

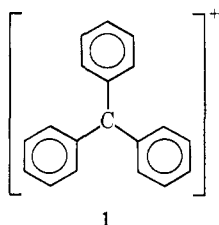
## Photolysis of Carbocationic Species. Triphenylcarbonium Ion

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**Abstract:** Triphenylcarbonium ion was photolyzed with visible light in various acidic media. In 72% aqueous sulfuric acid, bis-*p,p'*-diphenylmethylbiphenyl (3), *p*-diphenylcarbinol-*p'*-diphenylmethylbiphenyl (5), and bis-*p*-diphenylcarbinolbiphenyl (4) were formed, each in about 20% yield. Mechanistic investigations indicate that this dimerization involves interaction of an excited, triplet tritylcarbonium ion with a ground-state tritylcarbonium ion. Dimerization was suppressed by increasing the acidity of the medium, and in 96% sulfuric acid the only product obtained was 9-phenylfluoren-9-ol (formed in 60% yield). In the presence of acetic acid and lower concentrations of sulfuric acid, the excited triplet tritylcarbonium again plays a role, cyclizing to the 9-phenylfluorenyl system or oxidizing the solvent forming trityl radical, which then reacts further. In 3% sulfuric acid-acetic acid the products were 21% triphenylmethane, 22% 9-phenylfluorene, 17% bis-9-phenylfluorenyl peroxide, and 10% benzophenone. In 3% sulfuric acid-16% tolueneacetic acid the products were 20% of a mixture of 9-phenylfluorene and triphenylmethane, 45% 1,1,1,2-tetraphenylethane, and 11% 9-benzyl-9-phenylfluorene. In the presence of oxygen, photolysis of the tritylcarbonium ion in 3% sulfuric acid-acetic acid yielded 37% benzophenone, 28% 2,2-diphenylmethylenedioxybenzene, and 11% of the novel peroxide acetate 17. Under still more weakly acidic conditions the aldehyde acetate 18 was formed. In 30% sulfuric acid-acetic acid, diphenyl-*p*-tritylphenylcarbinol was formed in 30% yield, along with 12% 5, while in 60% sulfuric acid-acetic acid the only product isolated was 4.

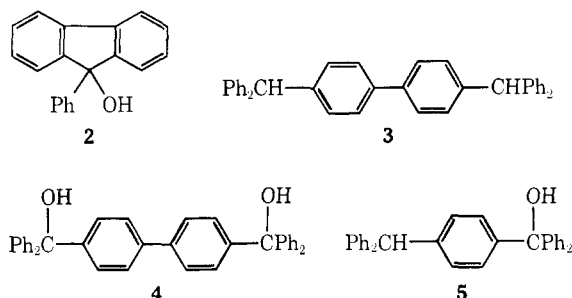
In connection with a general program concerned with the chemical behavior of photoexcited charged carbon species,<sup>1</sup> a study of the long-known, highly stable triphenylcarbonium ion 1 seemed in order. The



investigations described herein reveal that this familiar entity is capable of undergoing a great variety of photo-reactions, depending on such factors as the nature of the solvent, the pH of the medium, and the presence or absence of oxygen. Although this account touches on the complicated problem of mechanism, it mainly purposes to survey the products formed from 1 during irradiation under various conditions (Table I).<sup>2,3</sup>

In essentially all the photolyses carried out in this study, the light source (Hanovia medium-pressure lamp and U(VI) filter)<sup>4</sup> and triphenylcarbonium ion ( $\lambda_{\max}$  430 m $\mu$  ( $\epsilon$   $4 \times 10^4$ )) concentration ( $\sim 10^{-3}$  M) were invariant. However, the nature of products formed was highly dependent on the acidity of the medium. While in 96:4 sulfuric acid-water, 9-phenylfluoren-9-ol (2) was

formed, in 72:28 sulfuric acid-water dimer types 3, 4, and 5 were generated instead. In the first experiment,



irradiation was maintained for almost 40 hr, after which time there was secured a 60% yield (based on consumed trityl ion) of carbinol 2, identical with authentic material. The three products formed in the less acidic medium were isolated and purified by preparative tlc, each being secured in  $\sim 20\%$  yield. The least polar component was at first tentatively identified by means of its ir, uv, and nmr spectral properties, then compared spectrally and by mixture melting point with the known "Tschitschibabin's hydrocarbon" (3). Likewise, the most polar product was inspected initially by spectral means and then compared with a specimen of authentic ditertiary carbinol 4. The substance of intermediate polarity was obtained as an ethyl ether, almost certainly a consequence of long exposure of initially isolated tertiary carbinol 5 to chloroform-ethanol. Not a previously known compound, the ether of alcohol 5 was structurally clarified by means of its uv and nmr properties. 9-Phenylfluoren-9-ol was not detected as a product from the irradiation in 72% sulfuric acid, and no representative of the dimeric system was apparently formed in 96% sulfuric acid. Presumably biphenyls 3, 4, and 5 are interconverted by hydride transfer under the conditions of the experiment. However, because of adverse solubility properties, this relationship could not be tested conveniently.

Runs (72% acid) in which the concentration of carbonium ion only was varied indicate that the reaction is

(1) Other papers in this series: (a) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Amer. Chem. Soc.*, **87**, 4964 (1965); (b) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *ibid.*, **89**, 5073 (1967); (c) E. E. van Tamelen, T. M. Cole, Jr., R. Greeley, and H. Schumacher, *ibid.*, **90**, 1372 (1968); (d) J. I. Brauman, J. Schwartz, and E. E. van Tamelen, *ibid.*, **90**, 5328 (1968); (e) J. Schwartz, *Chem. Commun.*, 833 (1969); (f) E. E. van Tamelen and T. M. Cole, Jr., *J. Amer. Chem. Soc.*, **92**, 4123 (1970); (g) E. E. van Tamelen, J. Schwartz, and J. I. Brauman, *ibid.*, **92**, 5798 (1970).

(2) Part of this work was presented in preliminary form (ref 1c and 1f).

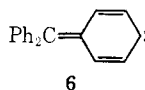
(3) H. Dauben, Jr., reported that 9-phenylfluorene was isolated after trityl perchlorate had lain on a desk top for 15 days: *J. Org. Chem.*, **25**, 1442 (1960).

(4) W. M. Hardham and G. S. Hammond, *J. Amer. Chem. Soc.*, **89**, 3200 (1967).

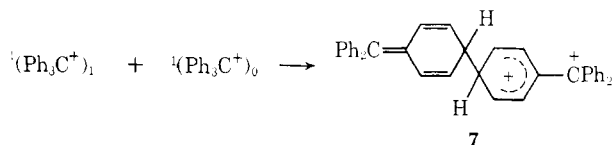
Table I

| Expt | Photolysis medium   | Product  | Yield, % |
|------|---|--|----------|
| 1    | 72% H <sub>2</sub> SO <sub>4</sub> (aqueous)  | <b>3</b>   | 19.5     |
|      |   | <b>4</b>   | 22       |
|      |   | <b>5</b>   | 22       |
| 2    | 96% H <sub>2</sub> SO <sub>4</sub> (aqueous)  | 9-Phenylfluoren-9-ol<br>(no <b>3</b> , <b>4</b> , <b>5</b> ) | 60       |
| 3    | 3.3% H <sub>2</sub> SO <sub>4</sub><br>96.5% CH <sub>3</sub> COOH<br>0.2% H <sub>2</sub> O  | Triphenylmethane   | 21       |
|      |   | 9-Phenylfluorene   | 22       |
|      |   | 9-Phenylfluorenyl peroxide                                   | 17       |
|      |   | Benzophenone   | 10       |
| 4    | 3.3% H <sub>2</sub> SO <sub>4</sub><br>80.1% CH <sub>3</sub> COOH<br>16.4% C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub><br>0.2% H <sub>2</sub> O | 1,1,1,2-Tetraphenylethane                                    | 45       |
|      |   | 9-Benzyl-9-phenylfluorene                                    | 11       |
|      |   | 9-Phenylfluorene (impure)                                    |          |
| 5    | 1.5% H <sub>2</sub> SO <sub>4</sub><br>96.2% CH <sub>3</sub> COOH<br>2.3% C <sub>6</sub> H <sub>6</sub>   | Tetraphenylmethane<br>(plus all products found<br>in expt 3) | 5-10     |
| 6    | 29.4% H <sub>2</sub> SO <sub>4</sub><br>69.4% CH <sub>3</sub> COOH<br>1.2% H <sub>2</sub> O   | <b>15</b>  | 30       |
| 7    | 61% H <sub>2</sub> SO <sub>4</sub><br>36.5% CH <sub>3</sub> COOH<br>2.5% H <sub>2</sub> O   | <b>5</b>   | 12       |
|      |   | <b>4</b>   | 56       |

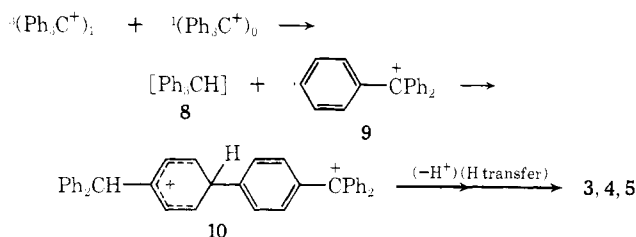
first order in this species. After the reaction was run to 40% completion in H<sub>2</sub>SO<sub>4</sub>-D<sub>2</sub>O, the recovered triphenylcarbinol showed no deuterium incorporation (by mass spectrum), indicating low proton affinity and therefore suggesting that the photocoupling mechanism does not involve a nucleophilic species such as an excited covalent triphenylcarbinyl type or carbene **6**. Negligible



quenching of the reaction by O<sub>2</sub> (saturated solution), I<sub>2</sub>, MnSO<sub>4</sub>, CoSO<sub>4</sub>, NiSO<sub>4</sub>, and CuSO<sub>4</sub> (each ~10<sup>-3</sup> M) was noted. Since the triphenylcarbinol concentration is exceedingly low (~10<sup>-9</sup> M), that ground- or excited-state molecule can hardly play an important role, and, therefore, the coupling process almost certainly features interaction of *two* trityl ions, presumably one in the ground state and the other, excited. Although originally thought<sup>1c</sup> to involve the first excited singlet of an electronically excited  $\sigma$  complex **7**, the mechanism now



appears, on the basis of additional experimental findings,<sup>5</sup> to proceed by interaction of triplet with ground-state carbonium ion, leading to radical cations **8** and **9**,

