ORGANIC AND BIOLOGICAL CHEMISTRY

Mechanistic Organic Photochemistry. II.[1,2] Solvolytic Photochemical Reactions

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A photochemical solvolytic reaction of substituted benzyl derivatives has been found having a substituent effect which is the reverse of ground state behavior. The observed photochemical reactivity, in which solvolysis is selectively enhanced by *m*-methoxyl substitution, is shown to accord with expectation based on the first electronic excited state LCAO MO electron distribution. Observation is shown to accord with predicted ease of electronically excited cation formation as well.

It has been noted in our first publication[2] of this series that organic photochemistry, although the subject of intensive investigation, has lacked the mechanistic sophistication of ordinary organic chemistry. Thus mechanistic organic photochemistry has been limited largely to specification of bonds broken and identification of the ensuing unstable species. This situation is not surprising for two reasons. First, in organic photochemistry the actual species undergoing transformation is electronically excited and therefore will have, in general, an electron distribution quite unlike that of its ground state progenitor. Since most often the electronic structure of the excited state of interest has not been readily describable, the organic chemist has had no opportunity to search for structure–reactivity relationships necessary for mechanistic development. Second, even were simple (*e.g.*, valence bond) structures available describing excited states of photochemical interest, there would be no *a priori* assurance that ground state experience would extend to excited states.

The excited states resulting from irradiation of substituted benzenes are of exceptional photochemical interest. It has been recognized in the literature (*e.g.*, ref. 4 and 5) that aromatic excited states are likely to exhibit reactivity different from that of the related ground states. However, a link between quantum mechanical description and experimental reality has been lacking.

The present paper deals with one of several investigations aimed at providing such a link. As a starting point and prior to presentation of our experimental findings, it is convenient to consider the theory of monosubstituted benzenes. Cases of substitution both by electron-withdrawing groups (W) and electron-donating groups (D) are pertinent. The former include $-NO_2$, $-CN$, $-CH_2^+$ while the latter might be taken as $-OCH_3$, $-NH_2$, $-CH_2^-$. For generality and simplicity one might take the withdrawing group $-W$ as $-CH_2^+$ and the electron-donating group $-D$ as $-CH_2:^-$, the aromatic compound then being the benzylcarbonium ion or the benzylcarbanion, respectively. In Fig. 1 LCAO MO π-electron densities are indicated for both types of aromatics; and ground states are included for comparison.[6]

Inspection of the ground states of these two systems indicates the expected *ortho–para* electron withdrawal by W– and *ortho–para* electron donation by D–. Contrariwise, the LCAO MO excited state electron distribution indicates a selective electron withdrawal from the *o*- and *m*-positions by W– and a selective electron transmission to the *o*- and *m*-positions by D–. This novel *ortho–meta* transmission, predicted to be characteristic of first excited state chemistry, contrasts with the long established *ortho–para* transmission of ground state chemistry.

That this prediction is not an isolated instance unique only to the benzyl system is seen in the LCAO MO calculations for anisole (Fig. 2)[7]; here electron transmission to the *m*-position is greater than that to the *o*-position.

To the chemist accustomed to thinking in terms of valence bond reasoning, the predictions derived from these calculations are less than satisfying. A better understanding of the nature of these calculations and the source of the *meta* transmission effect is derived from Fig. 3 which depicts the seven benzyl molecular orbitals resulting from interaction, or quantum mechanical "mixing," of the seven atomic *p*-orbitals of this species. These MO's, dissected on an energy basis, are actually superimposed on the same molecular framework. The π-electron distribution characteristic of each of the molecular orbitals is indicated schematically by a heavy electron cloud superimposed on a thin line sigma skeleton. The number adjacent to a particular atom indicates the contribution to the total electron density at that atom by an electron in the given molecular orbital; the total π-electron density at each atom is the sum of the individual contributions by all π-electrons in the species in Fig. 1 under consideration.[8]

For the case of the electron-withdrawing substituent (*i.e.*, the benzyl carbonium ion) there are six π-electrons, these being represented by solid dots in the

(1) (a) Presented in part at the 17th National Organic Symposium of the Am. Chem. Soc., June, 1961. (b) Taken in part from the Ph.D. Thesis of V. Sandel presented to Northwestern Univ. This research was begun at Northwestern and completed at the University of Wisconsin by the authors.

(2) Paper I, H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961).

(3) (a) University of Wisconsin Chemistry Department. (b) National Science Foundation Fellow 1958–1961.

(4) C. Reid, "Excited States in Chemistry and Biology," Academic Press, Inc., New York, N. Y., 1957, p. 66.

(5) J. Fernandez-Alonzo, *Compt. rend.*, **233**, 403 (1951).

(6) The benzyl species' molecular orbitals, used for these electron density calculations, are readily obtained from solution of the seventh order secular determinant. These LCAO wave functions have been previously described by W. Bingel, *Z. Naturforsch.*, **10A**, 462 (1955).

(7) The molecular orbitals obtained in these calculations and used for prediction of electron densities (*cf.* section on Calculations) parallel those described by K. Nishimoto and R. Fujishiro, *Bull. Chem. Soc. Japan*, **31**, 1036 (1958), for phenol.

(8) The ground state electron densities in Fig. 1 also can be obtained by the Dewar and Longuet-Higgens method of non-bonding MO's (*cf.* M. J. S. Dewar, "Progress in Organic Chemistry," Vol. II, Chapter 1, Academic Press, Inc., New York, N. Y., 1953). Here, since the benzyl radical has unit density at each atom, the electron densities of the benzyl cation and of the benzyl carbanion correspond to that of the extra electron removed or added, respectively. Because the electron is removed from or added to the non-bonding MO (zero level), the electron distribution for the cation and for the anion simply corresponds to unity at all atoms minus or plus the non-bonding MO densities (1/7 *ortho* and *para* and 4/7 benzylic). This approach can be extended to dealing with the two excited states of Fig. 1 once it is realized that the electron densities in the −1 and +1 energy levels are 1/4 at the *o*- and *m*-positions. Thus the first excited state for the eight electron species is constructed from the benzyl radical (π-electron density of one at each position) plus the 0.250 density *ortho* and *meta* due to the +1 level electron. The excited state for the six electron species results from subtracting the −1 energy level MO electron densities from unit densities of the benzyl radical.
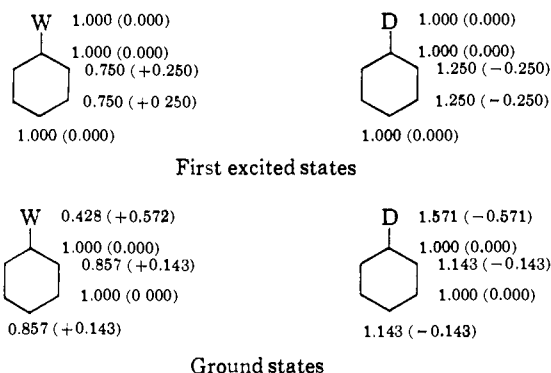
Fig. 1.—Monosubstituted benzene electron densities (W = CH₂⁺, D = CH₂⁻:). Unparenthesized numbers are π-electron densities; parenthesized numbers are formal charges.

