(aqueous Na_2CO_3) and extracted with several portions of $CHCl_3$. The combined extracts were dried (Na_2SO_4) and, after the $CHCl_3$ was removed at atmospheric pressure, the residue contained recovered 4-cyclopropylpyridine (0.65 g, 27.4% by comparison of its ir spectrum with that of an authentic sample) and 4-cyclopropylpyridine *N*-oxide (1.75 g, 65.8%, mp 163.4–164.6° from benzene). The structure of the product was confirmed by its elemental analysis, ir spectrum, and nmr spectrum.

Reaction of 4-Cyclopropylpyridine with *n*-Butyllithium.—4-Cyclopropylpyridine (0.02 mol, 2.38 g) was added to *n*-butyllithium (0.02 mol, 12.4 ml) and 100 ml of THF. The mixture was refluxed for 6 hr and cooled to room temperature and the THF was removed under reduced pressure (rotoevaporator). The residue was poured into water and extracted with several portions of $CHCl_3$ and the combined extracts were dried ($NaSO_4$). The solvent was removed at atmospheric pressure and the residue was vacuum distilled to give (1) recovered 4-cyclopropylpyridine, bp 74–76° (6.0 mm), 0.19 g, 8%, and (2) 2.06 g of material, bp 119–130° (5.6 mm). Glc analysis of fraction 2 showed three peaks. The peak with the shortest retention time corresponds to the retention time of an authentic sample of 4-cyclopropylpyridine. The smallest peak with an intermediate retention time was not identified. The largest peak with the longest retention time is 2-*n*-butyl-4-cyclopropylpyridine (65% based on glc analysis).

Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78. Found: C, 81.83; H, 9.65.

The picrate had mp 92.4–94.0° (from absolute ethanol). *Anal.* Calcd for $C_{18}H_{20}N_4O_7$: N, 13.86. Found: 13.86.

Registry No.—**3**, 6814-64-8; 2-vinylpyridine, 100-69-6; 4-vinylpyridine, 100-43-6; 2-methyl-6-vinylpyridine, 1122-70-9; 2-vinyl-5-ethylpyridine, 5408-74-2; 4-styrylpyridine, 103-31-1; 2-styrylpyridine, 714-08-9; 3-methyl-4-styrylpyridine, 13673-34-2; 3-methyl-2-styrylpyridine, 7433-87-6; 2-*n*-butyl-4-cyclopropylpyridine, 41764-88-9; 2-*n*-butyl-4-cyclopropylpyridine picrate, 41764-89-0.

Strained Ring Systems. XIV.[1a] Solvolysis of Arenesulfonate Derivatives of Benzobicyclo[2.2.0]hex-5-en-*exo*-2-ol

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The buffered acetolysis and formolysis of benzobicyclo[2.2.0]hex-5-en-*exo*-2-yl tosylate (1-OTs) and nosylate (1-ONs) were investigated. Buffered acetolysis of 1-OTs produced only naphthalene while 1-ONs yielded naphthalene (58%) and benzobicyclo[2.1.1]hex-2-en-*exo*-5-yl acetate (2-OAc, 37%). Buffered formolysis of 1-ONs gave exclusively 2-O_2CH in 97% yield. The effects of the benzo group in 1 are discussed.

We recently published the synthesis of benzobicyclo[2.2.0]hex-5-en-*exo*-2-ol (1-OH) by hydroboration–oxidation of benzobicyclo[2.2.0]hexa-2,5-diene.[2] We now wish to report the preparation and results of solvolytic studies of the tosylate (1-OTs) and nosylate (1-ONs) esters.

Alcohol 1-OH was converted into arenesulfonates 1-OTs and 1-ONs by standard methods. As is our practice with new substrates such as these, approximate rates of buffered acetolysis were determined at two temperatures with two weighed samples (0.005 *M* ROX, 0.006 *M* KOAc) each of 1-OTs and 1-ONs in separate ampoules using the sealed ampoule technique. These approximate rate constants are generally within ±10% of values determined for first-order rate constants from a full kinetic run.[3] These rate constants are listed in Table I.