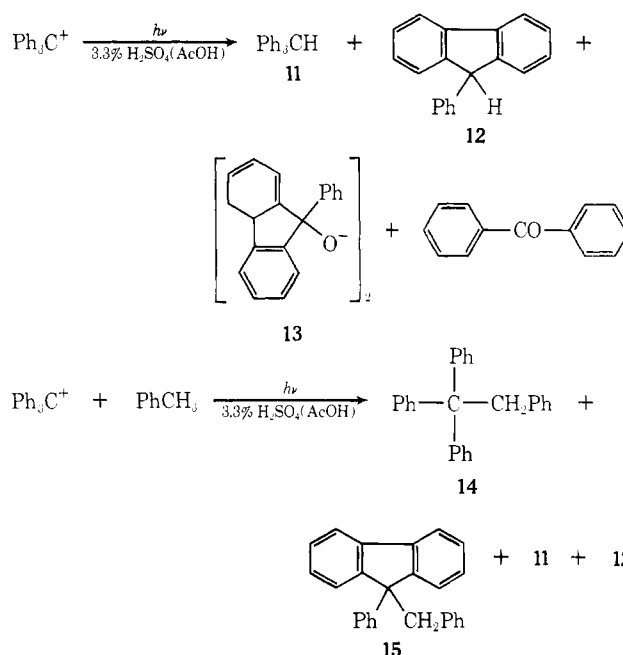


(5) T. M. Cole, Jr., *J. Amer. Chem. Soc.*, **92**, 4124 (1970), and unpublished results.

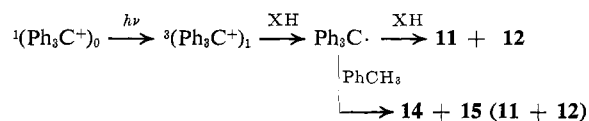
which then combine to precursor **10** of observed products.

Apparently, in an acid concentration of 96%, completion of the reaction sequence to dimers is suppressed, and a cyclization course is followed, at a rate 20 times slower than that of the coupling reaction. In the sulfuric acid medium used, subsequent oxidation of 9-phenylfluorene to the fluorenol might be required and can be observed as a separate reaction.

In the more weakly acidic systems which are about to be described, the dimerization, reaction characteristic of reactions in stronger, aqueous sulfuric acid and involving the excited triplet tritylcarbonium ion, did not occur. Instead, other reactions involving the triplet state supervened, *viz.*, cyclization to the 9-phenylfluorenyl system and reduction by the medium to trityl radical.

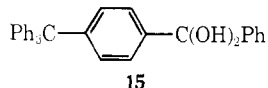


Photolysis of tritylcarbonium ion in 3.3% sulfuric acid, 96.5% acetic acid, and 0.2% water gave (after work-up in air) 21% triphenylmethane (**11**), 22% 9-phenylfluorene (**12**), 17% bis-9-phenylfluorenyl peroxide (**13**), and 10% benzophenone. When benzene was also present in a photolysis of the above sulfuric-acetic acid type, tetraphenylmethane was formed in addition to the above products. Tritylcarbonium ion, when irradiated in 3.3% sulfuric acid, 80.1% acetic acid, 16.4% toluene, and 0.2% water, gave rise to 45% 1,1,1,2-tetraphenylethane (**14**), 11% 9-benzyl-9-phenylfluorene (**15**), and 20% of a mixture of triphenylmethane and 9-phenylfluorene. It is evident from the nature of the products, especially those formed in the presence of toluene, that the photoreaction in the weakly acidic sulfuric-acetic acid medium involves incursion of radical species. That a triplet (excited) trityl ion is prominently involved in these reactions is indicated by the complete suppression, in the presence of oxygen, of reactions leading to the above products and promotion of quite different pathways (*vide infra*). In an overall sense, the



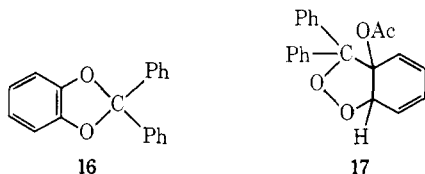
process can be viewed as involving the various reaction courses dependent upon initial, consecutive formation of triplet carbonium ion and trityl radical. However, this version is oversimplified, and the exact mechanism of such changes is taken up in more detail elsewhere.<sup>5</sup>

In 29% sulfuric acid in acetic acid (complete ionization), still a different coupling mode was displayed: the tetraphenylmethane derivative **15** was formed, in

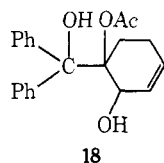


addition to the previously observed photoproduct **5**. It is noteworthy that in this system coupling involves the para site of the first trityl unit and the nonannular carbon in the second. The reasons for this behavior are not obvious. However, at higher mineral acid concentration (61%) in acetic acid, no **15** was formed, but rather a good yield of the original para-para dimer **4** was observed. Thus, as the acidity of the acetic acid system is increased, the photolysis reaction begins to parallel those in the aqueous sulfuric acid systems.

When triphenylcarbonium ion in 3.3%  $\text{H}_2\text{SO}_4$ -96.5%  $\text{CH}_3\text{CO}_2\text{H}$ -0.2%  $\text{H}_2\text{O}$  was photolyzed under oxygen with visible light,<sup>6</sup> there were formed benzophenone (37%), diphenylmethylenedioxybenzene (**16**) (30%), and a substance  $\text{C}_{21}\text{H}_{18}\text{O}_4$ , mp 116-118° (11%), assigned structure **17**. In addition to the molecular ion at 334



the mass spectrum of **17** displayed a first fragmentation peak at 302 ( $-\text{O}_2$ ), then *inter alia* 274 ( $-\text{CH}_3\text{COOH}$ ) and 243 (base peak,  $-\text{O}_2$  and  $\text{CH}_3\text{CO}_2$ ). The uv spectrum revealed maximal absorption at 260  $\text{m}\mu$  ( $\epsilon$  3600), while carbonyl absorption in the ir was located at 1747  $\text{cm}^{-1}$ . Proton resonances ( $\text{CDCl}_3$  solvent, 60 MHz) appeared at  $\tau$  7.92 (3 H, singlet, acetate), 4.85-3.90 (5 H, complex multiplet) and 2.67 (10 H, aromatic singlet). Catalytic reduction (5% Rh/C in aqueous methanol) led to a triol monoacetate (**18**) which was inert to sodium meta-



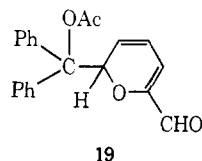
periodate. In the infrared, the reduction product displayed peak absorption at 2.92 ( $-\text{OH}$ ) and 5.81 (acetate)  $\mu$ . An nmr spectrum ( $\text{CDCl}_3$ , HA 100) included the following signals:  $\tau$  8.00 (3 H, singlet, acetate), 8.6-7.8 (4 H, multiplet, methylene), 6.65 (1 H, broad singlet, hydroxyl), 5.78 (1 H, multiplet,  $>\text{CHO}$ ), 5.47 (1 H,

(6) Control experiments indicated that covalent trityl compounds are not photolyzed under the conditions used in these experiments. Furthermore, energy transfer from triplet triphenylcarbonium ion to covalent trityl compounds would be highly endothermic. On the basis of phosphorescence spectra, trityl cation has  $E_t = 50$  kcal/mol (we thank Professor L. Stryer for fluorescence and phosphorescence measurements), while covalent trityl species have  $E_t = 70$  kcal/mol.<sup>7</sup>

(7) Yu. I. Kozlov and D. N. Shigorin, *Dokl. Acad. Nauk SSSR*, **161**, 871 (1965); *Chem. Abstr.*, **63**, 6528 (1965).

broad singlet, hydroxyl), 5.06 (1 H, multiplet, olefinic), 4.68 (1 H, multiplet, olefinic), and 2.76 (10 H, singlet, aromatic). After  $\text{D}_2\text{O}$  exchange, the  $\tau$  5.47 and 6.65 signals disappeared, while the  $\tau$  5.78 peak sharpened into a doublet. It was found that the peroxide **17** is stable in the dark to the reaction conditions and hence is apparently not an intermediate in the formation of the other products of the photolysis (sensitization of **17** by triphenylcarbonium ion would be expected to be endothermic, and **17** is nonabsorbing under the condition of the photolysis).

At lower acid concentrations (1%  $\text{H}_2\text{SO}_4$ ) triphenylcarbonium ion provided on photolysis an aldehyde acetate (**19**) in addition to the above products. This

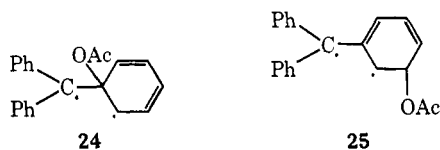


substance possessed (high-resolution mass spectrum) the formula  $\text{C}_{21}\text{H}_{18}\text{O}_4$ . In addition to the molecular ion, the low-resolution mass spectrum included fragmentation peaks at  $m/e$  292 ( $-\text{CH}_2\text{CO}$ ), 274 ( $-\text{CH}_3\text{CO}_2\text{H}$ ), and 245 ( $-\text{CH}_3\text{CO}_2\text{H}$  and  $\text{CHO}$ ). Carbonyl absorption appeared in the ir at 1750 and 1700  $\text{cm}^{-1}$  and in the uv at 298 and 309  $\text{m}\mu$  (conjugated). In an nmr analysis, the aldehyde displayed signals at  $\tau$  8.25 (3 H, singlet), 4.20-3.70 (4 H, complex multiplet), 2.81 (10 H, singlet), and 0.75 (1 H, singlet). Saponification provided the expected aldehyde alcohol, whereas reduction with sodium borohydride effected simple conversion of the aldehyde function to the corresponding alcohol ( $\lambda_{\text{max}}$  264, 270  $\text{m}\mu$ ).

