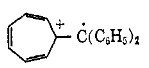
(3)

Radical cations such as II have been produced by electron impact,[5a,b] by photoionization,[5b] by electrolysis,[6a,7] and in a few instances by chemical oxidation.[5c,8,9] However, radical cations have seldom been implicated in simple ionic or free-radical reactions.

The purpose of the present work is to briefly explore, by HMO methods, the possible kinds of reactions in which radical-cation intermediates might be expected to occur and to examine one such reaction, the homolysis of a stable carbonium ion.

Calculations. We have used simple HMO and HMO ω techniques[6] to calculate the total π energy (M) of several radical cations and some possible precursors. Some of the data are listed in Table I. Because such comparisons of charged and uncharged systems are subject to large errors, we will not draw firm conclusions from this table but will use the data as a guide to possible reactions which we might investigate experimentally.

Table I. π Energies of Radical Carbonium Ions and Possible Precursors in Units of β_0[a]

No.	Structure	π energy[a] HMO	π energy[a] HMO ω
1		8.00	8.00
2		5.464	. . .
3		8.7206	. . .
4		8.7206	9.7680
5		9.6137	10.7604
6		10.4244	. . .
7		9.7622	10.9296
8		8.9880	10.188
9		6.5428	7.6831
10		9.7781	10.9938
11	$(C_6H_5)_3C^+$	25.8004	27.0612
12		23.4817	24.7584
13	$(C_6H_5)_3C\cdot$	25.8004	. . .
14		26.6757	27.9465
15		26.8457	28.1155

[a] See ref 6, Chapters 2 and 4.

The difference, ΔM, in the π energy of the radical ion and its precursor is considered to be the change in delocalization for the reaction. For example, in the treatment of electrochemical oxidations of aromatic hydrocarbons (ArH)

$$ArH \xrightarrow{-e} ArH\cdot^+ \qquad (4)$$

the difference $M_{ArH\cdot^+} - M_{ArH} = \Delta M$ has been successfully correlated with oxidation potentials.[6a,7] To illustrate our interests we list below a few hypothetical reactions and the ΔM for each (eq 5–8). The number in parentheses is the ΔM for the reaction using a phenyl substituent.

Reactions 5–8 and several others derivable from Table I appear to be rather favorable by these calculations. For example, III should decompose faster than *t*-butyl phenylperacetate, and we have therefore investigated reaction 5 in order to make this comparison.

Results

Preparation and Identification of Tropenium Derivatives. We have prepared cycloheptatrienylacetic acid derivatives by the reaction sequence 9–12.

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(5) (a) F. W. McLafferty, "Mass Spectrometry of Organic Ions," Academic Press Inc., New York, N. Y., 1963; (b) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957; (c) H. Hart, J. S. Fleming, and J. L. Dye, *J. Am. Chem. Soc.*, **86**, 2079 (1964).

(6) (a) A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley and Sons, Inc., New York, N. Y., 1961, p 185; (b) p 33; (c) p 115. (d) R. Ettinger, *Tetrahedron*, **20**, 1579 (1964). (e) We are grateful to Dr. Arnold Factor for the HMO ω program and for helpful discussions.

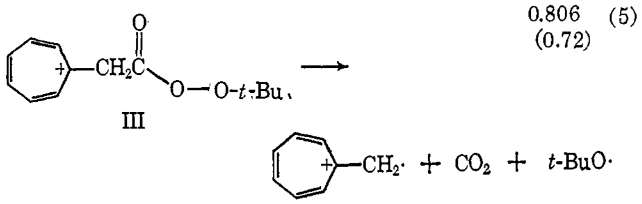
(7) E. S. Pysh and N. C. Yang, *J. Am. Chem. Soc.*, **85**, 2124 (1963).

(8) H. M. Buck, H. P. J. M. Dekkers, and L. J. Oosterhoff, *Tetrahedron Letters*, 505 (1965).

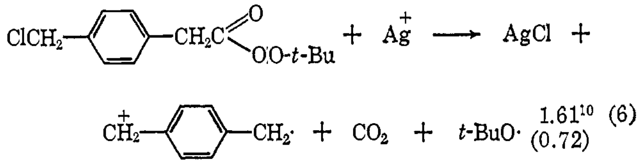
(9) A. A. Medzhidov, A. L. Buchachenko, and M. B. Neiman, *Dokl. Akad. Nauk SSSR*, [4] 161, 878 (1965).

Carbonium ion homolysis

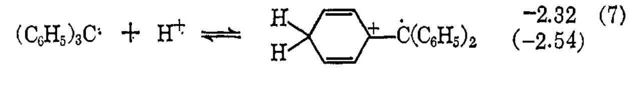
ΔM_1 (β_0)



Concerted homoheterolysis



Radical protonation



Hydrogen abstraction

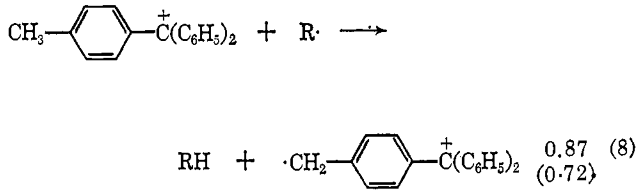
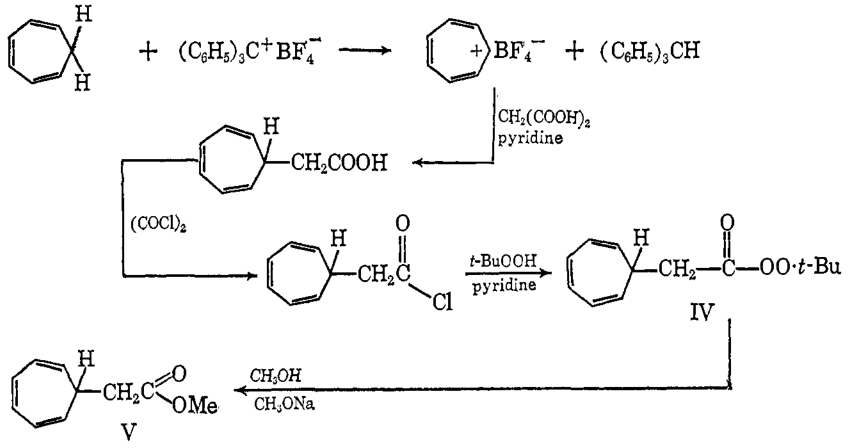