Fig. 2.—Unparenthesized numbers are π-electron densities; parenthesized numbers give formal charges.

center, energy level column of Fig. 3. For this case the circular dots are ignored. π–π* excitation involves promotion of one electron as depicted by arrow a. In this process an electron is removed from the −1 MO in which the electron can appear *meta* and is promoted to the non-bonding (zero) level in which the electron cannot appear *meta*. Herein is the source of the low *meta* electron density in the first excited state.

For the benzyl carbanion, where the donating substituent is –CH₂:⁻, there are eight π-electrons; here the six solid dots plus the two circled dots of Fig. 3 must be considered. Excitation is now indicated by arrow b. It is noted that an electron is removed from the non-bonding (zero) level in which it cannot appear *meta* and is promoted to the +1 level in which it can appear *meta*. Thus excitation enhances the *meta* electron density. The exact change in densities at the ring positions on excitation may be calculated from a comparison of the electron densities in the MO receiving the electron compared with the densities in the MO losing the electron.

In order to predict reactivity for the excited states of monosubstituted benzenes it is convenient to paraphrase the molecular orbital description in the form of the following type valence bond structures

While not deriving from any quantitative valence bond calculation, these do have the virtue of indicating transmission of electron density to and from the *meta* positions and they allow one to formulate an excited state in the form of one convenient, although admittedly approximate, structure.

As an experimental test of the reality of this concept of *meta* electron transmission, it was decided to examine the photochemical behavior of methoxyl substituted benzyl derivatives in ionic media. It seemed
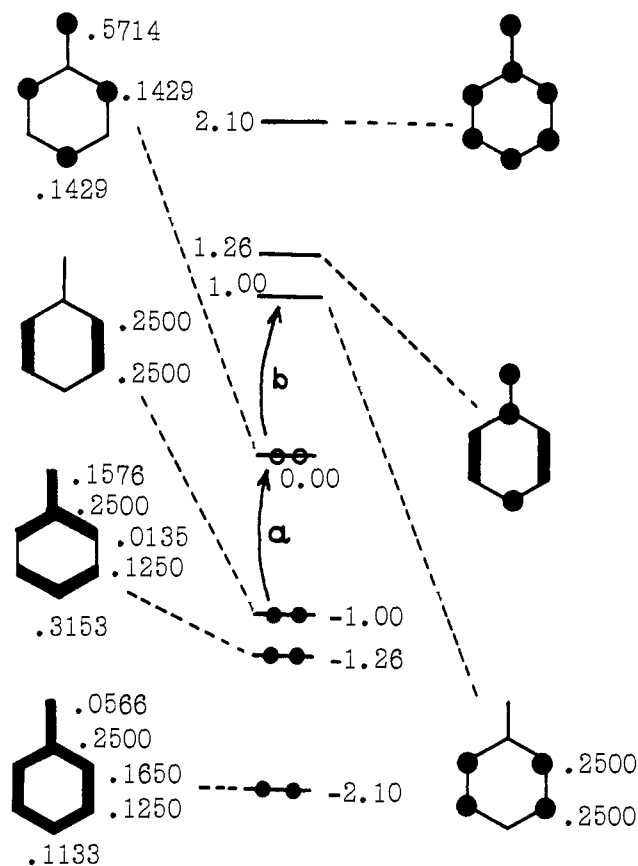

Fig. 3.—Benzyl MO's and excitation processes for the six and eight electron species. Blackened portions and numbers indicate LCAO MO electron densities. Energies given in the central column are in units of the absolute value of beta with the energy of an isolated *p*-orbital taken as the zero.

possible that transmission of electrons to a ring position bearing the grouping –CH₂–Y might effect an anionic expulsion of Y, where Y:⁻ might be chloride, acetate, etc.
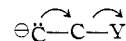

Such a β-elimination of Y could serve as a probe for excited state electron density and availability at different positions with respect to an electron-donating substituent.

In striking agreement with theoretical suggestion, it was found that benzyl derivatives bearing methoxyl groups did undergo photochemical solvolysis, and *meta* placement of methoxyl substituents was found to favor this reaction.

In these experiments, 3-methoxybenzyl chloride, 3-methoxybenzyl acetate, 4-methoxybenzyl acetate, 3,5-dimethoxybenzyl acetate, 3-dimethylaminobenzyl acetate, 3-methoxybenzyl methyl ether and 3-methoxyphenylacetonitrile were irradiated. Except for the last two compounds, these benzyl derivatives underwent solvolysis to varying extents. Preliminary studies were carried out with 3-methoxybenzhydryl acetate, (3-methoxyphenyl)-diphenylmethyl acetate, (3-methoxyphenyl)-diphenylacetonitrile and (4-methoxyphenyl)-diphenylacetonitrile. In most of these experiments filters were used to give light corresponding to the longest wave length π–π* singlet absorption band. Products were isolated and in the more interesting cases quantum yields were determined.

The most pertinent and interesting series consists of the photolyses in aqueous dioxane of 4-methoxybenzyl acetate (III), 3-methoxybenzyl acetate (IV) and 3,5-dimethoxybenzyl acetate (V). In preparative scale

runs it was found that 4-methoxybenzyl acetate afforded essentially exclusively free radical products expected from homolytic generation of 4-methoxybenzyl and acetoxyl radicals. Thus there were isolated 4,4'-dimethoxybibenzyl (VI), 4-methoxybenzyldioxane (VII) and dioxanyldioxane (VIII) (cf. Chart I).

CHART I
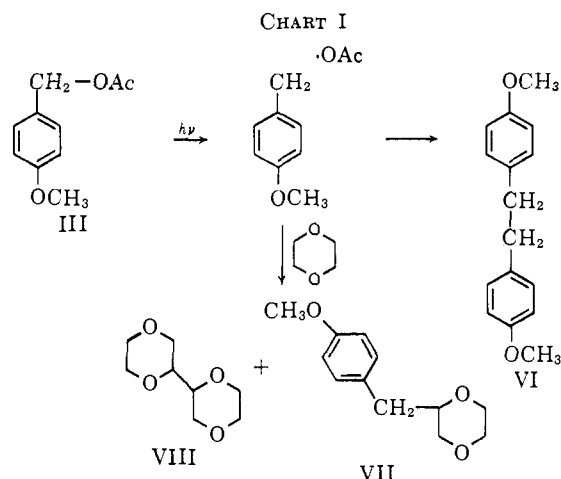
The formation of the bibenzyl derivative VI clearly results from dimerization of 4-methoxybenzyl free radicals. Similarly, dioxanyldioxane (VIII) logically derives from dimerization of dioxanyl free radicals, and these in turn seem likely to result from hydrogen abstraction from solvent dioxane by acetoxyl radicals (and possibly methyl radicals derived from acetoxyl by decarboxylation). 4-Methoxybenzyldioxane (VII) results in this scheme by combination of dioxanyl and 4-methoxybenzyl radicals.