*A priori*, there appear to be only two reasonable mechanisms which might account for these products. One involves the interaction of triplet carbonium ion with ground-state oxygen (triplet) to give singlet oxygen, which could then react with ground-state tritylcarbonium ion, producing peroxide **20**. The other mechanism involves the direct combination of triplet tritylcarbonium ion with ground-state molecular oxygen, again forming **20**. The latter mechanism is favored on the basis of the following considerations. The ready reaction of singlet oxygen with triphenylcarbonium ion might not be expected, as singlet oxygen is thought to be electrophilic.<sup>8a</sup> In addition, to the extent that the analogy of singlet oxygen to ethylene is valid, addition in the necessary fashion to triphenylcarbonium ion would be symmetry forbidden.<sup>8b</sup> Further, under conditions in which all of the incident light is being absorbed (in the absorption range of tritylcarbonium ion) the rate of excitation of tritylcarbonium ion and ultimately the rate of triplet formation would not change. Since the concentration of oxygen does not vary, the rate of formation of singlet molecular oxygen would remain constant, and the rate of formation of **20** would then depend on the concentration of ground-state tritylcarbonium ion, since the reaction of singlet oxygen with tritylium ion is a bimolecular reaction in competition with the unimolecular decay of the singlet oxygen. However, when the photolysis was

(8) (a) C. S. Foote, *Accounts Chem. Res.*, **1**, 104 (1968); (b) however, for exceptions, see P. D. Bartlett and A. P. Schaap *J. Amer. Chem. Soc.*, **92**, 3223 (1970).

carried out at different tritylcarbonium ion concentrations, the rate of disappearance of tritylium ion did not change. Thus, it appears that the oxygenated products do not arise by a singlet oxygen mechanism and hence, probably arise from the direct interaction of ground-state molecular oxygen with either excited triplet carbonium ion or possibly a diradical intermediate such as **24** to **25**, formed by addition of acetate to the excited



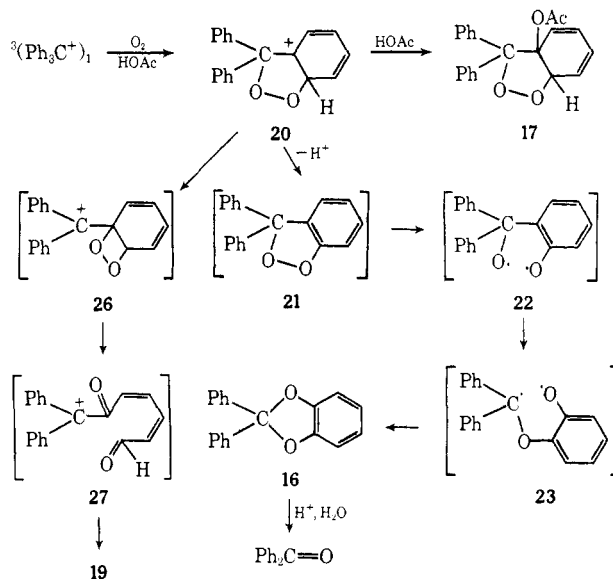
triplet carbonium ion. However, since the formation of diphenylmethylenedioxybenzene (**16**) and benzophenone can be rationalized most easily by postulating deprotonation and rearrangement of carbonium ion **20**, the simplest explanation for formation of these oxygenated products involves *initial capture of oxygen* by the triplet carbonium ion. Such a mechanism is consistent with all available data. In addition, the following considerations weigh against prior acetate capture by the triplet carbonium ion. As has been discussed earlier, in the absence of oxygen the triplet tritylcarbonium is reduced to trityl radical. The rate of the electron-transfer reaction appears to be comparable with the net rate of the reaction of the carbonium ion with oxygen. If, when oxygen is present, the triplet carbonium ion were reacting first with some species other than oxygen, there would be no reason for the electron-transfer reaction not to occur. In that case, trityl peroxide would be expected as a product, but in fact is not found. The only explanation for the complete suppression of the electron-transfer reaction by oxygen is that oxygen is the first species to react with the excited triplet carbonium ion.

The addition of oxygen to the excited triplet carbonium ion could proceed either by the concerted formation of both carbon-oxygen bonds, or by a two-step process in which one oxygen-carbon bond is formed at a time. Once the peroxide bridge is formed, the positive charge will be localized in the carbocyclic nonbenzenoid ring. Attack of acetate or acetic acid could presumably occur at the 1, 3, or 5 positions of this ring, the first possibility apparently being favored.

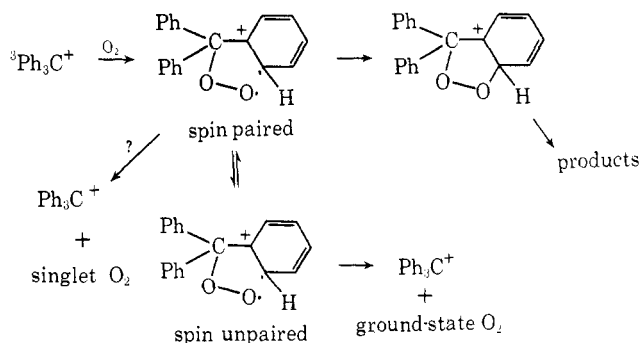
Aside from acquiring acetate, carbonium ion **20** would be expected to lose a proton, forming the fully aromatic peroxide **21**. This substance was not isolated, but is strongly implicated as an intermediate in the formation of diphenylmethylenedioxybenzene and benzophenone. Walling<sup>9</sup> has shown that diaryl peroxides are stable only at very low temperature, decomposing upon warming to aryloxy radicals (due to the weakness of the peroxide oxygen-oxygen bond and to the stability of the resulting aryloxy radicals). As illustrated, a similar homolytic cleavage of the peroxide bond of **21** would lead to diradical **22**. Since triphenylmethoxy radical is known to undergo phenyl migration to form the more stable diphenylphenoxymethyl radical the analogous aryl migration in the present case would be expected, forming **23**.<sup>10</sup> The latter would cyclize to diphenylmethylenedioxybenzene (**16**).

dioxybenzene, some of which would be hydrolyzed during the work-up, forming observed benzophenone.

Under more weakly acidic conditions the aldehyde acetate **19** (see above) was isolated in about 5% yield, in addition to the above-mentioned oxygen-derived products. The skeleton of **19** is consistent with its formation from carbonium ion **20**, suggesting the mechanism for its formation as shown. On the basis of precedent, the four-membered peroxide **26** would be expected to cleave to keto aldehyde **27**, the precursor of observed product **19**.<sup>11-14</sup>



In an attempt to determine whether carbonium **20** was being formed reversibly, the photolysis was carried out using ortho- and para-deuterated triphenylcarbonium ion. The isotopic species disappeared at the same rate as nondeuterated triphenylcarbonium ion, suggesting that **20** does not lose oxygen to any significant extent. If the formation of **20** were to a large extent reversible, one would find a rate-determining proton removal in going from **20** to **21**. Since most of the products are formed from **21**, ortho deuteration would be expected to slow the rate of photolysis of triphenylcarbonium ion. (Deuteration would not be expected to affect the rate of formation of **26** and **17**). It is tempting to speculate that the formation of **20** is a two-step process as shown below, thus providing a method for deactivation of the triplet without necessarily leading to products **6** and **17**.



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

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

(11) 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).

## Experimental Section

**General Procedure for Photolyses.** Unless otherwise stated, the following procedure was used for the photolyses. Triphenylcarbinol was recrystallized from hot benzene, and the resulting crystals were dried at 100° *in vacuo* (ca. 0.1 mm). The appropriate amount of triphenylcarbinol was then dissolved (in the dark) in 250–300 ml of the acidic medium. The resulting solution was placed in a three-necked Pyrex outer jacket, fitted with a quartz immersion well. The solution was stirred both by a magnetic stirrer and by the stream of nitrogen gas introduced near the bottom of the reaction vessel. The exit nitrogen stream was passed into water in all open flask to remove traces of the reaction solvent and to provide an indication of the nitrogen flow rate. A third neck of the reaction vessel was used to remove aliquots to check on the progress of the reaction.

The light source for the photolyses was a 450-W Hanovia medium pressure mercury lamp, surrounded by a uranium(VI) glass filter and located inside the quartz immersion well. The entire system was cooled by a stream of water running through the (double-jacketed) immersion well. The entire apparatus was covered with aluminum foil.

Before commencing each photolysis, nitrogen was bubbled through the reaction medium for at least 15 min to remove dissolved gases. As soon as each preparative photolysis was complete, the reaction medium was poured into 300 ml of an ice-water mixture. The resulting solution-suspension was then extracted two times with 200 ml of benzene and then one time with 100 ml of benzene. The combined organic phase was then washed with water and saturated sodium bicarbonate solution (until the aqueous phase remained neutral). The organic phase was then dried with anhydrous sodium sulfate and concentrated on a rotary evaporator at aspirator vacuum. The concentrate was then subjected to continuous preparative thin-layer chromatography, using Merck silica gel GF. Solvents, non-absorbing in the ultraviolet, were normally used to develop the preparative thin-layer plates, so that the chromatographic development could be followed by examining the plate under ultraviolet light. As soon as well-resolved bands were observed, the thin-layer plate was dried, and the separated products were eluted from the silica gel with acetone. If necessary, the isolated products were further purified by crystallization or further chromatography. Since *continuous* preparative thin-layer chromatography was normally employed, *R<sub>f</sub>*'s were meaningless and were not recorded.

