TABLE II

VALUES OF ν_H, $\nu_H - \nu_{CH_3}$, AND $\nu_{CD_3} - \nu_{CH_3}$ IN CM^{-1} FOR p-RC$_6$H$_4$OCH$_3$ IN VARIOUS SOLVENTS[a-c]

Solvent	ν_H	$\nu_H - \nu_{CH_3}$	$\nu_{CD_3} - \nu_{CH}$
Gas phase	46,510	1010	130[d]
Heptane	45,530	1090	80
MeCN	45,530	770	80
Dioxane	45,350	730	80
EtOH	45,570	860	80
H$_2$O	46,180	910	100

[a] Values of ν_{max}, determined as previously described,[5] are averages of two determinations, duplicable to ±20 cm^{-1} except where noted. [b] Compound preparation and purification also previously described.[5] [c] The isotopic composition of the sample of p-methylanisole-α-d_3 was: d_3, 85.0%; d_2, 9.8%; d_1, 0.7%; d_0, 4.5%.[5] [d] Value of ref 5, duplicable to ±20–30 cm^{-1}.

experimental error no solvent effect on $\nu_{CD_3} - \nu_{CH_3}$ is discernible. The interesting fact that p-alkyl lowers the principal electronic excitation energy of anisole and similar compounds,[8] and that both for compounds of the anisole type and nitrobenzene, p-CD$_3$ derivatives have a slightly higher excitation energy than the p-CH$_3$ derivatives, has been commented upon previously.[5,9]

Although base solvation of p-CH$_3$ is indetectable in this particular system, the pronounced lowering of the excitation energy of each nitrobenzene as solvent acidity is increased[10] indicates that acidic hydrogen bond solvation of the nitro oxygens is highly important in the total solvent effect.[2] The *increase* in excitation energy of the anisoles in proceeding from heptane to water solvent is attributable to acidic hydrogen bond solvation of the ether oxygen.[5]

Registry No.—p-Nitrotoluene-α-d_3, 23346-24-9; p-methylanisole-α-d_3, 23346-26-1.

Acknowledgment.—Financial support by the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.

[10] For nitrobenzene itself, the excitation energy is 14.6 kcal mol^{-1} less in 96% sulfuric acid than in heptane.

Protonation and Methylation of Dianions Derived from 1,4-Bisbiphenylenebutatriene and 1,4-Bisbiphenylene-1,3-butadiene

JOHN M. EDINGER AND ALLAN R. DAY*

Department of Chemistry,
University of Pennsylvania, Philadelphia, Pennsylvania 19104

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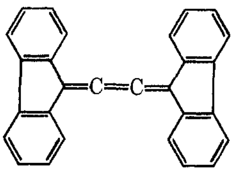
It was the purpose of this investigation to extend our knowledge of the chemical reactions of the dianions generated from aryl-substituted butatrienes. The chemical reactivity of the dianion derived from tetraphenylbutatriene has been the subject of several papers.[1]

The butatriene chosen for the present study was 1,4-bisbiphenylenebutatriene (II). It is a planar molecule

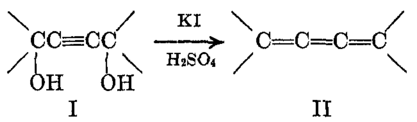


II

and extensive resonance delocalization is possible. This fact is clearly indicated by the colors of tetraphenylbutatriene and 1,4-bisbiphenylenebutatriene. The first is bright yellow and absorbs in the visible at 408 mμ, whereas the second is deep red with a visible absorption at 483 mμ. Due to some steric inhibition of resonance, delocalization is less in the first compound.

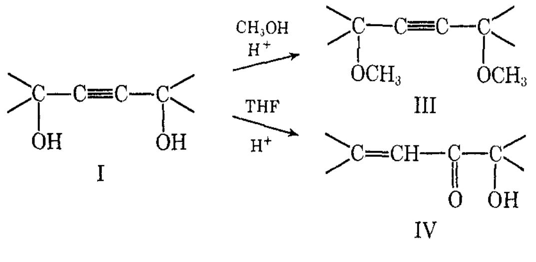
1,4-Bisbiphenylenebutatriene was prepared from 1,4-bisbiphenylene-2-butyne-1,4-diol by the potassium iodide–sulfuric acid method described by Wolinski[2] (Scheme I).

