o-Benzenedisulfonimide and Its Derivatives

JAMES B. HENDRICKSON, SHIGERU OKANO, AND RITA K. BLOOM

Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154

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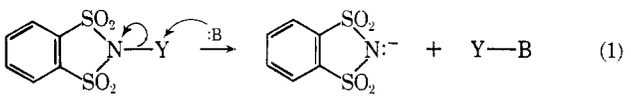
o-Benzenedisulfonimide is a strong acid, completely ionized in water, implying that the sulfonimide anion ($Z:^-$) is highly stabilized. Several N-substituted derivatives of *o*-benzenedisulfonimide (Z-H) were made to examine the activity of $Z:^-$ as a leaving group in these compounds, which include Z-Cl, Z-Br, Z-OH, Z-OCH_3, and Z-R; several other derivatives could not be prepared. The halides, Z-Cl and Z-Br, are very active sources of ionic positive halogen and halogenate aromatic rings with ease. The other derivatives were found not to have striking reactivity as reagents, and the leaving group activity of $Z:^-$ is inferred to be low.

The derivatives of *o*-benzenedisulfonimide (eq 1) should be especially attractive as synthetic tools, since the two sulfonyl groups flanking nitrogen provide substantial anionic charge stabilization so that the imide anion should be a good leaving group; furthermore, the diffusion of this charge should, conversely, make the imide anion a poor nucleophile[1] (*cf.* sulfate anion). These considerations can be synthetically useful in several ways, for the group Y is provided as certifiably cationic in reactions (eq 1) with anionic sites (:B), and



(1)

$$(Z{-}Y + :B \longrightarrow Z:^- + Y{-}B)$$

the imide anion product might be essentially uninvolvable as a nucleophile in subsequent reactions. Thus, a series of reagents, to act as Y^+, could be created with Y = halogen, OH, OR, CN, CHO, COOR, NO, NO_2, NH_2, etc.; furthermore, such reagents would be crystalline and so relatively easy to handle. Finally, relatively easy solvolytic cleavage of a C–N single bond should be made possible by conversion of a primary amine (RNH_2) to a sulfonimide (Y = R, eq 1) in order to take advantage of the better leaving group properties of the sulfonimide for displacement or elimination reactions. We have simplified discussion of these compounds by abbreviating the benzenedisulfonimido group as "Z" (eq 1) so that the parent imide is ZH, its salts $Z:^-$, and the reagents Z-Cl, Z-OH, Z-OR, etc.

o-Benzenedisulfonimide (ZH) was prepared as its ammonium salt from the action of ammonia on the disulfonyl chloride by Holleman[2] and by Hurtley and Smiles.[3] The free imide was shown to be fully ionized in (and not extractable from) water and said to possess acidity comparable to that of hydrochloric acid.[3,4]

The free imide, prepared by ion exchange, is a hydrate (hydronium salt, $H_3O^+Z:^-$), showing the same infrared bands for $Z:^-$ anion that are seen in the ammonium and silver salts. Anhydrous imide (ZH) may be crystallized from benzene after azeotropic water removal and shows a different infrared spectrum. The silver salt prepared from silver oxide and the ammonium salt ($NH_4^+Z:^-$)[3] is a silver–ammine complex,[6] while that from silver oxide and the hydrate is a hydrate. Anhydrous silver salt, required for the preparation of various Z-Y derivatives from Y-Cl, was obtained by heating the hydrated silver salt at 250° *in vacuo*.

N-Haloimides (Z-Cl, Z-Br).—In most common anhydrous solvents, halogenation of the dry silver salt yielded only free imide (and silver halide).[7] When the anhydrous silver imide was treated with chlorine in trifluoroacetic anhydride, however, the N-chloroimide (Z-Cl) was formed cleanly and could be separated in crystalline form by direct sublimation or, better (in over 80% yield), by evaporation, solution in phosphorus oxychloride to separate silver chloride, and subsequent recrystallization from trifluoroacetic acid to yield colorless crystals, mp 152–154°. Using bromine in the same procedure produced the N-bromoimide (Z-Br), mp 145–147°.

Both compounds gave a strong positive test with starch–iodide paper and reacted rapidly with tetrahydrofuran to negative starch–iodide and the production of Z-H. In methylene chloride, Z-Cl was stable overnight, but Z-Br had gone to negative starch–iodide in several hours. That Z-Cl was in fact a stronger chlorinating agent than chlorine was shown by the production of chlorine when Z-Cl was allowed to react with HCl.[8] Since the bromoimide was generally more reactive and unstable than the chloro derivative, it was no surprise that comparable iodination of the silver imide produced no iodoimide. The haloimides dissolve slowly in water to yield the free imide, ZH; they are not hygroscopic and keep very well in a refrigerated desiccator.