Table I

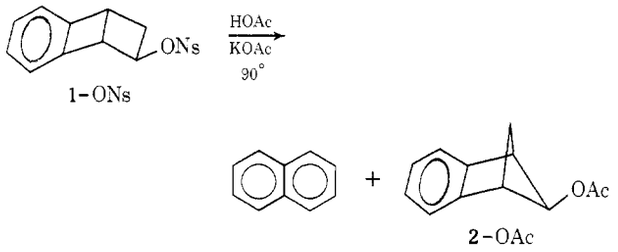
Approximate Buffered Acetolysis Rate Constants for 1-OTs and 1-ONs[a]

Compd	Temp, °C	k,[a] sec^{-1}
1-OTs	90.0	1.8×10^{-5}
	120.0	4.2×10^{-4}
1-ONs	70.0	4.6×10^{-6}
	90.0	4.7×10^{-5}

[a] Determined from only two kinetic points. The instantaneous rate constants from each point based on the initial concentration of substrate agreed within ±3% of these figures.

It was immediately obvious that more than a simple solvolysis reaction was occurring in either 1-OTs or 1-ONs or both from the ratio $k_{1\text{-ONs}}/k_{1\text{-OTs}} = 2.6$. We had previously found the nosylate–tosylate rate ratio to be about 10 for "normal" solvolyses for several primary derivatives,[4] and the same rate ratio was expected for these secondary derivatives.

Isolation of the materials from an interrupted buffered acetolysis of 1-OTs showed the presence of 1-OTs, naphthalene, and decomposition material. A preparative buffered acetolysis of 1-ONs at 90° for approximately 10 solvolytic half-lives (based on approximate k, Table I) yielded naphthalene (58%) and benzobicyclo[2.1.1]hex-2-en-*exo*-5-yl acetate (2-OAc, 37%).[5]



The thermal stabilities of 1-OTs and 1-ONs were determined by heating them in hydrocarbon solvents for the time required for approximately 10 buffered acetolysis half-lives of that arenesulfonate. Heating 1-OTs in xylene at 120° and 1-ONs in toluene at 90° produced naphthalene and the corresponding arenesulfonic acid in excellent yields with no recovery of the starting arenesulfonate. From these results it was

(1) (a) Paper XIII: R. N. McDonald and G. E. Davis, *J. Amer. Chem. Soc.*, **94**, 5078 (1972). (b) NDEA Fellow, 1966–1969.

(2) R. N. McDonald, D. G. Frickey, and G. M. Muschik, *J. Org. Chem.*, **37**, 1304 (1972).

(3) R. N. McDonald and G. E. Davis, *J. Org. Chem.*, **38**, 138 (1973).

(4) R. N. McDonald, N. L. Wolfe, and H. E. Petty, *J. Org. Chem.*, **38**, 1106 (1973).

(5) Y. Hata and H. Tanida, *J. Amer. Chem. Soc.*, **91**, 1170 (1969).

TABLE II

BUFFERED FORMOLYSIS DATA FOR BENZOBICYCLO[2.2.0]HEX-5-EN-*exo*-2-YL NOSYLATE (1-ONs)[a]

Temp, °C	k, sec^{-1}	Av k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
25.0		1.3×10^{-6} [b]		
50.0	$(3.91 \pm 0.05) \times 10^{-5}$	3.94×10^{-5}	25.4 ± 0.1	-0.4 ± 0.4
	$(3.97 + 0.05) \times 10^{-5}$			
70.0	$(4.17 \pm 0.05) \times 10^{-4}$	4.18×10^{-4}		
	$(4.20 \pm 0.07) \times 10^{-4}$			

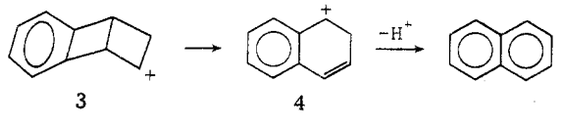
[a] 0.00516 *M* 1-ONs, 0.00646 *M* HCO_2K. [b] Extrapolated from data at other temperatures.

obvious that we were not looking at a purely solvolytic reaction in these buffered acetolyses.

