

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 results³ of the photo-

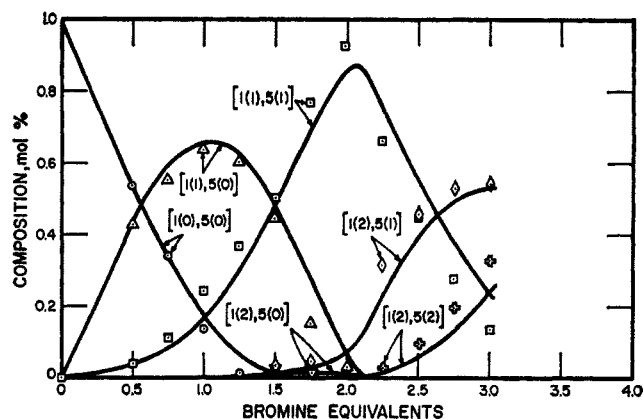


Figure 1.—Photobromination of 1,5-dimethylnaphthalene, [1(0), 5(0)].

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.

A *sym*-Dibenzfulvalene^{1a}

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We wish to report the isolation and characterization of a hitherto unknown² 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

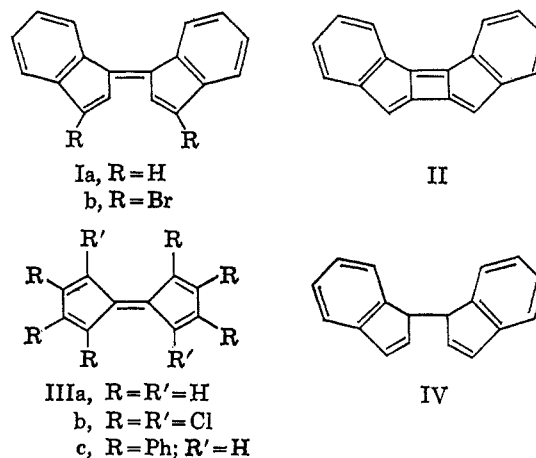


TABLE I
PHOTOBROMINATION OF 1,5-DIMETHYLNAPHTHALENE

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

bromination 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

(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.

(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.

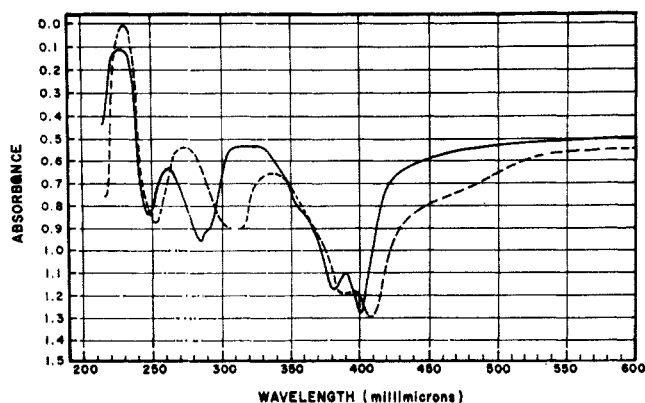
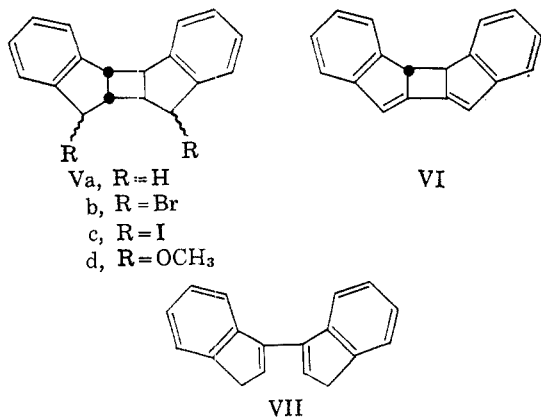


Figure 1.—Ultraviolet-visible spectra of *sym*-dibenzfulvalene Ia (solid line) and the dibromide Ib (dashed line) in *n*-hexane as recorded on a Perkin-Elmer Model 202 ultraviolet-visible spectrophotometer.

solutions,³ Ia manifests great stability both in solution and in the solid state.⁴ Other stable fulvalenes reported in recent years include the octachloro derivative IIIb⁵ and the hexaphenylfulvalene IIIc.⁶ The stability of Ia is in agreement with the results of molecular orbital calculations which predict a delocalization energy of 6.73β , as well as reasonable values of electron densities, free valence indices, and π -bond orders.⁷ It is noteworthy that earlier attempts to synthesize Ia by subjecting 1,1'-biindenyl (IV) to a variety of dehydrogenation conditions proved unrewarding.⁸