Halogenation of unactivated aromatic compounds proceeded efficiently with the N-haloimides in several exploratory experiments. With toluene, reaction is complete in less than 1 min (with benzene in *ca.* 0.5 hr) and the crude product contained no benzyl chloride, only nuclear-chlorinated products. This is confirmed by the isolation of a 4:7 mixture of *o*- and *p*-chlorophenylacetic acids, but no α-chlorophenylacetic acid, from the reaction with phenylacetic acid. Similarly, β-methylnaphthalene afforded a mixture of nuclear-chlorinated derivatives and no α-chloro derivatives in a very fast reaction. With Z-Br, some bromination on methyl was observed. Halogenation α to a ketone was also shown to be relatively easy in the reaction between

(1) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(2) A. F. Holleman, *Rec. Trav. Chim. Pays-Bas*, **40**, 446 (1921).

(3) W. R. H. Hurtley and S. Smiles, *J. Chem. Soc.*, 1821 (1926).

(4) The cyclic imide is too acidic to measure in water and is a much stronger acid than the acyclic bis(*p*-toluenesulfonyl)imide,[5] which is not substantially dissociated in water and is readily extractable with organic solvents.

(5) K. Ziegler, A. Späth, E. Schaaf, W. Schumann, and E. Winkelmann, *Ann. Chem.*, **551**, 80 (1942).

(6) This was shown by the isolation of the ammonium salt of the imide ($NH_4^+Z:^-$) after chlorination of this dried silver salt in anhydrous media.

(7) Bromination of ZH under conditions which N-brominated succinimide[5] similarly yielded only starting imide, as did the chlorination with calcium hypochlorite which had served to N-chlorinate bis(*p*-toluenesulfonyl)imide.[5]

(8) Z-Cl can in fact be isolated in this preparation only by virtue of the insolubility (and consequent slow reactivity) of the silver chloride produced.

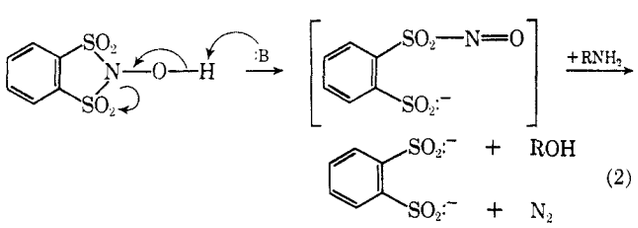
acetophenone and excess Z-Cl in refluxing methylene chloride overnight; these conditions produced phenacyl chloride in good yield even though no attempt was made to optimize the conditions. Z-H crystallized out during the reaction and presumably provided the acid catalysis required for initial enol formation.

The delocalization of charge in the imide ion led us to hope that the Z-Cl reagent might attack an isolated double bond by addition of Cl^+ and subsequent deprotonation to an allylic or vinylic chloride rather than by classical addition of the elements of Z and Cl. However, reaction with stilbene or cyclohexene at room temperature gave crystalline classical adducts (from both Z-Br and X-Cl) very rapidly and in good yield. We made a number of attempts to eliminate Z-H from these adducts (see Experimental Section), but recorded no practical success; in one instance, elimination of HCl rather than Z-H occurred in hot pyridine. The best procedure for elimination of Z-H from the stilbene adduct (Ph-CHCl-CHZ-Ph) was vacuum sublimation at 170°. Solvolysis of the stilbene adduct in boiling aqueous ethanol afforded Z-H quantitatively as well as a mixture of products, including diphenylacetaldehyde and 1-hydroxy-2-chloro-1,2-diphenylethane.

N-Hydroxyimide (Z-OH).—This compound was first prepared by Hurtley and Smiles[3] by reduction of *o*-benzenedisulfonyl chloride with sodium sulfite followed by nitrosation. The first step affords *o*-benzenedisulfinic acid, which we have isolated and characterized; the isolated acid reacts smoothly with nitrous acid to produce Z-OH.[9] It is a rather strong acid ($pK_a \sim 1$; compare HOCl, $pK_a = 7.5$) and is reduced to Z-H by sulfur dioxide.[3]

The hydroxyimide was investigated as a potential source of "$^+$OH," similar to a peracid, but showed no practical success either as a Baeyer–Villiger reagent or as a useful agent to convert aldehydes to acids. In most instances, under acidic or neutral conditions, the Z-OH was largely consumed or destroyed without substantial change in the substrate. On long standing at room temperature, crystalline Z-OH produced Z-H and *o*-benzenedisulfinic acid in fair quantities.

