tions[22] is a slow process. This is very likely a consequence of the pronounced steric hindrance imposed by the geminal methyl group. For the same reasons one would expect the acetal to be very reactive. Indeed, camphor diethyl acetal is hydrolyzed in the presence of a catalytic amount of acid, or sulfur dioxide, to camphor and ethanol with extreme ease.

(8) We did not investigate this particular reaction in any detail.
(9) A similar mixture of these eight ortho esters was also found when a drop of methanesulfonic acid was added to a mixture of the same two ortho esters.
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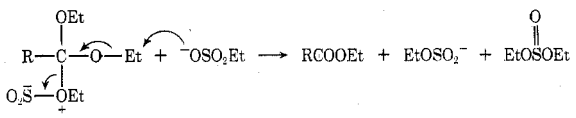
(14) This may be an oversimplification and certainly there are alternative possibilities. For example, the reaction between the ethyl sulfite anion and the ortho ester coordinated with sulfur dioxide may provide the same products.



(15) M. Kobayashi, *Bull. Chem. Soc. Jpn.*, **39**, 1296 (1966).
(16) The relative amounts varied from experiment to experiment.
(17) See, for example, E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 227.
(18) For the same reason one would not expect that the corresponding dicyclohexyl sulfite would be formed in the reaction, and indeed it was not observed among the reaction products.
(19) Clearly, the extent of the exchange reaction, i.e., the formation of the *trans*-4-*tert*-butylcyclohexanol (eq 11), will be a function of the relative rates of the respective processes. The relative amounts of the products varied from experiment to experiment and the ratio of ethanol/*trans*-4-*tert*-butylcyclohexanol was not constant.
(20) See, for example, E. H. Cordes in "The Chemistry of Carboxylic Acids and Esters", S. Patal, Ed., Interscience, New York, N.Y., 1967, pp 632–656.
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(23) Ethyl nitrite was prepared from sodium nitrite and ethanol according to the procedure of W. L. Semon and V. R. Damerell, "Organic Syntheses", Collect. Vol. II, Wiley, New York, N.Y., 1943, p 204.
(24) *Caution:* excessive pressure!
(25) The same eight peaks were also present in the reaction mixture of the same two ortho esters a short time after a catalytic amount of methanesulfonic acid was added.

Cyclobutylcarbinyl *p*-Bromobenzenesulfonate Solvolysis. 1-Aryl Substituent Effect upon Product Distribution

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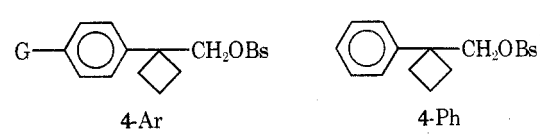
The acetolysis products of 1-phenylcyclobutylcarbinyl (4-Ph), 1-*p*-nitrophenylcyclobutylcarbinyl (4-NPh), and 1-*p*-methoxyphenylcyclobutylcarbinyl (4-MPh) brosylates have been determined in the presence of urea. All of the substrates give 1,2-phenyl rearranged products. The products of the reactions along with previously determined kinetic data[1] suggest that ionization occurs prior to rearrangement. In turn, the phenonium ion intermediate (II) partitions itself among the various product pathways. The mechanistic details are discussed in terms of the Winstein solvolysis scheme.

In a previous[1] solvolytic investigation, it was reported that the transition state for the acetolysis of 4-Ar has little phenonium ion character. Support for this postulate was afforded by the Hammett behavior of 4-Ar ($\rho = -1$), which reveals little direct conjugation between the para substituent and the developing cationic center. For example, the Hammett behavior of a series[2] of para-substituted neophyl tosylates and related systems, solvolyzing with aryl participation, is characterized by ρ values of about -3; while other related systems, solvolyzing without aryl participation, are characterized[2] by ρ values of about -1.



4-Ar 4-Ph

On the other hand, the fact that only 1,2-phenyl rearranged products were isolated[1a] from the acetolysis of 4-Ph provides strong evidence for phenyl bridging in the transition state leading to the intermediate which reacts with solvent.