The ultraviolet and visible spectra described were obtained either on a Cary recording spectrophotometer, Model 14M, or on a Bausch and Lomb Spectronic 505. The infrared spectra described were obtained either on a Perkin-Elmer 137 infrared spectrophotometer (PE 137), or on a Perkin-Elmer 421 infrared spectrophotometer (PE 421).

**Photolysis in 72% Aqueous Sulfuric Acid.** A solution of 0.050 g of triphenylcarbinol in 180 ml of 96% sulfuric acid and 120 ml of distilled water was photolyzed under nitrogen for 2 hr. The reaction was worked up (as described in the general procedure), leaving 0.050 g of yellow oil. This yellow oil was then subjected to non-continuous preparative thin-layer chromatography, using benzene as the solvent, resulting in the separation of four compounds.

The least polar compound (*R<sub>f</sub>*: 0.75–0.95), after elution from the silica gel by acetone, was crystallized from methanol-water, yielding crystals melting on a hot stage at 163–165°. The ultraviolet spectrum in cyclohexane for this product had  $\lambda_{\text{max}}$  269 (shoulder), 265, and 262 m $\mu$  (shoulder). The infrared spectrum in chloroform had bands at 3.27 (shoulder), 3.30, 3.46, 5.11, 5.25, 5.50, 5.67, 6.24, 6.71, 6.92, 7.15, 7.50, 7.60, 7.72, 7.94, 8.45, 8.55, 8.97, 9.29, 9.70, 9.93, 10.85, 11.42, 12.00, and 14.35  $\mu$ . The nmr spectrum in CDCl<sub>3</sub> (A-60) had in the aromatic region a pattern of three broad singlets: the resonances at  $\tau$  2.42 and at 2.57 totaled four hydrogens, while the resonance at 2.77 integrated for 24 hydrogens. In addition there was a singlet at  $\tau$  4.41 integrating for two hydrogens. These spectral properties indicated that the compound was bis-4,4'-diphenylmethylbiphenyl (lit.<sup>15</sup> mp 162–163° from benzene), which had been prepared by Tschitschibabin.<sup>15</sup> The "authentic" material was prepared by formic acid-sodium formate reduction (the reduction method of Kovache),<sup>16</sup> of bis-4,4'-diphenylcarbinolbiphenyl. The ir, uv, and nmr of the authentic bis-4,4'-diphenylmethylbiphenyl were identical with the corresponding spectra of the

photoproduct. However, the melting point (on a hot stage) of this compound (crystallized from benzene) was 150–151°. When the photoproduct and the authentic material were mixed, melted, and allowed to resolidify, the hot-stage melting point of the resolidified mixture was 161–163°. The yield of the bis-4,4'-diphenylmethylbiphenyl (before crystallization) was 0.007 g, which represents ca. 20% conversion from triphenylcarbinol.

The compound of *R<sub>f</sub>* 0.48–0.55, after elution from the silica gel by acetone, weighed 0.008 g. As a result of standing in chloroform for 2 weeks, it was converted to its ethyl ether (by the ethanol in the chloroform). The nmr of the ethyl ether in CDCl<sub>3</sub> (A-60) had a moderately complex pattern in the aromatic region from  $\tau$  2.3 to 3.0 integrating for 28 protons, a methine C–H singlet at 4.41 integrating for one proton, a methylene quartet at 6.84 (*J* = 7 Hz) integrating for two protons, and a methyl triplet at 8.77 (*J* = 7 Hz) integrating for three protons. The infrared spectrum in chloroform had bands at 3.27, 3.33, 3.40, 3.46, 5.10, 5.26, 5.50, 5.85, 6.25, 6.72, 6.93, 7.21, 7.62, 8.50, 8.67, 9.00, 9.40, 9.70, 9.95, 10.50, 10.90, 11.07, 11.41, 12.03, and 14.38  $\mu$ . The ultraviolet spectrum in cyclohexane had  $\lambda_{\text{max}}$  at 268 (shoulder), 263, and 260 m $\mu$ . These spectral data indicate that the compound is 4-diphenylmethyl-4'-diphenylethoxymethylbiphenyl. Presumably the corresponding alcohol, 4-diphenylcarbinol-4'-diphenylmethylbiphenol, was the product originally obtained from the preparative thin-layer chromatography. The yield of 0.008 g represents ca. 22% conversion from triphenylcarbinol.

The compound of *R<sub>f</sub>* 0.40–0.50, after elution from the silica gel by acetone, weighed 0.014 g, and was shown to be unreacted triphenylcarbinol by its infrared spectrum, melting point, and mixture melting point with authentic triphenylcarbinol (161–162°).

The most polar product (*R<sub>f</sub>* 0.02–0.05), after elution from the silica gel by acetone, weighed 0.008 g. This product was crystallized from absolute ethanol, yielding crystals which melted at 160–165°, resolidified, and then remelted at 184–186°. The infrared spectrum of this product in chloroform had bands at 2.76, 3.25, 3.30, 3.39, 3.49 (shoulder), 5.11, 5.23, 5.51, 5.86, 6.23, 6.71, 6.92, 7.20, 7.55, 8.43, 8.60, 8.65 (shoulder), 9.25, 9.68, 9.76 (shoulder), 9.85 (shoulder), 9.92, 10.60, 11.14, 11.73, 12.16, and 14.37  $\mu$ . The ultraviolet spectrum in cyclohexane had  $\lambda_{\text{max}}$  at 268 (shoulder), 263, and 260 m $\mu$ . The visible spectrum in concentrated sulfuric acid had  $\lambda_{\text{max}}$  at 525 ( $\epsilon$  93,500), 443 ( $\epsilon$  55,900), and 410 m $\mu$  (shoulder). The nmr spectrum in acetone-*d*<sub>6</sub> (A-60) had a moderately complex pattern in the aromatic region from  $\tau$  2.3 to 2.9, integrating for 28 protons, and a singlet at  $\tau$  4.82, integrating for two protons. Both melting points for this photoproduct corresponded to the melting points of bis-4,4'-diphenylcarbinolbiphenyl, which had been prepared by Tschitschibabin.<sup>15</sup> This compound was prepared by the method of Tschitschibabin, and crystallized from ethanol, yielding a crystalline product which melted at 162–165°, resolidified, and then remelted at 182–185°. The mixture of this compound and the photoproduct melted at 160–165°, resolidified, and then remelted at 182–185°. The infrared, ultraviolet, and visible spectra of the authentic compound were identical with the corresponding spectra of the photoproduct. The yield of 0.008 g of bis-4,4'-diphenylcarbinolbiphenyl represents a conversion of 22% from triphenylcarbinol.

**Preparation of Ortho- and Para-Deuterated Bromobenzene.** The method of Akawie was used to prepare 2,4,6-trideuteriobromobenzene.<sup>17</sup> Aniline hydrobromide, prepared from 0.2 mol of aniline (18.6 g), was heated five times with D<sub>2</sub>O (99.8% from Stohler Isotope Chemicals, Azusa, Calif. 91702), yielding 36.0 g (0.2 mol) of aniline-*N,N*,2,4,6-*d*<sub>3</sub> hydrobromide. This hydrobromide was diazotized and then added to CuBr, giving 13.2 g of the tri-deuterated bromobenzene. The nmr spectrum (A-60) of the neat bromobenzene showed only one signal—at  $\tau$  3.33 (meta protons)—indicating that the bromobenzene is completely deuterated in the ortho and para positions.

**Preparation of Ortho- and Para-Deuterated Triphenylcarbinol.** The triphenylcarbinol preparation of Shamshurin was used.<sup>18</sup> Trideuterated phenyl Grignard was prepared by treating 11.9 g of the deuterated bromobenzene with 1.99 g of magnesium in ether. To the resulting Grignard reagent was added 2.93 g of diethylcarbonate. Work-up, followed by crystallization of the product from carbon tetrachloride, yielded 4.216 g (mp 160–162°, after drying at 100° *in vacuo*) of ortho- and para-deuterated triphenylcarbinol. The nmr spectrum of the carbonium ion showed a single

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(16) A. Kovache, *Ann. Chem.*, **10**, 205 (1918).

(17) R. I. Akawie, J. M. Scarborough, and J. G. Burr, *J. Org. Chem.*, **24**, 946 (1959).

(18) A. A. Shamshurin, *J. Gen. Chem. USSR*, **13**, 569 (1943); *Chem. Abstr.*, **39**, 700 (1945).

signal at  $\tau$  2.12. The mass spectrum of the carbinol (taken on the MS-9 direct inlet machine) had  $m/e$  (intensity relative to base peak, %) 270 (6.2), 269  $M^+$  (28.1), 268 (3.8), 252 (3.8), 251 (3.1), 190 (15.6), 189 (100), 188 (26.2), 187 (3.8), 186 (2.5), 171 (6.2), 170 (6.2), 162 (3.8), 161 (2.3), 160 (23.7), 159 (12.5), 109 (8.8), 108 (95.0), 107 (8.8), 94 (5.0), 81 (8.8), 80 (53.7), 79 (7.5), 53 (71.5), and 52 (5.6). Metastable ions were observed at  $m/e$  131.4, 95.2, 61, 8, 59.3, 43.7, 35.2, and 33.7. The mass spectrum of nondeuterated triphenylcarbinol (taken on the MS-9 direct inlet machine) had  $m/e$  (per cent of base peak) 261 (5.0), 260  $M^+$  (22.9), 259 (1.8), 184 (12.4), 183 (82.1), 182 (16.1), 181 (4.1), 165 (9.6), 155 (1.9), 154 (22.9), 106 (8.7), 105 (100), 91 (3.7), 78 (9.2), 77 (6.9), and 51 (16.1). Metastable ions were observed at  $m/e$  127.5, 91.3, 60.2, 56.4, 42.5, and 33.8.

