

Irradiation of (4-Methoxyphenyl)-diphenylacetonitrile.—A solution of 1.818 g. (0.00618 mole) of (4-methoxyphenyl)-diphenylacetonitrile in 450 ml. of dioxane and 300 ml. of water was irradiated for 6 hr. at 25°. Work-up and chromatography afforded 0.28 g. (15%) of starting material and 0.72 g. (47%) of (4-methoxyphenyl)-diphenylcarbinol.

Quantum Yield Photolysis of 3-Methoxybenzyl Acetate.—The irradiation procedure described in the section on quantum yields was followed. In a 1-hr. irradiation 1.71 g. (87%) of recovered 3-methoxybenzyl acetate and 56 mg. (29% based on 13% conversion) of 3-methoxybenzyl alcohol were isolated; 4.2 meiv. of light was used. This indicated a quantum yield of 0.099 mole/ein.

In a second run V.P.C. analysis of the irradiation mixture was employed, making use of a benzyl acetate internal standard. Here 3.7 meiv. gave $3.34 \pm 0.09\%$ 3-methoxybenzyl alcohol and $96 \pm 3\%$ 3-methoxybenzyl acetate, and a quantum yield of 0.13 mole/ein.

Quantum Yield Photolysis of 3-Methoxybenzyl Acetate in 50% Ethanol.—Following the same general procedure and using V.P.C. analysis, 3.2 meiv. of light gave from 2.002 g. (0.0111 mole) of reactant $0.99 \pm 0.03\%$ of 3-methoxybenzyl ethyl ether, $1.50 \pm 0.05\%$ of 3-methoxybenzyl alcohol and $94 \pm 3\%$ 3-methoxybenzyl acetate. The quantum yield of the two solvolysis products was 0.10 mole/ein.

Ethyl 3-methoxybenzyl ether was prepared by adding 4.80 g. (0.100 mole) of 50% sodium hydride in mineral oil to 110 ml. of *t*-butyl alcohol, followed by 10.0 g. (0.0724 mole) of 3-methoxybenzyl alcohol and 12.4 g. (0.0796 mole) of ethyl iodide. Refluxing for 5 hr. followed by benzene-water extraction, drying and distillation afforded 6.81 g. (57%) of ethyl 3-methoxybenzyl ether, b.p. 122° at 15 mm., n_D^{20} 1.5065.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.26; H, 8.53.

Quantum Yield Photolysis of 4-Methoxybenzyl Acetate.—With the same procedure used for the *m*-isomer, 4.4 meiv. was found to give 0.056 g. of 1,2-di-(4-methoxyphenyl)-ethane; V.P.C. analysis indicated $0.52 \pm 0.03\%$ of 4-methoxybenzyl alcohol and a quantum yield of 0.016 mole/ein. However, similar amounts of 4-methoxybenzyl alcohol were observed in dark control runs. Also, when 4-methoxybenzyl alcohol was photolyzed together with 3.23% 4-methoxybenzyl alcohol, the V.P.C. analysis after photolysis indicated $3.42 \pm 0.06\%$ of this alcohol, showing that 4-methoxybenzyl alcohol was not being photolytically destroyed.

Quantum Yield Photolysis of 3,5-Dimethoxybenzyl Acetate.—In this case quantum yield determination was effected by column chromatography and V.P.C.; 0.10 mole/ein. was obtained.

Calculations.—The calculations were carried out by the simple LCAO MO method with neglect of overlap. The coulomb integral for methoxyl oxygen was taken as that for carbon plus 1.5 beta. The carbon-oxygen exchange integral was taken as 0.6 beta. In each case the secular determinant was simplified as far as possible by group theory and the residual determinants were diagonalized by the Jacobi method using a Control Data Corp. 1604 computer.

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Mechanistic Organic Photochemistry. III. Excited State Solvolyses¹

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Photochemical solvolyses of substituted-phenyl trityl ethers were uncovered. In contrast to the non-photochemical situation, *meta*-nitrophenyl trityl ether underwent a more efficient photochemical solvolysis than the *p*-isomer. Similar reversal of ground state behavior was observed for the cyanophenyl trityl ether isomers. A LCAO MO treatment of the excited states involved is given, and a rationale is presented for the observed *meta* electron transmission effect.

The present paper is one of a series³ describing exploratory and theoretical photochemical research stimulated by the realization that corresponding to each ordinary, ground state organic molecule there exists an excited state relative having the same gross structural features but differing in bond orders, electron distribution and reactivity.⁴ These studies have had as their objectives: (a) elucidation of the electronic structures of excited states of photochemical interest and (b) exploration of structure-reactivity relationships for such excited state species.

In view of these objectives and during some related photochemical investigations, it was with special interest that a most intriguing publication came to our attention in 1956. This was a report by Havinga⁵ of a

photochemical hydrolysis of isomeric nitrophenyl phosphate and sulfate esters. While these compounds were found to be stable in aqueous solution over a fairly wide pH range, on irradiation a photochemical hydrolysis to the corresponding nitrophenol and inorganic acid was observed. Especially fascinating was the finding that the *m*-nitrophenyl esters underwent the most efficient photochemical hydrolysis. This is, of course, the reverse of ground state⁶ expectation as Havinga noted. Whether the hydrolysis proceeds by unimolecular fission into phenolate and an inorganic species or instead requires concerted nucleophilic attack of water on phosphorus or sulfur, in ground state⁶ chemistry *p*-nitrophenolate is the better departing anion and the *p*-nitrophenyl ester would in any event be expected to hydrolyze more rapidly than the *m*-isomer. This derives from the well known selective electron transmission from phenoxy oxygen to a *para* electron-withdrawing group.⁷ Analogous direct electron delocaliza-

(1) Presented in part at the 17th National Organic Symposium of the Amer. Chem. Soc. This research was begun at Northwestern University and completed at the University of Wisconsin.

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(3) (a) Paper I, H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (b) paper II, H. E. Zimmerman and V. R. Sandel, *ibid.*, **85**, 915 (1963); (c) paper IV, H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962); (d) *cf.* also H. E. Zimmerman, *Tetrahedron*, in press.