Table II. Spectra of Methyl Tropeniumacetate Fluoroborate (VI) and *t*-Butyl Tropeniumperacetate Fluoroborate (III) Solutions in Acetonitrile[a]

	VI	III
Ultraviolet max, mμ	283^{c} (257)^{b}	278–280^{c} (257)^{b}
Infrared carbonyl peak, μ	5.74 (5.74)^{b}	5.62 (5.62)^{b} 11.8 (11.84)^{b}
Nmr, cps^{e}	555 (singlet, area 6) 267 c (singlet, area 2) 222 c (singlet, area 2.9)	550 c (singlet) 263 (singlet) 78.5 (singlet) (76.5)^{b,d}

[a] These salts were prepared through reaction 13 in acetonitrile. Therefore, the spectra of triphenylmethane is also observed but is not indicated here. [b] Peaks in the corresponding cycloheptatriene derivatives IV and V. [c] These peaks are removed upon addition of methanol. [d] *t*-Butyl protons in IV. [e] Downfield from TMS at 60 Mc.

Due to its extreme reactivity, first attempts to prepare perester III led to decomposition products, and subsequent attempts to isolate this salt proved futile. The isolation was made especially difficult by the induced decomposition noted below. However, the structure of the perester and its presence in solution can be demonstrated by comparison of a solution of III with that of VI which can be isolated. A comparison of these two tropenium compounds in solution is shown in Table II.



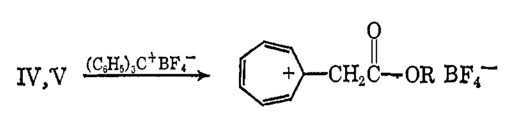
(9)

(10)

(11)

(12)

The cycloheptatrienes IV and V were then converted to the tropenium derivatives by treatment with trityl fluoroborate.



(13)

VI, R=CH$_3$
III, R=O-t-Bu

The cycloheptatriene derivatives had ultraviolet maxima at 257–270 mμ and displayed infrared and nmr spectra consistent with the assigned structure.[11]

It is clear from Table II that treatment of the cycloheptatrienyl perester (IV) with trityl fluoroborate in acetonitrile has removed both the ultraviolet and nmr spectra of the cycloheptatriene group and shifted the *t*-butyl protons in the expected downfield direction. There appear both ultraviolet and nmr absorptions typical and definitive for the tropenium group. The surprising observation of unchanged carbonyl-stretching frequency in going from IV to III is also noted in the change V to VI adding another corroboration to the assigned structure III.

Further evidence that the peroxide function is not changed during this hydride abstraction is seen in the titration for peroxide and in observation of two polarographic waves at −0.125 and −0.91 v, typical of tropenium and peroxy functions, respectively. The

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(10) We have prepared *t*-butyl *p*-chloromethylphenylperacetate and found it to decompose at a rate comparable to that of *t*-butyl phenylperacetate in acetonitrile or in acetic acid containing silver nitrate. This failure is probably due to the large decrease in entropy associated with such a highly concerted process.

(11) Because perester IV decomposed at a rate $k = 4 \times 10^{-5}$ sec^{-1} (100°) similar to *t*-butyl peracetate and much slower than *t*-butyl per-3-butenoate,[12b] structure IV seems highly probable. In addition, this rate indicates that decomposition proceeds without appreciable double bond participation.

(12) (a) P. D. Bartlett and C. Rüchardt, *J. Am. Chem. Soc.*, **82**, 1756 (1960); (b) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958); (c) P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960); (d) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *ibid.*, **82**, 1762 (1960); (e) P. D. Bartlett and H. Minato, *ibid.*, **85**, 1858 (1963).

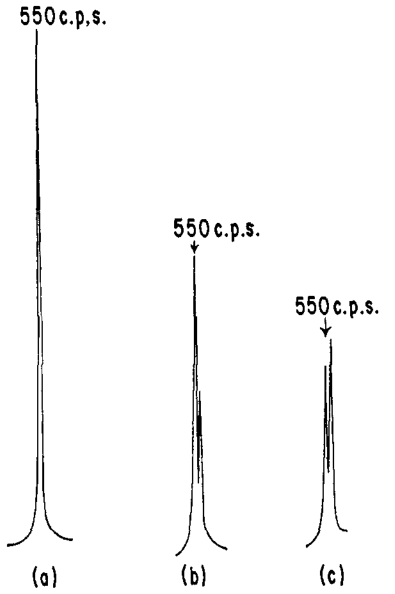

Figure 1. Tropenium nmr peaks (550 cps) during the decomposition of *t*-butyl tropeniumperacetate fluoroborate: (a) at the beginning of the run, (b) during the run, and (c) toward the end of the run.

observed infrared absorption at 11.8 μ is also diagnostic of peroxy groups.

Kinetics of Thermal Decomposition of III. The hydride abstraction reaction (13) can be carried to completion at 0° in 3 hr without appreciable decomposition of III. The perester III is then warmed quickly to the reaction temperature and the loss of the tropenium peak at 550 cps or the *t*-butyl peak at 78.5 cps is followed by repetitive scanning. The change in this peak and the appearance of a new tropenium peak with time are shown in Figure 1. A typical kinetic plot is shown in Figure 2, and the rate constants from several such plots are shown in Table III. Plotting peak heights or areas gave the same results. The reproducibility is estimated to be ±15%. The rate measured by using the 78.5-cps peak is acceptably close to those measured with the 550-cps peak.

Table III. The First-Order Decompositions of *t*-Butyl Tropeniumperacetate Fluoroborate in Acetonitrile

Perester,[a] M	Temp, °C	10^3k_1, sec^{-1}
0.157	37.2	1.61
0.157	37.2	1.40
0.157[b]	37.2	1.02
0.0785	37.2	1.38
0.0785	37.2	0.85
1.24	37.2	8.8
0.205[d]	33.8	1.27
0.205[c]	33.8	1.31
0.103	33.8	1.24
0.0501	33.8	0.705
0.205	23.5	0.665
0.205	29.0	0.980
0.103	29.0	0.522
0.0501	29.0	0.441
0.205	37.0	1.71

[a] Maximum possible concentration obtainable, based on the initial concentration of trityl fluoroborate.[d] [b] The peak scanned with time was the *t*-butyl peak at 78.5 cps. [c] Plot of peak area (550 cps) *vs.* time. [d] All runs below the first six were on solutions originally 0.205 M in trityl fluoroborate and 0.23 M in IV. Others were originally 0.157 and 0.21 M in these reagents.