We then turned our attention to buffered formolysis, since formolysis kinetic data was available for the parent bicyclo[2.2.0]hex-*exo*-2-yl tosylate.[6] The buffered formolysis data on **1**-ONs are listed in Table II. A preparative buffered formolysis (60°, 10 solvolytic half-lives) produced the single formate product, **2**-O_2CH, in 97% yield; nmr spectral analysis failed to show the presence of naphthalene or **1**-O_2CH. Formate **2**-O_2CH was shown to be stable to the formolysis conditions while **1**-O_2CH partially gave naphthalene plus unidentified materials. **1**-ONs was shown to be thermally stable in benzene at 70° for 10 formolysis half-lives. The structure of the formolysis product **2**-O_2CH was assigned on the basis of close similarities of the pmr chemical shifts and general peak multiplicities of **2**-OAc and **2**-O_2CH and from spin decoupling of the protons in **2**-O_2CH.

Two features of the product and kinetic data are evident: (1) the exclusive formation of **2**-O_2CH in the buffered formolysis of **1**-ONs readily demonstrates the requirement of Wagner–Meerwein rearrangement sometime during the solvolytic processes, and (2) the relatively abnormal effect of olefinic *vs.* arene double bond involvements in such participation compared with those in related bicyclic systems.

Tanida[5] has pointed out that should the classical benzobicyclo[2.2.0]hex-5-en-2-yl cation (**3**) be produced, naphthalene formed *via* benzylic cation **4** would be an



3 **4**

expected product; we agree. This expectation is given credence from the results of the solvolysis of bicyclo[2.2.0]hex-*endo*-2-yl 3,5-dinitrobenzoate yielding *only* products resulting from disrotatory zero-bridge opening,[7] which we believe would be representative of the classical [2.2.0]-2-yl cation and **3**. Principle sources of naphthalene in the buffered acetic acid media were probably thermal and/or base-induced eliminations.

If we assume that the k_{RONs}/k_{ROTs} ratio for formolysis of derivatives of **1**-OH is that found for acetolysis of several primary systems,[4] we calculate that introduction of the 5,6-ethylenic[8] and 5,6-benzo groups depresses the rate of solvolysis of bicyclo[2.2.0]hex-*exo*-2-yl OTs (**5**-OTs) by factors of 28 and $(28)^2$, respectively, with each $\Delta\Delta F^{\ddagger}$ of about 2 kcal/mol. Even applying an inductive correction factor of 10 for the β-aryl group[9] in **1**-ONs leaves us with a rate retardation of 78 for **1**-ONs compared to that calculated for **5**-ONs. The effects caused by such β-olefinic and β-aryl groups in related systems are listed in Table III.

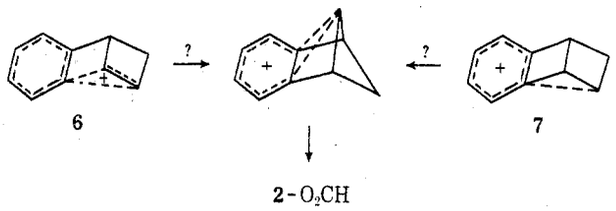
TABLE III

ACETOLYSIS RATE RATIOS OF SATURATED, β-OLEFINIC, AND β-ARYL DERIVATIVES IN BICYCLO[2.2.*n*]ALKYL SYSTEMS[a]

Structure	k_{satd}/k_{unsatd}	k_{unsatd}/k_{arene}	Ref
exo-2-[2.2.0]	28[b]	28[c]	6, 8, this work
exo-2-[2.2.1][d]	2.0	6.0	*e, f, g*
endo-2-[2.2.1][d]	44	5.7	*e, f, g*
exo-2-[2.2.2][d]	0.0038	100	*h*
endo-2-[2.2.2][d]	0.20	5.5	*h*

[a] Some rate data were determined in buffered solvent, while others come from unbuffered determinations. [b] Ratio at 90°. [c] Formolysis comparison at 25°. [d] Ratios at 25°. [e] S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1127 (1952). [f] S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956). [g] P. D. Bartlett and W. P. Giddings, *ibid.*, **82**, 1240 (1960). [h] H. Tanida, K. Tori, and K. Kitahonoki, *ibid.*, **89**, 3212 (1967).