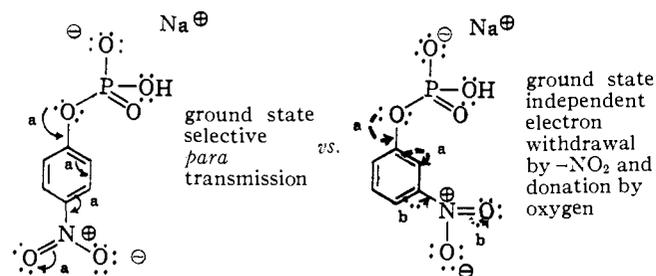
(4) The expectation of novel excited state reactivity has received notice by a number of authors, e.g., C. Reid, "Excited States in Chemistry and Biology," Academic Press, Inc., New York, N. Y., 1957, p. 66; J. Fernandez-Alonso, *Compt. rend.*, **233**, 403 (1951); R. Daudel, R. LeFebvre and C. Moser, "Quantum Chemistry, Methods and Applications," Interscience Publishers, Inc., New York, N. Y., 1959, p. 265; C. Sandorfy, *Can. J. Chem.*, **31**, 439 (1953). However, general correlations with experimental observation have been lacking.

(5) E. Havinga, R. O. de Jongh and W. Dorst, *Rec. trav. chim.*, **75**, 378 (1956).

(6) The term "ground state" in the present discussion is used to refer to the electronic ground state. The term "starting state" will be used to categorize the initial species of a chemical transformation.

(7) A more precise statement would recognize that the presence of the *p*-nitro group leads to stabilization of both starting and transition states. However, in such heterolyses the anionic moiety is more electron rich in the transition state with the result of greater stabilization by nitro in the transition state than in the starting state. Thus, introduction of a *p*-nitro group leads to a decreased energy of activation.

tion and stabilization is not possible for *meta* related groups. Havinga noted⁵ that an understanding of this effect was not to be had from qualitative valence bond reasoning.

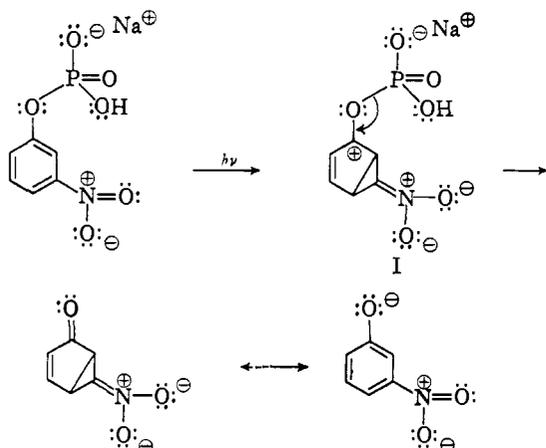


Our investigation in this area had the goals of determining if this unusual photochemical behavior could be understood on a quantum mechanical basis and whether the phenomenon was general.

The previous paper of this series outlined some selective electron donation effects in which it is the position *meta* with respect to an electron donor which becomes electron rich in the first excited state.^{3b} Also briefly mentioned was a selective withdrawal of electrons from the position *meta* to an electron-withdrawing substituent ($-W$) when the molecule is in the first excited state.

The simplest example of C_6H_5-W is the benzyl cation; here $-W$ is the $-CH_2^+$ group. Expectedly, in the LCAO MO picture of the ground state of the benzyl cation there is a selective withdrawal of electrons from the *o*- and *p*-positions. One can arrive at the ground state benzyl cation electron densities (Fig. 1) either by complete LCAO MO calculation or more simply by the method of non-bonding molecular orbitals.⁵ The first excited state electron densities are also given in Fig. 1. These may be obtained by LCAO MO calculation or by the simplified approach outlined in paper II of this series.⁹

The excited state electron distribution of Fig. 1 indicates that the withdrawing group (here $-CH_2^+$) has selectively diminished the electron density *ortho* and *meta* in contrast to the *ortho-para* withdrawal of ground state chemistry. It seemed likely that herein lay the reason for the intriguing reversal of ground state transmission effects in the nitrophenyl phosphate and sulfate hydrolyses. Thus the photochemical reaction could be depicted as



where the excited state MO description is roughly paraphrased^{9a} by structure I. The electron distribution

(8) (a) M. J. S. Dewar, "Progress in Organic Chemistry," Vol. II, Chapter 1, Academic Press, Inc., New York, N. Y., 1953; (b) H. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265, 275, 283 (1950); (c) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3341 (1952).

(9) Cf. footnote 8b of ref. 3b.

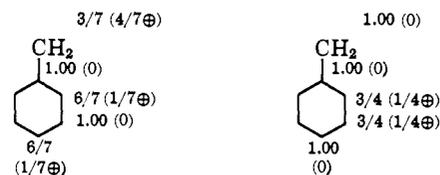
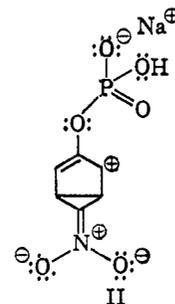


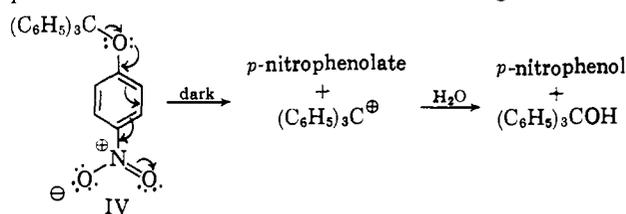
Fig. 1.—Benzyl carbonium ion ground state and excited state electron densities. Numbers adjacent to atoms are the π -electron densities; numbers in parentheses are formal charges.

in the excited state II of the *p*-isomer is inappropriate for heterolytic fission of the P-O bond.¹⁰



It seemed of considerable interest to determine whether or not the phenomenon of *meta*¹⁰ electron withdrawal was general, in which case moieties other than phosphate and sulfate bonded to the oxygen atom of the *m*-nitrophenyl group might be subject to photochemical heterolytic cleavage. The isomeric *m*-nitrophenyl and *p*-nitrophenyl trityl ethers were chosen for initial study, since here the relatively stable trityl carbonium ion might be engendered in such a heterolysis. Additionally, the isomeric *m*-cyanophenyl and *p*-cyanophenyl trityl ethers and the isomeric *m*-acetyl and *p*-acetylphenyl trityl ethers were investigated. In each case preparative scale photolyses were run. Additionally, quantum efficiencies were determined. The details are given in the Experimental section and summarized in Table I.