The silver salt (Z-OAg) was explored for oxidative halide displacement (*cf.* $R\text{-}CH_2X + Z\text{-}OAg \rightarrow AgX + [R\text{-}CH_2\text{-}O\text{-}Z] \rightarrow RCHO + ZH$). However, it was not possible to prepare an anhydrous silver salt, and the desired reaction was not observed. The hydroxyimide does, however, react as a nitrosating agent, bubbling immediately on contact with ammonia and primary amines and yielding the N-nitroso derivative with dicyclohexylamine in moderate yield. The reaction appears to proceed as outlined in eq 2.

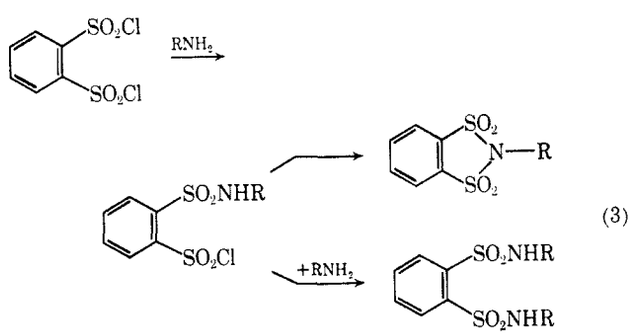


(2)

(9) The original authors reported the hydroxyimide as a hydrate, mp 90°, whereas their procedure in our hands produces a solid melting at 128–130°, also clearly a hydrate from the ir spectrum. With acetyl chloride, the compound forms an acetate, with correct analyses by combustion, mass spectrum, and nmr, which may be saponified to the starting Z-OH, so that we feel that its constitution is clear despite the melting-point discrepancy.

The methoxyimide ($Z\text{-}OCH_3$) was successfully prepared only with diazomethane on Z-OH. This derivative was inert to reaction with amines and was generally more stable than Z-OH. It showed no activity as a transfer agent for positive methoxyl with substrates like dimethylaniline and dimedone triethylamine. In the latter case, small amounts of the formaldehyde–dimedone adduct were obtained, but no trace of methoxydimedone.

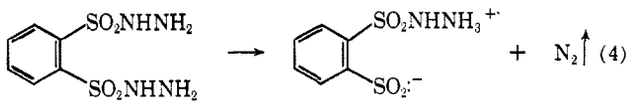
N-Alkylimides (Z-R).—Conversion of a primary amine into a leaving group to facilitate a C–N bond cleavage is at present a synthetically difficult or unreliable process. We considered conversion into a cyclic disulfonimide for this purpose; *i.e.*, reaction with *o*-benzenedisulfonyl chloride to convert $R\text{-}NH_2$ into R-Z. With ammonia and with aniline[3] the reaction is essentially quantitative, but with other primary amines we obtained mixtures of the cyclic imide (Z-R) and the bis-sulfonamide, *i.e.*, N,N′-dialkyl-*o*-benzenedisulfonamide, usually predominating in the latter. A series of experiments on benzylamine, altering conditions so as to favor internal over external sulfonation in the second mechanistic step (eq 3), led to very little variation in this result.



(3)

The best procedure afforded 35% cyclic imide from benzylamine, 51% from phenethylamine. The products were always easily separable chromatographically, so that pure imide samples were available for tests of the ease of C–N bond cleavage in these derivatives. In general, they were surprisingly inert. Reaction of the benzylimide ($Z\text{-}CH_2Ph$) with sodium cyanide for 5 hr at 100° in dimethylformamide resulted in recovery of 35% unchanged benzylimide. Elimination of Z-H from the phenethylimide ($PhCH_2CH_2Z$) was attempted using base or sublimation at elevated temperatures, but similarly resulted in very little styrene (<10% isolated as the dibromide). Thus, the initial trials do not support our original presumption that $Z:^-$ would act as a facile and useful leaving group.

