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PHOTOREARRANGEMENT OF BITOLYLS; EVIDENCE FOR A BENZVALENE MECHANISM

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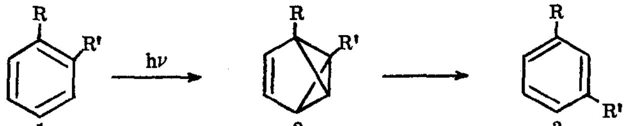
A study of the photochemistry of the six isomeric bitolyls 1a - f was initiated in connection with mechanistic studies on the photofragmentation of benzilides, in particular methyl labeled derivatives (tolilides), which give bitolyls among other products.[2-4]

The series of bitolyls was prepared from the appropriate lithiotoluenes and methylcyclohexanones using a modification of the procedure described by Abramovitch and Koleoso.[5] Complete gas-chromatographic resolution of the six isomers was achieved using a capillary column (0. 02 in) consisting of an initial 50 ft section coated with Apiezon L, a 50 ft unit coated with DC-200/500 and a terminal section of 100 ft coated with DC-550.[6]

The individual bitolyls 1 (40. 0 mg; 0. 22 mmole) in 4 ml of benzene were irradiated[2] with periodic sampling. Losses due to polymerization and other reactions were < 10%. It was observed that the photolability of these substrates is profoundly influenced by the substitution pattern of the methyl groups on the nuclei; those isomers having at least one ortho methyl group are most reactive and rearrange in a highly selective manner. A similar observation was made by Abramovitch in the monomethylbiphenyl series where 2-methylbiphenyl is more reactive than the other isomers.[4] In sharp contrast, the 3, 3'-, 3, 4'-, and 4, 4'-dimethylbiphenyls (1d, 1e and 1f, respectively) are comparatively photostable. Our results are presented graphically in Figures 1 and 2. Since the conversion levels observed under these conditions vary with light intensity (i. e., the number of lamps) and certainly must be a function of the extinction coefficients of the various isomers which vary greatly[7], absolute rate data cannot be inferred directly from Figures 1 and 2.



1 2 3

Equation 1

The formation of both primary and secondary photoproducts obtained from the 2, 2'-isomer (Figure 1) may be rationalized in terms of intermediates of the benzvalene type 2 produced through valence isomerization of the aromatic nucleus, which then may rearomatize to 3 with permutation of ring atoms. As a result of geometrical constraints imposed on the system, only 1, 2-transpositions of the ring atoms are allowed in a single cycle of the type shown in Equation 1.[8, 9]

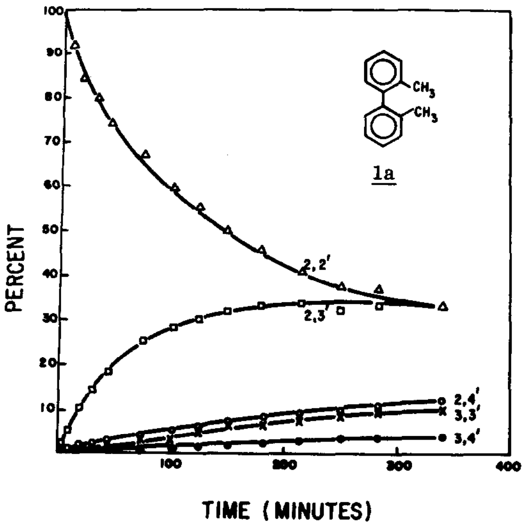


FIGURE 1

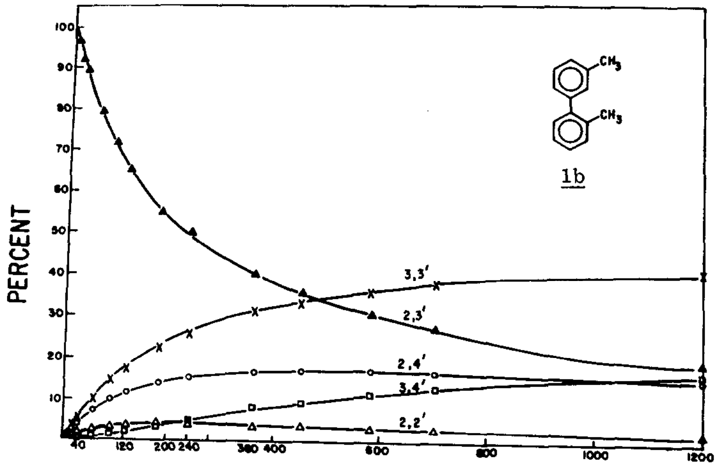
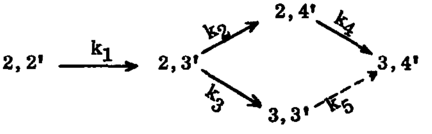
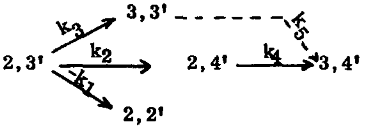


FIGURE 2

It is clear from the data in Figure 1 that the primary rearrangement product obtained from 2,2'-dimethylbiphenyl (1a) is the 2,3' isomer 1b which formally involves a 1,2-phototransposition of the type allowed. The concentrations of the 2,4', 3,3' and 3,4' isomers (1c, 1d and 1e, respectively) increase at a slower rate as expected if they are rearrangement products which arise from the primary product, or other secondary products. A proposed sequence of allowed conversions ("1,2-shifts") which accommodates all products is shown in Scheme 1 and all reactions are potentially reversible. It would appear that $k_2 > k_3$ although caution must be exercised in drawing such conclusions since λ_{max} and ϵ differ for the two isomers,[7,10] and such factors as selective sensitization by solvent or products and differential side reactions have not been



Scheme 1



Scheme 2

evaluated; however, it may be concluded that the 3,4' isomer 1e arises primarily from the 2,4' isomer (i.e., $k_5 \simeq 0$) in view of the relative photostability of the 3,3' as well as 3,4'-bitolyls. Since the 3,3' isomer is relatively stable and the 2,4' isomer is photolabile the differential between k_2 and k_3 is probably even greater than it might appear from Figure 1.