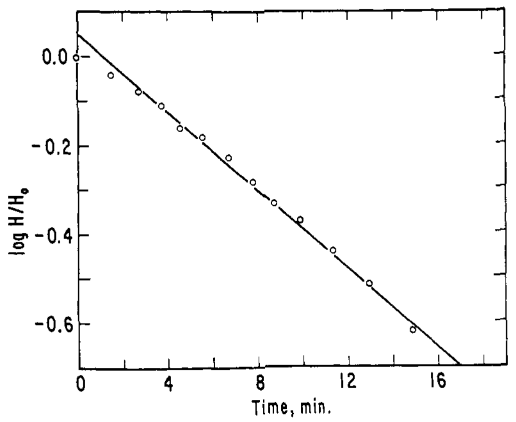

Figure 2. First-order rate plot of the thermal decomposition of 0.205 M *t*-butyl tropeniumperacetate fluoroborate in CH_3CN at 37°.

It should be noted that although rate constants determined at 0.05 to 0.1 M III are, within our accuracy, identical, a much faster decomposition occurs at higher concentrations.

Products of Thermal Decomposition of III. Both acetone and *t*-butyl alcohol are produced in this decomposition as might be expected for homolytic decomposition. We have determined the yields of these products by vapor phase chromatography of the volatiles after complete (in one case partial) decomposition. The results are tabulated in Table IV along with similar results for the decomposition of di-*t*-butyl peroxyoxalate (DBPO) in acetonitrile. A known concentration of benzene was added to some samples to determine absolute concentrations of acetone and *t*-butyl alcohol. Because *t*-butyl alcohol disappeared after it was formed, a series of control experiments were carried out to establish the amount formed in the reaction.

The behavior of DBPO is as expected (samples 1–4), the fraction of scission of *t*-butoxy radicals increasing with temperature and decreasing with concentration of triphenylmethane. Although the yield of acetone at 35° from III remains fairly constant at 30–35% with variations in reaction time, *t*-butyl alcohol yields are erratic (see samples 5, 6, 11) and the yield decreases with time (samples 5 *vs.* 11). These results indicate *t*-butyl alcohol is being removed during the course of the decomposition. *t*-Butyl alcohol reacts slowly with trityl cation. This is seen when *t*-butyl alcohol is mixed with trityl fluoroborate before analysis (samples 8 and 9). Parnes, *et al.*,[13] have shown that *t*-butyl alcohol reacts with tropenium bromide at a slow rate. It is also evident from samples 13–17 that substituted tropenium compounds react slowly with the alcohol. Thus, there are two possible methods of decreasing the *t*-butyl alcohol/acetone ratio as the decomposition occurs. We have obtained (sample 10) as high as 1.52 for this ratio early in the reaction. However, since acetone does not disappear, a better estimate of the actual ratio is (III–acetone)/acetone. Such an estimate gives a ratio of 2:1 at 0.153 M III. Under similar conditions (sample 3) DBPO decomposition yields a

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(13) Z. N. Parnes, G. D. Mur, R. V. Kudryatsev, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, **155**, 1371 (1964).

Table IV. Determination of *t*-BuOH and Acetone from Decomposition of III and of DBPO (in Acetonitrile)

Sample	DBPO, *M*	Perester III, *M*	Added materials, *M*	— Ratio of *t*-BuOH/acetone — 50°	40°	35°	0°	— *t*-BuOH, *M* — 35°	0°	— Acetone, *M* — 35°	0°
1	0.167	...	...	1.14	1.42	1.52	...	...	...	...	...
2	0.167	...	Ph_3CH, 0.050	1.01	1.32	1.49	...	...	...	...	...
3	0.167	...	Ph_3CH, 0.150	1.17	1.58	1.86	...	...	...	...	...
4	0.167	...	Ph_3CH, 0.450	1.61	2.27	2.35	...	...	...	...	...
5[c]	...	0.153	...	...	...	0.756	...	0.029	...	0.040	...
6	...	0.153	Styrene, 1.0	...	...	1.15	...	0.046	...	0.038	...
7	...	...	Acetone, 1.44 *t*-BuOH, 1.44	...	...	1.097	...	...	...	...	...
8[a]	...	...	Acetone, 1.44 *t*-BuOH, 1.44 $Ph_3{}^+BF_4$, 1.44	...	...	0.005	...	0.0	...	...	...
9[b]	...	...	Acetone, 1.44 *t*-BuOH, 1.44 $Ph_3{}^+BF_4$, 1.44	...	...	0.422	...	...	...	...	...
10[d]	...	0.153	...	...	...	...	1.52	...	0.0246	...	0.0147
11[c]	...	0.153	...	...	...	1.23	...	0.0581	...	0.0472	...
12[d]	...	0.157	...	...	...	...	0.47	...	...	...	...
13	0.129	...	...	...	...	1.21	...	0.1138	...	0.1025	...
14	0.0643	...	VI, 0.112	...	...	0.253	...	0.0114	...	0.0456	...
15	0.129	...	VI, 0.0745	...	...	0.249	...	0.0212	...	0.0916	...
16	0.129	...	VI, 0.0745; styrene, 1.0	...	...	2.05	...	0.0828	...	0.0472	...
17	0.167	...	VI, 0.33; Ph_3CH, 0.33	...	...	0.13	...	0.020	...	0.106	...

[a] Sample 8 was examined several hours after mixing. [b] Sample 9 was examined immediately after mixing. [c] Sample 11 was kept in a bath only 4 hr, whereas sample 5 remained about 12 hr at 35°. [d] Sample 12 was an infinity sample kept in the reaction flask, while sample 10 was kept in a sealed tube for a much shorter period of time at 0°.

1.86 *t*-butyl alcohol/acetone ratio. Thus, this criterion indicates homolysis of III.

Carbon dioxide was identified by its infrared spectrum which showed only traces of other gaseous products. After complete decomposition carbon dioxide yield was estimated to be 70% by measuring pressure of a known volume and 65% by weighing that which was absorbed on ascarite.