When irradiated under the same conditions 3-methoxybenzyl acetate (IV) afforded 3-methoxybenzyl alcohol (IX) along with somewhat smaller yields of 3,3'-dimethoxybibenzyl (X) and 3-methoxybenzyldioxane (XI). The latter two products X and XI clearly arise from free radical processes paralleling those of the 4-methoxybenzyl acetate photolysis and in the present instance can be ascribed to an initial homolytic fission into 3-methoxybenzyl and acetoxyl radicals.

On the contrary, the formation of 3-methoxybenzyl alcohol (IX) is suggestive of an ionic transformation of the electronically excited state giving rise to the 3-methoxybenzyl cation and acetate anion.[9]

Further evidence on this point was found in the irradiation of 3-methoxybenzyl acetate (IV) in 50% aqueous ethanol. In this instance both 3-methoxybenzyl alcohol (IX) and 3-methoxybenzyl ethyl ether (XII) were obtained as solvolysis products. This result is significant in ruling out acyl–oxygen fission as well as a homolytic acetoxy–carbon cleavage. Had acyl–oxygen fission occurred, only 3-methoxybenzyl alcohol (IX) and no ethyl ether (XII) would be observed. Regarding the second point, it may be

(9) The alternative of combination of hydroxyl and 3-methoxybenzyl radicals is ruled out for several reasons. In contrast to the stabilized benzylic and dioxanyl radicals postulated to combine, the hydroxyl radical is extraordinarily unstable and reactive. The energy of activation for hydrogen abstraction from even unactivated hydrocarbons is of the order of only 1 kcal./mole (ref. 10), and in the presence of highly abstractable hydrogen atoms of solvent dioxane it is highly unlikely that sufficient concentrations of hydroxyl radical could accumulate to combine with the higher, but still necessarily low, concentrations of 3-methoxybenzyl radical. Furthermore, benzyl alcohol product is not observed in the 4-methoxy series where free radicals are observed and where the more stabilized 4-methoxybenzyl radical is available. The most convincing argument favoring the ionic mechanism is the isolation of the corresponding ethyl ether from photolysis of 3-methoxybenzyl acetate in aqueous ethanol as discussed in the text.

(10) A. F. Trotman-Dickenson, "Free Radicals," John Wiley and Sons, Inc., New York, N. Y., 1959, p. 83.
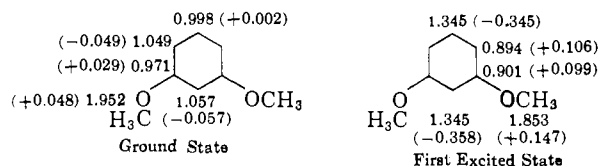
Fig. 4.—Unparenthesized numbers are π-electron densities; parenthesized numbers are formal charges.

concluded that homolytic- fission to acetoxy and 3-methoxybenzyl radicals cannot account for the 3-methoxybenzyl ether product (XII), since hydrogen abstraction from the α-carbon of alcohols is much more facile than from oxygen,[11] and as a consequence ethoxyl radicals, which would have to be postulated, would not be formed.

Additional evidence for formation of the 3-methoxybenzyl cation as an intermediate derives from the observation that 3-methoxybenzyl chloride (XIII) undergoes similar photochemical solvolysis in aqueous dioxane to afford 3-methoxybenzyl alcohol (IX).

+ lesser amounts of free radical prod.
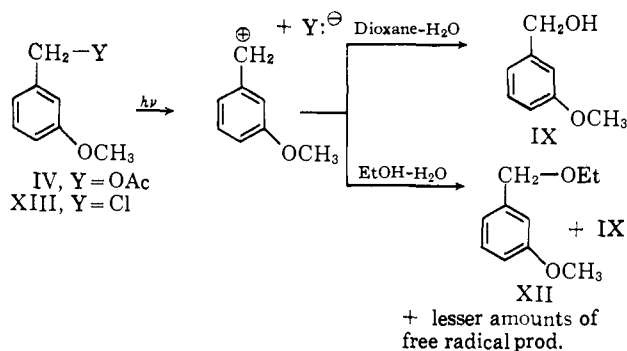
In each of these experiments, both in the 4- and 3-methoxy series, control runs were made to establish that no reaction occurred in the dark under the same solvent and temperature conditions and with similar workup. Beyond this, runs were made in which 4-methoxybenzyl alcohol was photolyzed alone and also with 4-methoxybenzyl acetate present under typical reaction conditions followed by the usual workup. These experiments demonstrated that 4-methoxybenzyl alcohol would have survived had it been formed.

Not unexpectedly, in the photolysis of 3-methoxybenzyl methyl ether and of 3-methoxyphenylacetonitrile in aqueous dioxane there were no detectable amounts of solvolysis products. Methoxide and cyanide, being higher energy anions, depart less readily than chloride and acetate.

Most strikingly, photolysis of 3,5-dimethoxybenzyl acetate (V) in 50% aqueous dioxane proceeded smoothly to afford as the only isolable product 3,5-dimethoxybenzyl alcohol (XIV). In this instance, products of free radical fission were not detected.
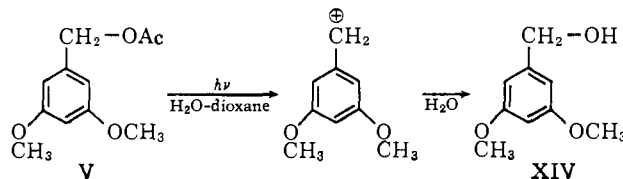
It is interesting to note that the LCAO MO calculations (cf. Fig. 4) for the first excited state of the 3,5-dimethoxy substituted aromatic ring show a further enhancement of the electron density at the carbon meta to the methoxyl group compared to the singly m-substituted case discussed earlier.

(11) M. S. Kharasch, J. L. Rowe and W. H. Urry, J. Org. Chem., 16, 905 (1951).

TABLE I

PHOTOLYSIS OF *meta*- AND *para*-METHOXYSUBSTITUTED BENZYL ACETATES

| Substituted benzyl acetate photolyzed[a]	Quantum yield of solvolysis product	Product distribution
4-Methoxy	0.016	31–36% 4,4'-dimethoxybibenzyl (VI), 23–31% 4-methoxybenzyldioxane (VII), dioxanyldioxane diastereomers,[b] minor amounts of 4-methoxybenzyl alcohol[c]
3-Methoxy	.13	29–35% 3-methoxybenzyl alcohol (IX), 8–18% 3,3'-dimethoxybibenzyl (X), 10% 3-methoxybenzyldioxane (XI), dioxanyldioxane[b]
3-Methoxy	.10[d]	3-methoxybenzyl alcohol:3-methoxybenzyl ethyl ether in 1.5:1.0 ratio[e]
3,5-Dimethoxy	.10	79% 3,5-dimethoxybenzyl alcohol[f]

[a] All runs except entry 2 made in 50% aqueous dioxane.   [b] Varying amounts isolated due to volatility.   [c] Detected only in V.P.C. analyses.   [d] Run in 50% aqueous ethanol and quantum yield is sum of ether and alcoholic products.   [e] No attempt to isolate homolytic products.   [f] Only discrete product detectable.

