67177-80-4; *i*-PrMe₂C=CNO₂, 107474-03-3; (*i*-Pr)₃SiC=CNO₂, 107474-05-5; $CH_3C \equiv CNO_2$, 107474-06-6; 2, 107474-09-9; (i-Pr)₃SiC=CH, 89343-06-6; cyclopentadiene, 542-92-7; 1,3-cyclohexadiene, 592-57-4; 2-nitro-3-(triisopropylsilyl)norbornadiene, 107474-07-7; 2-nitro-3-(trimethylsilyl)bicyclo[2.2.2]octa-2,5-diene, 107494-77-9; 2-nitro-3-(trimethylsilyl)norbornadiene, 107474-08-8.

Supplementary Material Available: IR spectral data for all new nitroacetylenes (Table II) and MS fragmentation patterns for nitroacetylenes and (trimethylsilyl)acetylenes (Table III) (3 pages). Ordering information is given on any current masthead page.

Synthesis of Monoalkyl Derivatives of 7,7,8,8-Tetracyano-p-quinodimethane from 2,5-Dimethoxybenzoic Acid

William P. Roberts* and Cynthia L. Ebner

W. R. Grace & Company, Washington Research Center, Columbia, Maryland 21044

Received November 10, 1986

7,7,8,8-Tetracyano-p-quinodimethane (TCNQ, 4a) and its derivatives have received much attention by virtue of their reversible stepwise two-electron redox chemistry,^{1,2a} their capacity to form electrically conductive chargetransfer complexes,² and the bistable electrical and photochemical switching behavior ascribed to certain metal-TCNQ salts.³ Although a large number of substituted TCNQ derivatives have been studied in these contexts, the great majority have been di- and tetrasubstituted, with only a few reports of the less symmetrical monosubstituted derivatives.4

Syntheses of the monosubstituted TCNQ derivatives 4b-d (Scheme I) have been reported by others.^{4c,d} These all employ a metal-ammonia reduction/hydrolysis sequence, starting from the correspondingly substituted derivatives of 1,4-dimethoxybenzene (1b-d), to arrive at the key 1.4-cyclohexanedione intermediates 2b-d. These cyclohexanediones are then converted to the corresponding TCNQ derivatives 4b-d by the classical condensation/ oxidation sequence of Acker and Hertler.¹ The utility of this general route to 1,4-cyclohexanediones is limited, however, by the availability of starting materials 1 and by the applicability of the metal-ammonia reduction to the chosen substrates. In our efforts to utilize the above procedure, we arrived at a convenient new method for synthesis of 1,4-cyclohexanediones that overcomes these limitations by employing 2,5-dimethoxybenzoic acid (5) as a universal starting material.

Results and Discussion

The method of Scheme I was used in our laboratories to prepare the hitherto unknown ethyl derivative of Scheme I





TCNQ. To accomplish this, we needed to synthesize 2ethyl-1,4-dimethoxybenzene $(1e)^5$ by reduction⁶ of the commercially available acetyl derivative 1h. In an analogous attempt to synthesize n-dodecyl-TCNQ, we prepared substrate 1f in two steps from 1a (acylation with lauroyl chloride⁷ to give 1i, followed by reduction⁶), only to find that the metal-ammonia reduction of 1i was hampered by solubility problems.

At this point, an examination of the literature on alternate metal-ammonia reduction methods led us to a reductive alkylation process based on 2,5-dimethoxybenzoic acid (5).⁸ As depicted in Scheme II, it was reasoned that hydrolyses of these reductive alkylation products, with concomitant decarboxylation, would afford 1,4-cyclohexanediones 2 directly. This dione formation had already been observed, as an undesired side reaction, by Hook and Mander.8a

In practice, diones 2e-g were successfully prepared from 5 and an alkyl iodide or bromide, each in a single synthetic operation, and in high yield. Table I summarizes the complete synthesis of monoalkyl-TCNQ derivatives 4e-g using this method. The overall yields of TCNQ derivatives based on 5 were 20-50%. In the malononitrile condensation step $(2 \rightarrow 3)$, it was found that aqueous THF was a useful solvent system for the β -alanine-catalyzed modification of Andersen and Jorgensen.^{4d}

Table II lists the cyclic voltammetric data for the newly synthesized TCNQ derivatives 4e-g and lists the first and second half-wave reduction potentials of (unsubstituted) TCNQ (4a), measured by us and by others,^{2a} for reference. The first reduction potentials observed for the new derivatives are consistent with expectations, based on the relative inductive effects of the substituents.