A new tropenium compound results from this decomposition as may be seen in the nmr spectrum of the product (Figure 1). Table V lists the aromatic hydrogen nmr positions for various tropenium salts.[14]

Table V. Chemical Shifts for Several Types of Tropenium Protons in Acetonitrile

	Compound	Chemical shift from TMS, cps
1	Tropenium fluoroborate	561
2	*t*-Butyl tropeniumperacetate fluoroborate (III)	550
3	Methyl tropeniumacetate fluoroborate (VI)	555
4	Isopropyl tropenium fluoroborate	543
5	Tropenium decomposition product appearing in the decomposition of the perester (III)	547
6	Allyltropenium fluoroborate[c]	542[14a]
7	1-Tropeniumylpropene-1 fluoroborate[a]	530[14a]
8	Phenyltropylium fluoroborate	554[14b]
9	Tropenium fluoroborate[b]	558[14c]

[a] In carbon tetrachloride as solvent. [b] Benzene used as internal standard, and 7.37 ppm (442.2 cps) used as shift for benzene to calculate tropenium shift from TMS. [c] In chloroform.

The position of the peak at 547 cps indicates an alkyltropenium salt. We attempted to isolate this tropenium compound by converting it first to a phenyl derivative by the reaction[15]

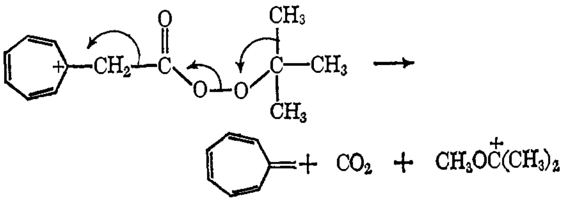
(14)

Treating the decomposition product of III with hydrogen peroxide produced a small (~10%) yield of material, mp 135–138°, mol wt 356, which has only aromatic protons as judged by nmr, contains a hydroxyl and carbonyl, and has not been identified.

In summary, the average product distribution from decomposition of solutions of III was acetone, 31%; *t*-butyl alcohol, 38%; carbon dioxide, 68%; triphenylmethane, 90%; and the unidentified solid product, 10–20%. All these yields are based on trityl fluoroborate which was usually the limiting reagent.

Discussion

The carbonium ion III might logically be expected to undergo ionic decomposition



(15)

However, in such decompositions methyl migration accompanies and provides driving force for breaking the O–O bond.[16] Thus our major product, *t*-butyl alcohol, would not be produced.

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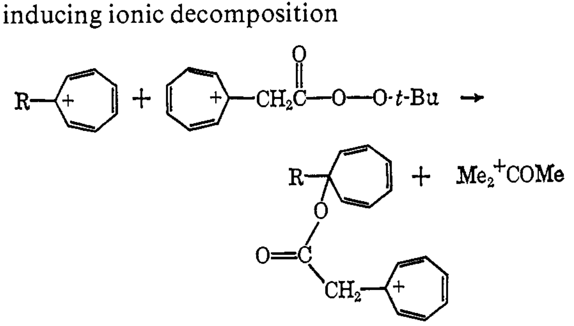
(14) (a) D. Bertelli, C. Golino, and D. L. Dreyer, *J. Am. Chem. Soc.*, **86**, 3329 (1964); (b) A. Cairncross, Thesis, Yale University, 1963; (c) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960).

(15) M. E. Volpin, D. N. Kursanov, and V. G. Dulova, *Tetrahedron*, **8**, 33 (1960).

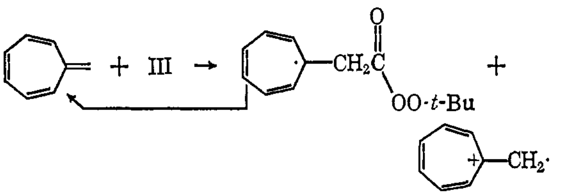
(16) P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **83**, 856 (1961).

The increase in rate of decomposition of III at high concentrations could also be explained by an attack of the tropenium ion on the oxygen of a second perester, inducing ionic decomposition



(16)

However, the rate of decomposition of *t*-butyl phenylperacetate in acetonitrile is increased only 40% at 80° upon the addition of 0.05 *M* tropenium fluoroborate. Furthermore, reaction 16 produces no *t*-butyl alcohol and results in a product whose tropenium nmr peak would not agree with our findings. Another possible induced decomposition might involve a rapid electron transfer with traces of heptafulvene.

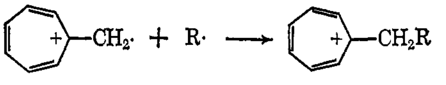


(17)

However, this reaction also requires that the radical cation have high stability. But the apparent lack of higher order induced decomposition at low concentration argues against this mechanism.

The increase in rate constant at high concentrations, typical of induced decomposition of peresters,[12] and the 2:1 ratio of *t*-butyl alcohol to acetone provide strong evidence for homolysis of III according to eq 5.

The fate of the tropeniummethyl radical (heptafulvene cation radical) cannot be decided from the data available. It presumably combines with another radical to give an alkyltropylium salt. The position of the new tropenium peak in the nmr (547 cps) and the production of carbon dioxide are strong inference that the carbonyl function has been removed.



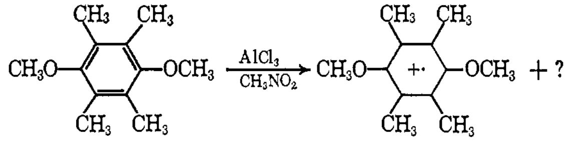
(18)

There remains the comparison of the rate of reaction 5 and the decomposition of *t*-butyl phenylperacetate. We may estimate the latter rate at 37° from the work of Bartlett and Rüchardt[12a] to be $k_3 = 6.36 \times 10^{-7}$ sec^{-1} with an activation enthalpy of 26 kcal/mole. The rate of decomposition of III at this temperature is $k_2 = 1.7 \times 10^{-3}$ sec^{-1}. Thus III decomposes about 2700 times faster than *t*-butyl phenylperacetate at 37°.

The polar effect on free-radical decompositions of peresters[12a] would predict that $k_2 << k_3$. We calculated the change in π energy for these two decompositions to be $0.806\beta_0$ and $0.72\beta_0$, respectively. From previous correlations of ΔE_π with rates of perester decompositions[6d,12b,17] we estimate a rate increase of 15 for each $0.1\beta_0$ We thus predicted a rate ratio $k_2/k_3 \cong$ 10 to 15.