SCHEME I



The dimethyl ether of I was readily prepared by treating the diol with methanol and sulfuric acid. The yellow color produced during the reaction was due to the formation of a small amount of 1,4-bisbiphenylene-1-buten-3-one-4-ol. The latter was formed as the result of an allylic-type rearrangement followed by a tautomeric shift to a keto structure. The keto alcohol was the main product when tetrahydrofuran was used in place of methanol (Scheme II).

SCHEME II



The hybrid dianion, $[\mathrm{C}\underline{\cdots}\mathrm{C}\underline{\underline{\cdots}}\mathrm{C}\underline{\cdots}\mathrm{C}]$,$^{2-}$ may be obtained directly from 1,4-bisbiphenylenebutatriene by treatment with sodium–potassium alloy but it is more readily prepared by treating the dimethyl ether III with sodium–potassium alloy.

Protonation of the dianion was first accomplished by the addition of methanol. The protonation was slow as evidenced by the very slow decolorization of the dianion solution. Only 1,4-bisbiphenylene-1,3-butadiene (V) was obtained from this reaction. When acetic acid was used as the protonating agent, decolorization occurred almost at once. In addition to the 1,3-diene V, 1,4-bisbiphenylene-2-butyne (VI) was isolated (Scheme III).

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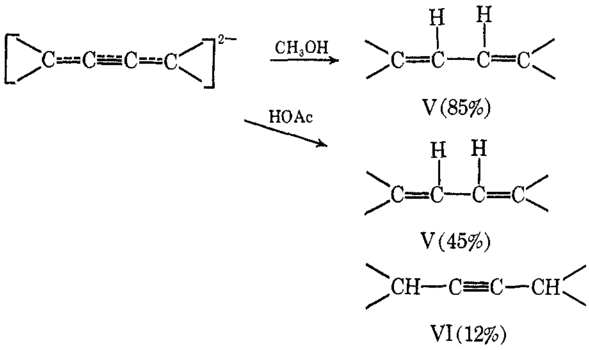
* To whom correspondence should be addressed.

(1) (a) A. Zweig and A. Hoffman, *J. Amer. Chem. Soc.*, **84**, 3278 (1962); (b) R. Nahon and A. R. Day, *J. Org. Chem.*, **30**, 1973 (1965); (c) S. Sisenwine and A. R. Day, *ibid.*, **32**, 1770 (1967).

(2) J. Wolinski, *Rocz. Chem.*, **29**, 23 (1955).

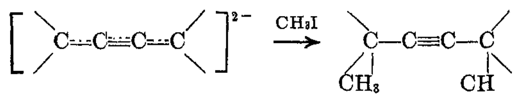
SCHEME III



Small amounts of impure 1,4-bisbiphenylene-1,2-butadiene (VII) were obtained from both methods of protonation. This was indicated by a strong infrared absorption at 1950 cm^{-1}, but a pure sample of VII could not be obtained. It was shown earlier[1c] that in the protonation of the dianion from tetraphenylbutatriene, an allene, 1,1,4,4-tetraphenyl-1,2-butadiene, was the kinetically favored product and could be obtained in good yields at low temperatures. The fact that no appreciable amount of the 1,2-diene could be obtained from the dianion corresponding to 1,4-bisbiphenylenebutatriene, even at low temperatures, suggests a greater increase in resonance stabilization when the entire system becomes conjugated than was the case with the tetraphenyl system.

Methylation of the dianion obtained from III, with methyl iodide, gave 2,5-bisbiphenylene-3-hexyne (VIII) as the only product (Scheme IV).

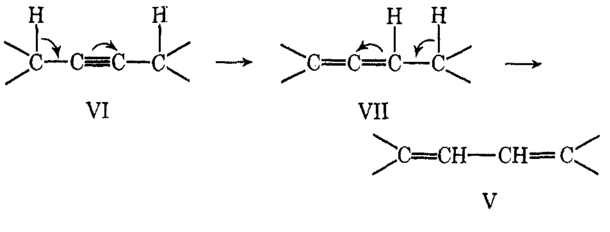
SCHEME IV



VIII

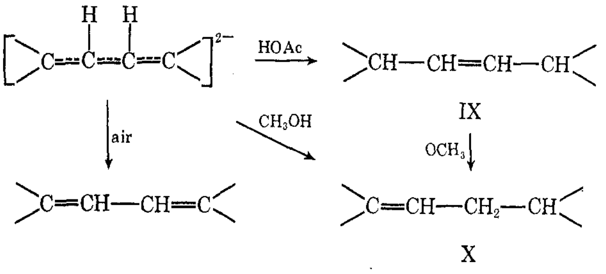
It is probable that protonation and methylation involve the same initial step, namely 1,4 addition. The 1,4-dihydro compound VI rearranges to the more stable system V, whereas the 1,4-dimethyl product VIII is stable under the conditions used (Scheme V).