It is obvious from the data in Table III that the total rate depression caused by the β-aryl group is largest in the *exo*-2-[2.2.0] system, $k_{satd}/k_{arene} = 780$. At the same time, the exclusive formolysis product from **1**-ONs is **2**-O_2CH, the product of Wagner–Meerwein (σ-bond) rearrangement. The question of whether the formolysis of **1**-ONs → **2**-O_2CH may involve σ-bond participation in concert with ionization (**6**)[11a] or proceeds by way of initial β-arylethyl type of participation[11b] (**7**) cannot yet be defined with the present limited data.



6 **7**

2-O_2CH

We plan to examine aryl substituent effects in **1**-ONs solvolysis. A "plus feature" of such a study is that we can then examine these same effects on derivatives of benzobicyclo[2.1.1]hex-2-en-*exo*-5-ol, the product of rearrangement, where solvolytic participation is *via* the aromatic ring π electrons.[5]

Experimental Section[12]

Benzobicyclo[2.2.0]hex-5-en-*exo*-2-yl Acetate (1-OAc). A.—To 407 mg (2.8 mmol) of **1**-OH[2] dissolved in 15 ml of dry pyridine

(6) R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967).

(7) R. N. McDonald and G. E. Davis, *J. Amer. Chem. Soc.*, **94**, 5078 (1972).

(8) S. Masamune, E. N. Cain, R. Vukov, S. Takada, and N. Nakatsuka, *Chem. Commun.*, 243 (1969).

(9) A more reasonable value for this inductive correction factor of 4–6 comes from the β-phenyl effects on the rate constants for k_s in 1-phenyl-2-propyl OTs and k_t in isopropyl OTs solvolyses.[10]

(10) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4294 (1969); C. J. Lancelot and P. v. R. Schleyer, *ibid.*, **91**, 4296 (1969).

(11) (a) The dashed delocalization indicated in the arene ring of **6** is to show possible arene-C_1 p orbital (filled) interaction with the π^* C_1–C_2 olefinic orbital (empty) similar to that suggested by Dewar [*J. Amer. Chem. Soc.*, **92**, 3996 (1970)] for β-arylethyl derivatives. (b) L. A. Paquette and I. R. Dunkin, *ibid.*, **95**, 3067 (1973), concluded that σ-bond participation was *not* involved in the solvolysis of benzobicyclo[2.2.1]hept-5-en-*exo*-2-yl derivatives but that β-arylethyl type participation was "entirely possible" with these substrates.

(12) Melting points were determined on a Kofler hot stage. Spectra were determined on commercial instruments (ir, P-E 137; nmr, Varian T-60). Nmr spectral data are listed as centers except for certain multiplets where the range of the signals is given.

(distilled from barium oxide and kept over potassium hydroxide pellets) at 5° was added 5.0 ml of reagent-grade acetic anhydride. The mixture was stirred for 12 hr and warmed to room temperature. The reaction mixture was dissolved in ether, washed with five 20-ml portions of 10% hydrochloric acid, two 10-ml portions of water, 10 ml of saturated aqueous sodium bicarbonate, and 10 ml of water, and dried ($MgSO_4$). Removal of the ether gave a liquid residue which was short-path distilled [40–60° (10^{-3} mm)] giving 513 mg (98%) of the desired acetate: ir (thin film) 1740 cm^{-1} (C=O); nmr (CCl_4, internal TMS) τ 2.75–3.05 (aromatic A_2B_2 pattern, 4), 5.05–5.30 (t, CHOAc, 1), 6.0–6.25 (m, bridgehead H's, 2), 7.50–7.75 (m, CH_2, 2), and 7.98 (s, CH_3, 3).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.44; H, 6.58.