The situation of the isomeric nitrophenyl trityl ethers proved especially illustrative of the sharp difference between ground state and excited state reactivity. Thus, in the dark the solvolysis of *p*-nitrophenyl trityl ether (IV) in 90% aqueous dioxane at 25°, forming triphenylcarbinol and *p*-nitrophenol, was rapid, with a half-life of *ca.* 5 hr.; under the same conditions *m*-nitrophenyl trityl ether (III) was essentially unreactive. This provides a typical example of ground state behavior, in which a nitro group withdraws electrons selectively from the position *para* with respect to its own location on an aromatic ring.⁷



The excited state situation contrasted with this ground state behavior. Thus, *m*-nitrophenyl trityl ether, unreactive in the dark, underwent a facile photochemical solvolysis to yield triphenylcarbinol, some 9-

(9a) Structures such as I provide crude but convenient symbolism conveying the idea of *meta*-transmission.

(10) In the study by Havinga and co-workers (ref. 5) *o*-nitrophenyl phosphate was found to be less reactive photochemically than the *m*-isomer. While more detailed calculations do indicate a somewhat smaller withdrawal from the *o*-position compared to *meta*, this effect is not subject to easy interpretation. This is because the theoretical model does not take into account the probable non-coplanarity of the nitro group when *ortho* to the bulky phosphate moiety.

TABLE I
 IRRADIATION OF ARYL TRITYL ETHERS

| Run ^a | Compound | Longest absorption maximum, m μ | Region irradiated, m μ | Product quantum efficiencies and % conversion in extended preparative runs | | |
|------------------|---|-------------------------------------|----------------------------|--|-----------------------|---------------|
| | | | | RPhOH | (Ph) ₃ COH | 9-Ph-fluorene |
| 1P | <i>m</i> -NO ₂ PhOC(Ph) ₃ | 324 (3.54) | >300 | 81 | 65 | 20 |
| 1Q | <i>m</i> -NO ₂ PhOC(Ph) ₃ | 324 (3.54) | 290-360 | 0.062 | 0.034 | 0.028 |
| 2P | <i>p</i> -NO ₂ PhOC(Ph) ₃ | 307 (3.38) | >300 | ... | ... | ... |
| 2Q | <i>p</i> -NO ₂ PhOC(Ph) ₃ | 307 (3.38) | 290-360 | Less than 0.0066 total | | |
| 3P | <i>m</i> -CNPhOC(Ph) ₃ | 288.5 (3.40) | >270 | 80 | 66 | 14 |
| 3Q | <i>m</i> -CNPhOC(Ph) ₃ | 288.5 (3.40) | 265-320 | 0.36 | 0.31 | 0.055 |
| 4P | <i>p</i> -CNPhOC(Ph) ₃ | 250.5 (4.16) | >230 | 72 | 65 | 19 |
| 4Q | <i>p</i> -CNPhOC(Ph) ₃ | 250.5 (4.16) | 240-270 | 0.15 | 0.15 | ... |

^a P refers to a preparative run while Q refers to a quantum yield determination. ^b Triphenylcarbinol and *p*-nitrophenol were isolated quantitatively; however, at least 91% derived from dark reaction. ^c Too little 9-phenylfluorene was isolated for quantum yield determination, but an estimation of 0.040 for the quantum yield of this compound can be made from the yields of run 4P.

phenylfluorene and *m*-nitrophenol when irradiated with light of wave length corresponding to its lowest energy $\pi-\pi^*$ transition. *p*-Nitrophenyl trityl ether, so reactive in the dark, was found to solvolyze only very slightly (if at all) more rapidly on irradiation. This qualitative observation made in preparative scale experiments was confirmed by determination of quantum efficiencies. The tenfold greater quantum efficiency observed for the *m*-isomer compared to the *p*-isomer is only a lower limit, since reduced accuracy of determination resulted from the competing rapid thermal (dark) reaction of the *para* compound. Significantly, 9-phenylfluorene, which was a product in the photochemical solvolysis of *m*-nitrophenyl trityl ether and the other compounds of the series undergoing photochemical solvolysis, was absent in the case of the photolysis of *p*-nitrophenyl trityl ether (cf. Table I, runs 1P, 1Q, 2P and 2Q).

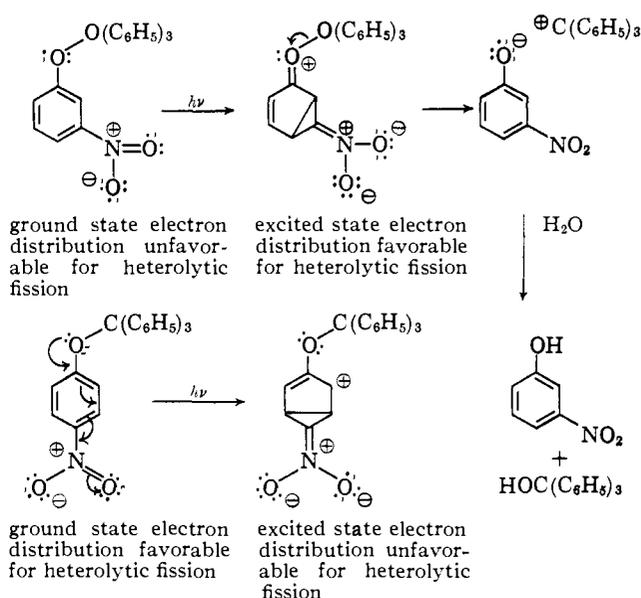
The photolysis of *m*-cyanophenyl trityl ether and *p*-cyanophenyl trityl ether proved qualitatively similar. In this instance both isomers were stable in the dark under the conditions of photolysis. However, again the quantum efficiency of the *meta* isomer was greater, although in this case the superiority of the *meta* reaction was less dramatic and the *para* isomer did undergo some photochemical reaction including formation of 9-phenylfluorene (cf. Table I, runs 3P, 3Q, 4P and 4Q).