Other Derivatives.—Generation of the N-aminoimide ($Z\text{-}NH_2$) was attempted *via* *o*-benzenedisulfonyl chloride reaction with hydrazine and its derivatives. In all cases, only bishydrazides were produced. The parent *o*-benzenedisulfonhydrazide, from hydrazine itself, yielded *o*-benzenedisulfonyl azide on reaction with nitrous acid, and also slowly dissolves in water with evolution of a gas. The product of this reaction is the rather unstable internal salt of *o*-sulfonhydrazidesulfinic acid (eq 4). Our efforts to close this salt to the N-amino



(4)

imide (Z-NH_2) with mild halogenation led only to the disulfonic acid. Some efforts were directed toward the synthesis of other reagents, Z-Y, where Y = CHO, CN, SO_2R, etc., but at present it is clear either that these compounds are not easily made or that their decomposition is extremely facile. In carbon tetrachloride, the anhydrous silver salt and gaseous nitrosyl chloride yielded only Z-H. In refluxing anhydrous acetonitrile, the silver salt was unaffected by cyanogen bromide, while in refluxing tetrachloroethane, silver bromide was precipitated but the filtrate yielded only Z-H on evaporation, a result which may reflect reaction with solvent. Similarly, the silver salt did not react with toluenesulfonyl chloride at room temperature in 2 days.

In summary, our initial trials seem to indicate that of the possible reagents, Z-Y, only the ionic halogenating agents, Z-Cl and Z-Br, have any reagent value, being very clean and active agents for halogenating unactivated aromatic rings. The hydroxyimide, Z-OH, decomposes by various routes, none of which is an active hydroxylating agent, while Z-R and Z-OCH_3 are surprisingly inert to nucleophilic attack aimed at releasing $Z:^-$. Z-NH_2 could not be prepared and no reliable route to Z-R applicable to all cases tried could be worked out.

Experimental Section[10]

o-Benzenedisulfonimide (ZH) and NH_4^+ Salt.—1.0 g o-benzenedisulfonyl chloride[2,3]/20 ml C_6H_6. Added 30 ml 3.4 *M* NH_3/C_2H_5OH in 10-ml portions. After 1 hr NH_4Cl ppt filtered and soln evap to 0.86 g (~100%) crystalline salt, mp 250–4° (lit.[2] 254°); sweet taste. Ir: 2.8, 3.2, 6.1 (w), 7.1, 7.8, 8.7–9.0, 9.5, 10.0 μ. Soln in H_2O and filtration yielded solid bisamide, 20 mg (2.3%), mp 330° dec (lit.[11] 335–8° dec). H_2O soln of salt through 30 g column/Dowex 50 × 8 resin (H^+), evap to hygroscopic crystals, dried/vac/100° to 0.59 g (79%), mp 190–3° (lit.[2] 192°). Ir: 2.8, 6.1, 7.8, 8.7–9.0, 9.5, 10.0 μ.

Anhydrous imide by boiling down C_6H_6 soln and cooling, crystals, mp 195–6°. Ir: 3.2, 7.30, 8.55, 9.50 μ. Nmr: imide hydrate (DMSO-d_6), 2.23 (s), 5.45 (m, disappears/D_2O); anhydrous (Me_2CO-d_6), 1.83 (s); NH_4^+ salt (Me_2CO-d_6), 2.10 (s), 6.48 (~s). Neither $NH_4^+Z^-$ nor *t*-$BuNH_3^+Z^-$ salts yielded ZH on pyrolysis/vac.

o-Benzenedisulfonimide Silver Salt (Z^-Ag^+).—Equimolar ZH (hydrate) and $AgNO_3/H_2O$ → ppt/$Z^-Ag^+ \cdot H_2O$. Ir: 2.8, 6.1, 7.8, 8.7–9.0, 9.5, 10.0 μ. Pulverize and Δ/vac/230–250°/1 hr to yellowish powder (loss of ir peaks at 2.8, 6.1 μ), used as is as anhydrous Z^-Ag^+. This salt with HCl/H_2O → ppt/AgCl (100%) and evap/filtrate → ZH (hydrate), mp and mmp 190–193°.

N-Chloro-o-benzenedisulfonimide (Z-Cl).—1.12 g anhyd ZAg/5 ml $(CF_3CO)_2O$. Passed in Cl_2 (dried/H_2SO_4)/3 hr. Evap, added 8 ml $POCl_3$, filtered AgCl ppt (~100%). Filtrate + large vol/CCl_4 → white crystals, 0.45 g, mp 150–1°; second crop/evap, 0.86 g, mp 132–7° (total >90%). Recryst/dry CF_3COOH, mp 152–4°, mmp with ZH, 133–5°. ZCl stable in desiccator/refrigerator, strong KI test. Ir: 7.3, 8.3, 8.4, 8.9 μ. Nmr ($CDCl_3$): τ 1.80 (s).

Anal. Calcd for $C_6H_4NS_2O_4Cl$: C, 28.45; H, 1.58; N, 5.54; Cl, 14.01. Found: C, 28.35; H, 1.58; N, 5.71; Cl, 13.92.