In conclusion, what we have demonstrated here is a route to 1,4-cyclohexanediones involving a common starting material and an alkyl halide, which considerably extends the range of easily accessible monosubstituted TCNQ derivatives.

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and were not corrected. Infrared spectra were recorded on a Nicolet 5DX FTIR spectrophotometer. NMR spectra were re-

Acker, D. S.; Hertler, W. R. J. Am. Chem. Soc. 1962, 84, 3370.
 (2) (a) Wheland, R. C.; Gillson, J. L. J. Am. Chem. Soc. 1976, 98, 3916.
 (b) Wheland, R. C. Ibid. 1976, 98, 3926. (c) Melby, L. R.; Harder, R. J.; Hertler, W. R.; Mahler, W.; Benson, R. E.; Mochel, W. E. Ibid. 1962, 84, 3374

⁽³⁾ Poehler, T. O.; Potember, R. S.; Hoffman, R.; Benson, R. C. Mol. Cryst. Liq. Cryst. 1984, 107, 91. Kamitsos, E. I.; Risen, W. M., Jr. Solid State Commun. 1983, 45, 165. Kamitsos, E. I.; Tzinis, C. H.; Risen, W. M., Jr. Ibid. 1982, 42, 561. Potember, R. S.; Poehler, T. O.; Cowan, D. O.; Bloch, A. N. In The Physics and Chemistry of Low-Dimensional

Solids; Alcacer, L., Ed.; Reidel: Boston, 1980; pp 419-428. (4) (a) Uno, M.; Seto, K.; Masuda, M.; Ueda, W.; Takahashi, S. Tetrahedron Lett. 1985, 26, 1553. (b) Kini, A.; Mays, M.; Cowan, D. J. Chem. Soc., Chem. Commun. 1985, 286. (c) Baghdadchi, J.; Panetta, C. A. J. Org. Chem. 1983, 48, 3852. (d) Andersen, J. R.; Jorgensen, O. J. Chem. Soc., Perkin Trans. 1 1979, 3095. (e) Wheland, R. C.; Martin, E. L. J. Org. Chem. 1975, 40, 3101.

^{(5) (}a) Shulgin, A. T. J. Med. Chem. 1975, 18, 1201. (b) Orlando, C. M., Jr.; Mark, H.; Bose, A. K.; Manhas, M. S. J. Org. Chem. 1968, 33, 2512. (c) Howe, C. A.; Hamel, C. R.; Stedman, E. D.; Hyman, F. Ibid. 1960, 25, 1245.

⁽⁶⁾ KOH, hydrazine, triethylene glycol, 190 °C; see: Huang-Minlon J. Am. Chem. Soc. 1946, 68, 2487. (7) Lauroyl chloride, AlCl₃, CHCl₃, reflux; see: Morimoto, K.; Furuya,

<sup>K.; Toriuchi, M. Ger. Offen. DE 3 437 545, 25 April 1985.
(8) (a) Hook, J. M.; Mander, L. N. J. Org. Chem. 1980, 45, 1722. (b) Hook, J. M.; Mander, L. N.; Urech, R. Synthesis 1979, 374.</sup>

Table I. Synthesis of Monoalkyl-TCNQ Derivatives

	$5 + \mathrm{RX} \rightarrow 2^a$			$2 \rightarrow 3^a$			$3 \rightarrow 4^a$		
RX	compd	yield from 5, %	mp, °C	compd	yield from 2, %	mp, °C	compd	yield from 3, %	mp, °C
CH ₃ CH ₂ I	2e	1.00	b	3e	75	153-154	4e	60	137-138
$n - C_{12}H_{25}I$	2 f	83	7070.5	3 f	73	98.5-99	4 f	72	119-120
$C_6H_5CH_2Br$	2g	94	67.5 - 68.5	3 g	56	218-219	4 g	40	165.5 - 167

^aSee the Experimental Section for details. ^bLiquid, bp 81-82 °C (0.45 mm).

