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

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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.

TABLE I

PRODUCTS FROM NUCLEOPHILIC SUBSTITUTIONS OF NITROTRIFLUOROMETHYLCHLOROBENZENES IN DMSO

Chlorobenzene substituents	Reagent	Temp, °C (time, hr)	Product	Yield, %	Mp, °C	Ref
2-NO_2-4-CF_3-	NaOH	20–25 (8)	2-Nitro-4-(trifluoromethyl)phenol	96.2	*a*	
4-NO_2-2-CF_3-	NaOH	20–25 (8)[b]	4-Nitro-2-(trifluoromethyl)phenol	40	133–134[g]	*h*
2,6-$(NO_2)_2$-4-CF_3-	NaOH	20–25 (4)[c]	2,6-Dinitro-4-(trifluoromethyl)phenol	92	46–48	*i*
4-NO_2-3-CF_3	NaSH	20–25 (8)	Bis(4-nitro-3-(trifluoromethyl)-phenyl) disulfide	45	119–120.5	*d*
2-NO_2-4-CF_3-	NaSCH	45–50 (22)	2-Nitro-4-(trifluoromethyl)phenylthiocyanate	70	74–77	*e*
4-NO_2-3-CF_3-	NaOH	20–25 (8)	5-Chloro-2-nitrophenol	93[f]	38.5–39	*j*

[a] The product is a dark red oil at 20°. [b] The product was actually isolated from the crude product oil after having been stored for 2 months at 20–25°. [c] Reverse addition required, with dinitro compound being added to a DMSO slurry of NaOH, in order to control extreme exotherm (fire). [d] *Anal.* Calcd for $C_{14}H_6F_6N_2O_4S_2$: S, 14.43. Found: S, 14.52. [e] *Anal.* Calcd for $C_8H_3F_3N_2O_2S$: S, 12.9; F, 23.0. Found: S, 12.9; F, 23.19. [f] The other major product was identified as fluoroform. [g] On several occasions, a solid, mp 63.5–64°, was isolated which on the basis of nmr spectrum and elemental analysis appears to be a 1:1 adduct of DMSO and 4-nitro-2-(trifluoromethyl)phenol (*Anal.* Calcd for $C_9H_{10}F_3NO_4S$: C, 37.89; H, 3.53; N, 4.91; F, 19.98. Found: C, 37.92; H, 3.95; N, 4.62; F, 19.84). [h] See ref 5. [i] L. M. Yaguipolskii and V. S. Mospan, *Ukr. Khim. Zh.*, **21**, 81 (1955); *Chem. Abstr.*, **49**, 8867*c* (1955). [j] Laubenheimer, *Chem. Ber.*, **9**, 768 (1876).

commercially as lamprecides,[2] agricultural chemicals,[3] and dyestuff intermediates.[4]

In the present work, nitrotrifluoromethylphenols were readily prepared by the reaction of sodium hydroxide with nitrotrifluoromethylchlorobenzenes in dimethyl sulfoxide. In general, the reactions proceeded best when 3 mol of sodium hydroxide was used for 1 mol of nitrotrifluoromethylchlorobenzene (see Table I).

Phenols of the type described are not new but have been prepared previously by tedious multistep reactions.[5]

Others[6] have attempted to produce nitrotrifluoromethylphenols directly in one step from nitrotrifluoromethylchlorobenzenes and hydroxide ions but in all cases found that the trifluoromethyl groups had been hydrolyzed. This is consistent with reports[7] that a trifluoromethyl group is invariably hydrolyzed by strong bases and with extraordinary facility if amino or hydroxyl groups are located ortho or para to the trifluoromethyl group. Such behavior has been attributed to "no-bond" resonance.[8]

In the course of this investigation, a novel reaction was observed when 4-nitro-3-trifluoromethylchlorobenzene was treated with sodium hydroxide in dimethyl sulfoxide. Upon the addition of the first portion of sodium hydroxide, gas evolution was noted. The two major products from this reaction were identified as fluoroform and 5-chloro-2-nitrophenol.

It is noteworthy that reaction of sodium sulfhydrate with 4-nitro-3-trifluoromethylchlorobenzene in dimethyl sulfoxide was normal.

In addition to the reactions described above, it was found that the use of sodium thiocyanate in place of sodium hydroxide produced nitrotrifluoromethylbenzenes containing the SCN moiety.

Experimental Section[9]

The preparation of 2-nitro-4-trifluoromethylphenol well illustrates the general technique followed in the preparation of those compounds shown in Table I. A 112.5-g (0.5 mol) quantity of 2-nitro-4-trifluoromethylchlorobenzene was dissolved in 150 ml of dimethyl sulfoxide, and 60 g (1.5 mol) of finely powdered sodium hydroxide was added with stirring over an 8-hr period. The reaction mixture was kept at 20–25° throughout the sodium hydroxide addition period. After standing overnight without stirring, the reaction mixture was poured into 1 l. of cold water, filtered through Dicalite, and acidified to pH 1 with concentrated hydrochloric acid. A dark red oil separated and was removed, dissolved in 50 ml of ether, and dried over Na_2SO_4; the ether was removed under reduced pressure. There remained 100 g (96.2% yield) of product, the ir spectrum of which was identical with the ir spectrum of a known pure sample of 2-nitro-4-trifluoromethylphenol.

Registry No.—2-Nitro-4-(trifluoromethyl)phenol, 400-99-7; 4-nitro-2-(trifluoromethyl)phenol, 1548-61-4; 2,6-dinitro-4-(trifluoromethyl)phenol, 393-77-1; bis-(4-nitro-3-(trifluoromethyl)phenyl) disulfide, 27006-08-2; 2-nitro-4-(trifluoromethyl)phenylthiocyanate, 26958-51-0; 5-chloro-2-nitrophenol, 611-07-4; 1:1 adduct of DMSO and 4-nitro-2-(trifluoromethyl)phenol, 26958-52-1.

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(2) O. Scherer, H. Frensch, and G. Stahler, German Patent 1,068,505 (Nov 5, 1969).

(3) J. Walker, M. Kerchersid, and M. Merkle, *J. Agr. Food Chem.*, **16**, 143 (1968).

(4) J. Dickey and J. McNally, U. S. Patent 2,442,345 (June 1, 1948).

(5) R. Filler, B. Khan, and C. W. McMullen, *J. Org. Chem.*, **27**, 4660 (1962).

(6) R. Filler and H. Novar, *ibid.*, **26**, 2707 (1961); *Chem. Ind. (London)*, 468, 1273 (1960).

(7) R. G. Jones, *J. Amer. Chem. Soc.*, **69**, 2346 (1947); J. Boynstein, S. A. Leone, W. F. Sullivan, and O. F. Bennett, *ibid.*, **79**, 1745 (1957).

(8) J. D. Roberts, R. L. Webb, and E. A. McElhill, *ibid.*, **72**, 408 (1950).

(9) Melting points are corrected and were determined in a Thomas-Hoover capillary melting point apparatus. Infrared spectra were obtained with a Perkin-Elmer infracord spectrophotometer and all compounds prepared had infrared spectra which agreed with the assigned structures. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. The mass spectrometric analysis was performed by Morgan-Schaffer Corp., Quebec, Canada.

A New Route to Brex-4-ene

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The continuing interest in the synthesis and rearrangements of alicyclic structures[1] has provided considerable information on the behavior of ionic intermediates in stereochemically defined systems. Several

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(1) P. de Mayo, "Molecular Rearrangements," Interscience, New York, N. Y., 1963.