These findings were rationalized[1b] in terms of Scheme I,

Scheme I

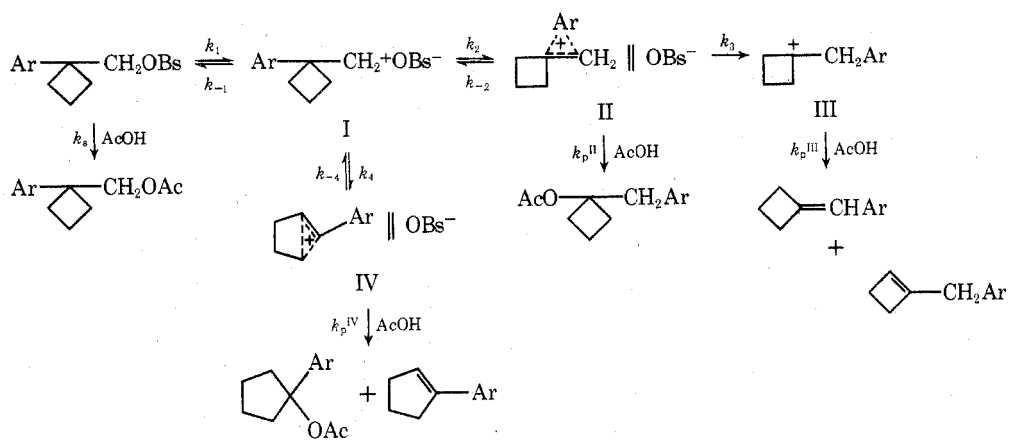


Table I
Acetolysis Products of Selected Tertiary-Carbinyl Systems

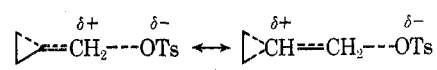
Substrate	% Ester	% Alkene	Ref
$CH_3CH_2\underset{\displaystyle Cl}{\underset{\vert}{C}}(CH_3)CH_3$	*a*	85	11a
$CH_3\underset{\displaystyle Cl}{\underset{\vert}{C}}(C_6H_5)CH_2CH_3$		95	11b
$CH_3CH_2\underset{\displaystyle Ph}{\underset{\vert}{C}}(CH_3)\underset{\displaystyle OBBZ}{\underset{\vert}{C}}(CH_3)CH_2CH_3$ [b]		100	11c

[a] Did not report substitution product. [b] p-Bromobenzoate.

which has been expanded to include ion-pair partitioning pathways.[3] Based upon the substrate's Hammett behavior, generation of the intimate ion pair (I) is considered rate determining, while aryl assistance controls ion-pair partitioning between the two bridging pathways: neighboring group participation (or internal displacement) by the cyclobutyl (k_4) or aryl (k_2) group. In turn, the phenonium ion intermediate (II) partitions itself among the product forming pathways k_p^{II} (solvent attack on the bridged ion) and k_p^{III} (rearrangment to open ion followed by solvent attack).

Basically, Scheme I rests on the mechanistic speculation of Sneen,[4] Shiner,[5] and Brown[3a] that solvolysis proceeds through a first-formed tight ion pair which partitions itself among the various product pathways. Furthermore, such a mechanistic scheme has been generally accepted[6] for solvolysis of the related substrate, the cyclopropylcarbinyl system.

The recent proposal of Traylor[7] that strained σ bonds, such as those in cyclopropylcarbinyl substrates, can afford stabilization of neighboring cationic centers via σ–π conjugation affords an interesting possibility for the structure of I. Thus it is speculated that I is stabilized by σ–π conjuga-



tion between the cyclobutyl group and the neighboring cationic center where little movement of the cyclobutyl group toward the developing cationic center occurs, i.e., vertical stabilization takes place in which the σ bond is delocalized without changing its bond length or angle significantly.

Delineation of all the mechanistic possibilities for product formation is assisted considerably by assessment of the various product distributions resulting from solvent interaction with each intermediate listed in Scheme I. Thus solvent attack on covalent substrate (k_s pathway) is eliminated from consideration by the absence of nonrearranged ester in the product. Furthermore, the absence of ring-expanded ester and/or alkene in the product mixture is evidence against reorganization of I to IV (k_p^{IV}pathway) or a ring-expanded open ion.