Table II. Reduction Potentials (mV vs. SCE) for TCNQ

Derivatives-							
compd	name	E°1	E°2				
4e	ethyl-TCNQ	140 ± 1	-376 ± 4				
4f	<i>n</i> -dodecyl- TCNQ	138 ± 2	-366 ± 2				
4g	benzyl-TCNQ	166 ± 2	-338 ± 1				
4a	TCNQ ^b	$171 \pm 1 \; (lit.^{\circ} \; 170)$	-374 ± 1 (lit.° -370)				

^aConditions: analyte concentration, 1×10^{-4} – 6×10^{-4} M; T, 25.0 \pm 0.2 °C; μ , 0.1 M Et₄NClO₄ in CH₃CN; scan rate, 50mV/s; Pt working and auxiliary electrodes. ^bSupplier Aldrich. ^cSee ref 2a.

corded on a Bruker AM 400MHz spectrometer. NMR chemical shifts are reported (ppm) vs. tetramethylsilane.

Elemental analyses for all new compounds reported were within 0.3% of the calculated values. Analyses were performed by Huffman Laboratories, Inc.

Cyclic voltammetry was performed with a BAS 100 electrochemical analyzer. All solutions were purged with N_2 .

Tetrahydrofuran (THF) was distilled from Na/benzophenone. Malononitrile (Aldrich) was vacuum distilled prior to use.

1-Ethyl-2,5-dimethoxybenzene (1e).⁵ To a mixture of 100 g (0.555 mol) of 2,5-dimethoxyacetophenone (1h) and 70.5 g (1.25 mol) of potassium hydroxide in 500 mL of triethylene glycol was added 80 mL of 85% hydrazine hydrate. The mixture was refluxed for 4 h with removal of water by distillation, allowing the pot temperature to reach 190 °C, and then refluxed for another 1 h. The cooled reaction mixture and aqueous distillate (which contained some codistilled product) were combined, diluted with 1 L of water, and extracted with CH₂Cl₂ (5 × 100 mL). The combined organic fraction was dried over MgSO₄, filtered, and reduced in vacuo to give an oil, which was further purified by vacuum distillation to give 73.4 g (80% yield) of a colorless oil: bp 104-105 °C (7mm); NMR (CDCl₃) δ 1.2 (t, 3 H), 2.6 (q, 2 H), 3.73 (s, 3 H), 6.73 (m, 3 H), in agreement with the literature.^{5b}

2-Ethyl-1,4-cyclohexanedione (2e; Method A). To a mechanically stirred mixture of 800 mL of liquid ammonia, 40.01 g (0.241 mol) of 1e, 90 mL of absolute ethanol, and 120 mL of ether at -73 °C was added 34.6 g (1.51 mol) of sodium metal in small pieces over 25 min. The resulting dark blue solution was stirred for 4 h at -73 °C and then quenched by slow addition (caution: foam) of 90 g of NH₄Cl over 20 min. The solvents were allowed to evaporate under a stream of N2 as the mixture warmed to room temperature, 700 mL of 4 N HCl was added, and the acidic solution was refluxed for 2 h. The cooled reaction mixture was extracted with CHCl_3 (4 \times 100 mL), and the combined organic fraction was dried over MgSO₄, filtered, and reduced in vacuo to give 33.7 g (quantitative yield) of a colorless oil: bp 81–82 $^{\circ}\mathrm{C}$ (0.45 mm); NMR (CDCl₂) δ 0.81 (t, 3 H), 1.35 (m, 1 H), 1.71 (m, 1 H), 2.36 (m, 1 H), 2.56 (br m, 6 H); IR (neat) 2967 (s), 2936 (sh), 2878 (m), 1714 (vs), 1461 (m), 1420 (m), 1307 (m), 1250 (m), 1150 (m), 969 (m) cm⁻¹. Anal. Caled for $C_8H_{12}O_2$: C, 68.54; H, 8.63; O, 22.83. Found: C, 68.45; H, 8.63; O, 22.67.