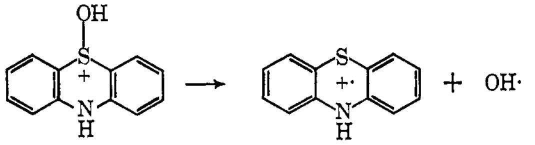
The observed factor surely justifies our intuitive feeling that k_2 should be greater than k_3. However, unless $\beta_0 > 70$ kcal, the observed rate increase far exceeds the prediction of our HMO or HMO ω calculations. It is possible that the ω technique does not properly account for changes in charge or that decrease in electron repulsions, which is not specifically treated, is a dominant factor in adding a positive charge to a delocalized free radical.

Other Radical Cations. There are several cases of protonation followed by electron transfer. Triphenylmethyl radical reacts with hydrochloric acid by an unknown mechanism to produce trityl chloride and triphenylmethane.[18] The first step in this reaction is very likely to be reaction 7. Electron spin resonance signals have been observed in many types of Friedel-Crafts conditions,[19] the latest being that shown below.[19c]



(19)

This reaction might occur through either mechanisms 1 or 2. Shine[20] has suggested the homolysis of a cation to produce the radical cation shown below.



(20)

In addition to these examples, the corresponding reactions which produce radical anions have been recognized and are under active study in several laboratories.[21]

Summary. We have observed a very strong stabilizing influence of a positive charge on a delocalized free radical which accords qualitatively with predictions from HMO calculations. Because the observed stability far exceeded our expectations, we are encouraged to believe that radical-ionic reaction mechanisms will be observed in many other systems.

Experimental Section

Instruments. The nuclear magnetic resonance spectra were taken on Varian A-60 and HR-60 spectrometers. A variable temperature probe (Varian) was used in some of the kinetic runs for temperatures below 35°. All nmr chemical shifts are given in cycles per second downfield from the internal standard tetramethylsilane (TMS).

A Perkin-Elmer Infracord Model 137B spectrophotomer was used for infrared spectra, and Cary Model 14 and Zeiss PMQ11 spectrophotometers were used for ultraviolet spectra.

An Aerograph Autoprep Model A-700 was used for vapor phase chromatography. Compounds which were sensitive to moisture were handled and stored under nitrogen in a drybox (D. L. Herring

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(17) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

(18) J. E. Leffler, "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1956.

(19) (a) R. E. Banks, L. F. Farnell, R. N. Hazeldine, P. N. Preston, and L. H. Sutcliffe, *Proc. Chem. Soc.*, 396 (1964); (b) J. Q. Adams and S W. Nicksic, *J. Am. Chem. Soc.*, **84**, 4355 (1962); (c) W. F. Forbes and P. D. Sullivan, *ibid.*, **88**, 2862 (1966).

(20) H. M. Shine and E. E. Mach, *J. Org. Chem.*, 30, 2130 (1965).

(21) (a) G. A. Russell and M. C. Young, *J. Am. Chem. Soc.*, **88**, 2007 (1966), and previous papers cited; (b) E. A. Chandross and F. I. Sonntag, *ibid.*, **88**, 1089 (1966); (c) N. L. Bauld, *ibid.*, **87**, 4788 (1965).

Dri-Lab HE-43 inert atmosphere chamber and Dri-Train HE-93 purification train).

Materials. The following reagents were used without purification: ethyl acetate (Fisher reagent grade), cycloheptatriene (Chemische Fabrik Triene), triphenylcarbinol (Eastman White Label), fluoroboric acid (J. T. Baker, purified, 48–50% aqueous solution), oxalyl chloride (Eastman Kodak White Label), methanol (Baker and Adamson reagent, absolute), sodium, Florisil (Floridin Co. 100–200 mesh), and silica gel G (Merck).

Eastman White Label propionic anhydride was distilled through a ten-plate Oldershaw column. The fraction boiling at 166.3–166.8° was retained. Malonic acid, Eastman White Label, was dried in a vacuum oven and used without further purification. Phillips 66 pure grade pentane was kept over sodium wire and used without further purification. Di-*t*-butyl peroxyoxalate (DBPO) and *t*-butyl hydroperoxide were made and purified by the method of Bartlett, Benzing, and Pincock.[12d] Baker and Adamson reagent grade pyridine was fractionally distilled over CaH_2 through a 45-cm Oldershaw column (bp 114.5°). Eastman White Label thionyl chloride was distilled from boiled linseed oil, using 10 g of $SOCl_2$ per ml of linseed oil. The fraction removed for use boiled at 76°.

Reagent grade acetonitrile was allowed to stand over $CaCl_2$ for several days. The liquid was decanted and distilled, the middle fraction being retained. This was allowed to stand over P_2O_5 for a few days and then distilled. The process was repeated until the P_2O_5 on standing did not discolor the solution. The last distillation over P_2O_5 was into K_2CO_3. The liquid was then decanted and fractionally distilled through an Oldershaw column, and the fraction boiling at 81.5° was retained.

Every batch of purified acetonitrile[22] was titrated with standardized Karl Fischer reagent to determine the amount of water present. The titrated water was always less than 0.01% by weight, which is within the experimental error of the method. The acetonitrile was then stored under an atmosphere of dry nitrogen.

Tropenium fluoroborate was prepared as described by Harmon, *et al.*,[23] from trityl fluoroborate which was prepared by the method of Dauben, Honnen, and Harmon.[24] The properties of both compounds were those previously reported.[23,24]

Cycloheptatrienylacetic Acid.[25a] To a stirred solution of 22.0 g of malonic acid in 105 ml of pyridine was added 21.7 g of tropenium fluoroborate. The mixture was placed on the steam bath to reflux overnight. The reflux condensor was fitted with a drying tube. After cooling, the reaction mixture was poured into 400 ml of 4.0 *N* HCl and extracted with several 50-ml portions of ether. The extracts were decolorized with charcoal and dried over $MgSO_4$; the ether was evaporated. A red-brown oily liquid remained. The acid was purified by recrystallizing from pentane at Dry Ice–acetone temperatures. In all cases yields of the recrystallized acid exceeded 90%. The purified white crystalline acid melted at 29–31° (lit.[25a] mp 30–33°). The infrared spectrum had an acid carbonyl peak at 5.82 μ in pentane. The ultraviolet spectrum in acetonitrile showed a single maximum at 257 mμ, in agreement with the value of 258 mμ obtained by Conrow.[25a] Conrow[25b] has shown the ultraviolet maxima for a number of 7-substituted tropilidenes to be between 255 and 269 mμ.