**Photolysis in 72% Aqueous Sulfuric Acid. Deuterium Isotope Effect.** A solution of 0.0500 g of triphenylcarbinol ( $1.92 \times 10^{-4}$  mol) in a solution of 120 ml of distilled water and 180 ml of 96% sulfuric acid was photolyzed under nitrogen for 1 hr. At the beginning and at the end of the photolysis a 0.1-ml aliquot was diluted to 5 ml with 96% sulfuric acid and the absorbance of the resulting solution was measured at 432  $m\mu$ . At the beginning of the reaction the absorbance at 432  $m\mu$  was 0.52, and at the end of 1-hr photolysis the absorbance at 432  $m\mu$  was 0.32 and the absorbance at 525  $m\mu$  (glycol) was 0.17. The decrease in absorbance at 432  $m\mu$  was 0.20.

Similarly a solution of 0.517 g ( $1.92 \times 10^{-4}$  mol) of ortho- and para-deuterated triphenylcarbinol in a solution of 120 ml of distilled water and 180 ml of 96% sulfuric acid was photolyzed under nitrogen for 1 hr. The decrease in absorbance at 432  $m\mu$  was 0.08. According to the decrease in absorbance of the triphenylcarbonium ion, the nondeuterated triphenylcarbinol disappeared 2.5 times faster than the ortho- and para-deuterated triphenylcarbinol.

**Photolysis of 77% Aqueous Sulfuric Acid.** A solution of 0.050 g ( $1.92 \times 10^{-4}$  mol) of triphenylcarbinol in a solution of 210 ml of 96% sulfuric acid and 90 ml of water was photolyzed under nitrogen for 1 hr. At the beginning of the reaction the absorbance (measured as above) at 432  $m\mu$  was 0.49. After 1 hr of photolysis the absorbance at 432  $m\mu$  was 0.42 while the absorbance at 525  $m\mu$  (glycol) was 0.06. The decrease in absorbance at 432  $m\mu$  was 0.07. The decrease in absorbance for triphenylcarbonium ion in 72% sulfuric acid had been 0.20. Thus the disappearance of triphenylcarbonium ion in 72% sulfuric acid is *ca.* 2.9 times faster than its disappearance in 77% sulfuric acid.

**Effect of Oxygen on the Photolysis in 72% Aqueous Sulfuric Acid.** A solution of 0.050 g of triphenylcarbinol ( $1.92 \times 10^{-4}$  mol) in a solution of 180 ml of 96% sulfuric acid and 120 ml of distilled water was photolyzed under nitrogen for 1 hr. At the beginning and at the end of the photolysis a 0.1-ml aliquot was diluted to 5 ml with 96% sulfuric acid, and the absorbance of the resulting solution at 432  $m\mu$  was measured. At the beginning of the photolysis the absorbance was 0.52 at 433  $m\mu$  and 0.0 at 525  $m\mu$ . After 1 hr of photolysis the absorbance at 433  $m\mu$  was 0.32 and at 525  $m\mu$  was 0.14. The decrease in absorbance at 433  $m\mu$  was 0.15.

Similarly 0.050 g of triphenylcarbinol was photolyzed under oxygen (after oxygen had been passed through the system for 15 min). At the beginning of the photolysis the absorbance at 433  $m\mu$  was 0.55. After 1 hr of photolysis the absorbance at 433  $m\mu$  was 0.51 and at 525  $m\mu$  was 0.04. The decrease in absorbance for triphenylcarbonium ion was 0.04. Thus the disappearance of triphenylcarbonium ion is slowed down by a factor of *ca.* 3.8 when the system is saturated with oxygen.

**Photolysis in Sulfuric Acid-Deuterium Oxide.** A solution of 0.050 g of triphenylcarbinol in 32 ml of 96% sulfuric acid plus 8 ml of deuterium oxide (99.8%  $D_2O$ ) was photolyzed for 1 hr. At the end of this time the formation of the para-para dimer was indicated by absorption at 525  $m\mu$ . The solution was subjected to the usual work-up, and the product was subjected to preparative thin-layer chromatography using chloroform as solvent. The yield of recovered triphenylcarbinol was 0.029 g. (That this was triphenylcarbinol was confirmed by its infrared spectrum in chloroform and its melting point (161–162°). The mass spectrum of the recovered triphenylcarbinol, obtained on the MS-9 (direct inlet system), indicated (by comparison with the mass spectrum of authentic triphenylcarbinol) that no incorporation of deuterium had occurred.

**Effect of Triphenylcarbonium Ion Concentration on Its Rate of Photolysis in 72% Aqueous Sulfuric Acid.** A solution of 0.050 g of triphenylcarbinol was photolyzed for 1 hr under nitrogen in a solution of 180 ml of 96% sulfuric acid plus 120 ml of distilled water. At the beginning and end of the photolysis a 0.1-ml aliquot was diluted to 5 ml with 96% sulfuric acid and the optical density

of the resulting solution was determined at 433 and 525  $m\mu$ . At the beginning of the photolysis the absorbance of triphenylcarbonium ion (at 433  $m\mu$ ) was 0.48. At the end of 1 hr of photolysis the absorbance at 433  $m\mu$  was 0.33 and the absorbance at 525  $m\mu$  was 0.14. The decrease in absorbance for triphenylcarbonium ion was 0.15.

Similarly a solution of 0.025 g of triphenylcarbinol was photolyzed under nitrogen in a medium of the same composition. The absorbancies were determined, as described above. At the beginning of the photolysis the absorbance at 433  $m\mu$  was 0.24. At the end of 1 hr of photolysis the absorbance at 433  $m\mu$  was 0.16, and the absorbance at 525  $m\mu$  was 0.07. The decrease in absorbance for triphenylcarbonium ion was 0.08.

This experiment indicates that the rate of disappearance of tritylcarbonium ion is dependent of its concentration. It appears that when the concentration of triphenylcarbonium ion was halved, its rate of disappearance (and also the rate of dimer formation) was halved.

**Photolysis in 3.3% Sulfuric Acid, 96.5% Acetic Acid, and 0.2% Water.** A solution of 0.100 g of triphenylcarbinol in 294 ml of glacial acetic acid plus 6 ml of 96% sulfuric acid was photolyzed for 1 hr and 30 min. The reaction was then worked up in the usual manner (see general procedure). The crude product was then subjected to continuous preparative thin-layer chromatography, using carbon tetrachloride as the solvent. Three intensely ultraviolet-active bands separated.

The least polar material was eluted from the silica gel by acetone yielding 0.047 g of oil which crystallized. This material was again subjected to continuous preparative thin-layer chromatography, using hexane as the solvent. Two poorly separated bands were obtained. The least polar product, which weighed 0.010 g, was discarded. The second product weighed 0.039 g. Its ultraviolet spectrum in cyclohexane was virtually identical with that of 9-phenylfluorene. Vapor phase chromatography on a 6-ft column ( $\frac{1}{4}$  in. diameter) of 5% Apiezon L-Chromosorb G (the F & M Model 700 thermal conductivity instrument was used, with an oven temperature of 285°, a detector temperature of 320°, an injector temperature of 295°, and a helium flow rate of 40 ml/min) showed that the 0.039 g was a mixture of 0.0195 g of triphenylmethane and 0.0195 g of 9-phenylfluorene. (The retention time for the triphenylmethane was 9.3 min and for the 9-phenylfluorene was 15.9 min). The identity of the products was confirmed by coinjection of the photoproducts with a mixture of authentic triphenylmethane and 9-phenylfluorene.

The material of intermediate polarity was eluted from the silica gel by acetone. This material was crystalline (mp 175–185°) and weighed 0.017 g. Recrystallization from benzene yielded crystals which, after drying at 100° under high vacuum, melted at 191–192° (oil bath). Authentic bis-9-phenylfluorenyl peroxide melted (oil bath) at 191–192°. The mixture melting point of the photoproduct and authentic material was 191–192°. The infrared spectrum of authentic bis-9-phenylfluorenyl peroxide, taken under identical conditions, was identical with that of the photoproduct.

The most polar product was eluted from the silica gel by acetone, and weighed 0.004 g. This product was identified as benzophenone by its infrared spectrum in chloroform and by its 2,4-dinitrophenylhydrazone.

**Photolysis in 3.3% Sulfuric Acid, 80% Acetic Acid, 16.4% Toluene, and 0.2% Water.** A solution of 0.200 g of triphenylcarbinol in 50 ml of toluene, 200 ml of glacial acetic acid, and 2 ml of 96% sulfuric acid was gas photolyzed for 2 hr 15 min under nitrogen. The reaction was worked up in the usual manner (see general procedure), and the resulting product was divided into four equal portions, which were each subjected to an 8-hr continuous preparative thin-layer chromatography using 60–68° petroleum ether as solvent. In each chromatography three main ultraviolet-active bands were observed.

The least polar material from the four plates was eluted from the silica gel by acetone, yielding 0.046 g of white crystalline solid. This solid was crystallized twice from cyclohexane, yielding a product melting at 143–144°. The ultraviolet spectrum of this recrystallized product in cyclohexane had  $\lambda_{max}$  304, 297 (shoulder), 293, 281 (shoulder), 276, 269, 265, 260 (shoulder), and 231  $m\mu$ . This was identical with the ultraviolet spectrum of authentic 9-phenylfluorene taken under identical conditions (the authentic material was prepared by the method of Kovache).<sup>16</sup> The melting point of the authentic 9-phenylfluorene was 146–148°, and the mixture melting point of the photoproduct and the authentic material was 144–147°.