2-Ethyl-1,4-cyclohexanedione (2e; Method B). To 400 mL of liquid ammonia, mechanically stirred at -33 °C (CO₂/acetonitrile), was added a solution of 5.00 g (0.0274 mol) of 5 in 30 mL of dry THF, followed by 0.48 g (0.069 mol) of lithium wire. After the mixture was stirred for 20 min at -33 °C, a solution of 3.1 mL (0.38 mol) of ethyl iodide in 20 mL of dry THF was added, dropwise, over 20 min. After stirring had continued for 2 h further at -33 °C, the solvent was allowed to evaporate under a stream of N₂ as the mixture warmed to room temperature. Water (100 mL) was added, and the mixture was extracted with CHCl₃ (2 × 60 mL) to remove neutral impurities. The remaining aqueous fraction was acidified (cautiously) with 33.3 mL of concentrated HCl and then heated at reflux for 1.5 h. The cooled reaction mixture was extracted with $CHCl_3$ (4×50 mL), and the combined organic fraction was dried over MgSO₄, filtered, and reduced in vacuo to give 3.84 g (quantitative yield) of a colorless oil, identical with the product from the preceding reaction.

1,4-Bis(dicyanomethylene)-2-ethylcyclohexane (3e). A mixture of 5.02 g (0.0358 mol) of 2e, 0.20 g of β -alanine, 25 mL of water, and 5.15 g (0.779 mol) of malononitrile was refluxed for 30 min. The resulting slurry was cooled and washed (by decantation) with water (300 mL) and ether (200 mL). The solid was collected by filtration, washed with cold ether, and dried in vacuo to give 6.34 g (75% yield) of an off-white powder: mp 153–154 °C; NMR (CD₂Cl₂) δ 0.96 (t, 3 H), 1.50 (m, 1 H), 1.61 (m, 1 H), 2.65 (br m, 3 H), 3.21 (br m, 3 H), 3.33 (m, 1 H); IR (cast film, CH₂Cl₂) 2987 (s), 2921 (s), 2876 (s), 2232 (vs, C=N), 1610 (s), 1593 (s), 1454 (s), 1434 (s), 1381 (m), 1349 (s), 1096 (s), 979 (s), 776 (m), 571 (m) cm⁻¹. Anal. Calcd for C₁₄H₁₂N₄: C, 71.17; H, 5.12; N, 23.71. Found: C, 70.88; H, 5.09; N, 23.65.

Ethyl-TCNQ (4e). A mixture of 5.6 g (0.024 mol) of 3e, 75 mL of acetonitrile, and 7.9 g (0.05 mol) of bromine was stirred under a nitrogen atmosphere and cooled to 0-10 °C in an ice bath. A solution of 7.9 g (0.099 mol) of pyridine in 15 mL of acetonitrile was added dropwise over 15 min, while the temperature was maintained below 10 °C. Stirring at 0-10 °C was continued for 45 min, followed by 2 h at room temperature. At this time, 125 mL of cold water was added, and the mixture was stirred for 3 h. The product was collected by vacuum filtration and washed successively with 700 mL of water and 250 mL of cold water. The resulting crude material was purified by filtration through silica gel (70-230 mesh, CH₂Cl₂ eluent) and reduction in vacuo to give 3.3 g (60%) of a yellow crystalline solid: mp 137.5–138 °C; NMR $(CD_2Cl_2) \delta 1.42 (t, 3 H), 3.16 (q, 2 H), 7.32 (s, 1 H), 7.48 (d, 1 H),$ 7.64 (d, 1 H); IR (KBr) 3059 (w), 3048 (w), 2986 (w), 2220 (s, $C \equiv N$), 1546 (s), 1528 (s), 1474 (m), 1447 (m), 1050 (m), 915 (s), 833 (s) cm⁻¹. Anal. Calcd for $C_{14}H_8N_4$: C, 72.40; H, 3.47; N, 24.12. Found: C, 72.19; H, 3.60; N, 23.90.

2-*n***-Dodecyl-1,4-cyclohexanedione (2f)** was prepared from 5 and *n*-dodecyl iodide by the procedure given for **2e**, method B. Crude yield: 95.5% of an off-white solid. Recrystallization (ether/pentane) afforded white needles: 83% yield; mp 70–70.5 °C; NMR (CDCl₃) δ 0.82 (t, 3 H), 1.19 (m, 20 H), 1.74 (m, 2 H), 2.41 (m, 1 H), 2.57–2.75 (m, 6 H); IR (cast film, CH₂Cl₂) 2917 (s), 2849 (s), 1705 (s), 1470 (m), 1427 (m), 1149 (m), 1086 (w), 718 (m) cm⁻¹. Anal. Calcd for C₁₈H₃₂O₂: C, 77.09; H, 11.5; O, 11.41. Found: C, 77.06; H, 11.45; O, 11.40.

