Photobromination of 1,5-Dimethylnaphthalene

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Based upon a study of the reaction kinetics of the photobromination of 1-methylnaphthalene, 2-methylnaphthalene, and 2,6-dimethylnaphthalene, we previously reported the predicted product composition resulting from the photobromination of 1,5-dimethylnaphthalene.[1] Of interest is the comparison of relative reactivity of α- and β-methyl groups (the α reaction proceeds 2.8 times faster than the β reaction) to that of α- and β-bromomethyl groups (in which it was found that the β reaction is about twice as fast as the α reaction).

In the case of 2,6-dimethylnaphthalene, [2(0),6(0)], the bis(bromomethyl)naphthalene, [2(1),6(1)], was formed in about a 9:1 mole ratio compared with the unsymmetric compound, [2(2),6(0)], as is to be expected.[2] However, in the case of 1,5-dimethylnaphthalene, [1(0),5(0)], the bis(bromomethyl)naphthalene, [1(1),5(1)], was predicted to form in about a 70:1 mole ratio compared to [1(2),5(0)] which is in agreement with the observation that secondary bromination is less favored at the α than the β position.

The predicted product composition of [1(0),5(0)] as a result of photobromination is given by the curves of Figure 1. The prediction was made using the relative rate constants determined from our previous work.[1] Table I presents the experimental results[3] of the photobromination of [1(0),5(0)]. These data are also presented as points in Figure 1. Agreement between the predicted composition and experimentally observed composition is good indicating that the method by which the relative rate constants were evaluated is sound. This strengthens our belief that the product composition of 1,4-dimethylnaphthalene subject to photobromination should be similar to that of 1,5-dimethylnaphthalene and further that our predictions regarding 1,6-dimethylnaphthalene are also sound.

TABLE I

PHOTOBROMINATION OF 1,5-DIMETHYLNAPHTHALENE

Br equiv reacted	Brominate analysis, mole % [1(0), 5(0)]	[1(1), 5(0)]	[1(1), 5(1)]	[1(2), 5(1)]	[1(2), 5(1)]	[1(2), 5(2)]
0.50	53.2	42.3	4.0	0	0	0
0.75	33.9	55.0	11.0	0	0	0
1.00	13.6	63.5	24.0	0	0	0
1.25	1.2	60.0	36.5	1.0	1.2	0
1.50	0	44.6	49.9	2.6	3.2	0
1.75	0	15.1	76.8	1.0	7.0	0
2.00	0	2.7	92.2	0	4.9	0
2.25	0	0	66.0	0	31.2	2.9
2.50	0	0	44.3	0	45.9	9.7
2.75	0	0	27.8	0	53.0	19.5
3.00	0	0	13.2	0	54.0	32.9

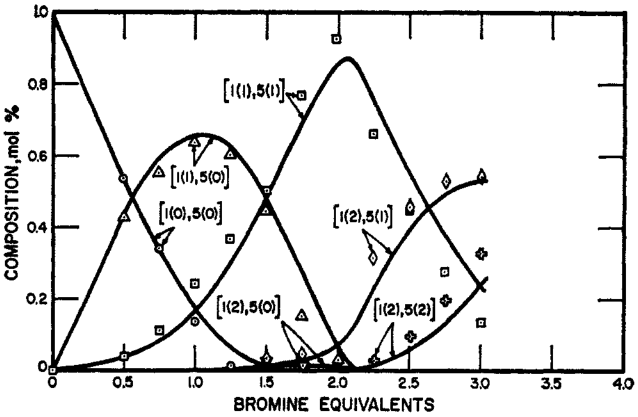

Figure 1.—Photobromination of 1,5-dimethylnaphthalene, [1(0), 5(0)].

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[1] P. R. Taussig, G. B. Miller, and P. W. Storms, *J. Org. Chem.*, **30**, 3122 (1965). Figure 6 in this reference is incorrect. An inadvertent numerical error in the computer program produced erroneous predictions for 1,5-dimethylnaphthalene. As a check we repeated all of the computations and obtained exact agreement for all of the data reported except in the case of Figure 6. The rate constants given in Table VII were found to be correct.

[2] The notational scheme for identifying compounds and reaction rate constants is the same as that defined in ref 1.

[3] The experimental and analytical procedures for this study are the same as those described in ref 1.

A *sym*-Dibenzfulvalene[1a]

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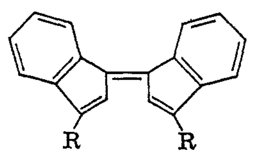
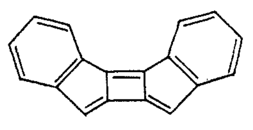
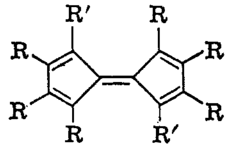
We wish to report the isolation and characterization of a hitherto unknown[2] symmetrical dibenzfulvalene Ia (hereafter referred to as *sym*-dibenzfulvalene) obtained unexpectedly during the course of efforts to synthesize the novel aromatic system II. In contrast to fulvalene (IIIa) which has been reported to exist only in dilute



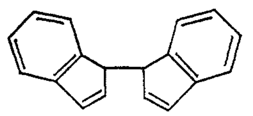
Ia, R=H
b, R=Br



II



IIIa, R=R'=H
b, R=R'=Cl
c, R=Ph; R'=H



IV

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[1] (a) Taken in part from the dissertations of A. G. A., submitted to the Graduate School of Yale University, New Haven, Conn., 1963, and F. L. S. submitted to the Graduate School of Tulane University, New Orleans, La., in partial fulfillment for degrees of Doctor of Philosophy. (b) Author to whom requests for reprints should be directed at the Department of Chemistry, Louisiana State University in New Orleans, New Orleans, La.

[2] Although Ia had eluded synthesis, several substituted dibenzfulvalenes have been reported. See, for example, E. D. Bergmann in "Progress in Organic Chemistry," Vol. 3, Butterworth and Co. (Publishers) Ltd., London, 1955, p 81.