The photochemical results obtained with 2,3'-dimethylbiphenyl (1b) also are consistent with a benzvalene mechanism. The results depicted in Figure 2 show that the 2,2', 2,4' and 3,3' isomers are primary reaction products. As anticipated an induction period is clearly evident in the case of the 3,4' isomer which cannot be a primary product of a single "1,2-shift" and probably arises predominantly from the 2,4' isomer since the other potential precursor, the 3,3' isomer, is substantially more photostable under these conditions. Maxima are observable in the curves for two of the primary products, namely the 2,2' and 2,4' isomers (1a and 1c, respectively) which is consistent with expectations in view of their photolability albeit relatively low extinction coefficients (*vide supra*). The interconversions of Figure 2 are summarized in Scheme 2.

Preliminary rate data obtained on the photolabile 2,4'-dimethylbiphenyl (1c) indicate that the only significant rearrangement product formed after 480 mins is 3,4'-dimethylbiphenyl (38%) with traces of the 4,4'-isomer derived from it. The fact that only traces of 2,3'-dimethylbiphenyl (1b) are detected when monitored throughout the course of the 2,4'-reaction suggests that a substituent effect is operative and a *para* methyl group stabilizes the ring toward reorganization of the benzvalene type.[11] Further quantitative discussion of these complicated series of interrelated transformations which involve reversible reactions seems unwarranted at the present time.

That photolability appears to be conferred upon biphenyls by the presence of an *ortho* methyl substituent is worthy of note. It has been suggested that the rearrangement of simple polyalkyl aromatics proceeds through a singlet excited state or a short-lived triplet state.[8b,12] Theoretical considerations support a planar or nearly planar geometry for the lowest excited states of biphenyl[13] and from experimental data it was concluded that this is the case for the lowest triplet state.[14] Conceivably rearrangement occurs preferentially with 2-substituted biphenyls because the requirements for coplanarity are less stringent in the singlet state and as a result the preferred triplet state geometry is less readily achieved with concomitant inhibition of competitive intersystem crossing. Alternatively, the system simply may be more favorably disposed toward rearrangement as the aromatic rings approach orthogonality for simple steric reasons. Experiments designed to test these hypotheses are in progress. While quantum yields have not been measured they appear qualitatively to be sufficiently high to utilize the rearrangement to synthesize interesting bridged biphenyls.

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REFERENCES

1. Author to whom inquiries should be directed.
2. Irradiations were conducted in benzene at 40° in serum-capped quartz test tubes employing a Rayonet Chamber Reactor equipped with sixteen 8-w 2537Å lamps and a Merry-Go-Round apparatus.
3. U. Mende and G. W. Griffin, unpublished results.
4. 1- and 2-Methylbiphenyl rearrange under similar conditions. See R. A. Abramovitch and T. Takaya, Chem. Commun., 1369 (1969).
5. R. A. Abramovitch and O. A. Koleoso, J. Chem. Soc., B, 779 (1969).
6. Analyses were performed using SCOT columns on a Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector temperature-programmed from 140° to 160° at 0.5°/min. Benzene (the reaction solvent) was used as the internal standard in all runs. Response factors for the bitolyls were the same within ± 1%.
7. H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, N.Y., 1967, p 282. The dihedral angle between the aromatic rings calculated for 2-methylbiphenyl and 2,2'-dimethylbiphenyl are 58° and 70°, respectively, and the absence of coplanarity is reflected in the ultraviolet spectra.
8. Irradiation of substituted benzene derivatives at 2537Å and 1850Å generally results in isomerization with 1,2- and 1,3-translocations of groups and concomitant ring carbon interchanges: (a) A. W. Burgstahler and P. L. Chien, J. Amer. Chem. Soc., **86**, 2940 (1964); (b) K. E. Wilzbach and L. Kaplan, J. Amer. Chem. Soc., **81**, 4004 (1965).
9. Although the same limitation may apply if a fulvene intermediate is invoked reversion of fulvene to benzene does not appear to occur at least in solution. L. Kaplan, S. P. Walch, and K. E. Wilzbach, J. Amer. Chem. Soc., **90**, 5646 (1968).
10. The symmetrically disubstituted isomers 1a and 1f have extinction coefficients of 6,800 (λ_{max}^{EtOH} 227) and 20,500 (λ_{max}^{EtOH} 255.6), respectively.
11. It has been noted by Kaplan and Wilzbach (personal communication) that relative rearrangement rates for m-, o-, and p-xylenes are 10:4:1.
12. N. Leroy, J. Chim. Phys., **64**, 1390 (1967); R. B. Cundall and J. R. Voss, Chem. Commun., 902 (1968).
13. A. Imamura and R. Hoffmann, J. Amer. Chem. Soc., **90**, 5379 (1968).
14. P. S. Wagner, J. Amer. Chem. Soc., **89**, 2820 (1967).