1,4-Bis(dicyanomethylene)-2-*n*-dodecylcyclohexane (3f). A mixture of 1.00 g (3.57 mmol) of 2f, 0.58 g (8.7 mmol) of malononitrile, 0.02 g of β -alanine, 10 mL of THF, and 3 mL of water was refluxed for 3 h. The cooled reaction mixture was reduced in vacuo, and the residue was triturated with 35 mL of water, then suspended in 40% ether/hexane, and filtered, giving 0.98 g (73% yield) of a white solid: mp 98.5–99 °C; NMR (CD₂Cl₂) δ 0.98 (t, 3 H), 1.28 (m, 20 H), 1.58 (m, 2 H), 2.67 (m, 3 H), 3.22 (m, 3 H), 3.43 (m, 1 H); IR (KBr) 2956 (sh), 2923 (s), 2852 (s), 2234 (s, C=N), 1606 (s), 1468 (m), 1436 (m), 1364 (w), 1339 (m), 989 (m), 931 (w), 771 (w), 721 (m), 578 (m) cm⁻¹. Anal. Calcd for C₂₄H₃₂N₄: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.49; H, 8.47; N, 14.84.

n-Dodecyl-TCNQ (4f) was prepared from 3f by the method given for 4e, with stirring of the reaction for 22 h, followed by addition of water and collection of the precipitate. Recrystallization (acetonitrile) afforded yellow needles: 72% yield; mp 119-120 °C; NMR (CDCl₃) δ 0.90 (t, 3 H), 1.30 (s, 16 H), 1.48 (m, 2 H), 1.65 (m, 2 H), 3.01 (t, 2 H), 7.28 (s, 1 H), 7.45 (d, 1 H), 7.62 (d, 1 H); IR (KBr) 3049 (w), 2955 (w), 2920 (s), 2850 (s), 2220 (m, C=N), 1545 (m), 1529 (m), 1472 (sh), 1462 (m), 908 (m), 833 (m),

723 (w), 463 (m) cm⁻¹. Anal. Calcd for $C_{24}H_{28}N_4$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.48; H, 7.59; N, 15.02.

2-Benzyl-1,4-cyclohexanedione (2g) was prepared from 5 and benzyl bromide by the procedure given for 2e, method B. A white, crystalline product was obtained directly: 94% yield; mp 67.5-68.5 °C; NMR (CD₂Cl₂) δ 2.38 (dd, 2 H), 2.68 (br m, 4 H), 2.93 (m, 1 H), 3.20 (dd, 2 H), 7.18 (br m, 5 H); IR (cast film, CH₂Cl₂) 3028 (m), 2956 (m), 2916 (m), 2852 (m), 1707 (vs), 1496 (m), 1456 (m), 1418 (m), 1330 (m), 1309 (m), 1278 (m), 1142 (m), 1081 (m), 986 (m), 914 (m), 829 (m), 755 (s), 733 (s), 698 (s), 630 (m), 595 (m), 560 (m) cm⁻¹. Anal. Calcd for C₁₃H₁₄O₂: C, 77.20; H, 6.98; O, 15.82. Found: C, 77.17; H, 6.92; O, 15.90.

1,4-Bis(dicyanomethylene)-2-benzylcyclohexane (3g). A mixture of 2.13 g (0.011 mol) of 2g, 1.50 g (0.023 mol) of malononitrile, 0.08 g of β -alanine, 10 mL of THF, and 4 mL of water was stirred at room temperature for 7 h and then diluted with 25 mL of water, and the precipitate was collected and washed with 200 mL of water followed by 200 mL of ether, giving 1.76 g (56% yield) of a white, crystalline product: mp 218-219 °C dec; NMR (CD₃CN) δ 2.8-3.3 (m, 7 H), 3.70 (m, 2 H), 7.32 (d, 2 H), 7.45 (m, 3 H); IR (KBr) 2959 (sh), 2924 (s), 2854 (m), 2232 (s, C=N), 1605 (s), 1497 (m), 1459 (m), 1442 (m), 1420 (m), 976 (m), 752 (s), 708 (m) cm⁻¹. Anal. Calcd for $C_{19}H_{14}N_4$: C, 76.49; H, 4.73; N, 18.78. Found: C, 76.33; H, 4.76; N, 18.74.