Z-Cl: sol/CH_2Cl_2 or $CHCl_3$, retaining KI-positive overnight, sol/C_6H_6 but destroyed overnight (or 0.5 hr/reflux). Reaction/H_2O or THF exothermic and → ZH, mp 191–4°. Reaction/CH_3OH required 3 days. Reaction/HCl (anhyd): 0.13 ml H_2O/8 ml $SOCl_2$ stood 4 hr, then 25 mg ZCl, reflux 0.5 hr, evap to white crystals, mp and mmp 194–6° (no reaction/$SOCl_2$ alone).

N-Bromo-o-benzenedisulfonimide (Z-Br).—1.16 g anhyd ZAg/5 ml $(CF_3CO)_2O$. Added 0.62 g Br_2, stirred 4 hr: Br_2 color gone and no Ag^+ ppt/HCl. Evap, added 10 ml $POCl_3$, filtered AgBr ppt (0.63 g, 94%), evap to residue. Sublimed to 0.89 g (84%) white crystals/ZBr, mp 137–42°. Recryst/dry CF_3COOH, mp 145–9°. Ir: <12 μ very similar to Z-Cl.

Reactions of Z-Cl with Aromatics.—Reaction/$C_6H_5CH_3$ very fast/25°. Nmr: τ 2.7 (m), 7.62–7.67 (3 singlets), no $C_6H_5CH_2Cl$ methylene. Reaction/2-methylnaphthalene (50 mg)/3 ml CH_2Cl_2 + 89 mg Z-Cl exothermic. Partition/H_2O–CH_2Cl_2 gave 75 mg ZH (~100%) from H_2O, and from CH_2Cl_2 55 mg oil (no starting material). Nmr: τ 2.0–2.7 (m, ~6 H), 7.40 (s, 3 H), no aromatic $-CH_2Cl$. With Z-Br ~1:4 mix/aliphatic: aromatic from nmr singlets at τ 5.28 and 7.35.

Reaction/$C_6H_5CH_2COOH$ (30 mg)/1 ml CH_2Cl_2 + 56 mg Z-Cl/1 ml CH_2Cl_2 6 hr/25° (positive KI), then overnight/reflux. Crystalline ppt/ZH (mp 192–3°) filtered, H_2O added and partitioned. CH_2Cl_2 evap to 37 mg colorless crystals, mp 55–75°. Ir 3.3 (broad), 5.82 μ. Nmr: τ 2.77 (m), 6.21 (s), 6.36 (s); intensities (resp) = 47, 14, 3, 5, indicating 13% starting acid (τ 6.36) owing to insufficient Z-Cl, 23% *ortho*, and 64% *p*-chlorophenylacetic acids and no α-chloro acid.

Reaction/$C_6H_5COCH_3$ (10 mg) + 25 mg Z-Cl/2 ml CH_2Cl_2 required overnight/reflux for completion (by KI). Washed/H_2O + evap to 10 mg, recryst/petrol ether to mp 52–3°, mmp (with $C_6H_5COCH_2Cl$, mp 53–5°) 53–5°.

Reaction of Z-Cl with Olefins. A. Cyclohexene.—1.0 g ZCl + 3 ml C_6H_{10}/10 ml CH_2Cl_2 exothermic, KI neg. Turned dark blue/standing, some ppt/ZH. Washed/H_2O, dried, evap to 0.87 g (67%) dark crystals; recryst/C_6H_6–Et_2O to white crystals mp 202–4°. Ir: 7.45, 8.30, 8.50, 9.35 μ. Nmr: τ 1.90 (s, 4 H), 5.0–6.0 (m, 2 H), 7.3–8.8 (m, 8 H).

Anal. Calcd for $C_{12}H_{14}S_2O_2NCl$: C, 42.93; H, 4.20; N, 4.17. Found: C, 43.17; H, 4.02; N, 3.91.

Adduct (82 mg) + 28 mg *t*-BuOK/5 ml dry *t*-BuOH/3 days/25°: tlc showed unchanged adduct. Reflux/2 hr, normal work-up → adduct unchanged (ir). Adduct refluxed/5 hr/50% aq HOAc + 1 hr/70% also unchanged. 50 mg adduct/1 ml quinoline/200°/1 hr and dark mixture partitioned/H_2O–CH_2Cl_2, washed/HCl, dried + evap to 34 mg, largely starting adduct by ir + tlc. Adduct sublimed unchanged at 120–180°/~40 μ.