The qualitative and preparative experiments described thus far clearly suggest an increasing facility of the photochemical solvolysis reaction relative to free radical fission in the sequence: 4-methoxybenzyl acetate < 3-methoxybenzyl acetate < 3,5-dimethoxybenzyl acetate. This conclusion was confirmed quantitatively with uranyl oxalate actinometric determination of quantum yields for the three reactions. The results of the isolative and quantum yield runs on the three compounds are summarized in Table I.

The facile *m*-substituted benzyl derivative solvolysis reaction may be qualitatively formulated in valence bond notation as
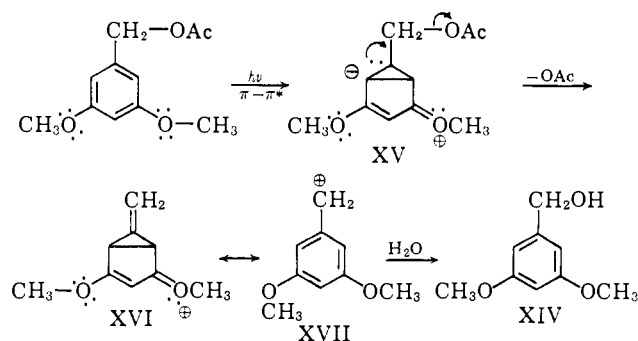
Here, using structures as XV to represent the excited state, one notes that an easy elimination of an anionic moiety as acetate should occur readily only where the benzylic position is *meta* with respect to the methoxyl groups, for only then is the benzylic position bonded to an electron-rich ring carbon atom. Thus the excited state XVIII from *p*-methoxybenzyl acetate does not have the proper electron distribution for anionic expulsion.
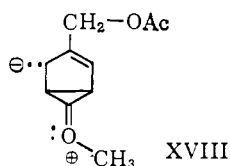
In assessing this rationale, one notes that in proceeding from *p*-methoxy to *m*-methoxy to 3,5-dimethoxy photolyses, the ratio of solvolysis to free radical fission efficiencies increases dramatically while the absolute quantum efficiency of solvolysis alone increases only in proceeding from the *p*-methoxy case to the singly *m*-substituted example. Introduction of the second methoxyl group does not lead to further enhancement of solvolysis quantum efficiency while it does result in further increase in the solvolysis to homolysis ratio. By way of comparison, one notes that in the LCAO MO excited state π-electron density at the benzylic bearing carbon for the three examples increases as 0.76 (for *p*-MeO) <1.20 (for *m*-MeO) <1.35 (for 3,5-di-MeO); here the large increase in electron density occurs on replacement of the *p*-methoxyl

by *meta* and a lesser increase results on introduction of the second *m*-methoxyl.

The preceding interpretive discussion makes use of the electron distribution of an electronically excited reactant in understanding the photochemical behavior of this reactant. In ground state chemistry an interpretation based only on the nature of the reactant can be naïve.[12] However, in the case of photochemical reactions the general importance of energy barriers separating electronically excited species from product has not been defined, and such reactant-based treatments cannot be considered to be unnecessarily naïve. Furthermore, knowledge of the make-up of the real photochemical reactant, the excited state, is certainly of interest.

Nevertheless, it is worthwhile to consider a more sophisticated approach. While, as noted, it is not clear that there are generally thermal barriers of importance in excited state reactants, it is quite clear that excited state reactions follow relatively low energy routes, or channels, along energy surfaces. Thus, in photochemical reactions bonds are not randomly broken; and, in general, photochemical reactions seem to proceed with minimum electron localization. This is one theme of the present sequence of publications. Phrased differently, photochemical reactions proceed by "smooth electron redistribution processes."[1a,2,13,14]

Tables II and III provide pertinent LCAO MO data allowing one to envisage part of the potential energy surface of the first electronically excited state systems. Table II gives the calculated LCAO MO π-energies[15] of the excited states of systems undergoing reaction as well as the energies of the related first excited cationic and free radical species formed in the ionic and radical reactions. Table III gives the LCAO MO π-energy change in each of the excited state reactions, heterolytic and homolytic. Because it is not certain that heterolytic or homolytic fission of the excited state reactant leads to a carbonium ion or radical which is still electronically excited, the value of this data is in allowing a comparison of one possible model with experimental fact.

As in the earlier consideration of electron distribution of reacting excited states, inspection of Tables II and III reveals some interesting parallelisms of LCAO MO theory with photochemical observation.

First, in contrast with the expected ground state situation (column 1, Table II) where the 4-methoxybenzyl cation has a lower π-energy than the 3-methoxybenzyl cation, column 2 of Table II reveals the first

(12) Such interpretations are valid for cases where there is evidence that the transition state closely resembles the reactant.

(13) Paper III of this series, H. E. Zimmerman and S. Somasekhara, *J. Am. Chem. Soc.*, **85**, 922 (1963).

(14) Paper IV of this series, H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962).

(15) Because these data are derived from the LCAO MO approximation with no allowance for electron repulsion or correlation, the calculations are of qualitative rather than quantitative significance.

TABLE II

LCAO MO ENERGIES OF SPECIES OF INTEREST

Cationic and radical species	Ground state cation energy[a]	1st excited state cation energy[a]	1st excited state radical energy[a,b]
4-MeO-benzyl	−11.8938	−10.8604	−10.8270, −10.8938
3-MeO-benzyl	−11.8504	−11.0024	−11.0024, −10.8170
3,5-DiMeO-benzyl	−14.9806	−14.2000	−14.2000, −13.9082
4-MeO-benzhydryl	−20.4618	−19.5441	−19.5205, −19.4618
3-MeO-benzhydryl	−20.4304	−19.5903	−19.5903, −19.4304

STANDARD SPECIES FOR COMPARISON PURPOSES

	Ground state energy	1st excited state energy
Benzene	− 8.0000	....
Anisole	−11.1306	− 9.3007
3,5-DiMeO-benzene	−14.2612	−12.4573
Benzyl cation	− 8.7206	− 7.7206
Benzyl radical	− 8.7206	− 7.7206, −7.7206[b]
Isolated MeO group	− 3.0000[c]	....

[a] All energies in units of the absolute value of beta. [b] Free radical energies are given for two excited states, first for promotion of the highest energy electron to the lowest vacant MO and second for promotion of the next lower energy electron to the odd electron-containing MO. [c] Based on coulomb integral of 1.5 beta used in calculations.