B.—To a solution of 11.0 g (98 mmol) of Δ^2-cyclobutenyl acetate[13] and 60 ml of analytical grade ethylene dichloride under nitrogen was added 4.0 g (27 mmol) of benzenediazonium 2-carboxylate. The slurry was stirred at 40–41° for 3 hr. Removal of solvent and recovered Δ^2-cyclobutenyl acetate and short-path distillation gave 1.40 g (28%) of volatile materials [53–100° (10^{-3}–10^{-4} mm)]. These volatile materials were chromatographed on silica gel where petroleum ether (bp 30–60°) eluted 0.20 g (4%) of naphthalene, and a 15:85 mixture of benzene–carbon tetrachloride eluted 0.02 g (>1%) of 3-phenyl-Δ^1-cyclobutenyl acetate: ir (thin film) 1750 cm^{-1} (C=O); nmr (CCl_4, internal TMS) τ 2.83 (m, aromatic H's, 5), 4.57 (broadened s, olefinic H, 1), 6.2–6.38 (m, $J_{2,3}$ = 4.5, $J_{2,4}$ = 2.0 Hz, –CHPh, 1), 6.6–7.65 (m, $J_{3,4}$ = 13.0 Hz, CH_2, 2), and 7.90 (s, CH_3, 3).

A 30:70 mixture of benzene–carbon tetrachloride eluted 200 mg (4%) of 1-OAc, while a 1:1 mixture of benzene–carbon tetrachloride eluted 340 mg (7%) of 4-phenyl-Δ^2-cyclobutenyl acetate: ir (thin film) 1710 cm^{-1} (C=O); nmr (CCl_4, internal TMS) τ 2.87 (m, aromatic H's, 5), 3.58–3.82 (doublet of triplets and doublet of doublets, $J_{2,3}$ = 0.8 Hz, olefinic H's, 2), 4.32–4.47 (doublet of triplets, $J_{1,2}$ = 2.8, $J_{1,3}$ = 1.0, $J_{1,4}$ = 0.7 Hz, CHOAc, 1), and 5.59–5.75 (s, CH_3, 3). The 1:1 benzene–carbon tetrachloride also eluted a 0.095-g (2%) mixture of unknown acetates.

To a solution of 11.40 g (0.11 mol) of Δ^2-cyclobutenyl acetate and 80 ml of analytical grade ethylene dichloride under nitrogen was added 7.1 g (0.048 mol) of benzenediazonium 2-carboxylate at 39–40° with another 7.4 g (0.05 mol) added after an additional 2 hr. Removal of solvent and excess Δ^2-cyclobutenyl acetate and distillation [40–100° (10^{-3} mm)] of the remaining residue yielded 4.95 g (38%) of volatile material which gave 493 mg (4%) of 1-OAc.

Benzobicyclo[2.2.0]hex-5-en-*exo*-2-yl Tosylate (1-OTs).—To a solution of 200 mg (1.35 mmol) of 1-OH in 25 ml of dry pyridine (distilled from barium oxide) at 5° was added 267 mg (1.4 mmol) of sublimed tosyl chloride. The mixture was stirred for 3 days and warmed to room temperature. Ether was added, and the mixture was washed with five 20-ml portions of water and dried ($MgSO_4$). Removal of solvent gave 279 mg of crude material which was chromatographed on activity 3–4 basic alumina, where carbon tetrachloride eluted 240 mg of product. Recrystallization from pentane–ether gave 185 mg (46%) of 1-OTs: mp 65.5–66°; ir (KBr disk) 1350 (S=O) and 1175 cm^{-1} (CO); nmr (CCl_4, internal TMS) τ 2.5–2.80 (A_2B_2, tosyl H's, 4), 2.85–3.10 (A_2B_2, aromatic H's, 4), 5.15–5.40 (t, CHOTs, 1), 6.0–6.3 (m, bridgehead H's, 2), 7.4–7.75 (m, CH_2, 2), and 7.55 (s, CH_3, 3).

Anal. Calcd for $C_{17}H_{16}SO_3$: C, 67.98; H, 5.37. Found: C, 67.74; H, 5.19.