B. Stilbene.—0.50 g *trans*-stilbene/10 ml CH_2Cl_2 + 1.05 g (1.5 equiv) Z-Cl added in portions and boiled. First portions = immediate KI neg. Final = KI pos and no stilbene/tlc. Washed/H_2O and recovered 0.41 g ZH/H_2O. CH_2Cl_2 evap to 1.20 g (~100%) colorless crystals (one spot/tlc), mp 110–150° after recryst/C_6H_6–C_2H_5OH; second crop, mp 158–161°. Fortuitous crystallization in some runs yielded mp 70–90°. All had similar ir (7.4, 8.3, 8.5 μ). Nmr showed mixture/diastereomers: τ 2.0–3.0 (m, ~14 H), 3.75 (d, *J* = 1.5), 3.93 (d, *J* = 1.5), 4.22 (d, *J* = 4.5), 4.40 (d, *J* = 4.5). Sum of doublets ~2 H in varying ratios. Positive Beilstein test.

Adduct, mp 70–90°, refluxed/C_5H_5N. No change/20 hr. Adduct, mp 110–150°, refluxed/C_5H_5N/4 hr, partitioned/HCl_{aq}–CH_2Cl_2 to oil (~50% wt) which yielded 8 mg crystals (from 21 mg/oil), mp 160–1°, from C_2H_5OH, neg Beilstein test. Ir: 7.30, 8.50 μ; λ_{max} 230, 310 mμ. Nmr: τ 212 (s, 4 H), 2.3–2.8 (m, ~11 H) and no other peaks.

Adduct (50 mg), mp 70–90°, refluxed/95% C_2H_5OH/1 hr, partitioned/H_2O–C_6H_6 to 26 mg (~100%) ZH, mp 189–191°, from H_2O, from C_6H_6, 26 mg (colorless oil, pos Beilstein test. Ir: 2.80, 5.80 μ (no SO_2 peaks). Nmr: τ 0.12 (d, *J* = 2.5), 2.7–2.9 (m), 5.0–5.3 (m), intensities ~0.3, 12, 2 (resp). 2,4-DNPH yielded 10 mg golden crystals, recryst to 147–9° [lit.[12] for $(C_6H_5)_2CHCHO$ deriv, 149–50°].

Adduct (80 mg), mp 110–150°, sublimed (160–170°/~20 μ) to 22 mg (56%) $C_6H_5CH{=}CClC_6H_5$, mp 40–42°. Nmr: τ 2–2.8 (m, 10 H), 8.95 (s, 1 H) and 37 mg off-white solid which yielded 30 mg (74%) ZH, mp and mmp 193–5° and 7 mg (8%) of starting adduct (by ir).

N-Hydroxy-o-benzenedisulfonimide (Z-OH).—Reduction/disulfonyl chloride by Na_2SO_3 followed by HNO_2 gave Z-OH (83%), white crystals, mp 128–130° (lit.[3,9] 90–1°). Ir: 2.80, 6.15 (w), 7.20, 7.35, 8.30, 8.50 μ. Nmr: τ 1.5–2.1 (sym multiplet). Reduction/Z-OH with 10% aq SO_2 in C_2H_5OH/50–60°/3 hr, evap + recrystallize to ZH, mp 190°. Analysis showed ZOH·H_2O[3] and efforts to dehydrate failed, usually giving ZH.

(10) Melting points on Fisher-Johns block, uncorrected. Ir in KBr unless noted, on a Perkin-Elmer Infracord; nmr with Me_4Si on Varian A-60A given in τ units.

(11) W. V. Farrav, *J. Chem. Soc.*, 3063 (1960).

(12) T. A. Favorskaya and L. A. Remizova, *Zh. Obshch. Khim.*, **23**, 817 (1953).

TABLE I
OXIDATIONS WITH N-HYDROXYIMIDE (Z-OH)

Substrate	Acid catalyst	Solvent	Reaction temp and time, hr	Acid yield, %	Recovered Z-OH, %	Recovered substrate, %
Anisaldehyde	Toluenesulfonic acid (catalytic)	THF	RT, 18	0	40	100
Anisaldehyde	Toluenesulfonic acid (catalytic)	THF	Reflux, 4	0	24	90
Phenylacetaldehyde	Toluenesulfonic acid (catalytic)	THF	RT, 16	0	35	50
Anisaldehyde	Boron trifluoride etherate (1 equiv)	Acetonitrile	Reflux, 6.5	13	0	60
Anisaldehyde	Boron trifluoride etherate (1 equiv)	Acetonitrile	Reflux, 23	12	0	81
Anisaldehyde[a]	Boron trifluoride etherate (1 equiv)	Acetonitrile	Reflux, 16	0		
Phenylacetaldehyde	Boron trifluoride etherate (1 equiv)	Acetonitrile	Reflux, 17	0		
Deoxybenzoin	Boron trifluoride etherate (1 equiv)	Acetonitrile	Reflux, 16			73

[a] No Z-OH.