The basic carbon skeleton for II may be acquired by the photosensitized dimerization of indene.⁹ The indene photodimer, referred to as a truxane, was rigorously shown¹⁰ to possess the *syn* (head to head), *trans* configuration Va by degradative ozonolysis to *cis,trans,cis*-1,2,3,4-tetracarboxycyclobutane and conversion to a truxone (in the formal sense an indenone dimer) of *syn* orientation.¹⁰ Treatment of Va with 2 equiv of *N*-bromosuccinimide afforded the dibromide Vb which in turn



(3) W. von E. Doering, the Kekulé Symposium, Butterworth and Co. (Publishers) Ltd., London, 1959, p 35; W. B. De More, H. O. Pritchard, and N. Davidson, *J. Am. Chem. Soc.*, **81**, 5874 (1959); E. M. Kosower and B. G. Ramsey, *ibid.*, **81**, 856 (1959).

(4) The ultraviolet spectrum of a heptane solution of Ia remained unchanged after 24 hr at the reflux temperature.

(5) V. Mark, *Tetrahedron Letters*, No. 10, 333 (1961).

(6) P. L. Pauson and B. J. Williams, *J. Chem. Soc.*, 4153, 4158 (1961).

(7) C. Sandorfy, *Compt. Rend.*, **230**, 961 (1950). Although Ia is conveniently depicted in the *cis* form there is no evidence to preclude the *trans* configuration.

(8) C. Dufraisse, A. Etienne, and P. Vallette, *ibid.*, **231**, 1379 (1950).

(9) G. O. Schenck, W. Hartmann, S. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962). We are indebted to Professor Schenck for making available a generous sample of the dimer.

(10) A. G. Anastassiou and G. W. Griffin, unpublished results. See also C. H. Krauch and W. Metzner, *Chem. Ber.*, **98**, 2762 (1965).

was transformed to the extremely light-sensitive diiodide Vc upon treatment with sodium iodide in acetone.

The orientation of the bromine and iodine atoms in Vb and Vc was established by examination of their nmr spectra. It should be noted that, *a priori*, three modes of substituent orientation are possible in the case of 1,1'-disubstituted *syn,trans* truxanes such as Vb or Vc: two symmetrical orientations either *exo,exo* (both substituents directed away from the cyclobutane ring) or *endo,endo* (both substituents directed toward the cyclobutane ring) and one unsymmetrical orientation *exo,endo*. Inspection of simple molecular models indicates that in the *endo,endo* substituent disposition the dihedral angle between the $>CHX$ proton and the adjacent cyclobutane proton is nearly 0° , while the corresponding angle for these protons in the *exo,exo* substituent orientation is of the order of 100° . The coupling constants associated with these dihedral angles should be approximately 8 cps for the *endo,endo* disposition and less than 2 cps for the *exo,exo* orientation.¹¹ The sharp singlets assignable to the $>CHX$ protons in Vb (τ 4.45) and Vc (τ 4.25) indicate that the halogen atoms in these dihalotruxanes are symmetrically disposed and *exo,exo*. All three isomeric dimethoxy derivatives Vd have been synthesized and their nmr spectra support the validity of this dihedral angle-coupling constant relationship.¹²

To date attempts to prepare the diene VI from Vb and Vc by employing various base-catalyzed dehydrohalogenation procedures have proved unsuccessful. However, our efforts have not been entirely unrewarding since in two cases Ia was obtained as a product. On treatment with excess potassium amide in liquid ammonia the dibromide Vb yielded two crystalline products, the dibenzfulvalene Ia and the known 3,3'-biindenyl (VII), which were separated by elution chromatography. The action of potassium *t*-butoxide in *t*-butyl alcohol on Vb gave only intractable materials; however, Ia may be generated in low yield from the diiodide Vc under these conditions.

The diene VII was characterized by a mixture melting point determination and direct comparison of its infrared spectrum with that of an authentic sample prepared from Ib by the method of Straus, Kühnel, and Haensel.¹³ The elemental analysis was also consistent as was the nmr spectrum which exhibited absorption at τ 2.6–3.1 (multiplet, aromatic protons), 3.50 (singlet, vinyl protons), and 6.55 (singlet, methylene protons) in the respective ratio of 4:1:2.