The third parallelism is the sequence of excited state cation formation energies relative to the corresponding excited state free radical formation energies. Because there are two configurations of radical excited states which can be written in each case with not too different energies and the same symmetry, configuration interaction is bound to modify the approximate LCAO MO predictions. With this in mind, both radical-excited state reaction energies are given as well as the average value in the last column of Table III. Inspection of the excited cation versus excited radical formation energies shows that the excited cation becomes more favorable relative to the excited radical in the sequence 4-methoxybenzyl, 3-methoxybenzyl, 3,5-dimethoxybenzyl.

Thus, on three bases the experimental enhancement of photochemical solvolysis over homolysis by m-methoxyl groups correlates with the LCAO MO picture[17] defining the low energy surfaces available for solvolysis.

As a matter of interest, the calculations have been extended to consider the effect of added phenyl groups at the benzylic position. Table II shows that the difference in excited cation energies due to meta versus para placement of the methoxyl group becomes considerably smaller. Also, the preference for excited cation versus excited radical formation in any one case diminishes. Preliminary studies on benzhydryl and trityl derivatives having one methoxy group are sug-

TABLE III

LCAO MO π ENERGY CHANGES FOR EXCITED STATE HETEROLYSES AND HOMOLYSES

Excited state reactant (and energy model used)	Energy of formation of derived species[a,b]	
	Cation	Radical
4-MeO-benzyl acetate (excited anisole model)	−1.5597	−1.5263, −1.5931 (1.5597)
3-MeO-benzyl acetate (excited anisole model)	−1.7017	−1.7017, −1.5163 (−1.6090)
3,5-DiMeO-benzyl acetate (excited 3,5-DiMeO-benzene)	−1.7427	−1.7427, −1.4509 (−1.5968)
4-MeO-benzhydryl acetate (ground state benzene + excited state anisole)	−2.2434	−2.2198, −2.1611 (−2.1905)
3-MeO-benzhydryl acetate (ground state benzene + excited state anisole)	−2.2896	−2.2896, −2.1297 (−2.2097)

[a] For the $n \rightarrow n+1$ and $n-1 \rightarrow n$ excitation processes where n is the odd electron-containing level in the radical ground state. [b] Average values parenthesized.

excited state of the 3-methoxybenzyl carbonium ion to be of lower energy than that of the 4-methoxybenzyl carbonium ion. In continuing the comparison to include the excited 3,5-dimethoxybenzyl cation, one finds a value of −14.2000 for the π-energy of the excited 3,5-dimethoxybenzyl cation. However, the π-energy of this species would in any event be lowered to the extent of −3.000 from the monomethoxybenzyl values exclusive of any electronic interaction of this second methoxyl group; this derives from the mere presence of two additional isolated, low energy electrons. With this correction of −3.000 in mind, one finds that the first excited state benzyl cation energies fall in the decreasing energy sequence: 4-methoxybenzyl (−10.8604) > 3-methoxybenzyl (−11.0024) > 3,5-dimethoxybenzyl (corrected for comparison) (−11.2000).

In a second parallelism, the same sequence is noted in Table III for the energies of formation of the excited state substituted benzyl cations from the respective excited substituted benzyl acetates.[16] Here the decreasing sequence is 4-methoxybenzyl (−1.5597) > 3-methoxybenzyl (−1.7017) > 3,5-dimethoxybenzyl (−1.7427).

(16) The energy of the acetate anion common to the heterolytic fission processes and the energy of the acetoxyl radical common to the homolytic processes are ignored. This means that one can compare the energies of different examples of each type of process, but that in comparing energies of heterolytic versus homolytic fission, there is a constant energy correction term to be taken into account.

gestive of such an effect.[18] These experiments are described in the Experimental section.

In conclusion, it may be stated that there is support developing from a number of directions to indicate that photochemical reactions do occur by smooth electron reorganization processes with minimum electron localization. As in ground state chemistry, energy valleys and mountain passes are followed except that in photochemistry one is dealing with the terrain of excited states.

(17) Actually, the exact way in which control is exercised is uncertain. Thus it is possible that unimolecular heterolysis of a singlet excited state is competing with unimolecular homolysis. Or, alternatively, it is possible that heterolysis is competing with intersystem crossing to give a triplet which undergoes homolysis. Furthermore, the possibility that it is a triplet which undergoes solvolysis cannot be excluded.

(18) Not only does the theory predict that the m- and p-substituted derivatives will approach one another in ease of heterolysis as well as in ease of homolysis but also it suggests that these processes become energetically more favorable. There is indeed literature on the photochemistry of triarylmethyl derivatives such as the photochemical ionization of the leuco cyanide and hydroxide bases of the triphenylmethane dyes; these derivatives have generally had p-substituted amino groups and the quantum yields of ionization have been high. The triarylmethyl situation will not be discussed here. However, for leading references cf. A. H. Sporer, Trans. Faraday Soc., 57, 983 (1961); O. E. Holmes, J. Chem. Phys., 62, 884 (1958), and 61, 434 (1957).

(19) (a) All melting points were taken on Fisher–Johns or Monoscope IV blocks, both of which were calibrated with compounds of known melting points. (b) This section has been abbreviated at the request of the Editor and referees; additional details are available in the Ph.D. thesis of V. Sandel (ref. 1b).

Experimental[19a,b]

3-Methoxybenzyl acetate[20] was prepared by the reaction of 3-methoxybenzyl alcohol[21] with acetic anhydride and a catalytic quantity of pyridine. The product was purified by fractionation with a 62-cm. Martin spinning band column and shown to be free of starting 3-methoxybenzyl alcohol by V.P.C. analysis; ultraviolet λ_{max} (95% ethanol) 274 mμ (3.30), 280 mμ (3.26).

3-Methoxybenzyl Chloride.—A slight modification of the method of Cornforth and Robinson[22] was used; ultraviolet, λ_{max} (95% ethanol) 279 mμ (3.28).

Methyl 3-methoxybenzyl ether[23] was prepared from the reaction of sodium hydride, t-butyl alcohol, 3-methoxybenzyl alcohol and methyl iodide; ultraviolet, λ_{max} (95% ethanol) 273 mμ (3.30), 280 mμ (3.25).

4-Methoxybenzyl Acetate.[24]—The same preparation and purification employed with the m-isomer was used; V.P.C. analysis showed the absence of 4-methoxybenzyl alcohol; ultraviolet λ_{max} (95% ethanol) 274 mμ (3.17), 280 mμ (3.11).

3-Dimethylaminobenzyl Acetate.—A solution of 10.0 g. (1.066 moles) of 3-dimethylaminobenzyl alcohol,[25] 8.1 g. (0.080 mole) of acetic anhydride and 0.06 ml. of pyridine was heated for 4 hr. on a steam-bath. Distillation using a 25-cm. Vigreux column yielded 3-dimethylaminobenzyl acetate slightly contaminated with a carbonyl compound absorbing at 6.03 μ in the infrared. A second distillation with the same column eliminated this impurity. A 6.7-g. (44%) yield of the pure ester, b.p. 109° at 0.5 mm., was obtained.