Attempts to extend the reaction to include the *meta* and *para* acetylphenyl trityl ethers were only partially successful. *m*-Acetylphenyl trityl ether underwent a normal photochemical solvolysis to afford *m*-acetylphenol, triphenylcarbinol and 9-phenylfluorene. However, the photolysis of *p*-acetylphenyl trityl ether was anomalous. In addition to the expected *p*-acetylphenol and triphenylcarbinol there was isolated trityl peroxide despite the rigorous exclusion of air during photolysis and there was isolated none of the 9-phenylfluorene characteristic of the other photochemical solvolyses.¹¹

The photochemical solvolytic behavior of the *m*- and *p*-isomers of the nitrophenyl and cyanophenyl trityl ethers provides additional examples of the unusual excited state behavior first observed by Havinga. In the present instance the preference for disengagement of a trityl carbonium ion from the $\pi-\pi^*$ excited state

(11) It is to be noted that an $n-\pi^*$ band is expected in the 300 m μ region. Whether direct excitation to the $n-\pi^*$ species is effected with a given filter may not be consequential, due to rapid internal conversion of the initially formed high energy (*i.e.*, 274 m μ) $\pi-\pi^*$ state to give the lower energy (*ca.* 300 m μ) $n-\pi^*$ state. In the present instance intervention of the $n-\pi^*$ species could well be responsible for the differing behavior of *p*-acetylphenyl trityl ether. Application of the mechanistic reasoning in ref. 1, 3a, 3c and 3d to the $n-\pi^*$ excited state from *p*-acetylphenyl trityl ether leads to a prediction of homolytic fission to give *p*-acetylphenoxy and trityl free radicals, whose disproportionation in the presence of water could give the observed *p*-acetylphenol and the triphenylcarbinol. Fission into trityloxy radicals could lead to the observed trityl peroxide. Similar reactions would not be expected from any $n-\pi^*$ species formed from the *m*-isomer.

having the electron-withdrawing group *meta* rather than *para* quite clearly results from the diminution of electron density at the ring position *meta* with respect to this group W. Using qualitative valence bond terminology one may write the reaction as



The formation of 9-phenylfluorene as one of the by-products may be interpreted in several ways.¹²

The discussion above has been limited to discussion of mono-substituted aromatics, and one might note that (*e.g.*) in the case of the nitrophenyl trityl ethers it is the entire nitrophenyl alkoxy π -system which is the chromophore absorbing light and being excited. A more accurate description would include both nitro and alkoxy substituents and determine whether the alkoxy oxygen is indeed more electron deficient in the

(12) Thus it is possible that the trityl carbonium disengaged from the excited state species is itself electronically excited and undergoes, to some extent, the *ortho-ortho* cyclization process reaction which in ground state chemistry is kinetically inferior to nucleophilic pickup of water. Evidence for this ground state kinetic inferiority of cyclization is found in the dark solvolysis of *p*-nitrophenyl trityl ether where only triphenylcarbinol and no 9-phenylfluorene is isolated. However, when the trityl cation is formed reversibly, as in the high temperature reaction of triphenylcarbinol with phosphoric acid (A. Kliegl, *Chem. Ber.*, **38**, 284 (1905)), each cation species has many opportunities to cyclize and the slower cyclization process yielding 9-phenylfluorene does occur. It is less likely that a kinetically excited, and hence less discriminant, trityl cation can account for the 9-phenylfluorene, since in solution dissipation of excess kinetic energy should be rapid. A third and attractive possibility is that the 9-phenylfluorene results from homolysis of the excited state with *ortho-ortho* cyclization of the trityl radical and then disproportionation of the cyclized radical-aryloxy radical pair. It is significant that the photolysis of hexaphenylethane has been reported (R. L. Letsinger, R. Collat and M. Magnusson, *J. Am. Chem. Soc.*, **76**, 4185 (1954)) to afford 9-phenylfluorene and triphenylmethane. In the present case, as a result of the availability of the aryloxy radical, no triphenylmethane would be expected and none was found.

excited state having the *meta* electron-withdrawing group. LCAO MO calculations of the electron distribution in *m*-nitro- and *p*-nitro-substituted phenyl ethers do suggest such a preferential electron withdrawal from the *meta* placed ether oxygen. Furthermore, this prediction is relatively independent of the choice of LCAO MO parameters (note Table II). Thus the conclusion is again reached that excited state transmission is best between *meta* placed groups W and D.

TABLE II

ALKOXYL OXYGEN ELECTRON DENSITIES FOR *m*- AND *p*-NITRO-PHENYL TRITYL ETHERS

| Choice of coulomb parameters (δ 's) | | | Alkoxy oxygen electron density | | |
|---|-----|------------------------|--------------------------------|--------------|---------------|
| CH ₃ O | N | NO ₂ oxygen | Isomer | Ground state | Excited state |
| 0.65 ^a | 0.5 | 1 | <i>meta</i> | 1.764 | 1.279 |
| | | | <i>para</i> | 1.703 | 1.307 |
| 1 | 0.5 | 1 | <i>meta</i> | 1.821 | 1.437 |
| | | | <i>para</i> | 1.784 | 1.461 |
| 1.5 | 0.5 | 1 | <i>meta</i> | 1.875 | 1.632 |
| | | | <i>para</i> | 1.854 | 1.654 |
| 1.0 | 2 | 1 | <i>meta</i> | 1.822 | 1.435 |
| | | | <i>para</i> | 1.735 | 1.449 |
| 1.5 | 2 | 1 | <i>meta</i> | 1.875 | 1.631 |
| | | | <i>para</i> | 1.834 | 1.645 |

^a Cf. footnote 13.