Ag salt (Z-OAg): 100 mg Z-OH + 54 mg Ag_2CO_3/3.5 ml H_2O/N_2/stirring 1 hr. Gas evolved and color = brown → white, 117 mg (87%) solid filtered. Attempts to dry gave dec. Ir showed H_2O (2.9, 6.1, 7.2, 7.35, 8.3, 8.5 μ).

o-Benzenedisulfinic Acid.—Reduction/disulfonyl chloride by Na_2SO_3 and evap H_2O to syrup. Added CH_2Cl_2 and 30% H_2SO_4/0°. Satd H_2O/NaCl and ext/CH_2Cl_2, dried + evap to 0.30 g crystals, mp 113–5° from 0.50 g disulfonyl chloride (80%). Ir: 2.85, 3.2, 8.75, 8.85 μ. Suspension in dil aq H_2SO_4 and addn/$NaNO_2$ gave Z-OH. Disulfinic acid stable in refrigerator.

Reactions of Z-OH. A. With Amines.—Z-OH bubbles (odorless, not SO_2) vigorously with aq NH_3 or RNH_2/Et_2O (used as diagnostic). $C_6H_5CH_2NH_2$ yielded white ppt (ir: 3–3.7, 3.85, 10, 10.6 μ) identical (ir) to ppt from o-benzenedisulfonic acid + the amine. Z-OH (100 mg, 0.4 mmol) + 790 mg (4.1 mmol) dicyclohexylamine mixed/15 min. Partitioned/Et_2O–2% HCl to 15 mg crystals (17%) from Et_2O, recryst $(CH_3)_2CO$, mp 105–6°. Mmp/authentic N-nitroso-dicyclohexylamine (mp 104.5–6°), 104.5–6°.

B. With Aldehydes.—Equimolar Z-OH + aldehydes (with added acid) stirred as shown in Table I. Work-up by pouring on Et_2O–ice and ext Et_2O/aq $NaHCO_3$, dried + evap to unchanged aldehyde. Acidification/aq $NaHCO_3$ and extn/CH_2Cl_2 gave Z-OH and/or acid.

N-Methoxy-o-benzenedisulfonimide (Z-OCH$_3$).—Excess CH_2N_2/Et_2O (dried/KOH) added to 0.30 g Z-OH; N_2 bubbled vigorously. After 0.5 hr, filtered + evap to 0.20 g crystals, recryst/hexane–CCl_4 to mp 180–3°. Ir: 7.15, 7.30, 8.30, 8.50 μ. Nmr ($CDCl_3$): τ 2.06 (s, 4 H), 5.90 (s, 3 H).

A. With $C_6H_5N(CH_3)_2$.—60 mg (0.24 mmol) Z-OH + 29 mg (0.24 mmol) $C_6H_5N(CH_3)_2$/2 ml CH_2Cl_2/24 hr. Tlc shows starting materials still present. 2 ml s-$C_2H_2Cl_4$ added and evap CH_2Cl_2. Refluxed/5 hr. Purple mix onto ice–10% HCl and ext/CH_2Cl_2, dried + evap to dark solid, 40 mg (66%), ir and tlc identical with Z-OCH$_3$. Acid layer + 50% NaOH and ext/CH_2Cl_2 to 15 mg residue, seven spots/tlc.

B. With Dimedone.—100 mg (0.4 mmol) ZOCH$_3$ + 56 mg (0.4 mmol) dimedone + 43 mg (0.43 mmol) Et_3N/5 ml CH_3CN refluxed 40 hr. Evap, partitioned/CH_2Cl_2–10% NaOH. Evap/CH_2Cl_2 gave 22 mg (22%) Z-OCH$_3$. Aq NaOH acidified/conc HCl + ext/CH_2Cl_2 to 43 mg yellow solid. Nmr (C_5D_5N): τ 7.65 (s), 7.70 (m), 8.98 (s), 9.07 (m). Tlc gave 10 mg (18%) dimedone and 7 mg (6%) dimedone–CH_2O adduct, recryst/C_2H_5OH to mp 194°, mmp/authentic sample (mp 194°), 194°.

N-Acetoxy-o-benzenedisulfonimide (Z-OCOCH$_3$).—0.50 g Z-OH + 10 ml CH_3COCl/stirred 2 days, mostly dissolved. Filtered + evap to 0.58 g crystals, mp 128–132°, recryst/C_6H_6 to mp 128–130°, mmp/Z-OH, 118–119°. Ir: 5.50, 7.15, 7.30, 8.3, 8.4, 8.6 μ. Nmr ($CDCl_3$): τ 2.00 (s, 4 H), 7.80 (s, 3 H). Crystals slowly dissolved/10% NaOH. After 15 min, acidified to crystalline ppt, mp 128–130°, identical with Z-OH by ir.