The dibenzfulvalene was isolated in the form of golden orange leaflets (mp >300). In addition to the consistency of the elemental analysis and the nmr spectrum, which shows two signals (multiplets) at τ 2.0–2.3 and 2.5–3.1 in the respective ratio of 1:5, convincing evidence for structure Ia is provided by the similarity of its ultraviolet-visible spectrum to that of the known¹³ dibromo analog Ib¹⁴ (Figure 1). Both Ia and VII, a diene of known structure, are transformed to the same material, undoubtedly 1,1'-biindanyl, upon catalytic hydrogenation. Moreover, treatment of VII with *o*-chloranil afforded an orange oil whose ultraviolet spec-

(11) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

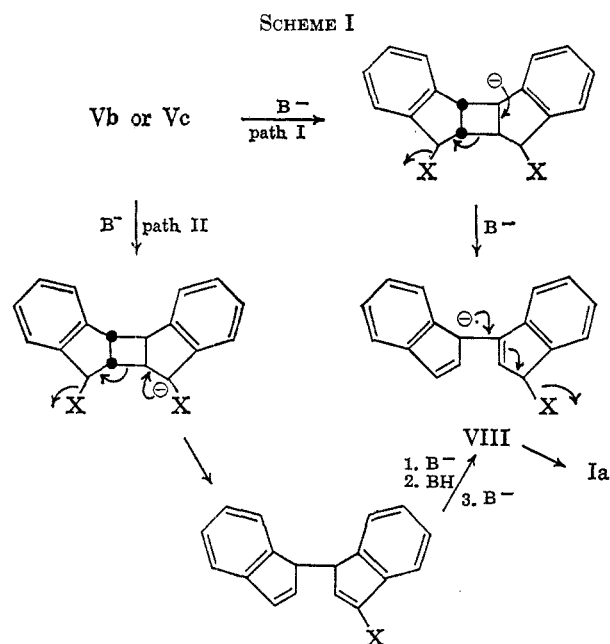
(12) F. L. Setliff and G. W. Griffin, unpublished results.

(13) F. Straus, R. Kühnel, and R. Haensel, *Chem. Ber.*, **66**, 1847 (1933).

(14) Attempts to convert Ib to Ia by conventional dehalogenation procedures failed.

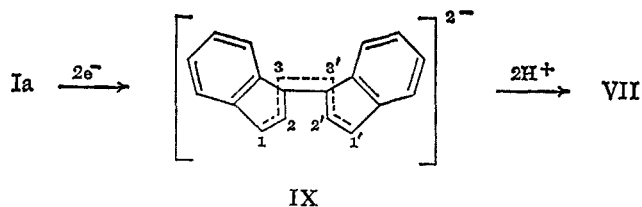
trum was virtually superimposable above 300 μ on that of Ia.

We wish to propose Scheme I to account for the formation of Ia.¹⁵ As indicated in the scheme below,



abstraction of either the tertiary benzylic (path I) or the halobenzylic (path II) protons may lead to the reactive intermediate VIII which would then collapse to afford the observed product.

To explain the formation of 3,3'-biindenyl (VII) a Birch-type reduction¹⁶ of the dibenzfulvalene to yield the dianion IX may be invoked. Subsequent protonation of IX at sites 1 and 1' would then account for the observed product. Molecular orbital calculations suggest that these sites possess the highest electron densities in IX. Support for the proposal that VII is formed by reduction of Ia was obtained by treating the dibromide Vb with a limited quantity (2 equiv) of potassium amide. In this case Ia is formed without contamination by VII.



Experimental Section¹⁷

Photodimerization of Indene. Formation of *syn,trans*-Truxane (Va).—Four serum-capped, 200-ml Pyrex round-bottom flasks,

(15) There is no evidence available at present to support or refute a concerted process in the two elimination steps or a prior epimerization at one or more centers.

(16) A. J. Birch, *J. Chem. Soc.*, 430 (1944); *ibid.*, 593 (1946). Unreacted potassium metal probably serves as the reducing agent.

(17) All melting points are uncorrected. Infrared spectra were determined in potassium bromide on a Perkin-Elmer Model 337 spectrophotometer. Ultraviolet spectra were recorded on a Perkin-Elmer Model 202 ultraviolet-visible spectrophotometer and a Cary Model 14 spectrophotometer. All nmr spectra were obtained on a Varian A-60 instrument with tetramethylsilane as internal standard. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y., or Galbraith Laboratories, Knoxville, Tenn.

each containing freshly distilled indene (20.3 g, 0.175 mole), benzophenone (3.0 g), and benzene (150 ml) were placed in a Rayonet photochemical reactor¹⁸ equipped with 16 8-w, 3500-A lamps and irradiated for 24 hr. The contents of the flasks were then subjected to slow evaporation in an air stream and the residual crystals were washed free of adhering oil with cold acetone. Recrystallization from acetone afforded a total of 21.0 g (26%) of Va as colorless crystals, mp 109–111° (lit.⁹ mp 110°).