The product of intermediate polarity (from the four plates) was eluted from the silica gel, yielding 0.115 g of light-yellow oil which crystallized. The ultraviolet spectrum in cyclohexane had  $\lambda_{\max}$  270, 265, 260, and 255  $m\mu$ . The nmr spectrum (A-60) in  $CDCl_3$  had signals for 20 aromatic protons (a 14-proton singlet at  $\tau$  2.81, a 4-proton, complex pattern at 3.0, and a 2-proton, complex pattern at 3.35), and two benzylic protons (a 2-proton singlet at  $\tau$  6.09). After crystallization from ethanol-hexane, this photoproduct had mp 141–142°. The melting point of authentic 1,1,1,2-tetraphenylethane, prepared by the method of Fuson,<sup>19</sup> was 142–143°, and the mixture melting point of the photoproduct and authentic 1,1,1,2-tetraphenylethane was 141–143°. The ultraviolet spectrum in cyclohexane and the nmr in  $CDCl_3$  of authentic 1,1,1,2-tetraphenylethane were identical with the corresponding spectra of the photoproduct. The yield of 0.115 g of this photoproduct represents a 45% yield from starting triphenylcarbinol.

The most polar material (from the four plates) was eluted from the silica gel by acetone, yielding 0.028 g of light yellow oil. This oil was then subjected to a 24-hr continuous preparative thin-layer chromatography using (60–68°) petroleum ether as solvent. Two bands were obtained. The least polar, after elution from the silica gel, was shown to be more 1,1,1,2-tetraphenylethane. The most polar material was eluted from the silica gel by acetone, yielding 0.019 g of oil. This oil was then subjected to noncontinuous preparative thin-layer chromatography (benzene), yielding ( $R_f$  0.65–0.75) 0.012 g of oil. A further noncontinuous preparative thin-layer chromatography, using carbon tetrachloride, yielded 0.012 g of material, and indicated that the material was now homogeneous. This material was crystallized from hexane, yielding crystals melting at 136–137°. The ultraviolet spectrum in cyclohexane of this photoproduct had  $\lambda_{\max}$  307, 300, 295, 278 (shoulder), 271, 267, 263 (shoulder), and 239  $m\mu$ . The nmr spectrum (A-60) had signals for 18 aromatic protons (10 protons from  $\tau$  2.4 to 2.9, mainly a singlet at 2.74, a five-proton complex pattern centered at 3.20, and a three-proton complex pattern centered at 3.53, and two benzylic protons (a singlet at 6.22). The ultraviolet and nmr spectra obtained for the photoproduct were identical with those of authentic 9-benzyl-9-phenylfluorene prepared by the method of Bachmann<sup>20</sup> (mp 136–137°). The mixture melting point of the photoproduct and authentic material was (undepressed) 136–137°.

In a control experiment, 0.020 g of triphenylcarbinol was dissolved in a solvent mixture of 20 ml of glacial acetic acid, 5 ml of toluene, and 0.5 ml of 96% sulfuric acid, and allowed to stand in the dark for 3 hr. At the beginning and at the end of this experiment, the absorbance at 433  $m\mu$  of a 0.5-ml aliquot diluted to 5 ml with concentrated sulfuric acid was measured. The absorbance at the beginning of the experiment was 1.13 and at the end of the experiment was 1.15. This indicated that no destruction of the triphenylcarbinol had occurred.

**Photolysis in 1.5% Sulfuric Acid, 96.2% Acetic Acid, and 2.3% Benzene.** A solution of 0.200 g of triphenylcarbinol in 250 ml of glacial acetic acid, 2 ml of 96% sulfuric acid, and 8 ml of benzene was photolyzed under nitrogen for 1 hr, 15 min. The reaction was worked up in the usual manner (see general procedure). Vapor phase chromatography on a 6-ft column of 5% Apiezon L-Chromosorb G, using a column temperature of 280°, indicated by co-injection the presence of triphenylmethane, 9-phenylmethane, and tetraphenylmethane plus unidentified products in the reaction mixture. Upon removing the benzene solvent, an oil was obtained which partially crystallized. Trituration with benzene left crystals, which were recrystallized twice from hot benzene, yielding 0.012 g (5% of tetraphenylmethane, mp 280–282° (hot stage)). The melting point of authentic tetraphenylmethane was 283–285°, and the mixture melting point of the authentic tetraphenylmethane and the phototetraphenylmethane was 280–285°.

**Photolysis in 3.3% Sulfuric Acid, 96.5% Acetic Acid, and 0.2% Water in the Presence of Oxygen.** A solution was made of 0.050 g of triphenylcarbinol in 294 ml of glacial acetic acid and 6 ml of 96% sulfuric acid. After oxygen had been bubbled through the solution for 15 min, the solution was photolyzed under oxygen for 15 min, after which time the color due to the carbonium ion had disappeared. The reaction was worked up in the usual manner (see general procedure) yielding 0.044 g of yellow oil. This oil was subjected to a noncontinuous preparative thin-layer chromatography, using chloroform as the solvent. Three intensely ultraviolet-active bands were obtained.

The least polar material (at the solvent front) was eluted from the silica gel by acetone, yielding 0.015 g of crystals melting at 92–94° (hot stage). The infrared spectrum of this product in chloroform was identical with that for authentic 2,2-diphenylmethylenedioxybenzene and had bands at 3.28, 6.13, 6.75, 6.92, 7.36, 7.63, 7.95 (shoulder), 8.25, 8.48, 9.12, 9.28, 9.60, 9.82, 10.53, 10.90, 10.96, and 14.38  $\mu$ . The ultraviolet spectrum in cyclohexane had  $\lambda_{\max}$  290, 289, 280, 273 (shoulder), 268 (shoulder), and 258 (shoulder)  $m\mu$ . The A-60 nmr in  $CDCl_3$  showed a complex pattern of ten aromatic protons from 2.20 to 2.85 and a four-proton singlet at 3.17. An HR-100 spectrum resolved the low-field multiplet into two multiplets (the lower field multiplet had four protons and the other had six protons), and split the singlet at  $\tau$  3.17 into a complex  $A_2B_2$  pattern characteristic of symmetrically ortho-disubstituted benzenes. An oil-bath melting point determination gave 91–92°, as the melting point for the photoproduct, authentic 1,2-diphenylmethylenedioxybenzene,<sup>21</sup> and a mixture of the photoproduct and authentic material.

The material of intermediate polarity was eluted from the silica gel by acetone, yielding 0.013 g of benzophenone (the infrared spectrum in chloroform was identical with that of authentic benzophenone).

The most polar material (slightly separated from the benzophenone) was eluted from the silica gel by acetone, yielding 0.006 g of light-yellow oil which crystallized. The infrared spectrum of this product in carbon tetrachloride had bands at 3.27, 3.42, 3.50, 5.74 (acetate carbonyl), 6.25, 6.71, 6.93, 7.33, 7.60, 8.20, 8.49, 8.81, 9.55, 10.00, 10.98, 11.07, 11.40, 11.60, and 14.35  $\mu$ . This acetate **17** was subjected to a further noncontinuous preparative thin-layer chromatography using carbon tetrachloride, yielding after elution by acetone 0.004 g of crystals, melting at 116–118°. (The infrared spectrum of this rechromatographed material was the same as that of the crude crystalline material.) The nmr in  $CDCl_3$  had a ten-proton singlet at  $\tau$  2.67, a complex multiplet of five protons from 3.9 to 4.85, and a three-proton singlet at 7.92 (acetate methyl).

The ultraviolet spectrum in methanol had  $\lambda_{\max}$  260  $m\mu$  ( $\epsilon$  3620). The mass spectrum (Atlas Direct Inlet) had the molecular ion at  $M + 334$  (the high-resolution mass spectrum of the molecular ion gave a measured mass of 334.12063; calcd for  $C_{21}H_{18}O_4$ : 334.12050). In the low-resolution spectrum, fragmentation peaks occurred at  $m/e$  302 ( $M - O_2$ ), 301, 264 ( $M - \text{acetic acid}$ ), 263, 260, 259, 243 — base peak ( $M - O_2 - \text{acetate}$ ), 197, 183, 165, 105, 77, 44, and 43. The physical data are consistent with the peroxide-acetate structure **17**.

**Hydrogenation of the Peroxide Acetate 17.** A mixture of triphenylcarbinol and peroxide acetate was hydrogenated at atmospheric pressure in about 20 ml of aqueous ethanol (the oil was dissolved in ethanol and then water was added until the solute began to come out of solution) using 0.010 g of 5% rhodium-on-carbon catalyst. The material was hydrogenated for 4 hr at room temperature and atmospheric pressure. The catalyst was then filtered off, the solvent was removed, and the product was subjected to preparative tlc (noncontinuously) with 5% (by volume) methanol-chloroform. Two bands were observed. The top band upon elution with acetone yielded 0.017 g of triphenylcarbinol. The second band yielded an almost colorless oil (0.016 g). This oil had infrared absorption ( $CHCl_3$ ) at 2.92 (hydrogen bonded OH), 3.31, 3.41, 5.81 (hydrogen bonded acetate carbonyl), 6.24, 6.71, 6.92, 7.33, 8.15 (broad), 8.51, 8.91, 9.52, 9.81, 10.17, 10.93, 11.08, 11.30, 11.80, 12.00, and 14.36  $\mu$ . The nmr spectrum in  $CDCl_3$  (HA-100) contained a ten-proton singlet at  $\tau$  2.76, a one-proton multiplet at 4.68 (vinyl H), a one-proton multiplet at 5.06 (vinyl H), a one-proton broad singlet at 5.47 (OH), a one-proton multiplet at 5.78 (proton on carbon bearing OH), a one-proton broad singlet at 6.65 (OH), and a complex pattern of seven protons from 7.8 to 8.6 (acetate and methylene protons) including a sharp three-proton peak at 8.00 (acetate). Upon  $D_2O$  exchange, the signals at 5.47 and 6.65 disappeared, and the signal at 5.78 became a sharp doublet. This spectrum suggests the structure **18** for the glycol acetate formed in this reduction.