The assessment that solvent interaction with II leads to exclusively aryl rearranged esters and that interaction with III leads to predominantly aryl rearranged alkenes is based upon less compelling arguments than the above owing to the paucity[8] of product distribution data in acetolysis studies, but nevertheless, the data collected in Table I make such an assessment attractive. Not only are high percentages of alkene products obtained from the acetolysis of the listed tertiary-carbinyl compounds, but also there is a growing body of evidence[11] that in the solvolysis of tertiary-carbinyl substrates a more reactive leaving group produces a higher percentage of alkene. This evidence suggests

Table II
Acetolysis Products for 1-p-X-Phenylcyclobutylcarbinyl Brosylates[a]

X	p-XPhCH=	p-XPhCH$_2$–	p-XPH–	p-XPhCH$_2$–OAc
MeO	0	0	10[b]	90
H	92	8	0	0
NO_2	100	0	0	0

[a] All product studies carried out at 65°C in the presence of urea. [b] See ref 17.

that greater progress along the traditional Winstein solvolysis scheme,[12] as would be the case[13] for a brosylate ion pair compared to a chloride ion pair, leads to an increasing percentage of alkene in the product distribution.

Furthermore, examination of the structure of II reveals that it is stereoelectronically unfavorable[14] for an E1 elimination, that is, the relevant σ bonds are not in the colinear relationship necessary for π-bond formation. This expectation was confirmed recently by the observed[15] solvolytic behavior of the parent compound, cyclobutylcarbinyl brosylate, which produced no cyclopentene while cyclopentyl brosylate, under the same reaction conditions, yielded 20% cyclopentene.

To further test Scheme I, the acetolysis products of 1-p-nitrophenylcyclobutylcarbinyl brosylate (4-NPh) and 1-p-methoxyphenylcyclobutylcarbinyl brosylate (4-MPh) have been determined in the presence of urea. Also, as a control experiment, the acetolysis products of 1-phenylcyclobutylcarbinyl brosylate (4-Ph) were redetermined in the presence of urea.

Based upon the known[1] product partitioning behavior of 4-Ph in acetic acid (without buffer) and the normal para-substituent effect behavior,[16] it was anticipated that acetolysis of 4-NPh would produce some ring-expanded ester while acetolysis of 4-MPh would yield some phenyl-rearranged ester.

As seen by the product data listed in Table II, the latter expectation was fulfilled but not the former. Thus the acetolysis of 4-MPh yielded 1-p-methoxybenzylcyclobutyl acetate (5) and a small amount[17] of 1-p-methoxyphenylcyclopentene, while acetolysis of 4-NPh yielded a single product, identified as 1-p-nitrobenzalcyclobutane (6).[18] The previously reported[1] products for the acetolysis of 4-Ph, in the absence of buffer, were replicated in the presence of urea.

The structures of the alkene products were identified by comparison of their GLC, ir, and NMR data with that of authentic reference samples. The structure of 1-p-nitrobenzalcyclobutane was established by oxidative cleavage of the 1,2-diol derivative to p-nitrobenzoic acid, and confirmed by mass spectral evidence (see Experimental Section for details); while the structure of 1-p-methoxybenzylcyclobutyl acetate was confirmed by GLC, ir, and NMR analysis (see Experimental Section for detail).

On the basis that cyclobutyl participation is more effective than methyl participation (cyclobutylcarbinyl brosylate solvolyzes some 200 times faster than isobutyl brosylate via a nearly exclusive k_Δ pathway in formic acid[15,19]), and the demonstrated[20] ability of a neighboring methyl group to compete with a neighboring p-nitrophenyl group in anchimerically assisting the solvolysis of p-nitroneophyl brosylate, it is intriguing that solvolysis of 4-NPh yields no detectable amount of ring-expanded product. Despite the p-nitro group's deactivation of the benzene ring in 4-NPh, aryl participation (k_2) dominates completely over cyclobutyl participation (k_4) in the partitioning of the first formed intimate ion-pair species.