Benzyl-TCNQ (4g) was prepared from 3g by the method given above for 4e. Rapid filtration through silica gel $(CH_2Cl_2, some$ decomposition on column apparent) afforded an orange crystalline solid: 40% yield; mp 165.5–167 °C; NMR (CD_2Cl_2) δ 4.42 (s, 2 H), 7.04 (s, 1 H), 7.16 (d, 2 H), 7.4 (m, 4 H), 7.66 (d, 1 H); IR (KBr) 3060 (w), 2220 vs, C=N), 1609 (vw), 1552 (m), 1533 (s), 1493 (m), 1453 (m), 875 (m), 808 (s), 764 (m), 708 (s) cm⁻¹. Anal. Calcd for $C_{19}H_{10}N_4$: C, 77.54; H, 3.42; N, 19.04. Found: C, 76.91; H, 3.48; N, 19.07.

Acknowledgment. We thank Dr. Mark Nemeth for cyclic voltammetry, Dr. Narender Luthra and Susan Campbell for NMR spectroscopy, and Joseph Slanga for IR spectroscopy.

Registry No. 1e, 1199-08-2; 1h, 1201-38-3; 2e, 107616-65-9; 2f, 105314-19-0; 2g, 107616-67-1; 3e, 107616-66-0; 3f, 105314-20-3; 3g, 107616-68-2; 4e, 97221-64-2; 4f, 105314-21-4; 4g, 107616-69-3; 5, 2785-98-0; C_2H_5I , 75-03-6; $C_{12}H_{25}I$, 4292-19-7; $C_6H_5CH_2Br$, 100-39-0; NCCH₂CN, 109-77-3.

Leaving Group Rate Ratios in Solvolytic **Displacement Reactions.** The Effect of **Neighboring Sulfur**

Dionis E. Sunko,* Branko Juršić, and Mladen Ladika

Laboratory of Organic Chemistry, Faculty of Science, University of Zagreb, Strossmayerov trg 14, 41000 Zagreb, Yugoslavia

Received June 11, 1986

One of intriguing problems in the study of solvolytic reactivity of organic substrates in nucleophilic substitution is the choice of proper rate ratios for various leaving groups.¹ Although some authors claim^{2,3} that leaving group effects in solvolytic reactions are not very sensitive to mechanistic changes, these effects often depend on various reaction characteristics such as a type of substrate,

Table I. Solvolysis Rate Constants of Various 2-(Methylthio)ethyl Substrates, CH₃SCH₂CH₂Y

· · ·		, <u> </u>	, , , , , , , , , , , , , , , , , , , ,	
Y	solvent ^a	<i>t</i> , ℃	k, s^{-1}	$k_{97\mathrm{T}}/k_{80\mathrm{E}}$
OTs	80E	25	$(1.69 \pm 0.05) \times 10^{-4}$	
• • •	97T	25	$(2.74 \pm 0.05) \times 10^{-5}$	0.162
I	80E	25	$(2.70 \pm 0.07) \times 10^{-3}$	
	97T	25	$(2.63 \pm 0.05) \times 10^{-3}$	0.974
Br	80E	25	$(4.48 \pm 0.05) \times 10^{-4}$	
	97T	25	$(3.41 \pm 0.07) \times 10^{-4}$	0.761
		50	$(2.61 \pm 0.07) \times 10^{-3}$	
		65	$8.52 \times 10^{-3 b}$	
Cl	96E	25	$(1.02 \pm 0.02) \times 10^{-4}$	
	80E	25	$(1.97 \pm 0.02) \times 10^{-4}$	
		50	$(1.39 \pm 0.06) \times 10^{-3}$	
		70	5.43×10^{-3b}	
	60A	25	$(1.69 \pm 0.05) \times 10^{-4}$	
	97T	25	$(1.69 \pm 0.01) \times 10^{-4}$	0.858
		50	$(1.36 \pm 0.01) \times 10^{-3}$	0.978
		65	4.15×10^{-3b}	
	97H	25	$(1.91 \pm 0.07) \times 10^{-4}$	
ODNB	80E	70	$(4.05 \pm 0.06) \times 10^{-5}$	
	97T	65	$(3.58 \pm 0.11) \times 10^{-5}$	
OPNB	80E	70	$(1.43 \pm 0.07) \times 10^{-5}$	
	97T	65	$(1.36 \pm 0.03) \times 10^{-5}$	
			. ,	