**Attempted Sodium Periodate Cleavage of the Glycol Acetate.** In an attempt to determine whether the two hydroxyl groups of the glycol acetone were on adjacent carbon atoms, 0.017 g of the glycol acetate was subjected for 12 hr at room temperature to the action of 0.011 g of sodium metaperiodate (3:1 mol ratio of iodate to

(19) R. C. Fuson and P. E. Weigert, *J. Amer. Chem. Soc.*, **77**, 1138 (1955).

(20) W. E. Bachmann, *ibid.*, **52**, 3290 (1930).

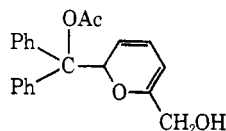
(21) H. S. Mason, *ibid.*, **66**, 1156 (1944).

glycol) in 10 ml of a 50:50 (by volume) mixture of water and tetrahydrofuran. Upon addition of 50 ml of ether, extraction five times with 50 ml of water, drying of the ether (and THF) phase with anhydrous sodium sulfate, and removal of the ether on the rotary evaporator, the glycol acetates were recovered unchanged.

**Aldehyde Acetate 19.** This product was the most polar one isolated from the photolysis of 0.400 g of triphenylcarbinol in 294 ml of glacial acetic acid and 2 ml of 96% sulfuric acid. The aldehyde acetate (0.012 g) (obtained by noncontinuous preparative tlc using chloroform) was further purified by a continuous tlc using carbon tetrachloride as the solvent. The product was 0.009 g of almost colorless oil. The ultraviolet absorption in cyclohexane had  $\lambda_{\max}$  330 (shoulder), 309, 298, 285 (shoulder), 272, 265, and 260  $m\mu$ . The A-60 nmr ( $CDCl_3$ ) had a one-proton singlet at  $\tau$  0.75 (aldehyde), a ten-proton singlet at 2.81, a four-proton complex multiplet from 3.70 to 4.20, and a three-proton singlet at 8.25. The infrared spectrum in carbon tetrachloride (P and E-421) had bands at 3.24, 3.26, 3.29, 3.41, 3.68, 5.71 (acetate carbonyl), 5.88 (unsaturated aldehyde carbonyl), 6.01, 6.11, 6.26, 6.71, 6.90, 6.98, 7.30, 7.50, 8.28, 8.49, 8.83, 9.05, 9.71, 10.47, and 14.37  $\mu$ . The mass spectrum of the product gave the molecular ion at  $M + 334$  (Atlas Direct Inlet). The high-resolution mass spectrum (MS-9 direct inlet machine) of the molecular ion gave a measured mass of 334.12094 (calcd molecular weight for  $C_{21}H_{18}O_4$ : 334.12050). In the low-resolution spectrum, fragmentation peaks occurred at  $m/e$  292 ( $M - \text{ketene}$ ), 274 base peak ( $M - \text{HOAc}$ ), 245 ( $M - \text{acetic acid} - \text{formyl}$ ), 218, 217, 215, 214, 213, 167, 165, 105, 77, and 43.

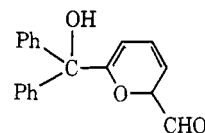
**Sodium Borohydride Reduction of the Aldehyde Acetate 19.** A solution of 0.012 g of the aldehyde in 20 ml of absolute methanol was treated with excess sodium borohydride for 5 min. The solution was then made slightly acidic with 6 *N* hydrochloric acid, and the methanol was then azeotroped off with water on a rotary evaporator. The organic material was then extracted into ether and the ether was washed with water, dried with anhydrous sodium sulfate, and finally removed on a rotary evaporator. The product residue was then subjected to a noncontinuous preparative tlc using 5% methanol-chloroform (by volume) as the solvent. Two bands were obtained, and elution of the least polar band with acetone provided 0.006 g of light-yellow oil.

The infrared spectrum of this material (0.006 g), taken in carbon tetrachloride (P-E 421), had bands at 2.77 (free OH), 2.88 broad (hydrogen-bonded OH), 3.24, 3.27, 3.30, 3.42, 3.50, 5.73 (acetate carbonyl), 6.05, 6.18, 6.70, 6.90, 7.07, 7.31, 7.56, 8.17, 8.51, 8.85, 9.03, 9.29, 9.76, 10.47, 10.64, 11.01, and 14.37  $\mu$ . The HA-100 nmr spectrum in  $CDCl_3$  had a ten-proton singlet at 2.74, a three-proton multiplet of seven major lines (vinyl hydrogens) from 3.8 to 5.0, a one-proton doublet (7 Hz) at  $\tau$  4.82 (hydrogen allylic and on carbon-bearing oxygen), a two-proton singlet at 5.72 (alcohol methylene group), a broad 1-H singlet at 7.95 (OH), and a three-proton singlet at 8.24 (acetate methyl). When the upfield proton of the vinyl multiplet was irradiated in a double resonance experiment, the 1-H doublet at 4.82 collapsed to a singlet. Similarly when the proton at 4.82 was irradiated, the vinyl multiplet was changed from seven major lines to six major lines. The ultraviolet spectrum in cyclohexane had absorption at 270 (shoulder), 264, and 260  $m\mu$  (shoulder). The structure of this reduction product appears to be



**Saponification of the Aldehyde Acetate 19.** A solution of 0.008 g of the aldehyde acetate in 20 ml of aqueous methanol to which a sodium hydroxide pellet had been added was allowed to stand for 12 hr at room temperature. More water was then added, and the methanol was azeotroped off on a rotary evaporator. The aqueous phase was extracted with ether. The ether phase was washed with water and then dried over anhydrous sodium sulfate, and the ether was removed on a rotary evaporator leaving a light yellow oil. This oil was tlc chromatographed continuously using chloroform as the solvent. The single major band obtained was eluted with acetone, and provided 0.004 g of almost colorless oil. The infrared spectrum in carbon tetrachloride (P-E 421) had bands at 2.79 (free OH), 2.92 (hydrogen-bonded OH), 3.25, 3.27, 3.32, 3.42, 3.55, 3.68, 5.92 (unsaturated aldehyde carbonyl), 6.12, 6.30, 6.72, 6.92, 7.03, 7.14, 7.55, 8.04, 8.26, 8.52, 9.43, 9.77, 10.53, 10.87, 10.99, 11.14, and 14.39  $\mu$ . The HA-100 nmr spectrum in  $CDCl_3$  had a 1-H singlet at  $\tau$  0.78 (aldehyde H), a 10-H singlet at 2.78, a 10-H multiplet centered at

3.44 (vinyl H), a 2-H multiplet centered at 4.12 (vinyl H), a 1-H doublet at 5.24 (hydrogen allylic and on carbon bearing oxygen), and a 1-H broad singlet at 8.13 which exchanges when  $D_2O$  is added to the solvent (OH proton). The ultraviolet absorption in cyclohexane had absorption at 330 (sh), 311, 298, 285 (sh), 272, 265, and 263 (sh)  $m\mu$ . The structure of saponification product appears to be



**Effect of Triphenylcarbinol Concentration on the Rate of Reaction with Oxygen in 3.3% Acetic Acid-Sulfuric Acid.** A solution of 0.400 g of triphenylcarbinol in 294 ml of glacial acetic acid plus 6 ml of 96% sulfuric acid was used in this experiment. Oxygen was bubbled through the solution for 15 min before photolyzing and during the 1-hr photolysis. At the beginning and end of the photolysis a 0.1-ml aliquot was diluted to 5 ml with 96% sulfuric acid, and 1 ml of this resulting solution was diluted again to 5 ml with 96% sulfuric acid. The initial absorbance of the resulting solution at 430  $m\mu$  was 0.73 at the start and 0.15 at the end of 1 hr of photolysis. The decrease in absorbance of 0.58 corresponds to the destruction of 0.318 g of triphenylcarbinol. The initial temperature was 18.5° and that at the end of 1 hr of photolysis was 25.0°.

In like manner, an identical system, except that it contained 0.800 g of triphenylcarbinol, was photolyzed for 1 hr. The temperature at the beginning was 18.5° and after 1 hr of photolysis was 28.0°. In this case a 0.1-ml aliquot was diluted to 5 ml, and 1 ml of the resulting solution was diluted to 10 ml with sulfuric acid. The initial absorbance of the resulting solution at 430  $m\mu$  was 0.75 at the start and 0.45 at the end of 1 hr of photolysis. The decrease in absorbance of 0.30 corresponds to the destruction of 0.320 g of triphenylcarbinol.

**Effect of Phenyl Deuteration on the Reaction with Oxygen in 3% Sulfuric Acid-Acetic Acid.** A solution of 0.4003 g of triphenylcarbinol ( $1.54 \times 10^{-3}$  mol) in 270 ml of acetic acid plus 5 ml of 96% sulfuric acid was photolyzed under oxygen for 1 hr. The absorbance at 432  $m\mu$  was measured for 0.1 ml aliquots diluted to 5 ml with 96% sulfuric acid and then diluted again—1 ml to 5 ml with 96% sulfuric acid. The absorbance at the beginning of the reaction was 0.86 and at the end of the photolysis was 0.18. The decrease in absorbance of 0.68 corresponds to the destruction of 0.316 g of triphenylcarbinol ( $1.225 \times 10^{-3}$ , 79.0%).

Similarly 0.4141 g of ortho and para 9-deuterated triphenylcarbinol ( $1.54 \times 10^{-3}$  mol) in 270 ml of glacial acetic acid plus 5 ml of 96% sulfuric acid was photolyzed under oxygen for 1 hr. The absorbance at the beginning of the reaction was 0.84 and after 1 hr of photolysis was 0.15. The decrease in absorbance of 0.69 corresponds to the destruction of 0.340 g of deuterated triphenylcarbinol ( $1.26 \times 10^{-3}$  mol, 82.0%).