TABLE III

ARYL TRITYL ETHER SYNTHESSES

| Compound | M.p., °C. | λ_{\max} , m μ ^a | Elemental analyses, % | | | Yield, % ^d |
|---|-----------|---|-----------------------|--------|--------|-----------------------|
| | | | C | H | N | |
| <i>p</i> -NO ₂ C ₆ H ₄ OC(Ph) ₃ | 149-150 | 307 (3.38) | (78.74) | (4.99) | (3.67) | 64 |
| | | | 78.61 | 4.79 | 3.68 | |
| <i>m</i> -NO ₂ C ₆ H ₄ OC(Ph) ₃ | 92-94 | 324 (3.54) ^b | (78.74) | (4.99) | (3.67) | 42 |
| | | | 78.61 | 4.61 | 3.92 | |
| <i>p</i> -CNC ₆ H ₄ OC(Ph) ₃ | 133-135 | 250.5 (4.16) | (86.44) | (5.26) | (3.88) | 53 |
| | | | 86.10 | 5.27 | 4.11 | |
| <i>m</i> -CNC ₆ H ₄ OC(Ph) ₃ | 143-145 | 288.5 (3.40) | (86.44) | (5.26) | (3.88) | 35 |
| | | | 86.27 | 5.23 | 3.63 | |
| <i>p</i> -AcC ₆ H ₄ OC(Ph) ₃ | 94-96 | 274 (4.51) | (85.70) | (5.82) | | 63 |
| | | | 85.80 | 6.34 | | |
| <i>m</i> -AcC ₆ H ₄ OC(Ph) ₃ | 89-90 | 305 (3.21) | (85.70) | (5.82) | | 35 |
| | | | 85.83 | 5.75 | | |

^a Longest wave length band; 95% ethanol except as noted. ^b 95% dioxane. ^c Calcd. in parentheses. ^d After recrystallization to constant m.p.

In conclusion, it may be stated that despite some still unanswered questions¹⁴ parallelism between calculated charge distribution of aromatic excited states and reactivity of these excited states exists, and additional theoretical and experimental efforts to explore further such structure-reactivity relationships seem likely to be rewarding.

Experimental^{15a,b}

Irradiation Procedure.—All irradiations were carried out in the apparatus described in detail in the preceding paper of this series.^{15b} Benzophenone ketyl-purified nitrogen was used and thermostating was to $25 \pm 0.2^\circ$.

(13) The parameters in entry one of Table II were chosen equal to those used by J. I. Fernandez-Alonso and R. Domingo, *Anal. Roy. Soc. Espan. Fis. y Quim.*, **B51**, 321 (1955), for the nitroanilines. The results agree closely with the charge distribution calculated by these authors, who suggested that the excited state behavior might differ from that of the ground state as a result of differing charge distribution.

(14) No firm decision has been reached concerning the singlet *vs.* triplet characterization of the excited states involved. Although Hückel calculations do not distinguish between these, when a full linear combination of Slater determinantal wave functions is used, prediction of energy and electron distribution will depend on which species is represented. Experimental and theoretical work in this direction is being pursued.

(15) (a) All melting points were taken on a Fisher-Johns block checked with compounds of known m.p. (b) The Experimental section has been abbreviated at the request of the editor and referees; further details may be obtained, where lacking, from the senior author.

Preparation of Aryl Trityl Ethers.—The following procedure described for the preparation of *p*-nitrophenyl trityl ether is typical. A 16.0-g. (0.10 mole) sample of sodium *p*-nitrophenolate was dried at 150° and 0.3 mm. for 12 hr. and then was refluxed for 3 hr. in 100 ml. of benzene together with 28.0 g. (0.10 mole) of trityl chloride. The reaction mixture was filtered hot. The cooled filtrate was washed with three 50-ml. portions of cold 10% potassium hydroxide solution. The benzene layer was then washed with cold water and dried over anhydrous sodium sulfate. Concentration of the extracts *in vacuo* afforded 38.0 g. of crude product melting at $90-98^\circ$. Two crystallizations from benzene-heptane (1:4) afforded 24.5 g. (64%) of crystalline *p*-nitrophenyl trityl ether, m.p. $149-150^\circ$.

Irradiation of *m*-Nitrophenyl Trityl Ether without Filter.—A 670-ml. portion of a solution of 1.670 g. (4.38 mmoles) of *m*-nitrophenyl trityl ether in 630 ml. of pure¹⁶ dioxane and 70 ml. of distilled water was flushed with ketyl-purified nitrogen for 15 min. and irradiated for 2 hr., at the end of which time titration of an aliquot against standard sodium hydroxide indicated completion of solvolysis. During the reaction period of 2 hr., there was no change in the titration value of a control sample of the solution kept dark.

The reaction product had turned brownish-yellow. The solution was concentrated *in vacuo* at 50° . The residue was chromatographed on a 2×55 cm. column of silica gel slurry packed in 1:19 ether-hexane; 200-ml. fractions were collected. The column was eluted as follows: 0.6 l. of 1:19 ether-hexane, 0.4 l. of 1:9 ether-hexane, 0.4 l. of 1:4 ether-hexane, 0.4 l. of 2:3 ether-hexane, 0.4 l. of 1:1 ether-hexane, 0.4 l. of 3:1 ether-hexane, 0.4 l. of ether and 1 l. of CHCl₃. Fraction 1 afforded 98.2 mg. of a solid melting at $110-118^\circ$ purified by crystallizing from ethanol to give 0.540 g. (0.22 mmole) of a colorless, crystalline solid melting at 145° . The infrared spectrum was identical with that of authentic 9-phenylfluorene (reported¹⁷ 148°). Frac-

tions 2 and 3 gave 0.210 g. of an oily product which could not be crystallized. Fractions 4 and 5 yielded 0.1280 g. (0.49 mmole) of a crystalline solid melting at $154-156^\circ$. Its infrared spectrum was identical with that of an authentic sample of triphenylcarbinol (reported¹⁸ $158-160^\circ$). Fraction 6 afforded 0.1120 g. of an uncharacterized oily material. Fraction 7 afforded 0.139 g. (1.00 mmole) of *m*-nitrophenol melting at $94-95^\circ$. Its infrared spectrum was that of *m*-nitrophenol. The subsequent fractions yielded small amounts of brown oils which were not identified, and quite a bit of the material, tarry in appearance, was firmly held on the column.