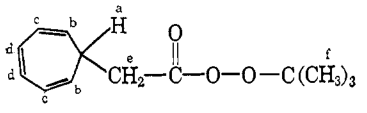
Cycloheptatrienylacetyl Chloride. An attempt to make cycloheptatrienylacetyl chloride from the acid with thionyl chloride proved unsuccessful. Only a small trace of acid chloride was obtained, with a majority of the product being polymer.

The cycloheptatrienylacetyl chloride was prepared using the general method of Adams and Ulich.[26] Oxalyl chloride (18.81 g) was added to a flask containing 9.0 g of purified cycloheptatrienylacetic acid, protected by a reflux condenser fitted with a drying tube. After 30 min of gas evolution, the mixture was refluxed on a steam bath for 2–5 hr. After the excess oxalyl chloride had been removed by evaporation, the dark reaction mixture was extracted several times with dry pentane. The pentane was evaporated leaving a light orange-red liquid which was found to be pure acid chloride as judged by its infrared spectrum (one carbonyl peak in the infrared at 5.52 μ). The yield of acid chloride from acid was almost 100%. It was found that the acid chloride decomposed on standing within a few weeks even when purified and kept under nitrogen. The ultraviolet spectrum was that of a 7-substituted cycloheptatriene, having a maximum at 255 mμ in CH_3CN.

***t*-Butyl Phenylperacetate** was prepared by the method of Bartlett and Hiatt.[12b]

***t*-Butyl Cycloheptatrienylperacetate** (IV). The cycloheptatriene perester was made by the general method for the synthesis of peresters described by Bartlett and Hiatt.[12b] From a typical preparation using 50 ml of pentane, 10 ml of pyridine, 8.00 g of *t*-butyl hydroperoxide, and 10.00 g of cycloheptatrienylacetyl chloride there were obtained 11.32 g (85.9%) of the perester after purification by chromatography. The ultraviolet spectrum in CH_3CN showed a maximum at 257 mμ. The perester purity by titration was 98.8%. The purified perester was a light orange liquid at room temperature, which remained a liquid in the freezer at −20°.

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 67.75; H, 7.91. The infrared spectrum in pentane showed a carbonyl band at 5.58 μ and an O–O perester band at 11.70 μ. In CH_3CN the carbonyl band is at 5.62 μ. The nmr spectrum showed the following peaks in CCl_4



IV

d, 400 cps (triplet)
c, 372 cps (multiplet)
b, 312 cps (multiplet)
a, 148 cps (multiplet)
e, 150 cps (multiplet)
f, 76.5 cps (singlet)

Protons a, b, c, and d on the cycloheptatriene group check with the literature values for these protons for cycloheptatriene.[27] In CH_3CN the *t*-butyl protons (f) are found at 76.5 cps.

The decomposition of this perester in acetonitrile at 100.0° was followed by titration for peroxide function.[28] First-order rate constants for two runs were 3.9 × 10^{-5} and 5.1 × 10^{-5} sec^{-1}. We have shown elsewhere that peresters decompose at similar rates in acetonitrile and in chlorobenzene.[29]

Methyl Cycloheptatrienylacetate (V). To a solution of 0.1 g of sodium in 10 ml of methanol was added 1.00 g of *t*-butyl cycloheptatrienylperacetate. The solution was allowed to stand overnight, then poured into 20 ml of water, and extracted several times with pentane. The pentane layer was washed several times with water, dried over $CaCl_2$, and evaporated under vacuum. The resulting yellow-orange liquid had a strong infrared band at 5.70 μ in pentane. In CH_3CN, this ester band appears at 5.74 μ. The ultraviolet spectrum showed a maximum at 257 mμ in CH_3CN.

Methyl Tropeniumacetate Fluoroborate (VI). Methyl cycloheptatrienylacetate (0.711 g) was added dropwise to a stirred mixture of trityl fluoroborate in 3.0 ml of acetonitrile. With the addition of each drop a red color was observed at the reaction surface. As ester was added, the trityl fluoroborate ultraviolet absorption began to disappear. When the addition was three-fourths complete, the trityl fluoroborate had completely disappeared and a white precipitate began to form. The reaction mixture was stirred overnight, then filtered under an atmosphere of dry nitrogen. A light tan solid was obtained. This solid contained both the methyl tropeniumacetate and triphenylmethane. The tan solid was washed with dry ether several times to remove the triphenylmethane, the identity of which was proved by its isolation. The light brown solid which remained after washing was dried under vacuum and stored under dry nitrogen. The infrared spectrum of the tan solid in CH_3CN showed a carbonyl band at 5.74 μ. The ultraviolet spectrum in CH_3CN showed maxima at 283 and 348 mμ. Addition of methyl alcohol to an acetonitrile solution of the tropenium salt caused the maximum at 283 mμ in the ultraviolet to disappear. The maximum at 348 mμ remained and a peak at 252 mμ began to form (this is in the region of 7-substituted cycloheptatrienes).[25] The tropenium compound was also titrated by dissolving it in an ethanol–water solution with NaOH. It gave a purity of 62.4%. The titration when checked against purified tropenium fluoroborate and trityl

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[22] G. J. Janz and S. S. Danyluk, *J. Am. Chem. Soc.*, **81**, 3846 (1959).

[23] (a) K. M. Harmon, F. E. Cummings, D. A. Davis, and D. J. Diestler, *ibid.*, **84**, 3349 (1962); (b) K. M. Harmon, Thesis, University of Washington, 1958.

[24] H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).

[25] (a) K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959); (b) K. Conrow, M. E. H. Howden, and D. Davis, *ibid.*, **85**, 1929 (1963).

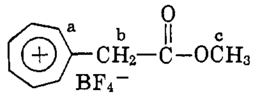
[26] R. Adams and L. H. Ulich, *ibid.*, **42**, 599 (1920).

[27] "Varian Spectra Catalog, No. 1," Varian Associates, Palo Alto Calif., spectrum 158.

[28] D. H. Wheeler, *Oil & Soap*, **9**, 89 (1932).

[29] G. R. Jurch, Jr., Ph.D. Thesis, University of California, San Diego, 1965.

fluoroborate gave very accurate results. The nmr spectrum taken in CH_3CN confirmed the structure of the methyl tropenium acetate salt.