**The Effect of Oxygen on the Rate of Disappearance of Triphenylcarbinol Ion in 3% Sulfuric Acid-Acetic Acid.** A solution of 0.2003 g of triphenylcarbinol ( $7.70 \times 10^{-4}$  mol) in a solution of 270 ml of glacial acetic acid and 5 ml of 96% sulfuric acid was photolyzed under nitrogen for 1 hr. Visible spectral absorbancies were measured at 432  $m\mu$  of 0.05-ml aliquots diluted to 5 ml with 96% sulfuric acid. The absorbance at the beginning of the reaction was 1.11 and after 1 hr of photolysis was 0.82. The decrease in absorbance of 0.29 corresponds to the destruction of 0.5022 g of triphenylcarbinol ( $2.01 \times 10^{-4}$  mol).

Using the same lamp, a solution of 0.4003 g of triphenylcarbinol ( $1.54 \times 10^{-3}$  mol) in a solution of 270 ml of glacial acetic acid and 5 ml of 96% sulfuric acid was photolyzed under oxygen for 1 hr. The absorbance at 432  $m\mu$  was measured for 0.1-ml aliquots diluted to 5 ml with 96% sulfuric acid and then diluted again—1 to 5 ml with 96% sulfuric acid. The absorbance at the beginning of the reaction was 0.86 and at the end of the photolysis was 0.18. The decrease in absorbance of 0.68 corresponds to the destruction of 0.316 g of triphenylcarbinol ( $1.22 \times 10^{-3}$  mol). Thus triphenylcarbinol ion disappears *ca.* 6.1 times faster under oxygen than under nitrogen.

**Photolysis in 29.4% Sulfuric Acid, 69.4% Acetic Acid, and 1.2% Water.** A solution of 0.101 g of triphenylcarbinol in 240 ml of glacial acetic acid and 60 ml of 96% sulfuric acid was photolyzed for 4 hr and 25 min. The reaction was then worked up in the usual manner (see general procedure). The crude product was then subjected to preparative tlc using chloroform as solvent. Four poorly separated uv-active bands were obtained.



The least polar "band" was eluted from the silica gel by acetone yielding 0.025 g of oil. This oil was then continuously preparatively thin-layered for 2 hr using carbon tetrachloride. Five uv-active bands were obtained. The least polar band contained 0.005 g of oil which had uv absorbance in cyclohexane at  $\lambda_{\max}$  303, 292, 280 (sh), 269, 266 (shoulder), 262, 251, and 245 (shoulder)  $m\mu$ . The second product (0.006 g) had uv absorption in cyclohexane at  $\lambda_{\max}$  303, 280 (sh), 269, and 264  $m\mu$ . The third product (0.005 g) had uv absorbance in cyclohexane at  $\lambda_{\max}$  308, 299, 285 (sh), 280 (sh), 273 (sh), 269, and 263  $m\mu$ . The fourth product (0.003 g) had uv absorption in cyclohexane at  $\lambda_{\max}$  314, 309, 301, and 270  $m\mu$ . The fifth product (most polar) (0.002 g) had uv absorption in cyclohexane at  $\lambda_{\max}$  314, 309, 300, and 270  $m\mu$ .

Elution of the "second least polar" band (from the original chromatography) with acetone gave 0.008 g of oil. The uv of this product in cyclohexane had absorption at  $\lambda_{\max}$  314, 308, 300, and 265  $m\mu$ . This material was not characterized further.

Elution of the "third least polar" band (from the original chromatography) with acetone gave 0.034 g of oil. This product was continuously preparatively thin-layered for 72 hr using carbon tetrachloride. Two main bands were observed. Elution of the upper band with acetone provided 0.009 g of oil. The infrared spectrum of this product in chloroform had bands at 2.79 (OH stretch), 3.28, 3.32, 5.11, 5.25, 5.52, 6.26, 6.73, 6.94, 7.20, 7.60, 8.45, 8.65, 9.00, 9.29, 9.70, 9.90 (shoulder), 9.96, 11.05 (shoulder), 12.06 (para disubstituted benzene ring), and 14.40  $\mu$ . The HA-100 nmr spectrum in  $CDCl_3$  had 28 aromatic protons from 2.4 to 3.1 and a one-proton singlet at 4.52. The uv spectrum in cyclohexane had absorption at  $\lambda_{\max}$  270 (sh) and 265  $m\mu$ . The visible spectrum 96% sulfuric acid had absorption at 527 and 425  $m\mu$ . On the basis of its spectral properties this compound appears to be 4-diphenylcarbinol-4'-diphenylmethylbiphenyl. Elution of the lower band with acetone gave 0.023 g of crystals of mp 208–210°. The infrared spectrum of this material in chloroform had bands at 2.78, 3.30, 5.10, 5.50, 6.25, 6.73, 6.95, 7.15, 7.55, 8.45, 8.65, 9.14, 9.70, 9.90, 9.96 (sh), 11.20, 12.08, and 14.40  $\mu$ . The ultraviolet spectrum of this material in cyclohexane had absorption at  $\lambda_{\max}$  272 (sh), 265 (sh), and 259  $m\mu$ . The visible spectrum in 96% sulfuric acid had absorption at  $\gamma_{\max}$  452 and 415 (br sh)  $m\mu$ . The mass spectrum (taken of the MS-9 direct inlet machine) had  $m/e$  (per cent of base peak) 504 (3.6), 503 (18.1), 502  $M^+$  (42.2), 427 (6.0), 426 (31.3), 425 (84.3), 410 (2.4), 409 (7.2), 348 (3.6), 347 (8.4), 320 (3.6), 319 (7.2), 244 (7.2), 243 (36.1), 242 (6.0), 241 (13.3), 240 (2.4), 239 (6.0), 183 (16.9), 167 (8.4), 166 (8.4), 165 (33.7), 106 (8.4), 105 (100), and 77 (25.4). The ir, uv and visible spectra of this photoproduct were identical with the corresponding spectra of authentic mono-*p*-trityltriphenylcarbinol prepared by the method of Tschitschibabin.<sup>22</sup> The melting point of this compound was shown to be identical with that of the photoproduct (a mixture melted at 219–220°).

The most polar product (band 4) from the original chromatography was unreacted triphenylcarbinol.

In a control, a solution of 0.010 mg of triphenylcarbinol in 24 ml of glacial acetic acid and 6 ml of 96% sulfuric acid was allowed to

stand in the dark for 4 hr and 25 min. At the beginning and end of the experiment a 0.1-ml aliquot was diluted to 5 ml with 96% sulfuric acid and the optical density at 432 nm measured. In both cases the absorbance was 1.17. Thus it is demonstrated that no reaction occurs in the dark.

**Photolysis of Triphenylcarbinol in 96% Sulfuric Acid.** A solution of 0.0502 g of triphenylcarbinol in 300 ml of 96% sulfuric acid was photolyzed for 39 hr and 20 min. The reaction was monitored by removing 0.1-ml aliquots, diluting them to 5 ml with 96% sulfuric acid, and then measuring the visible spectrum on the Bausch and Lomb spectrometer. During the course of the reaction the absorbance at  $\lambda_{\max}$  432  $m\mu$  gradually diminished and a new absorbance at  $\lambda_{\max}$  493  $m\mu$  increased. Reaction times and absorbancies are as follows: start, 432 ( $A = 0.49$ ), 493 ( $A = 0$ ); 6 hr, 432 ( $A = 0.40$ ), 493 ( $A = 0.06$ ); 17 hr, 432 ( $A = 0.32$ ), 493 ( $A = 0.13$ ); 27 hr 40 min, 432 ( $A = 0.28$ ), 493 ( $A = 0.20$ ); 39 hr 20 min, 432 ( $A = 0.24$ ), 493  $m\mu$  ( $A = 0.25$ ). After photolysis as described, the reaction was worked up in the usual manner (see general procedure), yielding 0.041 g of crystalline material. This was subjected to continuous preparative thin-layer chromatography using chloroform-carbon tetrachloride (50:50 by volume) as the developing solvent. Four uv-active bands were obtained. The first two (from the top) each yield 0.002 g of product and were discarded. The third band yielded 0.015 g of crystalline material, mp 160–162° (triphenylcarbinol). The most polar product weighed 0.021 g and was crystalline (mp 78–83° from carbon tetrachloride). The infrared spectrum in chloroform of this product had bands at 2.80 (free OH), 2.90 (hydrogen bonded OH), 3.30 (CH), 5.11, 5.21, 5.50, 5.85 (the last four are overtone or combination bands for the benzenoid system), 6.23, 6.74, 6.94 (the last three C=C aromatic stretch bands), 7.50, 7.80, 8.60, 9.10, 9.25, 10.91, 11.4 and 14.40  $\mu$ . The uv spectrum in cyclohexane was identical with the uv spectrum of 9-phenylfluoren-9-ol prepared by the method of Arcus, *et al.*<sup>23</sup> It had  $\lambda_{\max}$  310, 298, 293 (sh) 287 (sh), 282, 276, 270, 239, 232, and 225  $m\mu$ . The spectrum in concentrated sulfuric acid was identical with that of authentic 9-phenylfluoren-9-ol with  $\lambda_{\max}$  at 493, 465 (sh), 373, 305 (sh), 278, 269, and 248 (sh)  $m\mu$ . The A-60 nmr in  $CDCl_3$  had 13 aromatic hydrogens from 2.2 to 3.0 and one hydroxyl proton at 7.6 (exchanges with  $D_2O$ ). An oil-bath melting point determination gave 78–83° as the melting point for the photoproduct, 80–84° as the melting point for the authentic material, and 78–83° as the mixture melting point. The yield of 9-phenylfluorenol was 60% based on recovered triphenylcarbinol.

In a control, a solution of 0.0090 g of triphenylcarbinol in 50 ml of 96% sulfuric acid was allowed to stand in the dark for 96 hr. The absorbance at 432  $m\mu$  of a 0.1-ml aliquot diluted to 5 ml with 96% sulfuric acid was 0.51 at the start of the reaction and 0.43 after 96 hr. No new absorption peaks were observed in the visible range.

**Acknowledgment.** The authors appreciate financial aid from the Army Research Office (Durham) (5227-C) and the Petroleum Research Fund (2892), administered by the American Chemical Society.

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