This finding suggests that the relief of ring strain that normally[15,21] would accompany reorganization of I to IV is

reduced by the presence of the 1-*p*-nitrophenyl group, or more specifically the 1-*p*-nitrophenyl group introduces steric factors into the transition state leading to IV which reduce the magnitude of the expected steric strain relief associated with bridging. The present level of understanding[3c] of steric factors in intimate ion pairs is insufficient to permit productive speculation. Whatever the details as to the steric factors, the presence of the 1-*p*-nitrophenyl group in I unexpectedly inhibits ring expansion.

Experimental Section

Infrared spectra were obtained on a Bausch and Lomb IR-270 spectrophotometer, and the nuclear magnetic resonance spectra were taken on a Hitachi Perkin-Elmer R-24 instrument with tetramethylsilane as internal standard. A Beckman GC-4 chromatographic instrument equipped with a thermal conductivity detector, a Disc automatic integrator–printer, and a 6 ft × 0.125 in. column of 20% Carbowax 20M on Chromosorb W (80–100 mesh) was used for analytical GC work. The mass spectral analysis was carried out at Rockefeller University and the microanalysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

1-*p*-Methoxyphenylcyclobutylcarbinyl (4-MPh), 1-*p*-nitrophenylcyclobutylcarbinyl (4-NPh), and 1-*p*-phenylcyclobutylcarbinyl (4-Ph) brosylate were the same materials as previously described.[1]

Preparation of Reference Olefins and Esters. 1-Phenylcyclopentene was prepared via acid-catalyzed dehydration of 1-phenylcyclopentanol and the structure assignment was confirmed by NMR. 1-*p*-Anisylcyclopentene was prepared via acid-catalyzed dehydration of 1-*p*-anisylcyclopentanol, mp 86–86.5° (lit.[23] 87–90°). Analysis by GLC revealed the presence of a single compound and the NMR spectrum confirmed the structure assignment. 1-Phenylcyclobutylcarbinyl acetate, 1-*p*-methoxyphenylcyclobutylcarbinyl acetate, 1-*p*-nitrophenylcyclobutylcarbinyl acetate, and 1-phenylcyclopentyl acetate were prepared from their respective carbinols[1] with acetyl chloride in pyridine. Their purity and structure assignments were confirmed by GLC and NMR data.

Solvent. Acetic acid solvent was prepared from 994.9 ml of glacial acetic acid (Matheson Scientific, 99.8%) and 5.1 ml of acetic anhydride.

Acetolysis Product Studies. A. 1-Phenylcyclobutylcarbinyl Brosylate (4-Ph). A solution (50 ml, 0.25 *M*) of 1-phenylcyclobutylcarbinyl brosylate in acetic acid (0.3 *M* in urea) was sealed in ampoules under N_2 and immersed in a constant-temperature bath at 65 ± 0.1°. After 7 half-lives (ca. 22 hr) the solution was diluted with 200 ml of water and continuously extracted with ether for 48 hr. The ether extract was neutralized with cold saturated $NaHCO_3$ solution, washed four times with 60-ml portions of water, and dried ($MgSO_4$), and the solvent was removed by controlled distillation with a Nester-Faust NFA-200 annular still. The residue was further distilled to yield 1.75 g (97% yield) of distillate (boiling range 42–45°, 0.1 mm). The distillate on analysis by gas chromatography (175°, 35 ml/min He flow rate) gave rise to two peaks, A (4.2 min retention time) and B (7.1 min retention time), with 11.5:1 relative peak areas, in addition to the air peak. Under the same conditions 1-phenylcyclopentene gave rise to a peak with a 1.9-min retention time. Peak A was identified as 1-benzalcyclobutane and peak B as 1-benzylcyclobutene from the following facts: catalytic hydrogenation of the distillate over platinum oxide (Englehard Industries, 82.3%) in methanol (40 psi) yielded a product whose NMR spectrum agreed with that of benzylcyclobutane;[24] and 1-benzylcyclobutene was differentiated from 1-benzalcyclobutane by presence of benzylic protons (a sharp singlet at δ 3.12) in the NMR spectrum of peak B.