Anal. Calcd. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82. Found: C, 68.26; H, 7.87.

3,5-Dimethoxybenzyl alcohol[26] was prepared in 65% yield by the lithium aluminum hydride reduction of 3,5-dimethoxybenzoic acid; equimolar quantities of the reactants in ether were refluxed for 20 hr. The product melted at 49–50° (reported[26] 47–48°).

3,5-Dimethoxybenzyl Acetate.—A solution of 10.0 g. (0.0595 mole) of 3,5-dimethoxybenzyl alcohol, 15.0 g. (0.147 mole) of acetic anhydride and 0.06 ml. of pyridine was heated on a steam-bath for 4 hr. The flask was then attached to an aspirator and the excess acetic anhydride and acetic acid was distilled off. The residue was fractionated using a 62-cm. Martin spinning band column. A 12.2-g. (97%) yield of 3,5-dimethoxybenzyl acetate, b.p. 121.5° at 0.4 mm., n^{25}D 1.5164, was obtained; ultraviolet, λ_{max} (95% ethanol): 280 mμ (3.34).

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.84; H, 6.71. Found: C, 62.88; H, 6.68.

3-Methoxybenzhydrol was prepared by the method of Stoermer[27] using phenylmagnesium bromide and 3-methoxybenzaldehyde. 3-Methoxybenzhydrol, b.p. 162–165° at 1.0 mm., was obtained in 83% yield. The material did not crystallize (reported[27] m.p. 41°).

3-Methoxybenzhydryl Acetate.—In a 100-ml. flask fitted with a condenser, dropping funnel and magnetic stirrer, 5.00 g. (0.0234 mole) of 3-methoxybenzhydrol in 25 ml. of toluene was added to 1.22 g. (0.0234 mole) of 50% sodium hydride dispersion in mineral oil. After heating at reflux for 1 hr., the mixture was cooled in an ice-bath. The 2.38 g. (0.0234 mole) of acetic anhydride in 10 ml. of toluene was added dropwise, followed by another 20 ml. of toluene to facilitate stirring. The mixture was allowed to warm to room temperature and was stirred for another hour. Water was added, and the toluene layer was separated. After extracting the aqueous layer with ether, the extracts and toluene solution were combined, dried, and evaporated *in vacuo*. The residue was chromatographed using a 3.2 × 97 cm. silica gel column slurry packed with 4% ether in hexane. All solvents were equilibrated with ethylene glycol prior to use in packing and eluting; 500-ml. fractions were collected, using increasing amounts of ether in hexane. Fractions 12–14 had identical infrared spectra and contained 2.71 g. of 3-methoxybenzhydryl acetate; ultraviolet λ_{max} (95% ethanol) 274 mμ (3.39), 281 mμ (3.35).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.02; H, 6.20.

(3-Methoxyphenyl)-diphenylmethanol.—The preparation from phenylmagnesium bromide and methyl 3-methoxybenzoate gave material of m.p. 88.0–89.5° (reported 88°,[28] 90.5°[29]).

(3-Methoxyphenyl)-diphenylmethyl Acetate.—A modification of the general method of Schoepfle[30] was used. From 5.0 g. (0.017 mole) of acetyl chloride and 5.0 g. (0.084 mole) of acetic acid in 20 ml. of benzene, reacting for 5 min., there was obtained 3.2 g. (57%) of (3-methoxyphenyl)-diphenylmethyl acetate, m.p. 72–73° after crystallization from hexane. The hydrolysis of this compound in 3:1 dioxane–water at 26° was found to have a 12-hr. half-life.

Anal. Calcd. for $C_{22}H_{20}O_3$: C, 79.49; H, 6.06. Found: C, 79.34; H, 6.10.

(3-Methoxyphenyl)-diphenylacetonitrile.—To 6.4 g. (0.022 mole) of (3-methoxyphenyl)-diphenylmethanol was added 10.0 g. (0.094 mole) of thionyl chloride. Following the initial exothermic reaction, the mixture was refluxed for 20 min., and the excess thionyl chloride was removed *in vacuo*. Then 7.5 g. (0.030 mole) of mercuric cyanide was added to the residue. The slurry was stirred with oil-bath heating to 150–160° for 1 hr. The mixture was then extracted with hot benzene and the extracts were concentrated to leave 8.3 g. of material which was chromatographed on a 3.8 × 109 cm. silica gel column slurry packed with 5% ether in hexane; 500-ml. fractions were collected and the percentage of ether gradually increased. Fractions 11–14, obtained with 10–20% ether in hexane, showed nitrile absorption in the infrared; these totaled 2.58 g. Recrystallization from hexane afforded 1.93 g. (10%) of (3-methoxyphenyl)-diphenylacetonitrile, m.p. 105–107°; ultraviolet λ_{max} (95% ethanol) 276 mμ (3.42), 283 mμ (3.39).

Anal. Calcd. for $C_{21}H_{17}NO$: C, 84.25; H, 5.73. Found: C, 84.19; H, 5.62.

Methyl (3-Methoxyphenyl)-diphenylmethyl Ether.—A solution of 5.0 g. (0.017 mole) of (3-methoxyphenyl)-diphenylmethanol and 0.1 g. of p-toluenesulfonic acid in 70 ml. of methanol was heated at reflux for 13 hr. After cooling, the mixture was poured into 10% sodium carbonate solution and extracted with chloroform. The extracts were dried over sodium sulfate, concentrated *in vacuo*, and chromatographed on a 3.8 × 36 cm. column of silica gel, slurry packed with 3% ether in hexane; 500-ml. fractions were collected. Beginning with fraction 3, 6% ether in hexane was used. Fraction 3 contained 0.47 g. (79%) of methyl (3-methoxyphenyl)-diphenylmethyl ether, n^{25}D 1.5930; ultraviolet λ_{max} (95% ethanol) 277 mμ (3.24), 283 mμ (3.20).

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62. Found: C, 82.50; H, 6.75.

(4-Methoxyphenyl)-diphenylacetonitrile was prepared from (4-methoxyphenyl)-diphenylmethanol[31] *via* the corresponding chloride.[19b] Material of m.p. 119–120° was used (reported[32] 117–118°); ultraviolet λ_{max} (95% ethanol) 269 mμ (3.39), 277 mμ (3.47), 284 mμ (3.42).

Light Source.—A General Electric A-H6 high pressure mercury arc at the focus of a parabolic reflector 13.7 cm. long and 14.0 cm. in diameter was used. Light output was monitored with an RCA 935 phototube.

Irradiation and Filter Cells.—Three types of cylindrical cells were used: A filter cell was made up of three compartments, each with an optical path 12 cm. in diameter by 2.4 cm. thick, placed in series. Gasketed quartz disks separated the compartments and covered the ends. Each compartment was cooled internally with a cooling coil.

