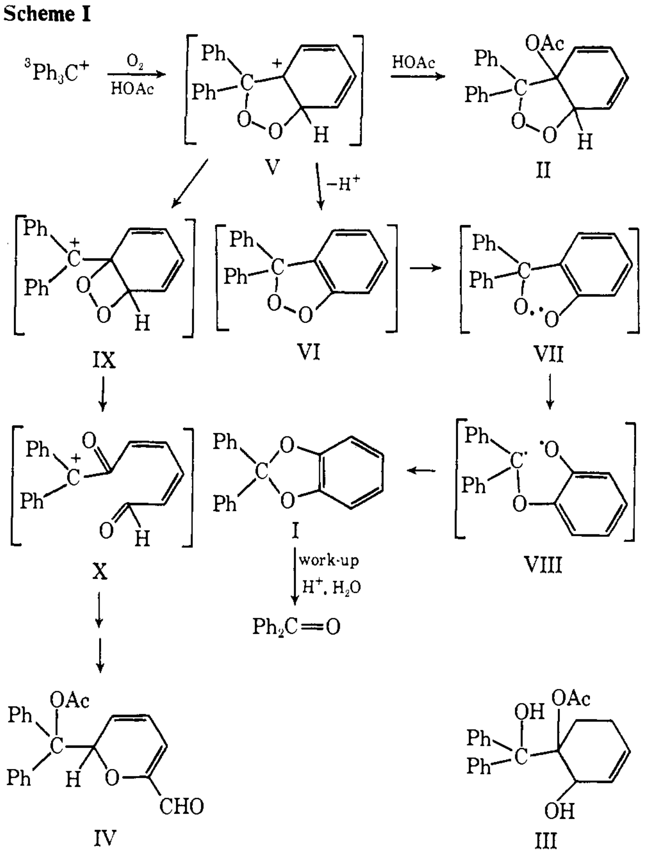
Scheme I



going this reaction, especially since in this system no fluorescence could be observed.[3] The homolysis of VI to VII would be expected on the basis of findings that diaryl peroxides are stable only at very low temperatures, decomposing upon warming to aryloxy radicals.[8,9] The conversion of VII to VIII is analogous to the known conversion of triphenylmethoxy radical to the more stable diphenylphenoxymethyl radical,[10] while the four-membered peroxide IX would be expected by precedent[11-14] to cleave to the keto aldehyde.

It has not yet been determined whether singlet oxygen is produced in this system. However, preliminary results indicate that the excited triplet carbonium ion is quenched by oxygen to an extent greater than can be accounted for by the formation of the peroxide-derived products.[15]

Acknowledgment. The authors are grateful to the Army Research Office—Durham (Project No. CRD-AA-5227-C) and the Petroleum Research Fund (Grant 2892 (A1,4)), administered by the American Chemical Society, for support. Also, thanks are due Dr. Lois Durham for consultation on nmr spectra and to Professor L. Altman for helpful discussions.

E. E. van Tamelen, T. M. Cole, Jr.[16]
Department of Chemistry, Stanford University
Stanford, California 94305

Received October 15, 1969

---

(8) C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 466.

(9) A heterolytic mechanism, perhaps involving initial protonation of a peroxide oxygen, could also be invoked to rationalize the formation of I from VI.

(10) H. Wieland, *Ber.*, **44**, 2533 (1911).

(11) Pitts, *et al.*, isolated succindialdehyde from the photooxidation of benzene and postulated a related four-member peroxide: K. Wei, J. Mani, and J. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 4225 (1967).

(12) E. H. White, J. Wiecko, and D. F. Roswell, *ibid.*, **91**, 5194 (1969).

(13) W. Fenical, D. R. Kearns, and P. Radlick, *ibid.*, **91**, 3398 (1969).

(14) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969).

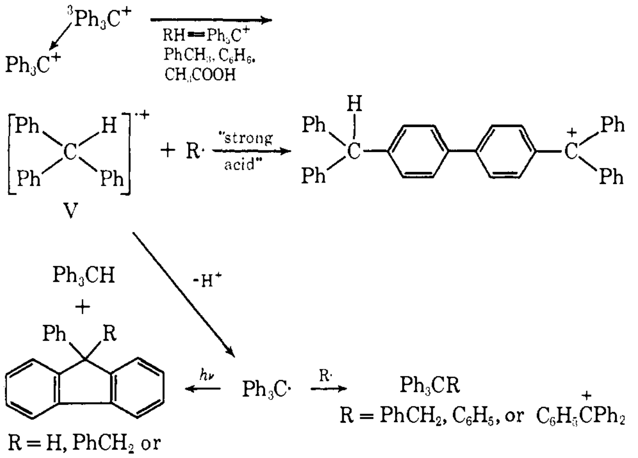
(15) For example, in 72% aqueous sulfuric acid oxygen slowed the photodimerization[1b] by a factor of 4 but did not form any adducts with triphenylcarbonium ion.