Benzobicyclo[2,2,0]hex-5-en-*exo*-2-yl Nosylate (1-ONs).—To a solution of 220 mg (1.51 mmol) of 1-OH in 3 ml of anhydrous ether (distilled from lithium aluminum hydride) was added 2.0 ml (3.2 mmol) of a 1.6 *M* solution of methyllithium in pentane at 4°.[4] The mixture was stirred for 15 min at 5° and then 331 mg (1.50 mol) of nosyl chloride (recrystallized from carbon tetrachloride) was added to the alkoxide solution. The solution was stirred at 5° for an additional 1 hr. Ether was added and then the mixture was washed with four 15-ml portions of water and dried (Na_2CO_3). Removal of solvent gave a yellow oil (465 mg) which was chromatographed on activity II–III, basic alumina where benzene eluted 0.307 g of crude material. Recrystallization from ether–methylene chloride–pentane gave 262 mg (53%) of 1-ONs: mp 100–101°; ir (KBr disk) 1520 (N=O), 1350 (S=O), and 1175 cm^{-1} (CO); nmr ($DCCl_3$, internal TMS) τ 1.5–2.0 (A_2B_2, nosyl H's, 4), 2.6–3.1 (A_2B_2, aromatic H's, 4), 5.0–5.25 (t, CHONs, 1), 5.85–6.20 (m, bridgehead H's, 2), and 7.35–7.65 (m, CH_2, 2).

Anal. Calcd for $C_{16}H_{13}O_5NS$: C, 58.00; H, 3.95. Found: C, 57.69; H, 3.95.

Benzobicyclo[2.2.0]hex-5-en-*exo*-2-yl Formate (1-O_2CH).—To a solution of 100 mg (0.675 mmol) of 1-OH in 20 ml of dry pyridine (distilled from barium oxide) at 5° was added 1.50 ml of acetic–formic anhydride.[14] The mixture was stirred for 12 hr at 5–10° and then at room temperature for 2 days. The reaction mixture was poured into ice–water and extracted with two 20-ml portions of ether. The ether extracts were combined and washed with five 15-ml portions of water, three 15-ml portions of cold 10% hydrochloric acid, 15 ml of saturated sodium bicarbonate, and two 15-ml portions of water, and dried ($MgSO_4$). Removal of the ether gave a colorless liquid that was short-path distilled [40° (10^{-3} mm)] yielding 94 mg (78%) of 1-O_2CH: ir (thin film) 1730 cm^{-1} (C=O); nmr (CCl_4, internal TMS) τ 2.95 (s, O_2CH, 1), 2.6–3.1 (m, aromatic H's, 4), 4.85–5.1 (t, –CHO$_2$CH, 1), 5.9–6.2 (m, bridgehead H's, 2), and 7.4–7.7 (m, CH_2, 2).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.90; H, 6.16.

Thermal Stability Check of 1-OTs.—A solution of 40 mg (0.133 mmol) of 1-OTs in 15 ml of xylene (distilled from sodium) was placed in a bath at 120.0 ± 0.1° for 280 min (approximately 10 $t_{1/2}$ for buffered acetolysis). The solvent was short-path distilled under vacuum, yielding 39 mg (99%) of crude product. The nmr in DMSO-d_6 showed the presence of naphthalene and *p*-toluenesulfonic acid which compared identically with spectra of known samples.

Preparative Buffered Acetolysis of 1-ONs.—A solution of 80 mg (0.242 mmol) of 1-ONs in 20 ml of 0.013 *M* potassium acetate–acetic acid (2% acetic anhydride) buffer solution was placed in a constant-temperature bath at 90.0 ± 0.1° for 50 hr (approximately 10 $t_{1/2}$ for buffered acetolysis). It was then cooled, placed in a separatory funnel with 20 ml of cold water, and extracted with three 20-ml portions of ether. The ether extracts were combined, washed with five 20-ml portions of water, two 10-ml portions of saturated sodium bicarbonate, two 20-ml portions of water, two 10-ml portions of saturated sodium bicarbonate, and 20 ml of water, and dried ($MgSO_4$). Removal of solvent gave a residue, which was chromatographed on activity II–III, basic alumina where petroleum ether eluted 18 mg (58%) of naphthalene while benzene eluted 17 mg (37%) of 1-OAc.

Thermal Stability Check of 1-ONs.—A solution of 40 mg (0.121 mmol) of 1-ONs was dissolved in 15 ml of toluene (analytical reagent) and placed in a constant-temperature bath at 90.0 ± 0.1° for 5 hr (approximately 10 $t_{1/2}$ for buffered acetolysis). The solvent was short-path distilled [50–60° (20 mm)] yielding 36 mg (90%) of a mixture of naphthalene and *p*-nitrobenzenesulfonic acid, as identified by nmr.