A single compartment irradiation cell was used for preparative runs. This had a 12-cm. diameter and 5-cm. optical path. The cell was equipped with a thermistor probe inlet, Trubore stirrer, heat exchanger coil, oxygen-free nitrogen inlet and capillary outlet device for obtaining aliquots with a hypodermic syringe. The cell temperature was maintained ±0.10° electronically by control of the temperature of the heat exchanger coil water. For quantum yield determinations, a double cell was used having a second compartment identical with the first already described.

Filters.—For quantum yield determinations, solution filters were used in the triple compartment filter cell as follows: cell 1, 0.0410 g. of acridine hydrochloride and 2.00 ml. of 12 N hydrochloric acid per l. of aqueous solution; cell 2, 0.0130 g. of 5,7-dimethyl-1,2,3-trihydro-1,4-diazepine hydroperchlorate[33] per l. of aqueous solution; cell 3, 460 g. of hexahydrated nickel sulfate, 140 g. of heptahydrated cobalt sulfate and 1.00 ml. of 36 N sulfuric acid dissolved in 1 l. of water. The perchlorate solution could not be stored more than a few days without decomposition and was prepared just before each experiment. This filter combination has a maximum transmission of 64% at 275 mμ and transmits less than 1% below 263 and above 312 mμ. Corning glass filters and filter solutions were used for preparative irradiations as indicated.

Quantum Yield Determinations.—The double compartmented cell was used and the temperature was maintained at

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(26) F. Mauthner, *J. prakt. Chem.*, [2] **100**, 178 (1920).

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(28) A. v. Baeyer, *Ann.*, **354**, 171 (1907).

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(30) C. Schoepfle, *J. Am. Chem. Soc.*, **47**, 1470 (1925).

(31) M. Gomberg and C. Buchler, *ibid.*, **45**, 217 (1923).

(32) I. Lifschitz and G. Girbes, *Chem. Ber.*, **61**, 1486 (1928).

(33) G. Schwarzenbach and K. Lutz, *Helv. Chim. Acta*, **23**, 1139 (1940).

25°. Each determination consisted of three irradiations: irradiation with both compartments containing uranyl oxalate solution, irradiation with cell 1 containing the organic reactant and cell 2 containing uranyl oxalate, irradiation with both cells containing uranyl oxalate solution. Fresh filter solutions were used for each of the three runs. Benzophenone–ketyl purified nitrogen[34] under slight positive pressure was used. In these runs cell 1 was found to absorb all the available light, and from the amount of uranyl oxalate consumed in the first and third irradiations, the amount of light available in run 2 was calculated. This assumed the quantum efficiency of destruction of uranyl oxalate to be 0.58[35] at 276 mμ.

Preparative Irradiation of 4-Methoxybenzyl Acetate.—A 20-ml. portion of a solution of 2.52 g. (0.0140 mole) of 4-methoxybenzyl acetate in 350 ml. of purified[36] dioxane and 350 ml. of distilled water was placed in darkness as a blank. The remainder was irradiated at 17–18° through 4 mm. of Corning 9-54 (7910) filter cutting off below 235 mμ. The reaction was followed by titration; the blank showed no change during the 18-hr. irradiation. A 0.423-g. crop of white crystalline solid, m.p. 125–127°, was filtered at the end of the run. The filtrate was concentrated *in vacuo* at 30°. The residue showed only weak absorption at 2.9–3.05 μ and lacked 9.9 μ absorption characteristic of 4-methoxybenzyl alcohol. This residue was chromatographed on a 2.1 × 104 cm. silica gel column slurry packed in 3% ether in hexane. All solvents were saturated with ethylene glycol and 250-ml. fractions were collected. Increasing amounts of ether were used. Fractions 6 and 7 (10%) contained 0.129 g. of solid, m.p. 125.5–127°; this melted at 129–130° after recrystallization from ethanol–benzene and was identified as 1,2-di-(4-methoxyphenyl)-ethane (reported[37] 130°) by mixed melting point and infrared comparison. The total yield was 36%. Fraction 13 (30%) contained 0.025 g. of 4-methoxybenzyl acetate. Fractions 17 and 18 (50%) weighed 0.820 g. and consisted mainly (0.620 g.) of 4-methoxybenzyldioxane which was obtained pure by chromatography on alumina. Additionally there was obtained from these fractions and from fractions 19 and 20 (50%) 0.010 g. (0.024 g. nearly pure) of the high melting diastereomer of dioxanyldioxane, m.p. 156–157° (reported[38] 157°). Fraction 27 weighed 0.058 g. and melted at 129–131° (reported 131° for the low melting diastereomer of dioxanyldioxane). In a control experiment, 4-methoxybenzyl acetate was shown to be stable to chromatographic conditions utilized.

In a second run using a Corning 9-53 filter (9700) cutting light off below 276 mμ, 2.52 g. of 4-methoxybenzyl acetate in 350 ml. dioxane and 350 ml. of water was irradiated for 3 hr. at 18–25°. There was obtained 0.443 g. (31%) of 1,2-di-(4-methoxyphenyl)-ethane, 0.313 g. (13%) of recovered 4-methoxybenzyl acetate and 0.74 g. (31%) of 4-methoxybenzyldioxane. It was found in a control run that 4-methoxybenzyl alcohol is unchanged under these reaction conditions.

1,2-Di-(4-methoxyphenyl)-ethane was prepared by the general method of Cornforth and Robinson[22] from the reaction of ferric chloride with 4-methoxybenzylmagnesium chloride; m.p. 129–130° (reported[39] 130°).

4-Methoxybenzyldioxane.—A slight modification of the general method of Summerbell and Umhoefer[40] was used. 2-Chlorodioxane[40] was prepared from *p*-dioxene[41] and added to ethereal 4-methoxybenzylmagnesium chloride to give after 24 hr. at room temperature and workup a 32% yield of 4-methoxybenzyldioxane, n^{25}D 1.5270.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.20; H, 7.75. Found: C, 69.03; H, 7.65.

Preparative Irradiation of 3-Methoxybenzyl Acetate.—A 20-ml. aliquot of a solution of 2.53 g. (0.0140 mole) of 3-methoxybenzyl acetate in 350 ml. of purified dioxane and 350 ml. of water was set aside as a blank. The remainder was irradiated at 17–24° using a 9-54 filter cutting light off below 235 mμ. The blank showed no change at the end of the 10 hr. used for irradiation. Following irradiation, the main portion was concentrated *in vacuo*. The crude concentrate in this case showed a medium intensity hydroxyl infrared band. This was chromatographed on a 2.2 × 102 cm. silica gel column slurry packed with 10% ether in hexane; however, all solvents were saturated with ethylene glycol. Fractions were 250 ml. and increasing concentrations of ether were used. Fractions 2–5 (10–15% ether) contained 0.257 g. (18%) of 1,2-di-(3-methoxyphenyl)-ethane having identical infrared with an authentic sample.[42]

(34) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1941, p. 396.

(35) W. A. Noyes, Jr., "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1950, p. 82.

(36) Reference 34, p. 369.