Treatment of Va with N-Bromosuccinimide. Formation of the Dibromide Vb.—To a solution of Va (10.0 g, 43.1 mmoles) in 150 ml of dry carbon tetrachloride (distilled from phosphorus pentoxide) was added N-bromosuccinimide (15.4 g, 86.4 mmoles) and a few small grains of benzoyl peroxide. The resulting reaction mixture was held at reflux with constant stirring for 10 hr. The suspension was cooled to room temperature, the succinimide was collected on a filter, and the clear yellow filtrate was evaporated on a rotary evaporator. The residual oil was subsequently digested with glacial acetic acid at 70° for 3 hr and the precipitated white solid was collected and recrystallized from methylcyclohexane to yield 8.2 g (49%) of Vb, mp 172–175°. An analytical sample was obtained after two recrystallizations from glacial acetic acid, mp 175–178°. The infrared spectrum of this material exhibits strong bands at 760, 733, 680, 630, and 500 cm^{-1} . The nmr spectrum (CDCl_3) exhibits signals at τ 2.60 (singlet), 4.45 (singlet), 6.25 (doublet), and 7.00 (doublet) in the respective peak area ratio 4:1:1:1.

Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{Br}_2$: C, 55.43; H, 3.62; Br, 40.96. Found: C, 55.38; H, 3.92; Br, 40.61.

Treatment of Vb with Sodium Iodide. Formation of the Diiodide Vc.—A mixture of Vb (6.0 g, 15.4 mmoles), sodium iodide (6.3 g, 42 mmoles), and 100 ml of dry acetone (distilled from potassium carbonate) was heated under reflux with stirring for 1.5 hr. The reddish brown reaction mixture was cooled to room temperature, the precipitated sodium bromide was collected on a filter, and the filtrate was subjected to slow evaporation in an air stream. The solid material remaining was washed in turn with water (50 ml) and cold, absolute ethanol (100 ml). The light yellow solid (5.7 g, 74%) decomposes¹⁹ at 83–85°, but remains unmelting up to 300°. The infrared spectrum of Vc is characterized by strong absorption at 760, 745, 615, and 495 cm^{-1} .

The nmr spectrum (CDCl_3) exhibits signals at τ 2.7 (singlet), 4.25 (singlet), 6.35 (doublet), and 6.95 (doublet) in the respective area ratio of 4:1:1:1. Two recrystallizations from cyclohexane afforded an analytical sample, that decomposed at 83–85°.

Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{I}_2$: C, 44.60; H, 2.89; I, 52.48. Found: C, 44.82; H, 3.01; I, 52.70.

Treatment of the Dibromide Vb with Excess Potassium Amide in Liquid Ammonia. Formation of 3,3'-Biindenyl (VII) and *syn*-Dibenzfulvalene (Ia).—Anhydrous liquid ammonia (250 ml) was placed in a dry, 500-ml, three-necked, round-bottom flask equipped with a Dry Ice condenser, drying tube, and mechanical stirrer (glass stirring blade). Potassium metal (8.0 g, 2.05 g-atoms) and iron powder (1.0 g) were then added successively and the reaction mixture was stirred vigorously for 0.5 hr. The dibromide (3.9 g, 10 mmoles) was then added in one operation and the resulting deep red suspension was stirred for an additional 2.5 hr. The reaction was subsequently quenched, under a blanket of nitrogen, by the careful addition of solid ammonium chloride (25.0 g) followed by ether (100 ml) and water (50 ml), and the solution was transferred to a separatory funnel. The dark residue in the flask was further extracted with ether (400 ml) and the ether extracts were transferred to the separatory funnel. Separation of the two layers was achieved by the addition of 5% hydrochloric acid. The aqueous phase was further extracted with ether and the combined deep red ether extracts were washed with water and dried over calcium sulfate. Evaporation of the ether afforded a dark residue which was dissolved in the minimum amount of 1:1 benzene-hexane and the solution was applied to a 60-cm chromatographic column packed with acid-washed aluminum oxide. Elution was then performed with 1:4 benzene-hexane. Evaporation of the initial colorless eluate (approximately 200 ml) afforded 530 mg (23%) of 3,3'-biindenyl in the form of pale yellow plates, which after recrystal-

(18) Southern New England Ultraviolet Co., Middletown, Conn.