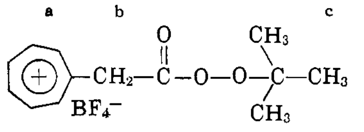


VI	area
a, 555 cps	5.98
b, 267 cps	2.00
c, 222 cps	2.91

Methyl tropeniumacetate fluoroborate is very sensitive to moisture.

***t*-Butyl Tropeniumperacetate Fluoroborate (III).** The perester was made by the hydride-exchange reaction.[30] Excess *t*-butyl cycloheptatrienylperacetate was added in 15 min to a stirred solution of trityl fluoroborate in CH_3CN, which was kept at 0° under dry nitrogen throughout the addition. The reaction mixture was stirred at 0° for 2–3 hr. The reaction was judged complete when the ultraviolet maxima of trityl fluoroborate disappeared from the reaction mixture. The fluoroborate salt of the perester was examined in the acetonitrile solution. The ultraviolet spectra of several batches of the tropenium perester reaction mixture showed a new maximum at 278–280 mμ, which was assigned to the tropenium perester. The peak could be removed from the spectrum by adding methyl alcohol to the perester solution. The infrared spectra of several samples of the tropenium perester reaction mixture in acetonitrile showed a strong carbonyl band at 5.62 μ.

The proton chemical shifts in the nmr were assigned as follows.



III

a, 550 cps (singlet)
b, 263 cps (singlet)
c, 78.5 cps (singlet)

Attempts to precipitate this salt by adding ether or pentane gave tars.

In one experiment a solution of 0.157 *M* trityl fluoroborate and 0.20 *M* *t*-butyl cycloheptatrienylperacetate (IV) made up quickly in dry acetonitrile at 0° was sampled at various times. The ultraviolet spectrum showed clearly that the trityl peak at 402 mμ decreased to a steady value (0.003 *M*) in 3 hr. The 256-mμ peak of IV disappeared during this time. The nmr peaks of IV at 300–400 cps disappeared in 3 hr while the singlet at 550 cps (III) reached a maximum at about 2.75 hr, as did the 78.5-cps *t*-butyl peak of III. At 3 hr the nmr spectrum is in agreement with a mixture of triphenylmethane and III. No acetone or *t*-butyl alcohol is observable. Samples of gas removed at various times indicated that no carbon dioxide appeared until about 5 hr from time of mixing.

Subsequently, carbon dioxide slowly evolved; the nmr peaks at 78.5 and 550 cps decreased and were replaced by new peaks at 70 (*t*-BuOH), 85, and 547 cps (see Figure 1), and the infrared absorbtion at 11.8 μ disappeared. Finally, at very long reaction times, all nmr peaks in the tropenium region disappeared.

In another experiment, 4.96 mmoles of IV was added to 4.69 mmoles of trityl fluoroborate in 15 ml of acetonitrile at 0° and the mixture stirred for 3 hr (A). The nmr spectrum (at 25°) showed peaks at 76.0, 78.5, 266, 334, 430, 432, and 550 cps which is consistent with a mixture of III, IV, and trityl fluoroborate. After 15 min at room temperature new peaks appeared at 73, 85, and 547 cps, and those at 78.5 and 550 cps were greatly decreased.

The solution (A) above was extracted several times at −30° with pentane. The extracts contained triphenylmethane and IV as indicated by the nmr of the nonvolatile products. The extracted acetonitrile solution showed the same peaks and same behavior with time in the nmr as did the unextracted solution except that there were much smaller peaks at 76 (IV) and 436 cps (triphenylmethane).

The solution of III decolorized galvinoxyl instantaneously.

Effect of Tropenium Fluoroborate on Perester Decompositions. The decomposition of *t*-butyl phenylperacetate at 80.0° in acetonitrile was followed by titrating aliquots removed from ampoules as described below. First-order rate plots for solutions 0.0548 *M* in the perester yield rate constants of 1.23×10^{-4} and 1.78×10^{-4} sec^{-1} in solutions containing no and 0.0521 *M* tropenium fluoroborate, respectively.

Procedures. In the following kinetic experiments the reaction of trityl fluoroborate with IV was allowed to run for 3 hr at 0° and the sample for kinetics warmed quickly to the reaction temperature.

The kinetics of the *t*-butyl tropeniumperacetate fluoroborate decomposition were followed by nmr by observing the disappearance of the tropenium peak (550 cps) with time (other methods failed). No other peak in the starting reaction mixture was within 100 cps of the tropenium peak. As the tropenium peak disappeared, another peak appeared about 2–3 cycles upfield from it which prevented our taking an infinity blank as a correction. Figure 1 is an example of three peaks in a kinetic run: (a) at the beginning of the run, (b) during the run, and (c) toward the end of the run.

An aliquot of the reaction mixture at 0° was syringed into an nmr tube under nitrogen and placed in the probe. When the perester had reached the temperature of the probe the region surrounding the tropenium protons was scanned with time. The time was measured with a stopwatch and recorded at the maximum of the tropenium peak. The temperature in the probe was measured directly and also by measuring the difference in chemical shifts in methanol.[31]

The rate was determined by measuring the peak height, *H*, for each scan. The determination of rate by peak height was compared with the determination by area under the peak, and the two methods agreed within the experimental error of 10 to 15%. Results are shown in Table II.

The decomposition of other peresters were followed by a modified Wheeler method.[19] Aliquots containing up to 0.1 mmole of perester were added to a 50-ml glass-stoppered flask containing 1 ml of methanol, 1 ml of saturated potassium iodide, and about 0.1 g of Dry Ice. Fifteen milliliters of acetic acid containing 0.003% ferric chloride was then added; the flask was stoppered, placed in the dark for 10 min, and titrated with standardized 0.01 *N* sodium thiosulfate.

A vapor phase chromatograph was used in the determination of *t*-butyl alcohol and acetone. Twenty-foot columns, $^1/_8$ in. in diameter and packed with Carbowax 20M on Chromosorb P 60–80 mesh, were operated at 90°. The amounts of acetone and *t*-butyl alcohol were obtained by measuring the areas under each peak and comparing them to a standard concentration of benzene which was added to each sample. The column was calibrated before each use by injecting a standard solution of acetone and *t*-butyl alcohol in acetonitrile.