(37) A. Sosa, *Ann. Chim.* (Paris), [11] **14**, 5 (1940).

(38) K. Pfordte, *Ann.*, **625**, 30 (1959).

(39) K. Rorig, J. Johnston, R. Hamilton and T. Telinski, *Org. Syntheses*, **36**, 50 (1956).

(40) R. Summerbell and R. Umhoefer, *J. Am. Chem. Soc.*, **61**, 3016 (1939).

(41) R. Summerbell and L. Bauer, *ibid.*, **57**, 2366 (1935).

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.30; H, 7.49. Found: C, 79.16; H, 7.50.

Fractions 16 and 17 (30%), weighing 0.722 g., had infrared spectra identical with 3-methoxybenzyl alcohol except for a doublet at 8.9 and 9.0 μ due to dioxane contamination; 0.580 g. on treatment with *p*-nitrobenzoyl chloride in pyridine gave 0.520 g. of 3-methoxybenzyl *p*-nitrobenzoate, m.p. 65–67°, plus 0.371 g., m.p. 53–63°, from the filtrate. An authentic sample prepared from 3-methoxybenzyl alcohol melted at 66–67°.

In a second run using a 9-53 filter cutting off below 276 mμ the same quantities as above were irradiated for 3 hr. Chromatography as before gave 0.151 g. (9.2%) of 1,2-di-(3-methoxyphenyl)-ethane, 0.55 g. (29%) of 3-methoxybenzyl alcohol and 0.29 g. (10%) of 3-methoxybenzyldioxane.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.20; H, 7.75. Found: C, 69.47; H, 7.75.

In a control run it was determined that irradiation left 3-methoxybenzyl alcohol unchanged.

Irradiation of 3-Methoxybenzyl Chloride.—A solution of 2.00 g. (0.0128 mole) of 3-methoxybenzyl chloride in 350 ml. of pure dioxane and 350 ml. of water, minus a 5-ml. sample removed as a control, was irradiated for 4 hr. at 18° using a 9-53 filter. The control showed no reaction at the end of this time. The irradiated solution was worked up as described. There resulted 0.59 g. (35%) of 3-methoxybenzyl alcohol and 0.53 g. (21%) of 3-methoxybenzyldioxane.

Non-reactive Compounds.—Irradiation of methyl 3-methoxybenzyl ether and separately of 3-methoxyphenylacetonitrile under conditions similar to those described above gave no reaction.

Preparative Irradiation of 3,5-Dimethoxybenzyl Acetate.—A 5.00-ml. sample was removed from a solution of 2.406 g. (0.0114 mole) of 3,5-dimethoxybenzyl acetate in 375 ml. of dioxane and 375 ml. of water. The 5.00-ml. control showed no change at the end of the 24 hr. The main portion was irradiated for 3 hr. at 25 ± 1°. Titration of aliquots indicated a nearly constant liberation of acid with time with a final titration corresponding to 52% solvolysis. Work-up and chromatography of the 2.218 g. of crude product afforded 1.093 g. (47%) of recovered 3,5-dimethoxybenzyl acetate (eluted with 50–70% ether in hexane) and 0.766 g. of 3,5-dimethoxybenzyl alcohol, m.p. 44–48° (reported[26] 47–48°). This corresponds to a 79% yield based on 53% conversion.

Irradiation of 3-Methoxybenzhydryl Acetate.—Irradiation at 25° of 2.38 g. of 3-methoxybenzhydryl acetate in 402 ml. each of dioxane and water, with a 24-ml. portion reserved as a control, followed by work-up and chromatography as before afforded 0.249 g. (19%) of *m*-benzylanisole as one product.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.81; H, 7.31.

Also obtained was 0.50 g. (23%) of unreacted 3-methoxybenzhydryl acetate and 0.45 g. (31%) of 3-methoxybenzhydrol. Additionally, 8 mg. of material, m.p. 168.5–170°, analyzing for $C_{28}H_{26}O_2$, was obtained; this is likely to be 1,2-diphenyl-1,2-di-(3-methoxyphenyl)-ethane.

3-Benzylanisole.—To 80 ml. of liquid ammonia containing 3.00 g. (0.0140 mole) of 3-methoxybenzhydrol and 1.40 g. (0.0308 mole) of ethanol was added with stirring 0.70 g. (0.031 g. atom) of sodium in small pieces. When the blue color had dissipated, the mixture was allowed to evaporate and the residue was chromatographed on silica gel. The fraction eluted with 3% ether in hexane was molecularly distilled at 105° and 6.5 mm. to give 1.09 g. of 3-benzylanisole, n^{25}D 1.5742.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.75; H, 7.24.

Irradiation of (3-Methoxyphenyl)-diphenylmethyl Acetate.—A 25-ml. portion of a solution of 1.500 g. (0.00452 mole) of (3-methoxyphenyl)-diphenylmethyl acetate in 563 ml. of dioxane and 187 ml. of water was set aside as a control. The remainder was irradiated at 25° for 3 hr. The irradiated portion was treated with refluxing methanol for 1 hr. to solvolyze unreacted (3-methoxyphenyl)-diphenyl acetate. Work-up and chromatography afforded 0.63 g. (50% after allowance for aliquots titrated) of (3-methoxyphenyl)-diphenylmethyl methyl ether indicating this percentage of acetate was unreacted on photolysis. Also isolated was 0.33 g. (55% based on a 50% conversion) of (3-methoxyphenyl)-diphenylmethanol. The control indicated that 62% of the solvolysis was photochemical.

Irradiation of (3-Methoxyphenyl)-diphenylacetonitrile.—A solution of 1.881 g. (0.00629 mole) of (3-methoxyphenyl)-diphenylacetonitrile in 450 ml. of dioxane and 300 ml. of water was irradiated at 25° for 7.5 hr. using a 9-53 filter. A control run indicated no dark reaction. Work-up and chromatography afforded 0.342 g. (19%) of recovered reactant and 0.87 g. (62% based on 81% conversion) of (3-methoxyphenyl)-diphenylmethanol.

(42) Prepared by Dr. T. Axenrod by the method of Cornforth and Robinson (ref. 22).

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 mein. 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 mein. gave 3.34 ± 0.09% 3-methoxybenzyl alcohol and 96 ± 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 mein. of light gave from 2.002 g. (0.0111 mole) of reactant 0.99 ± 0.03% of 3-methoxybenzyl ethyl ether, 1.50 ± 0.05% of 3-methoxybenzyl alcohol and 94 ± 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., $n^{25}D$ 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 mein. was found to give 0.056 g. of 1,2-di-(4-methoxyphenyl)-ethane; V.P.C. analysis indicated 0.52 ± 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 ± 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.

Mechanistic Organic Photochemistry. III. Excited State Solvolyses[1]

BY HOWARD E. ZIMMERMAN[2] AND S. SOMASEKHARA

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 series[3] 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 Havinga[5] 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 state[6] 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 state[6] 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.

(2) University of Wisconsin.

(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.