(16) National Institutes of Health Predoctoral Fellow, 1965–1968; address correspondence to Department of Chemistry, Columbia University, New York, N. Y. 10027.

Photolysis of Triphenylcarbonium Ion under Nitrogen[1]

Sir:

In Table I are listed the results of the photolysis of triphenylcarbonium ion in various systems under nitrogen.[2] These products are consistent with the mechanistic scheme shown below in which the primary photochemical process is the abstraction of a hydrogen atom by the excited triplet of triphenylcarbonium ion to form V. The acidity of the medium, the identity of the hydrogen donor RH, and the intensity of light capable of photolyzing trityl radical determine the ultimate product composition.



The following results support the involvement of the excited triplet state of triphenylcarbonium ion: in expt 4 the dimerization could be quenched (by FeSO$_4$, NaBr, and NaCl) without diminishing the trityl cation fluorescence; in expt 1–3 no fluorescence was observed, and when expt 1 was carried out under oxygen, none of the anaerobic products were obtained.[3]

The formation of cation-radical V from triplet trityl cation receives support from the formation of I–III in expt 4 and II in expt 6. When expt 4 was carried out using *ortho-* and *para*-deuterated triphenylcarbonium ion, the dimerization was slowed by a factor of 2.5, consistent with a rate-determining hydrogen atom abstraction from the *para* position of a ground-state

---

(1) Part III of a series concerned with the photolysis of triphenylcarbonium ion.

(2) E. E. van Tamelen, T. M. Cole, R. Greeley, and H. Schumacher, *J. Amer. Chem. Soc.*, **90**, 1372 (1968).

(3) E. E. van Tamelen and T. M. Cole, Jr., *ibid.*, **92**, 4123 (1970).

Table I

Expt	Photolysis medium	Product	Yield, %
1	3.3% H_2SO_4	Triphenylmethane	21
	96.5% CH_3COOH	9-Phenylfluorene	22
	0.2% H_2O	Bis(9-phenylfluorenyl) peroxide	17
2	3.3% H_2SO_4	1,1,1,2-Tetraphenylethane	45
	80.1% CH_3COOH	Triphenylmethane	8
	16.4% $C_6H_5CH_3$	9-Phenylfluorene	12
	0.2% H_2O	9-Benzyl-9-phenylfluorene	10
3	1.5% H_2SO_4	Tetraphenylmethane	5–10
	96.2% CH_3COOH	(plus all products found in	
	2.3% C_6H_6	expt 1)	
4	72% H_2SO_4 (aqueous)	$p\text{-}A(C_6H_5)_2CC_6H_4C_6H_4C(C_6H_5)_2A'\text{-}p$	
		I, A = A' = H	20
		II, A = A' = OH	22
		III, A = H; A' = OH	22
5	29.4% H_2SO_4	$p\text{-}(C_6H_5)_3CC_6H_4C(OH)(C_6H_5)_2$	
	69.4% CH_3COOH	IV	30
	1.2% H_2O	III	12
		Five hydrocarbons[a]	25
6	61% H_2SO_4	II	56
	36.5% CH_3COOH		
	2.5% H_2O		

[a] All appeared to be 9-phenylfluorene derivatives on the basis of their uv spectral properties, but were not characterized further.