Irradiation of *m*-Nitrophenyl Trityl Ether with Pyrex Filter.—A solution of 1.639 g. (4.30 mmoles) of *m*-nitrophenyl trityl ether dissolved in 630 ml. of pure¹⁶ dioxane and 70 ml. of distilled water was prepared. A dark control was set aside. The remaining 670 ml. of the solution was flushed with benzophenone ketyl-purified nitrogen for 15 min. and then irradiated, using a Pyrex filter, for 2.5 hr. by which time titration of an aliquot against standard sodium hydroxide indicated 90% solvolysis. Throughout the irradiation a positive pressure of N₂ was maintained. There was no change in the titration value of the blank. The reaction product had turned yellow. The irradiated solution was concentrated at water-pump vacuum at 50° . The 2.211 g. of partially crystalline residue was taken up in 200 ml. of ether and extracted with 5% aqueous potassium hydroxide. The ether layer was dried over anhydrous sodium sulfate and

(16) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957, p. 284.

(17) D. Vorländer and A. Pritzche, *Chem. Ber.*, **46**, 1793 (1913).

(18) A. A. Morton and J. R. Stevens, *J. Am. Chem. Soc.*, **53**, 4030 (1931).

concentrated to obtain 1.162 g. of a slightly gummy solid. The combined alkali extracts were made acidic to congo red with hydrochloric acid and ether extracted. The dried ether extracts gave 0.466 g. of a brown solid.

The acidic fraction (0.466 g.) was chromatographed on a 2.5 × 25 cm. silica gel column slurry packed in 1:4 ether-hexane; 200-ml. fractions were collected. The column was eluted with 0.6 l. of 1:4 ether-hexane and 0.4 l. of ether. Fractions 1 and 2 afforded 0.4352 g. (3.13 mmoles) of *m*-nitrophenol melting at 93–94°. The infrared spectrum of this material was identical with that of an authentic sample. Fractions 4 and 5 afforded 0.0236 g. of a dark brown viscous liquid which was not characterized.

The neutral fraction (1.1620 g.) was chromatographed on a 2 × 50 cm. column of silica gel slurry packed in 1:19 ether-hexane; 200 ml. fractions were collected. The column was eluted as follows: 0.4 l. of 1:19 ether-hexane, 1 l. of 1:9 ether-hexane, 0.4 l. of 3:7 ether-hexane, 0.2 l. of 3:2 ether-hexane, and 0.2 l. of ether. Fraction 1 afforded 0.1906 g. (0.788 mmole) of 9-phenylfluorene melting at 126–131° with an infrared spectrum identical with an authentic sample. Fractions 4–6 afforded 0.585 g. (2.25 mmoles) of triphenylcarbinol melting at 158–160° and with an infrared spectrum of triphenylcarbinol.

Control Run; Irradiation of Triphenylcarbinol.—Triphenylcarbinol (2.00 g., 7.70 mmoles) was dissolved in 630 ml. of dioxane and 70 ml. of water. The solution was irradiated for 2.5 hr. under the conditions of the previous experiment. The reaction solution was concentrated and the residue chromatographed on a 2.5 × 25 cm. silica gel column slurry packed in 1:19 ether-hexane; 200-ml. fractions were collected and the column was eluted as follows: 0.6 l. of 1:19 ether-hexane and 0.4 l. of 1:4 ether-hexane. Fractions 3–5 afforded 1.985 g. (7.69 mmoles) of triphenylcarbinol, m.p. 159–160°, but no 9-phenylfluorene could be found in fractions 1 and 2.

Control Run; Irradiation of *m*-Nitrophenol.—A 3.408-g. (0.0245 mole) sample of *m*-nitrophenol was dissolved in 650 ml. of 70% dioxane and irradiated for 6 hr. under the conditions of the previous experiment. The solution was concentrated and the residue, melting at 94–95°, weighed 3.310 g. (0.0238 mole). Its infrared spectrum was identical with that of *m*-nitrophenol.

Irradiation of *p*-Nitrophenyl Trityl Ether Using Pyrex Filter.—A 2.040-g. (5.30 mmoles) sample of *p*-nitrophenyl trityl ether was dissolved in 630 ml. of purified dioxane and 70 ml. of distilled water. Of this, 670 ml. was irradiated as described above at 25° for 3 hr., by which time titration with sodium hydroxide indicated 79% solvolysis. Titration with 0.0603 *M* NaOH of irradiation and control aliquots at increasing times gave: 0 min. irradiation, 0.382 ml., control 0.382 ml.; 15 min., 0.449 ml., 0.418 ml.; 45 min., 0.461 ml., 0.432 ml.; 75 min., 0.475 ml., 0.436 ml.; 120 min., 0.482 ml., 0.438 ml.; 180 min., 0.501 ml., 0.456 ml. At the end of 3 hr. of irradiation the reaction product had turned yellow; 600 ml. of this solution was concentrated at 35–40° *in vacuo*. The fraction soluble in 10% NaOH gave 0.546 g. (3.90 mmoles) of essentially pure *p*-nitrophenol. This melted at 110–112° (reported¹⁹ 114°; infrared check). The neutral fraction (1.250 g.) was chromatographed on a 2.5 × 115 cm. column of silica gel slurry packed in 1:19 ether-hexane; 200-ml. fractions were collected. The column was eluted as follows: 0.6 l. of 1:19 ether-hexane, 0.6 l. of 1:9 ether-hexane, and 1 l. of 1:4 ether-hexane. Fractions 4–10 afforded 1.0621 g. (4.08 mmoles) of triphenylcarbinol melting at 159–161°. A dark band stayed at the top of the column.

Irradiation of *m*-Acetylphenyl Trityl Ether.—Of 2.030 g. (5.30 mmoles) of *m*-acetylphenyl trityl ether in 700 ml. of 90% ethanol, 670 ml. was flushed and irradiated under nitrogen through Pyrex for 3.5 hr. at 24°. At the end of the run, titration of an aliquot with standard sodium hydroxide indicated 44.5% solvolysis. A dark control run liberated no acidic product.