B. 1-*p*-Methoxyphenylcyclobutylcarbinyl Brosylate (4-MPh). 1-*p*-Methoxyphenylcyclobutylcarbinyl brosylate was solvolyzed and worked up as in section A with the exception that 25 ml of a 0.10 *M* solution of 4-MPh (0.12 *M* in urea) was used and the residue (0.7 g) was not distilled. The residue on analysis by gas chromatography (150°, 35 ml/min He flow rate) gave rise to two major peaks,[25] A (4.3-min retention time) and B (8.5-min retention time), with 1.0:11.2 relative peak areas.[26] The retention time for peak A is identical with that of authentic 1-*p*-methoxyphenylcyclopentene, and analysis by NMR revealed the presence of a multiplet at δ 6.0, typical of vinylic protons. Peak B was identified as 1-*p*-methoxybenzylcyclobutyl acetate from the following facts. Analysis by ir revealed the presence of a strong carbonyl stretching absorption at 1740 cm^{-1} and analysis by NMR gave the following spectrum: δ 7.0 (q, 4 H, aromatic), 3.7 (s, 3 H, typical *p*-MeO aryl protons), 1.6–2.6 (broad, 6 H, typical cyclobutane ring pattern), and 1.9 (s, 3 H, CH_3COO).

C. 1-*p*-Nitrophenylcyclobutylcarbinyl Brosylate (4-NPh). 1-*p*-Nitrophenylcyclobutylcarbinyl brosylate was solvolyzed as in section A with the exception that 50 ml of a 0.15 *M* solution of 4-NPh (0.18 *M* in urea) was used. After 7 half-lives (ca. 7 days), the solution was diluted with 200 ml of water and extracted six times with 50-ml portions of ether. The combined ether extracts were neutralized with cold saturated $NaHCO_3$, washed three times with 50-ml portions of water, and dried ($MgSO_4$) and most of the solvent was removed via rotovaporization to yield a dark orange oil. The oil was dissolved in 95% ethanol, treated with Norite A, and upon cooling to −10° the alcohol solution gave 1.37 g (7.25 mmol, 96.5% yield) of 1-*p*-nitrobenzalcyclobutane (**6**), light yellow crystals, mp 95.5–95.6°. Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.90; H, 5.82; N, 7.40. Found: C, 69.79; H, 5.73; N, 7.21. NMR (CCl_4) δ 8.06 (d, 2 H, aromatic), 7.45 (d, 2 H, aromatic), 6.32 (s, 1 H, vinylic,[27] 2.9–2.3 (broad, 4 H, cyclobutyl), 2.3–2.1 (m, 2 H, cyclobutyl). The mass spectrum of **6** showed *m/e* 91 (tropylum cation)[28] in addition to the molecular ion peak at *m/e* 189 and many other peaks. Additional definitive evidence for the assigned product structure of **6** was provided by the isolation of *p*-nitrobenzoic acid (mp 240–241°, lit.[29] mp 240–242°)[30] from the reaction of **6** with a mixture of potassium permanganate and potassium periodate in aqueous solution at pH 7.7.[31]

Registry No.—4-Ph, 50978-05-7; 4-MPh, 50978-03-5; 4-NPh, 50978-07-9; **5**, 57573-61-2; **6**, 57573-62-3.

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(16) For a recent discussion see C. D. Johnson, "The Hammett Equation", Cambridge University Press, New York, N.Y., 1973.
(17) Stability experiments revealed that under product run conditions (cf. Experimental Section), 1-*p*-methoxyphenylcyclobutyl acetate is converted into 1-*p*-methoxyphenylcyclopentene.
(18) The acetolysis of 1-*p*-nitrophenylcyclobutylcarbinyl brosylate thus provides a convenient synthesis of this new four-membered ring compound.
(19) In formic acid at 35° (sec^{-1}), *k* (isobutyl brosylate) = 0.82 × 10^{-6}; at 45°, 2.4 × 10^{-6}; at 55°, 7.9 × 10^{-6} (D. D. Roberts, unreported data).
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(25) The sample was not stable on the gas chromatograph and with increas-

ing temperature and prolonged retention time tended to pyrolyze, yielding additional unidentified peaks.