^a96E = 96 vol % ethanol/water; 80E similarly; 60A = 60 vol % acetone/water; 97T = 97 wt % 2,2,2-trifluoroethanol/water; 97H = 97 wt % 1,1,1,3,3,3-hexafluoro-2-propanol/water. ^bExtrapolated from lower temperatures.

solvent, temperature, etc.⁴ For 2-adamantyl substrates the OTs/Br rate ratio of 240 for 97% CF₃CH₂OH (97% TFE)³ is similar to the value of 231 for 80% EtOH.⁵ On the contrary, the Br/Cl rate ratios for both tert-butyl halides and 2-adamantyl halides in 97% (CF₃)₂CHOH are³ about 9, whereas these ratios for tert-butyl halides in 97% TFE^{6,7} and EtOH⁸ are 22 and 50, respectively, indicating that the rate ratios in $\mathbf{S}_N \mathbf{1}$ reactions have smaller values in solvents of low nucleophilicity. Furthermore, while in S_{N1} reactions sulfonates are usually much better leaving groups than halides, in S_N2 reactions sulfonates and halides have comparable leaving-group ability and the relative reactivities of the leaving groups are considered to be dependent on the nucleophile as well as on solvent.^{1a} However, the OTs/Br rate ratio is often very low but variable (even smaller than unity) for both S_N1 and S_N2 reactions in various solvents.⁴

Until now leaving group rate ratios for $S_N 2$ solvolyses have been almost exclusively studied in reactions that include the nucleophilic attack of external nucleophile. For intramolecular displacement reactions such rate ratios were determined in very few cases.⁹⁻¹¹ In this work we report leaving group rate ratios for several common leaving groups (halides, sulfonates, and benzoates) in solvolyses of compounds with the methylthio group present as an internal nucleophile which can interact at the reaction center in the rate-determining step of solvolysis. For this

0022-3263/87/1952-2299\$01.50/0 © 1987 American Chemical Society

^{(1) (}a) Lowry, T. H.; Richardson, K. S. Mechanism and Theory in Organic Chemistry, 2nd ed.; Harper and Row: New York, 1981; pp 339-342. (b) Stirling, C. J. M. Acc. Chem. Res. 1979, 12, 198 and references cited therein.

⁽²⁾ Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. J. Am. Chem. Soc. 1979, 101, 3295.

⁽³⁾ Bentley, T. W.; Bowen, C. T.; Parker, W.; Watt, C. I. F. J. Chem. Soc., Perkin Trans. 2 1980, 1244.

^{(4) (}a) Hoffmann, H. M. R. J. Chem. Soc. 1965, 6753. (b) Hoffmann, (b) Romanni, I. M. R. Soc. 1965, 1963, 1963.
 (b) Hormanni, H. M. R. Soc. 1965, 1963.
 (c) Fry, J. L.; Lancelot, C. J.; Lam, L. K. M.; Harris, J. M.; Bingham,

R. C.; Raber, D. J.; Hall, R. E.; Schleyer, P. v. R. J. Am. Chem. Soc. 1970, 92, 2538

⁽⁶⁾ Shiner, V. J., Jr.; Dowd, W.; Fisher, R. D.; Hartshorn, S. R.; Kessick, M. A.; Milakofsky, L.; Rapp, M. W. J. Am. Chem. Soc. 1969, 91, 4838

⁽⁷⁾ Scott, F. L. Chem. Ind. (London) 1959, 224.
(8) (a) Fainberg, A. H.; Winstein, S. J. Am. Chem. Soc. 1956, 78, 2770.
(b) Fainberg, A. H.; Winstein, S. J. Am. Chem. Soc. 1957, 79, 1602.
(9) Knipe, A. C.; Stirling, C. J. M. J. Chem. Soc. B 1968, 67.
(10) (a) Bird, R.; Knipe, A. C.; Stirling, C. J. M. J. Chem. Soc., Perkin

Trans. 2 1973, 1215. (b) Bird, R.; Stirling, C. J. M. J. Chem. Soc., Perkin

Trans. 2 1973, 1221. (11) Bird, R.; Griffiths, G.; Griffiths, G. F.; Stirling, C. J. M. J. Chem. Soc., Perkin Trans. 2 1982, 579.