carbonium ion. (It had been noted previously that the rate of dimerization in expt 4 was first order in ground-state carbonium ion.[2]) The evidence obtained also indicates that trityl radical, implicated in the more weakly acidic systems (expt 1, 2, 3, and 5), arises from V. When expt 1 was carried out in the presence of toluene, cumene, or cyclohexane (each at *ca.* 10^{-2} *M*), the disappearance of the starting carbinol was accelerated. (This is apparently due to the added hydrocarbons' providing an additional reaction pathway for the excited trityl cation, as shown by the products obtained in expt 2).[4] Per mole, cumene is 11.2 times as efficient as toluene, and cyclohexane is 0.37 times as efficient as toluene in this acceleration. These selectivity results indicate that mechanisms involving electron transfer from acetate or bisulfate anions[5] or from toluene or cumene[6] to excited trityl cation are not involved, but are instead consistent with hydrogen atom abstraction by triplet triphenylcarbonium ion. That it is the methine position that is the site of hydrogen atom capture in these weakly acidic systems is supported by the observations that, when C_6D_6 was used in expt 3, the isolated tetraphenylmethane was entirely tetraphenylmethane-d_5, and that when *ortho*- and *para*-deuterated triphenylcarbonium ion was used in expt 2, no deuterium loss was noted in the isolated triphenylmethane and 1,1,1,2-tetraphenylethane.[7] The mechanism of formation of triphenylmethane and the 9-phenylfluorenyl system will be discussed later.

Acknowledgment. The author wishes to thank Professor E. E. van Tamelen for suggesting this study and for providing advice throughout its course. Thanks are also due Professors Lawrence Altman and Cheves Walling for many helpful suggestions. This project was supported by the Army Research Office–Durham (Project No. CRD-AA-5227-C) and the Petroleum Research Fund (Grant 2892 (A1,4)), administered by the American Chemical Society.

---

[4] Presumably in the absence of added hydrogen donors, the excited trityl cation abstracts a hydrogen atom from the methyl group of acetic acid. Due to the removal of all acids in the work-up procedure, products from the acetic acid derived radical were not characterized.

[5] Added hydrocarbons would react with the anion-derived radicals, thereby reducing the amount of electron "retransfer" to regenerate trityl cation and the anion. However, acetoxy or bisulfate radicals would not be expected to exhibit such a large hydrogen abstraction selectivity. The sulfate radical anion is known to be an extremely potent hydrogen abstractor, generating in aqueous base hydroxyl radicals from water (L. Dogliotti and E. Hayon, *J. Phys. Chem.*, **71**, 2611 (1967)). The observed selectivity is three times greater than that reported for methyl radical (W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 170) and still greater than that which would be expected for acetoxy radical. In addition, if acetoxy radical had been formed, considerable decarboxylation would have been expected (M. S. Kharasch and M. T. Gladstone, *J. Amer. Chem. Soc.*, **65**, 15 (1943); T. W. Martin, J. M. Buck, and A. Henshall, *ibid.*, **88**, 1097 (1966)). In expt 2 a maximum of 2% of the theoretical amount of carbon dioxide was obtained.

[6] It has been proposed recently (E. I. Heiba, R. M. Dessau, and W. J. Koehl, *ibid.*, **91**, 6830 (1969)) that the $Co(OAc)_3$ oxidation of alkylbenzenes in acetic acid proceeds *via* electron transfer from the arene to the cobalt(III), followed by proton loss from the resulting cation radical. These workers found that toluene is oxidized 3.3 times faster than cumene in that reaction. A mechanism of this type would also not account for the slight, but definite, effect of added cyclohexane in accelerating the disappearance of trityl cation.

[7] We thank Dr. Alan Duffield for taking the mass spectra (MS-9 direct inlet).

[8] National Institutes of Health Predoctoral Fellow, 1965–1968; address correspondence to Department of Chemistry, Columbia University, New York, N. Y. 10027.

T. M. Cole, Jr.[8]
Department of Chemistry, Stanford University
Stanford, California 94305

Received October 15, 1969

Tri-*t*-butylethylene[1]

Sir:

The members of the family of *t*-butylethylenes have remained elusive compounds; their facile synthesis, particularly of pure samples, has been balked by the bulky groups present and by the propensity of various precursors for rearrangement. Nevertheless *t*-butylethylene (**1**),[2a] 1,1-di-*t*-butylethylene (**2**),[2b] *cis*-1,2-di-*t*-butylethylene (**3**),[2c] and *trans*-1,2-di-*t*-butylethylene (**4**)[2d] have been previously prepared and have proven

---

[1] Presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969, Abstract ORGN 100.

[2] (a) M. Delacre, *Bull. Soc. Chim. Fr.*, **35** (3), 343 (1906); (b) F. C. Whitmore and K. C. Laughlin, *J. Amer. Chem. Soc.*, **55**, 3732 (1933); (c) G. F. Hennion and T. F. Banigan, Jr., *ibid.*, **68**, 1202 (1946); (d) F. L. Howard, T. W. Mears, A. Fookson, and P. Pomerantz, *ibid.*, **68**, 2121 (1946).