(19) This iodide is extremely sensitive to light and turns brown on prolonged exposure; however, it may be stored indefinitely without decomposition in an opaque container at 0°.

lization from absolute ethanol melted at 130–131° (lit.¹³ mp 130–131°). The infrared spectrum exhibits sharp absorption bands at 1445, 1385, 970, 775, 765, 745, and 720 cm⁻¹. The ultraviolet spectrum is characterized by absorption at $\lambda_{\text{max}}^{\text{EtOH}}$ 227 m μ (ϵ 30,300), 234 (29,500), and 255 (15,700). The nmr spectrum (CCl₄) exhibits signals at τ 2.6–3.1 (multiplet), 3.50 (singlet), and 6.55 (singlet) in the respective area ratio of 4:1:2. A mixture melting point determination with an authentic sample¹³ showed no depression, and the infrared spectrum was identical with that of authentic material.

Anal. Calcd for C₁₈H₁₄: C, 93.87; H, 6.13. Found: C, 93.58; H, 6.18.

Evaporation of the later chromatographic fractions afforded 330 mg (14.5%) of an orange, crystalline solid which was recrystallized from absolute ethanol but still melted over a wide range. Further purification of this material was achieved by chromatography through a 30-cm chromatographic column packed with acid-washed aluminum oxide. The central part of the bright orange band was collected and after removal of the volatile solvent, 45 mg of pure *sym*-dibenzfulvalene (Ia) remained. The golden orange leaflets of Ia upon heating begin to darken at 220° but do not melt up to 300°. The infrared spectrum of this material exhibits significant bands at 1445, 1370, 780, and 740 cm⁻¹. The ultraviolet spectrum is characterized by absorption at $\lambda_{\text{max}}^{\text{hexane}}$ 248 m μ (ϵ 19,300), 285 (22,300), 291 (shoulder) (20,900), 360 (shoulder) (18,300), 380 (27,200), and 401 (30,000). See Figure 1 for a comparison with Ib. The nmr spectrum (CCl₄) shows absorption at τ 2.0–2.3 (multiplet) and 2.5–3.1 (multiplet) in the respective ratio of 1:5.

Anal. Calcd for C₁₈H₁₂: C, 94.70; H, 5.30. Found: C, 94.86; H, 5.21.

Treatment of Vb with 2 Equiv of Potassium Amide in Liquid Ammonia.—By a procedure analogous to that above, the dibromide, Vb (2.5 g, 6.4 mmoles), on treatment with potassium amide generated from potassium metal (0.5 g, 0.125 g-atom), iron powder (1.0 g), and anhydrous liquid ammonia (50 ml), provided 100 mg (7%) of Ia. No traces of 3,3'-biindenyl (VII) could be detected.

Treatment of the Diiodide Vc with Potassium *t*-Butoxide.—To a solution of potassium *t*-butoxide, prepared from potassium metal (0.750 g, 0.019 g-atom) in 50 ml of dry *t*-butyl alcohol (distilled from sodium metal), was added the diiodide (1.5 g, 3.1 mmoles). The resulting mixture was stirred at 75° for 6 hr. After cooling to room temperature, the volatile solvents were removed under reduced pressure (rotary evaporator) and the residue was suspended in water (50 ml) and extracted with two 100-ml portions of ether. The ether extracts were combined and washed in turn with 5% hydrochloric acid (100 ml), 5% sodium thiosulfate solution (100 ml), and finally water (200 ml). After drying over sodium sulfate the ether solution was evaporated and the dark brownish orange residue was dissolved in the minimum amount of benzene. The benzene solution was then applied on a 30-cm column packed with neutral aluminum oxide. Elution was begun with 1:4 benzene-cyclohexane (100 ml) and continued with 1:3 benzene-cyclohexane (100 ml), 1:1 benzene-cyclohexane (200 ml), and pure benzene (200 ml). Evaporation of the first 100 ml of yellow-orange eluate afforded a total of 8 mg (1%) of the dibenzfulvalene (Ia) as an orange, crystalline solid. Later eluates afforded only dark, intractable oils.