Kinetic Method for Buffered Formolysis.—The buffered formolysis procedures were modifications of those developed by other workers.[15] All volumetric solutions were prepared in a dry, N_2-atmosphere glove box. The sealed ampoule technique was used for formolyses determined above 35°. Substrate solutions were prepared to be 0.005 *M* ROX and 0.006 *M* KO_2CH. Approximately 1.5 ml of the formolysis solution was removed per point with a constant-delivery pipette, quenched in 6 ml of purified dioxane, and titrated with $HClO_4$–acetic acid using a Metrohm Herisau E 436D automatic titrator.

The rate constants were calculated using the RATSOL2[3] computer program using experimental infinity titers. Thermochemical data and rate extrapolations were obtained from a computer program which calculated the energy of activation and its maximum error limits.

Using the above procedure, duplicate rate constants for cyclohexyl tosylate (mp 43–44°) were (4.14 ± 0.10) × 10^{-5} sec^{-1} and (4.05 ± 0.10) × 10^{-5} sec^{-1}; average k = 4.1 × 10^{-5} sec^{-1}. Both determinations had 101 ± 2% infinity titers. The unbuffered formolysis of cyclohexyl tosylate had k = (3.97 ± 0.05) × 10^{-5} sec^{-1} at 25°.

(13) K. B. Wiberg, V. Z. Williams, and L. E. Friedrich, *J. Amer. Chem. Soc.*, **92**, 564 (1970).

(14) L. I. Krimen, *Org. Syn.*, **50**, 1 (1970).

(15) S. Winstein and R. Heck, *J. Amer. Chem. Soc.*, **78**, 4801 (1956); S. Winstein and H. Marshall, *ibid.*, **74**, 1120 (1952).

Preparative Buffered Formolysis of 1-ONs.—To 30 ml of 0.103 *M* potassium formate–formic acid solution, which had been prepared and kept in a nitrogen atmosphere, was added 82 mg (0.247 mmol) of 1-ONs. The solution was placed in a constant-temperature bath at 60.00 ± 0.05° for 20 hr (approximately 10 $t_{1/2}$). It was then cooled and placed in a separatory funnel with 50 ml of ether. The ether solution was washed with four 20-ml portions of water, two 10-ml portions of 7% sodium bicarbonate solution, and 25 ml of water and dried (Na_2SO_4). Removal of solvent gave a residue which was short-path distilled [40–45° (10^{-3} mm)] yielding 40.5 mg (97%) of 2-O_2CH: ir (thin film) 1720 cm^{-1} (C=O); nmr (CCl_4, internal TMS) τ 1.95 (s, O_2CH, 1), 2.65–3.05 (m, aromatic H's, 4), 5.1–5.2 (d, CHO_2CH, 1), 6.4–6.6 (m, *exo*-methylene H, 1), 6.75 (d, bridgehead H's, 2), and 7.5–7.7 (t, *endo*-methylene H, 1); the chemical shifts and peak multiplicities agree closely with those of 2-OAc.[5]

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.70; H, 5.81.

Formolysis Stability Check of 2-O_2CH.—To a 25-ml solution of 0.0103 *M* potassium formate–formic acid in a 50-ml round-bottom flask was added 40 mg (0.225 mmol) of 2-O_2CH. The solution was placed in a constant-temperature bath at 60.00 ± 0.06° for 20 hr (approximately 10 $t_{1/2}$). At the end of 20 hr, the solution was placed in a separatory funnel with 50 ml of ether, and was washed with five 25-ml portions of water, 10 ml of saturated sodium bicarbonate, and 20 ml of water and dried ($MgSO_4$). Removal of solvent gave a 39.7-mg (99%) recovery of 2-O_2CH, as shown by ir and nmr spectroscopy.