A 620-ml. volume of the irradiated solution was worked up at room temperature under reduced pressure in the same general manner as described above. Acid-base separation gave 0.2960 g. (2.20 mmoles) of a solid melting at 88–90° (reported²⁰ m.p. for *m*-acetylphenol 96°) with infrared spectrum of *m*-acetylphenol. The neutral fraction (1.5270 g.) was chromatographed to give 0.2653 g. (1.10 mmoles) of 9-phenylfluorene, m.p. 135–137°; 0.5353 g. (2.06 mmoles) of triphenylcarbinol, m.p. 159–161°; and 0.620 g. (1.60 mmoles) of *m*-acetylphenyl trityl ether, m.p. 86–88°. Infrared comparisons of products were made.

Irradiation of *p*-Acetylphenyl Trityl Ether.—Of a 2.200-g. (5.80 mmoles) sample of *p*-acetylphenyl trityl ether in 20 ml. of purified¹⁶ dioxane, 643 ml. of 95% ethanol and 37 ml. of distilled water, a 670-ml. volume was irradiated for 1.75 hr. at 24° using a Pyrex filter. At the end of this time titration with sodium hydroxide indicated 89% solvolysis. The thermal contribution to solvolysis during the above time interval was 18% as determined by titration of a dark control.

A 630-ml. volume of the irradiated solution was concentrated *in vacuo* at 35° and the residue was worked up in the usual manner to give 0.6930 g. (5.10 mmoles) of *p*-acetylphenol, m.p. 107–108° (reported²¹ 107°); 0.8741 g. (3.36 mmoles) of triphenylcarbinol, m.p. 160–162°; and 0.137 g. (0.36 mmole) of *p*-acetylphenyl trityl ether, m.p. 90–92°. All identities were checked by infrared comparison.

Irradiation of *p*-Acetylphenyl Trityl Ether Using Solution Filters Transparent between λ 245 $m\mu$ and λ 295 $m\mu$.—A 2.0256-g. (5.3 mmoles) sample of *p*-acetylphenyl trityl ether was dissolved in 643 ml. of 95% ethanol, 20 ml. of purified dioxane and 37 ml. of distilled water. A 680-ml. volume of the above solution was irradiated for 2.5 hr. at 5.5°. Between the light source and the reaction cell was placed a triple decker arrangement of three 24-mm. thick cells filled with nickel sulfate solution (63.5 g. of NiSO₄·6H₂O in 500 ml. of water, cell I), cobalt sulfate solution (68.6 g. of CoSO₄·7H₂O in 500 ml. of water, cell II), and 2,7-dimethyldiaza(3,6)cycloheptadiene-1,6 perchlorate²² (0.0617 g./500 ml. of water, cell III). The thermal contribution to solvolysis during the above time interval was 2% based on titration of the dark control also kept at 5°.

Work-up gave 0.6473 g. (4.7 mmoles) of *p*-acetylphenol, m.p. 104–106°; 0.1960 g. (0.37 mmole) of trityl peroxide, m.p. 182–183° (reported²³ for trityl peroxide 185°); 0.6252 g. (2.4 mmoles) of triphenylcarbinol, m.p. 156–159°; and 0.4233 g. (1.1 mmoles) of *p*-acetylphenyl trityl ether, m.p. 88–90°. Trityl peroxide was analyzed and otherwise infrared comparisons were made.

Irradiation of *m*-Cyanophenyl Trityl Ether.—A 1.8169-g. (5.03 mmoles) sample of *m*-cyanophenyl trityl ether was dissolved in 630 ml. of purified¹⁶ dioxane and 70 ml. of distilled water; 660 ml. of the above solution was irradiated for 3.5 hr. at 21° using a Corning 9700 (9-53) filter. At the end of the run titration indicated 64% solvolysis. The thermal contribution to solvolysis during the above time interval was nil.

A 620-ml. volume of the irradiated solution was concentrated under vacuum at 30° using a rotary evaporator. The oily semi-solid residue was dissolved in ether and extracted with 10% potassium hydroxide. The dried ether layer gave 1.410 g. of a gummy solid. The alkaline extracts on acidification and ether extraction afforded 0.420 g. (3.5 mmoles) of *m*-cyanophenol, m.p. 76–78° (reported²⁴ 82°; infrared check). The neutral fraction (1.410 g.) was chromatographed on a 3.8 × 80 cm. column of silica gel slurry packed in 1:19 ether-hexane; 200-ml. fractions were collected, and the column was eluted as follows: 1 l. of 1:19 ether-hexane, 0.4 l. of 1:9 ether-hexane, 0.4 l. of 3:17 ether-hexane, 0.4 l. of 1:3 ether-hexane, 0.6 l. of 2:3 ether-hexane, 1 l. of 3:2 ether-hexane, 0.4 l. of 4:1 ether-hexane and 0.4 l. of ether. Fractions 4–5 afforded 0.1596 g. (0.66 mmole) of 9-phenylfluorene, m.p. 134–136° (infrared check). Fractions 8–12 afforded 0.7722 g. (2.9 mmoles) of triphenylcarbinol, m.p. 159–161° (infrared check). Fractions 16–19 afforded 0.2570 g. of an oily material which could not be made to crystallize. This oily fraction (0.257 g.) was chromatographed on a 2.5 × 25 cm. column of alumina without obtaining further solid product.

Irradiation of *p*-Cyanophenyl Trityl Ether.—A 1.8050-g. (5.00 mmoles) sample of *p*-cyanophenyl trityl ether was dissolved in 630 ml. of purified¹⁶ dioxane and 70 ml. of distilled water; 660 ml. of the above solution was irradiated with a Corning 7910 (9-54) filter at 20° for 3.5 hr., by which time titration of an aliquot indicated 61% solvolysis. The thermal contribution to solvolysis was nil.

A 610-ml. volume was concentrated at 28°. The 10% base-soluble fraction yielded 0.5120 g. of a viscous liquid.