SCHEME V



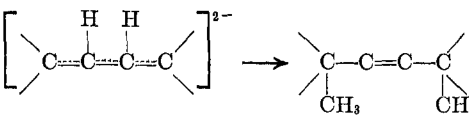
Protonation of the dianion derived from 1,4-bisbiphenylene-1,3-butadiene (V) led to some interesting results. Protonation with acetic acid gave an excellent yield of 1,4-bisbiphenylene-2-butene (IX). The compound was too insoluble for nmr analysis. The presence of an absorption at 957 cm^{-1} in the infrared indicated the 2-butene to be in the trans form. Protonation of the dianion from V with methanol gave only 1,4-bisbiphenylene-1-butene (X) (Scheme VI). In the conversion of V to X a small amount of 1,4-bisbiphenylene-1,3-butadiene (V) was isolated. This undoubtedly resulted from an electron-transfer reaction with air (O_2), since the conversion is efficiently accomplished by bubbling air through the solution.

SCHEME VI



Methylation of the dianion from V, with methyl iodide, gave an excellent yield of 2,4-bisbiphenylene-3-hexene (XI) (Scheme VII).

SCHEME VII



XI

Experimental Section

All melting points were taken in a Thomas-Hoover capillary melting point apparatus. The infrared spectra were obtained with a Perkin-Elmer 521, double beam, recording spectrophotometer using KBr disks, Nujol mulls, or thin films on sodium chloride disks. The ultraviolet spectra were recorded on a Cary 14 spectrophotometer. Nuclear magnetic resonance spectra were determined with a Varian Associates Model A-60A spectrophotometer at 60 MHz with tetramethylsilane as an internal standard.

Purification of Solvents.—Tetrahydrofuran and 1,2-dimethoxyethane were refluxed over lithium aluminum hydride and then distilled. The distillate was then redistilled over sodium–potassium alloy. Several crystals of benzophenone were added to the alloy–solvent mixture to signal complete dryness. If the intense blue-violet color of the anion-radical of the benzophenone disappeared at any time during the distillation, the drying process was repeated.

Preparation of Sodium–Potassium Alloy.—Four parts (12.0 g) of potassium and one part of sodium (3 g) were added to a 100-ml flask containing 60–70 ml of freshly distilled 1,2-dimethoxyethane. After refluxing for 2–3 hr, the flask was cooled and the liquid alloy was stored under nitrogen in the same flask in which it was prepared. The alloy was removed as needed with a glass pipet (eye dropper type) and transferred to a weighed, stoppered, 25-ml erlenmeyer flask containing 10 ml of dry tetrahydrofuran. The entire contents of this flask were then emptied into the reaction flask when needed.

1,4-Bisbiphenylene-2-butyne-1,4-diol (I).—This diol was prepared from fluorenone and acetylenedimagnesium bromide.[3]

1,4-Bisbiphenylenebutatriene (II).—This compound was prepared from I by the sulfuric acid–potassium iodide method.[1c,2] The red product was washed with ethanol, water, and again with ethanol, yield 78%, mp 316° (from xylene).[4] The ir spectrum of the triene was identical with that obtained by Otting.[5]

Anal. Calcd for $C_{28}H_{16}$: C, 95.41; H, 4.59. Found: C, 95.36; H, 4.64.

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(3) E. Bergmann, H. Hoffman, and D. Winter, *Chem. Ber.*, **50**, 3349 (1956).

(4) The melting points reported in the literature vary widely. Bergmann, Hoffman, and Winter (ref 3) report >300°; Wolinski[2] gives 324–336°; R. Kuhn and G. Platzer [*Chem. Ber.*, **73**, 1410 (1940)] report 330°; C. R. Hauser and D. Lednicer [*J. Org. Chem.*, **22**, 1248 (1957)] give 309°; D. Y. Curtin and E. W. Flynn [*J. Amer. Chem. Soc.*, **81**, 4714 (1959)] give 279–282°; and D. Lavie and E. D. Bergmann [*J. Org. Chem.*, **18**, 367 (1953)] report 300–302°.

(5) W. Otting, *Chem. Ber.*, **87**, 611 (1954).