Formolysis Stability Check of 1-O_2CH.—To a solution of 30 ml of 0.0103 *M* potassium formate–formic acid in a 50-ml round-bottom flask was added 43 mg (0.244 mmol) of 1-O_2CH. It was placed in a constant-temperature bath at 60.00 ± 0.06° for 20 hr (approximately 10 $t_{1/2}$). The cooled solution was placed in a separatory funnel with 50 ml of ether, and was washed with five 25-ml portions of water, 15 ml of saturated sodium bicarbonate, and 25 ml of water and dried ($MgSO_4$). Removal of the solvent gave 36.3 mg of product. The isolated product was dissolved in 1.0 ml of absolute ethanol and cooled to 5°. To this solution at 5° was added 0.15 ml of a 5% potassium hydroxide in absolute ethanol. The mixture was stirred and warmed to room temperature over 14 hr. The reaction mixture was transferred to a separatory funnel with 20 ml of ether and enough 10% hydrochloric acid to acidify the resulting aqueous solution. This mixture was washed with five 15-ml portions of water, 10 ml of saturated sodium bicarbonate, and 15 ml of water and dried ($MgSO_4$). Removal of solvent gave 28 mg of material which was chromatographed on activity II–III, basic alumina where petroleum ether eluted 5 mg of naphthalene and methylene chloride eluted 22 mg of 1-OH.

Thermal Stability of 1-ONs.—A solution of 40 mg (0.12 mmol) of the title compound in 15 ml of benzene (thiophene-free benzene distilled from sodium) was placed in a round-bottom flask and set in a constant-temperature bath at 70.00 ± 0.05° for 5 hr (approximately 10 $t_{1/2}$). Removal of solvent by short-path distillation gave 40 mg (100%) of recovered 1-ONs.

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Registry No.—1-OH, 33905-59-8; 1-OAc, 41562-89-4; 1-OTs, 41562-90-7; 1-ONs, 41562-91-8; 1-O_2CH, 41562-92-9; 2-O_2CH, 41562-93-0; Δ^2-cyclobutenyl acetate, 27238-02-4; benzenediazonium 2-carboxylate, 1608-42-0; 3-phenyl-Δ'-cyclobutenyl acetate, 41562-96-3; 4-phenyl-Δ^2-cyclobutenyl acetate, 41562-97-4; tosyl chloride, 98-59-9; nosyl chloride, 122-04-3; cyclohexyl tosylate, 953-91-3.

Notes

The Preparation of 2-Alkylamino-1,3,4-thiadiazoles

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Investigation of the chemical and antimicrobial properties of mesoionic 8-alkyl-1,3,4-thiadiazolo[3,2-*a*]pyrimidine-5,7-diones[1,2] required the preparation of 2-alkylamino-1,3,4-thiadiazoles, unsubstituted in the 5 position, as intermediates. We wish to report an improved procedure for the preparation of these thiadiazole derivatives.

Although 5-substituted 2-acylamino-1,3,4-thiadiazoles can be conveniently reduced to the corresponding amines with lithium aluminum hydride, the 5-unsubstituted amides are base sensitive and undergo extensive decomposition.[3] Formamidate esters undergo thermal rearrangement to *N*-alkylformamides which can be subsequently hydrolyzed to alkylamines.[4] Treatment of 2-amino-1,3,4-thiadiazole with a tenfold excess of trimethyl orthoformate gave as the sole product *N*,*N'*-bis(1,3,4-thiadiazol-2-yl)formamidine (**1**), instead of the desired methyl *N*-(1,3,4-thiadiazol-2-yl)-formamidate. Therefore, this method appears unsuitable for the preparation of the desired 2-alkylaminothiadiazoles.

2-*sec*-Amino-1,3,4-thiadiazoles have been prepared by the treatment of 4-substituted thiosemicarbazides **2** with triethyl orthoformate.[5a-e] Although this is a satisfactory method in the preparation of 2-arylamino derivatives,[5d] 2-alkylamino derivatives are obtained in low yield accompanied by nearly equivalent amounts of 4-alkyl-1,2,4-triazoline-3-thione (**5**). Thus treatment of **2** (R = CH_3) with a twofold excess of triethyl orthoformate results in the formation of both **4** (R = CH_3) and **5** (R = CH_3) in 39 and 34.5% yield, respectively. Heating of the presumed intermediate,[5a,b] ethyl formate 4-methylthiosemicarbazone (**3**, R =

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