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)phenyl-thiocyanate	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 $C_{14}H_8F_6N_2O_4S_2$: 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.

(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).

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.

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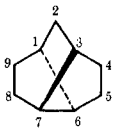
The continuing interest in the synthesis and rearrangements of alicyclic structures[1] has provided considerable information on the behavior of ionic intermediates in stereochemically defined systems. Several

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

years ago, the synthesis of a new tricyclic ring system, brexane (tricyclo[4.3.0.0.^{3,7}]nonane) (**1**), was announced by Nickon, *et al.*[2]

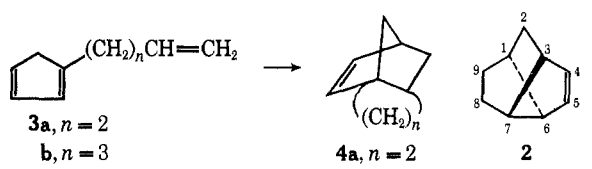
In our systematic pursuit of synthetic applications of the intramolecular Diels–Alder reaction,[3] we have found a convenient synthesis of the unsaturated derivative brex-4-ene (**2**).



1

Results and Discussion

The application of the intramolecular Diels–Alder reaction to a substituted cyclopentadienylhexene has been reported previously.[3a] A related synthetic application was reported by Corey,[4] utilizing 1-(4-pentenyl)-1,3-cyclopentadiene. On extending this reaction to the corresponding 1-(3-butenyl)-1,3-cyclopentadiene (**3a**), the product formed in quantitative yield was not the expected, albeit strained, tricyclo[4.2.1.0^{1,4}]-non-7-ene (**4a**) but instead the isomeric brex-4-ene (**2**).[5]



3a, $n = 2$
b, $n = 3$
c, $n = 4$

4a, $n = 2$
b, $n = 3$
c, $n = 4$

2

Presumably the starting olefin, **3a**, isomerizes to the 1-substituted cyclopentadiene prior to cyclization permitting the formation of the less strained brex-4-ene. The equilibration of alkylcyclopentadienes is well established, the free-energy difference between 1-methyl- and 5-methylcyclopentadiene being approximately 2.0–2.5 kcal/mol.[6] The structure of product **2** was established by direct gas chromatographic and spectroscopic comparison (ir and nmr) with an authentic sample.[7]

To confirm further the structure of the olefin, **2** was catalytically hydrogenated to the parent hydrocarbon brexane (**1**), identical with an authentic sample.[7] The presence of the double bond offers an opportunity or the introduction of other functional groups.[4]

(2) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. Di Giorgio, *J. Amer. Chem. Soc.*, **87**, 1613 (1965).

(3) (a) G. Brieger, *ibid.*, **85**, 3783 (1963); (b) G. Brieger, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, p D-29.

(4) E. J. Corey and R. S. Glass, *J. Amer. Chem. Soc.*, **89**, 2600 (1967).

(5) H. Scharf and G. Weisgerber, *Tetrahedron Lett.*, **16**, 1567 (1967).

(6) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

(7) Comparison with authentic samples of brex-4-ene and brexane was kindly performed by Professor A. Nickon.

Experimental Section[8]

1-(3-Butenyl)-1,3-cyclopentadiene (3a).—A solution of 3.25 g (0.0825 mol) of sodium amide in 85.0 ml of tetrahydrofuran was added, under nitrogen, to a stirred solution of 11.0 ml (0.125 mol) of cyclopentadiene in 10 ml of tetrahydrofuran with cooling. 4-Bromobutene, 11.1 g (0.0822 mol), was added over a 45-min period. The mixture was stirred for an additional 2.5 hr. The mixture was then extracted with 150 ml of petroleum ether. The extract was washed three times with water, dried ($MgSO_4$), and distilled to give 4.52 g (44.5% yield) of **3a**: bp 52–53° (14 mm); ir 3.30 (m), 3.48 (s), 6.12 (m), 6.24 (w), 6.98 (m), 7.34 (m), 10.06 (m), 10.55 (w), 10.98 (s), 12.33 (w), 13.38 (w), 14.81 μ (s); nmr δ 6.4–5.4, multiplet (4 H), 4.95, triplet (2 H), 2.82, doublet (2 H), 2.36, singlet (4 H).

Anal. Calcd for C_9H_{12}: C, 89.94; H, 10.06. Found: C, 89.83; H, 10.23.

1-(4-Pentenyl)-1,3-cyclopentadiene (3b).—The same procedure as above was followed, utilizing 5-bromopentene, for the preparation of **3b**, yield 77%, bp 69–71° (15 mm).[4]

1-(5-Hexenyl)-1,3-cyclopentadiene (3c).—The above procedure was followed for the preparation of **3c**, utilizing 5-bromohexene: yield 73%; bp 87–89° (12 mm); ir 3.27 (m), 3.41 (s), 6.10 (m), 6.20 (w), 6.97 (m), 7.32 (m), 10.07 (m), 10.53 (w), 10.97 (s), 11.12 (s), 12.34 (w), 13.62 (w), 14.85 μ (m); nmr δ 6.2–5.0, complex (4 H), 4.45, doublet, 4.95, singlet (2 H), 2.55, doublet (2 H), 2.3–1.22, complex (8 H).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.96; H, 11.04.

Brex-4-ene (2).—A 5.0% solution of **3a** in benzene was heated in a sealed tube at 180° for 4 hr. According to gas–liquid chromatographic analysis (15 ft × 0.25 in. column with 25% TCEPE/Chromosorb W), there was quantitative conversion to **5**. A sample collected by preparative glc had the following properties: ir 3.28 (m), 3.38 (s), 6.21 (w), 6.36 (w), 7.49 (m), 7.96 (w), 7.86 (w), 10.97 (w), 11.14 (w), 11.83 (m), 12.38 (m), 13.29 (w), 14.18 μ (s); nmr δ 5.94 doublet, (2 H), 2.40, singlet (1 H), 2.56, singlet (1 H), 2.08, singlet, (1 H), 1.8–0.6, several bands (7 H).[7]

Tricyclo[5.2.1.0^{1,5}]dec-8-ene (4b) was prepared as described above for **2** from **3b**. A quantitative conversion was noted.[4]

Tricyclo[6.2.1.0^{1,6}]undec-9-ene (4c) was prepared as above for **2** from **3c**: ir 3.29 (w), 3.42 (s), 3.51 (w), 6.91 (m), 7.49 (w), 11.0 (w), 11.71 (w), 13.35 (w), 14.20 μ (m); nmr δ 5.95–5.68, complex (2 H), 2.68, singlet (1 H), 2.4–1.0, complex (13 H).

Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.89; H, 11.12.

Brexane (1).—**2** (0.5 g) was hydrogenated in a Parr hydrogenator in 60.0 ml of diethyl ether with 0.5 g of 10% Pd/C. The ether was removed by distillation and the product analyzed by gas chromatography as above. A 95% yield was obtained: ir 3.38 (s), 3.47 (sh), 6.84 (w), 7.62 μ (w); nmr δ 2.88, singlet (4 H), 1.46, multiplet (8 H), 1.03, singlet (2 H).[7]

Registry No.—**2**, 15782-76-0; **3a**, 27017-52-3; **3c**, 27017-53-4; **4c**, 27017-54-5.

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(8) The boiling points are uncorrected. Infrared spectra in μ were determined as liquid films unless otherwise indicated. Nmr spectra were determined with a Varian T-60 spectrometer, 10% solutions in CCl_4 with TMS internal reference (δ = 0 ppm). Analyses were made by Spang Microanalytical Laboratories, Ann Arbor, Mich.