1,4-Bisbiphenylene-1,4-dimethoxy-2-butyne (III).—This ether was prepared by a previously reported method.[1c] The yield was 75%: mp 200° (from ethanol); ir (KBr) 2990–2820 (CH_3), 1090–1060 cm^{-1} (COC); nmr aromatic multiplet at δ 7.3 (16) and a methyl proton singlet at δ 3.0 (6).

Anal. Calcd for $C_{30}H_{22}O_2$: C, 86.92; H, 5.35. Found: C, 86.95; H, 5.40.

1,4-Bisbiphenylene-3-oxo-1-buten-4-ol (IV).—A tetrahydrofuran solution of sulfuric acid (2 ml of 96.4% H_2SO_4 in 10 ml of THF) was added with stirring to a solution of III (2 g, 0.005 mol) in 30 ml of THF. After refluxing for 30 min, the solution was poured into water. The resulting orange oil was taken up in ether, and washed with water, 10% $NaHCO_3$, and water, and dried ($CaCl_2$). The ether was evaporated and the resulting solid was recrystallized from petroleum ether (60–110°): yield 63%, orange crystals; mp 175°; ir (KBr) 1670 (C=CC=O) and 3440 cm^{-1} (OH); nmr aromatic multiplet at δ 7.2 (16), olefin proton singlet at δ 6 (1), and a hydroxyl proton singlet at δ 4.95 (1).

Anal. Calcd for $C_{28}H_{18}O_2$: C, 87.02; H, 4.69. Found: C, 86.89; H, 4.79.

Preparation of the Dianion from 1,4-Bisbiphenylene-1,4-dimethoxy-2-butyne (III).—Tetrahydrofuran (250 ml) was distilled, in a nitrogen atmosphere, into a dry 500-ml erlenmeyer flask containing a magnetic stirrer. Compound III (2.9 g, 0.007 mol) was then added and the flask was capped with a serum cap. The Na–K alloy (1.44 g, 0.042 g-atom), was preweighed in a 25-ml erlenmeyer flask containing 10 ml of dry THF and added quickly to the solution of III. The mixture was stirred for 12 hr at which time the solution was dark reddish brown (the color of the dianion). Stirring was continued for an additional 10 hr.

Protonation of the Dianion, from III, with Methanol. Preparation of 1,4-Bisbiphenylene-1,3-butadiene.—The dianion solution was transferred, under nitrogen, to another dry flask and protonation carried out as described in the protonation of the dianion from tetraphenylbutatriene.[1c] The solution was stirred for 1 hr and evaporated to about one-third of its initial volume. The solid so obtained was washed with methanol, water, and methanol and recrystallized from xylene, yield 85%, orange needles, mp 381°.[6] The ultraviolet spectrum for V was almost identical with that reported by Wieland and Kraus:[6] uv (dioxane) 241 mμ (log ϵ 4.82), 268 (4.71), 278 (4.65), 415 (4.63), and 442 (4.60).

Anal. Calcd for $C_{28}H_{18}$: C, 94.87; H, 5.13. Found: C, 94.78; H, 5.17.

Protonation of the Dianion from III with Acetic Acid. Preparation of 1,4-Bisbiphenylene-1,3-butadiene and 1,4-Bisbiphenylene-2-butyne (VI).—The only change in the above procedure was the use of acetic acid in place of methanol. The resulting solid was refluxed in THF and filtered hot to remove the 1,3-diene V which was identified by its melting point and uv spectrum. The filtrate deposited colorless crystals of 1,4-bisbiphenylene-2-butyne which were recrystallized from benzene until spectrally free of the 1,3-diene (uv) and of the 1,2-diene (no 1950 cm^{-1} absorption in the ir), yield 12%, mp 255–257°. A mixture melting point determination with an authentic sample, prepared by an aluminum amalgam–water reduction of bisbiphenylenebutatriene,[7] showed no depression.

Methylation of the Dianion from III. Preparation of 2,5-Bisbiphenylene-3-hexyne (VIII).—A solution of the dianion, prepared in the usual manner, was cooled in Dry Ice–acetone and 7 ml of methyl iodide was added by way of a syringe. The solution was stirred for 1 hr and cooled and the inorganic salts were removed. The filtrate was evaporated and the resulting solid was recrystallized from ethanol: yield 82%; mp 231°; ir (KBr) 2970–2860 cm^{-1}; nmr an aromatic multiplet at δ 7.4 (16) and a methyl proton singlet at δ 1.5 (6).

Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80. Found: C, 94.28; H, 5.87.