(26) As the sample aged, the ratio of the relative peak areas A:B increased; therefore, we assign production of 1-phenylcyclopentene to an isomerization reaction of 1-*p*-methoxybenzylcyclobutyl acetate. Such ready conversion of tertiary esters to alkenes has been previously observed.[15]

(27) The δ 6.32 value is consistent with that observed[20] for vinylic protons in β,β-dimethyl-*p*-nitrostyrene (a model for 1-*p*-nitrobenzalcyclobutane) and contrasts with the δ 5.97 value observed[20] for the vinylic protons in α,β-dimethyl-*p*-nitrostyrene (a model for 1-*p*-nitrophenylcyclopentene).

(28) The presence of the tropylium cation is consistent with a 1-*p*-nitrobenzalcyclobutane fragmentation reaction.

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1-Alkyl- (or aryl-) amino-2-methylpropane-2-thiols. Some Bi- and Tetradentate Nitrogen–Sulfur Ligands from Schiff's Base Disulfides

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Repetition of a published procedure for the preparation of several N-substituted 1-amino-2-methylpropane-2-thiols (**2a–d**) for use as bidentate ligands indicated that the products characterized therein were not thiols, but the corresponding disulfides (**3a–d**). Preparation of the authentic thiols was accomplished by reduction of the intermediate Schiff's bases (**1a–d**) with $LiAlH_4$ in refluxing tetrahydrofuran. The novel tetradentate **5** was also synthesized from **4** using the same procedure. The chelating ability of **5** was demonstrated by formation of a neutral Ni(II) complex. It was also shown that the 3-arylamino-5,5-dimethylthiazolidine-2-thiones (**6**) were obtained from both the thiols and disulfides, indicating that formation of this derivative does not prove the presence of a thiol function.

Nitrogen- and sulfur-donor ligand systems[1] are of continuing interest in coordination chemistry, and at our laboratory we are especially interested in complexes of molybdenum[2] and iron.[3] Recently, interesting properties have been found for complexes with tertiary thiol groups such as 3-mercaptovaline (penicillamine).[2c,4] We sought to synthesize a variety of such tertiary thiols (**2a–d**), and a straightforward route for these compounds had recently appeared in this journal.[5] This involved Schiff's base formation using α,α'-dithiodiisobutyraldehyde followed by reduction with $NaBH_4$ (Scheme I), and no difficulty was anticipated. This same route also appeared suitable for the novel tetradentate **5**, because the cyclic Schiff's base **4** was a known compound.[6] However, our attempts to repeat this synthetic sequence failed, and the preparation and characterization of these compounds by a revised procedure is the subject of this paper.

Attempts to make **2a** gave the viscous, pale yellow, nondistillable liquid previously described.[5] However, only 1–2% thiol was found (I_2 titration), and ir and NMR showed NH, but no SH. Molecular weight data were consistent with a dimer, which we assign as the disulfide **3a**. This is a surprising result because the reaction and subsequent work-up were conducted under argon. Neither diselenide-catalyzed hypophosphorous acid reduction[7] nor more vigorous $NaBH_4$ treatment (2 hr in refluxing acetonitrile) would cleave **3a**. The literature reveals tertiary disulfides to be fairly resistant to reduction; e.g., di-*tert*-butyl disulfide is resistant to $LiAlH_4$ in refluxing ether, but is reduced in refluxing tetrahydrofuran (THF),[8] and while penicillamine disulfide is little affected by $NaBH_4$ (50°),[9] it can be cleaved by Na–NH_3.[10] Treatment of either **3a** or its precursor **1a** with $LiAlH_4$ in THF gave the desired thiol as a distillable, mobile liquid (Table I), which exhibited an SH peak (NMR, ir) and the correct molecular weight, and consumed 2 equiv of iodine, a characteristic of some tertiary thiols (sulfenyl iodide formation).[11]

It was apparent that the previous report[5] of **2a** was in error, and that the others (**2b–d**) of interest to us were probably disulfides (**3b–d**) also. In order to test this, we repeated the synthesis of "**2b**", "**2c**", and "**2d**", reported to be a viscous, nondistillable liquid, a crystalline solid (mp 82–83°), and a volatile liquid [bp 113–114° (0.75 Torr)], respectively. Again the $NaBH_4$ reduction gave products with these same properties. These compounds were shown to be the disulfides **3b–d** by an analogous process. When these Schiff's bases (**1b–d**) were reduced with $LiAlH_4$ in THF,

Scheme I