The neutral fraction (1.410 g.) was chromatographed on a 3.8 × 80 cm. column of silica gel slurry packed in 1:19 ether-hexane; 200-ml. fractions were collected. The column was eluted as follows: 1 l. of 1:19 ether-hexane, 0.4 l. of 3:17 ether-hexane, 1 l. of 1:4 ether-hexane, 0.4 l. of 2:3 ether-hexane, 0.4 l. of 3:2 ether-hexane, 0.4 l. of 4:1 ether-hexane and 0.4 l. of ether. Fractions 2–4 afforded 0.2005 g. (0.82 mmole) of 9-phenylfluorene, m.p. 136–139°. Its infrared spectrum agreed with that of 9-phenylfluorene. Fractions 8–11 afforded 0.7471 g. (2.87 mmoles) of triphenylcarbinol melting at 160–162°. Fraction 20 yielded 0.0431 g. of a semi-solid which was not characterized.

The acidic fraction (0.512 g.) was chromatographed over a 2.5 × 25 cm. column of silica gel slurry packed in 1:19 ether-hexane; 200-ml. fractions were collected. The column was eluted as follows: 0.6 l. of 1:19 ether-hexane, 0.6 l. of 1:9 ether-hexane, 0.4 l. of 1:4 ether-hexane and 0.8 l. of 2:3 ether-hexane. Fractions 9–11 (600 ml.) yielded 0.3680 g. (3.1 mmoles) of *p*-cyanophenyl, m.p. 111–112°.

Actinometry.—The procedure used was essentially that described previously²⁵ using a double compartment cell for reaction

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and uranyl oxalate. The triple compartment cell was used for filter solutions. The filter solution combinations used and transparent wave length regions were as follows:

For the *m*- and *p*-nitrophenyl trityl ethers: cell I, solution of 63.5 g. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ /500 ml. of water; cell II, 68.6 g. of $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$ /500 ml. of water; cell III, 38.8 g. of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ /500 ml. of water. This system was transparent between 290 and 360 μ .

For *p*-cyanophenyl trityl ether: cell I, solution of 76.2 g. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 82.3 g. of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ /600 ml. of water; cell II, 0.0372 g. of quinoline hydrochloride/liter; cell III 1.00 g. of 2,7-dimethyldiaza(3,6)cycloheptadiene-1,6 perchlorate/600 ml. This filter combination was transparent between 240 and 270 μ .

For *m*-cyanophenyl trityl ether: cell I, 127.0 g. of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ /liter; cell II, 137.0 g. of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ /liter; cell III, 0.0366 g. of acridine hydrochloride/500 ml. of 1% hydrochloric acid. This filter combination was transparent in the region 265–320 μ .

In these quantum efficiency runs photolysis was continued to less than 20% reaction. Products were isolated in the same fashion as described in the preparative runs and quantum yields determined from the amount of product formed relative to the amount of light available with the given filter during the time of photolysis. Production of phenolic products was monitored

by titration. Light availability through each filter for the time of photolysis was determined using uranyl oxalate and potassium permanganate titration. The assumption²⁵ was made of 0.55 $\mu\text{ein./mmole}$ of oxalic acid utilized.

Calculations.—The calculation on the isomeric nitroanisoles was carried out by the simple LCAO MO method with neglect of overlap. Diagonalization of the secular determinant was by the Jacobi method using a Control Data Corp. 1604 computer.²⁶

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(26) We thank Mr. John Munch for his assistance in computing.

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Conformations. III. Estimation of Rotational Conformations of Phenyl in Substituted 1-Phenylcyclohexenes by Proton Magnetic Resonance

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Phenyl rotational conformations in twenty substituted 1-phenylcyclohexenes have been estimated by the interrelation of olefinic proton chemical shifts and dihedral angles ϕ (in I) using theoretical values of Johnson and Bovey for shieldings experienced by a nucleus in the neighborhood of a benzene ring. It was found that practically identical results were obtained when the point dipole approximation method was used.

Waugh and Fessenden² have experimentally estimated that the magnetic anisotropy of the benzene ring³ leads to a chemical shift (δ) of -1.50 p.p.m. (deshielding) for the benzene proton magnetic resonance. From this chemical shift, a spacing of 1.28 Å. between the maximum π -electron density of the two circular π -electron clouds in benzene was found.^{4,2} Using this model, Johnson and Bovey⁴ have calculated the magnetic field (resulting from the magnetically induced precession of three π -electrons in each of the circular loops) about a freely tumbling benzene ring in an external magnetic field. The Johnson and Bovey tables⁴ provide theoretical chemical shifts for protons in the neighborhood (in terms of coordinates ρ and z) of the benzene ring. For simple aromatic hydrocarbons agreement between theory and experiment is good.⁴

Non-coplanarity of conjugated systems is readily detectable through ultraviolet spectroscopy. The effects of non-coplanarity upon the spectra of conjugated systems are varied.⁵ The intensity of absorption (or more reliably the oscillator strength) is generally considered to be uniformly more sensitive to deviations from coplanarity of the conjugated system than is the transition energy^{6,6}; however, this generality is neither theoretically⁷ nor experimentally⁸ without exception.

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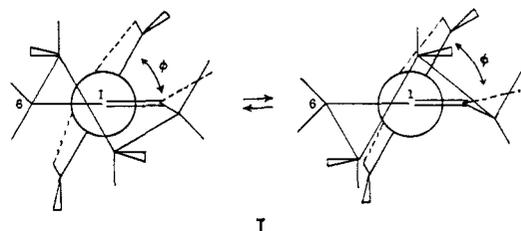
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Recently,⁹ simple LCAO–MO theory has been used to correlate the interplanar angle in biphenyls,^{9a} stilbenes and styrenes^{9b} with the wave length of maximum absorption.

This paper concerns itself with an estimation of the time-averaged dihedral angles (ϕ)^{10a} in *C*₆- and *ortho*-substituted 1-phenylcyclohexenes (I) through chemical shifts of the olefinic proton's magnetic resonance.^{10b}



Model and Anisotropy Calculations.—The cyclohexene model used is that derived from vector analysis by Corey and Sneen¹¹ in which total distortion (from normal tetrahedral) in all angles is approximately equal and as small as possible. The angle between each vinyl bond and the carbon–carbon double bond is taken as 122.5°. Bond lengths taken are: 1.54 Å. (C–C), 1.09 Å. (C–H), 1.48 Å. (C_{olefinic}–C_{Ar}),

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