Protonation of the Dianion from 1,4-Bisbiphenylene-1,3-butadiene with Methanol. Preparation of 1,4-Bisbiphenylene-1-butene (X).—Methanol was added to the cold (0°) dianion solution, prepared in the usual way[1c] from V, and the solution stirred for 1 hr. The mixture was filtered and the filtrate was evaporated. The resulting oil was taken up in benzene and a small amount of the 1,3-diene V (orange crystals, mp 381°) was removed. The benzene filtrate was evaporated and a yellow oil remained which crystallized from methanol. The product was recrystallized from ethanol: yield 85%, pale yellow needles; mp 163°; nmr an aromatic multiplet at δ 7.35 (16), an olefinic proton triplet at δ 6.45 (1, J = 7 Hz), a tertiary proton at δ 4.15 (1, J = 7 Hz), and a methylene proton triplet at δ 3.35 (2, J = 7 Hz); ir (KBr) 957 cm^{-1} (trans form).

Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.25; H, 5.69.

Protonation of the Dianion from 1,4-Bisbiphenylene-1,3-butadiene with Acetic Acid. Preparation of 1,4-Bisbiphenylene-2-butene (IX).—Acetic acid was added to the dianion solution from V at 0°. After stirring for 1 hr, the mixture was allowed to come to room temperature and was then filtered. The filtrate was evaporated to small volume and cooled and the solid removed. This solid was recrystallized from benzene, yield 84%, pale yellow crystals, mp 268° (Lavie and Bergmann[4] reported 267–268°). A mixture melting point determination with an authentic sample, prepared by the zinc–acetic acid reduction of 1,4-bisbiphenylene-1,3-butadiene,[4] showed no depression.

Base-Catalyzed Isomerization of 1,4-Bisbiphenylene-2-butene (IX) to 1,4-Bisbiphenylene-1-butene (X).—1,4-Bisbiphenylene-2-butene (0.1472 g, 0.004 mol) was dissolved in 10 ml of warm tetrahydrofuran and 0.121 g of sodium methoxide was added. Three drops of water were added to dissolve the sodium methoxide. After stirring for 15 min, the mixture was partially evaporated to give an orange product. After recrystallization from xylene this proved to be 1,4-bisbiphenylene-1,3-butadiene, yield 8%, mp 381°. The addition of methanol to the tetrahydrofuran filtrate precipitated a light yellow product which was recrystallized from ethanol, yield 43%, mp 163°. A mixture melting point determination proved this product to be bisbiphenylene-1-butene.

Methylation of the Dianion from 1,4-Bisbiphenylene-1,3-butadiene (V). Preparation of 2,5-Bisbiphenylene-3-hexene (XI).—Methyl iodide (10 ml) was added to the cold (0°) dianion solution. After stirring for 1 hr, the mixture was allowed to come to room temperature and filtered. The filtrate was evaporated and the resulting oil was crystallized by stirring with methanol. The product was recrystallized from methanol: yield 76%; mp 158°; nmr (CS_2) δ 7.7–7.1 (m, 16), 5.65 (s, 2, CH=CH), 1.4 (s, 6, CH_3).

Anal. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29. Found: C, 93.61; H, 6.25.

Registry No.—Dianion of II, 12441-29-1; IV, 26924-10-7; V, 4551-02-4; dianion of V, 12441-28-0; VIII, 26963-81-5; X, 26924-12-9; XI, 26924-13-0.

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(6) The melting points reported in the literature differ considerably from our value. Lavie and Bergmann (ref 4) report 355°; H. Wieland and E. Krause [*Justus Liebigs Ann. Chem.*, **443**, 129 (1925)] report 360°; and E. Bergmann and Y. Hirshberg [*Bull. Soc. Chim. Fr.*, **17**, 1091 (1950)] give 373°.

(7) R. Kuhn and H. Fischer, *Chem. Ber.*, **94**, 3060 (1961).

The Synthesis of Nitrotrifluoromethylphenols and Related Compounds from Nitrotrifluoromethylchlorobenzenes

RICHARD L. JACOBS

Toledo Laboratory, Sherwin Williams Chemicals,
Division of The Sherwin-Williams Company,
Toledo, Ohio 43608

Received January 26, 1970

The use of nitrotrifluoromethylchlorobenzenes as precursors for nitrotrifluoromethylphenols is of interest owing to the commercial availability[1] of the former and the lack of general synthesis procedures for the latter. In addition, nitrotrifluoromethylphenols are useful

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(1) The various nitrotrifluoromethylchlorobenzenes used as starting materials in the present work were obtained from Sherwin Williams Chemicals, Fine Chemicals Dept., Cincinnati, Ohio.