Treatment of 3,3'-Biindenyl (VII) with Tetrachloro-1,2-benzoquinone.—A solution of VII (70 mg, 0.3 mmole) and tetrachloro-1,2-benzoquinone (*o*-chloranil, 75 mg, 0.3 mmole) in 25 ml of dry benzene (distilled from sodium metal) was maintained at reflux for 20 hr. The light orange solution was subsequently evaporated to dryness, the residue was dissolved in the minimum amount of 1:1 benzene-hexane, and the resultant solution was applied on a 30-cm chromatographic column, packed with acid-washed aluminum oxide, and eluted with 1:5 benzene-hexane. Evaporation of the initial colorless eluate afforded 40 mg (57%) of unreacted diene VII. Evaporation of the yellow eluate that followed yielded a dark orange oil (25 mg) which could not be induced to crystallize. The ultraviolet spectrum of this material exhibited absorption at $\lambda_{\text{max}}^{\text{hexane}}$ 380 and 401 m μ , which is characteristic of the dibenzfulvalene.

Catalytic Hydrogenation of 3,3'-Biindenyl (VII) and of *sym*-Dibenzfulvalene (Ia).—3,3'-Biindenyl (30 mg, 0.13 mmole), heptane (60 ml), and 5% palladium on charcoal (50 mg) were placed in a hydrogenation flask and the pressure was raised to 50 psi of hydrogen at room temperature. The mixture was shaken for 24 hr. Removal of the catalyst by filtration afforded a colorless

heptane solution which exhibited ultraviolet absorption at λ_{max} 260.5, 267, and 273.5 m μ . *sym*-Dibenzfulvalene was hydrogenated as described above, and under a pressure of 63 psi of hydrogen. The ultraviolet spectrum of the resultant colorless heptane solution was qualitatively identical with that of the product obtained by reduction of 3,3'-biindenyl. After removal of most of the heptane under reduced pressure, the residual materials from the two hydrogenations exhibited identical infrared spectra (CCl₄).

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The Oxidation of Some Benzhydrols with Bromine in Methanol^{1a}

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A recent discovery in our laboratory of a novel synthesis of mixed ethers from the reaction of some arylcarbinols with simple aliphatic alcohols in the presence of iodine,² has prompted an investigation into the limitations of the reaction. It was found that benzhydrols which were substituted in the 4 position by electron-seeking groups gave reduced yields of mixed ethers and in the case of 4-nitrobenzhydrol no reaction was observed. The same carbinol, however, when treated with bromine in methanol was converted to 4-nitrobenzophenone in nearly quantitative yield. Table I indicates the results obtained from this very simple oxidation procedure with other benzhydrols as well as with benzyl alcohol, 4-nitrobenzyl alcohol, triphenylcarbinol, and phenyl-*p*-tolyl- α -naphthylcarbinol.

TABLE I

Alcohol ^a	Product	% yield
(R) ₂ CHOH	Benzophenone	45%
RR ₁ CHOH	4-Chlorobenzophenone	Ca. quant
RR ₂ CHOH	4-Bromobenzophenone	Ca. quant
R ₁ R ₂ CHOH	4-Chloro-4'-bromobenzophenone	Ca. quant
RR ₃ CHOH	4-Nitrobenzophenone	Ca. quant
R ₂ R ₃ CHOH	4-Bromo-4'-nitrobenzophenone	Ca. quant
RR ₄ CHOH	4-Methylbenzophenone	81%
R ₃ R ₅ CHOH	4-Nitro-4'- <i>t</i> -butylbenzophenone	95%
RCH ₂ OH	Benzaldehyde	20%
R ₂ CH ₂ OH	4-Bromobenzaldehyde	40%
R ₃ CH ₂ OH	4-Nitrobenzaldehyde	80%
(R) ₃ COH	Methyl ether	Ca. quant
RR ₄ R ₆ COH	Methyl ether	80%

^a R = C₆H₅; R₁ = 4-ClC₆H₄; R₂ = 4-BrC₆H₄; R₃ = 4-NO₂-C₆H₄; R₄ = 4-CH₃C₆H₄; R₅ = 4-*t*-BuC₆H₄; R₆ = α -naphthyl.

As can be seen from the table, the yields of oxidation product are excellent in all cases where the algebraic sums of the Hammett σ values of the ring substituents

(1) (a) This research was supported in part by a grant from the Petroleum Research Fund of the American Chemical Society and in part by the Ontario Research Foundation. Grateful acknowledgement is hereby rendered to both granting agencies. (b) Holder of a National Research Council of Canada Studentship.

(2) K. G. Rutherford and O. A. Mamer, submitted for publication.