Solutions of III or of DBPO were allowed to decompose completely at the desired temperature; then the sealed tubes containing the samples were broken and the samples injected immediately into the glc. In some cases, known amounts of benzene were added prior to analysis. Results are shown in Table III.

The quantitative determination of carbon dioxide was done as described by Bartlett and Minato.[12e]

Nonvolatile Products of III Decomposition. The conversion of tropenium compounds to phenyl derivatives was done with H_2O_2.[15] A 15-ml sample of III which originally was 0.156 *M* in trityl fluoroborate and 0.21 *M* in IV but had formed III was placed in a flask under a stream of dry nitrogen. While the flask was kept at −20 to −40°, the reaction mixture was pumped with a vacuum pump to remove all but a few milliliters of acetonitrile. The sample was then washed several times with 10–15-ml portions of dry pentane to remove the excess cycloheptatriene perester and the triphenylmethane. After the sample was washed with pentane, enough acetonitrile was added to the mixture to bring it to its original concentration. An nmr spectrum of the washed sample now showed no cycloheptatriene perester and only a small amount of triphenylmethane at the spectrum amplitude where all of the samples were to be compared.

The washed perester solution, still under a stream of dry nitrogen, was allowed to decompose completely at room temperature. To the decomposed mixture was added, slowly, an excess of 5% aqueous H_2O_2. The reaction was moderated by cooling to prevent the reaction mixture from becoming warm. After the addition of hydrogen peroxide the mixture was extracted several times with ether. The ether extracts were washed with 10% aqueous NaOH and then with water to remove H_2O_2 and all water-soluble products

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(30) H. J. Dauben, Jr., F. A. Gadecki, K. M. Harmon, and D. L. Pearson, *J. Am. Chem. Soc.*, 79, 4557 (1957).

(31) Technical Information, Publication No. 87-100-110, Varian Associates, Palo Alto, Calif.

such as acids and phenols, and dried over $MgSO_4$. Upon evaporation of the ether, 0.0946 g (10–20%) of a light yellow solid was obtained, mp 110–130°. Thin layer chromatography on silica gel using 90:10:1 volume ratio of hexane–ether–acetic acid indicated this product to be mostly one component. The solid was washed with pentane and recrystallized from chloroform–petroleum ether to give a lighter yellow product, mp 135–138°. It had infrared peaks at 2.74, 5.64, 5.84, 6.25, 6.70, 6.91, 7.97, and 9.23 μ. A large nmr peak at 439 cps and very small peaks at 437 and 440 cps were observed in $CDCl_3$ solvent. *Anal.* Found: C, 77.05; H, 5.99; mol wt, 356.

The data are not consistent with *t*-butyl benzyl ether or with 1,2-diphenylethane.

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Mechanisms of Substitution Reactions at Sulfinyl Sulfur. II. Concomitant Electrophilic and Nucleophilic Catalysis of the Solvolysis of Aryl Sulfinyl Sulfones in Acetic Acid–Water[1]

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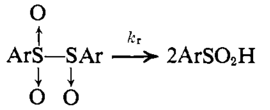
Abstract: In acetic acid–1% water the rate of acid-catalyzed solvolysis (eq 1) of aryl sulfinyl sulfones (II) can be rather dramatically accelerated by the addition of small amounts of various alkyl sulfides. The sulfide-catalyzed solvolysis is first order in both sulfide and sulfinyl sulfone; its rate is proportional to the Hammett acidity function and is strongly dependent on the structure of the sulfide ($\rho^* = -1.6$). Electron-withdrawing substituents in the aromatic ring attached to the sulfonyl sulfur of II enhance the rate of reaction with a given sulfide while the same substituents in the ring attached to the sulfinyl sulfur retard the reaction somewhat. The reaction shows a small solvent isotope effect, $k_H/k_D = 1.15$. Several mechanisms (eq 6 or 8) can be written which are consistent with these data. In each of them one has a nucleophilic attack by the sulfide on the sulfinyl group of II, which displaces the $ArSO_2$ group; this displacement is significantly assisted by the transfer of a proton to the departing $ArSO_2$ group. The mechanisms differ only in the details of how this proton transfer is effected. The sulfide-catalyzed solvolysis of II is thus an example of concomitant nucleophilic and electrophilic catalysis of the scission of a sulfur–sulfur bond involving substitution at sulfinyl sulfur. It is compared with earlier examples[4,5] of such catalysis involving substitution at sulfenyl sulfur.

In moist acetic acid an aryl sulfinyl sulfone (II) hydrolyzes readily to two molecules of the corresponding sulfinic acid (I). In two other papers[2,3] we



$$\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{ArS}}}\text{—}\underset{\underset{O}{\downarrow}}{SAr} \xrightarrow{k_r} 2ArSO_2H \qquad (1)$$

II I

a, Ar = p-$CH_3C_6H_4$
b, Ar = C_6H_5
c, Ar = p-ClC_6H_4
d, Ar = p-$CH_3OC_6H_4$

have shown that one can easily determine the rate of this reaction under a wide variety of reaction conditions. In connection with this work we discovered that the presence of very small amounts of certain alkyl sulfides can profoundly accelerate the rate of acid-catalyzed solvolysis of a sulfinyl sulfone. Investigation of the nature of this catalysis by added sulfides reveals that the phenomenon bears a striking resemblance to several earlier examples of concomitant nucleophilic and electrophilic catalysis of the scission of a sulfur–sulfur bond.[4,5] These other cases, however, involved a substitution at a sulfenyl rather than a sulfinyl sulfur. The similarity in the behavior of the various systems suggests the important conclusion that this type of catalysis is a more general phenomenon in sulfur–sulfur bond scissions that might previously have been suspected.

Study of the mechanism of sulfide catalysis of the solvolysis of II is also of considerable interest in connection with both the mechanism of the normal acid catalyzed solvolysis of sulfinyl sulfones[3] and the general question of mechanisms of substitution at sulfinyl sulfur. The latter area has been the subject of much recent investigation.[6–9]

Results

Kinetic Study of the Solvolysis of II. All the sulfinyl sulfones exhibit a strong absorption maximum near 300 mμ. At the same wavelength, a solution of the corresponding sulfinic acid of comparable concentration is completely transparent. Thus their solvolysis

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[1] (a) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-106-65. (b) Part of this work appeared in preliminary form: J. L. Kice and G. Guaraldi, *Tetrahedron Letters*, 501 (1966).

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