Anal. Calcd for $C_8H_7NS_2O_6$: C, 34.68; H, 2.53; N, 5.08; S, 23.10. Found: C, 34.62; H, 2.37; N, 5.61; S, 23.04.

N-Benzyl-o-benzenedisulfonimide (ZCH$_2$Ph) and N,N'-Dibenzyl-o-benzenedisulfonamide. A.—Following lit.[3]: 160 mg o-benzenedisulfonyl chloride added to C_2H_5OH soln of 320 mg (4 equiv) $PhCH_2NH_2$ and 320 mg NaOAc. 3 hr/reflux, filtered + cooled: 62 mg (36%) ZCH_2Ph crystals, mp 150–1°. Ir: 7.45, 8.35, 8.50 μ. Nmr ($CDCl_3$): τ 2.33 (d, 4 H), 2.53 (m, 5 H), 5.10 (s, 2 H).

Anal. Calcd for $C_{13}H_{11}S_2O_4N$: C, 50.48; H, 3.58; N, 4.53. Found: C, 50.61; H, 3.52; N, 4.37.

Filtrate evap + crystallized/aq C_2H_5OH to 28 mg (12%) bisamide, mp 105–7°. Ir: 2.98, 7.55, 8.60, 8.70 μ. Nmr ($CDCl_3$): 2 equiv groups (~4 peaks each) at τ 1.96, 2.48 (total = 4 H), 2.87 (s, 10 H), 3.36 (t, 2 H, J = 6, disappeared/D_2O), 5.84 (d, 4 H, J = 6, → singlet/D_2O). In general, all imides observed showed a singlet (4 H) ~τ 2 and o-sulfonyl bis derivatives a broad multiplet ~1.8–2.4. Mother liquors = only these two spots/tlc (bis amide predominant).

B.—A series of efforts made to favor cyclization (eq 3) are shown in Table II.

C.—o-Benzenedisulfonic anhydride (56 mg) + 36 mg $C_6H_5CH_2NH_2/CH_2Cl_2$ refluxed/3 hr. Evap, added THF, refluxed 1 hr; added 0.5 g PCl_5, refluxed 1 hr. Poured/H_2O, ext/C_6H_6 to dark oil containing phosphorus: Tlc = ZCH_2Ph, no bis amide; other side products were present and product did not crystallize.

Reactions of N-Benzyl-o-benzenedisulfonimide (ZCH$_2$Ph). A.—NaCN (163 mg, 0.33 mmol, finely ground) + 103 mg (0.33 mmol) ZCH_2Ph/3.5 ml DMF stirred/95°/5 hr. Cooled, partitioned/10% $NaHCO_3$–CH_2Cl_2. CH_2Cl_2 washed/HCl, dried, evap to 36 mg (35%) recovered ZCH_2Ph.

B.—ZCH_2Ph (77 mg, 0.25 mmol) refluxed (suspension) 20 hr in 5 ml 50% aq C_2H_5OH. Cooled, crystallized 16 mg (21%) $ZCH_2C_6H_5$. Filtrate evap and partitioned/H_2O–CH_2Cl_2 gave 8 mg colorless oil. Reaction/3,5-dinitrobenzoyl Cl and tlc gave 8 mg solid, recryst/C_2H_5OH–H_2O to 5 mg mp 112.5–113°. Mmp/authentic benzyl 3,5-dinitrobenzoate (mp 113°), 114.5–115°.

N-(β-Phenethyl)-o-benzenedisulfonimide (ZCH$_2$CH$_2$Ph).—o-Benzenedisulfonyl chloride (100 mg, 0.36 mmol) added to 177 mg (1.46 mmol) $PhCH_2CH_2NH_2$ + 177 mg (2.18 mmol) NaOAc/10 ml EtOH, refluxed 3 hr, cooled, filtered. 9 mg (6%) crystals of bis amide, recryst/EtOH, mp 176–8°. Ir: 3.0, 7.55, 8.65 μ. Nmr ($CDCl_3$): two groups at τ 2 (4 H), 2.75 (m, 10 H), 3.75 (2 H, disappeared/D_2O, 6.8 (m, 4 H), 7.25 (m, 4 H). Filtrate

TABLE II

BENZYLAMINE REACTION WITH *o*-BENZENEDISULFONYL CHLORIDE

No.	Mole ratio of amine:chloride	Solvent	Base[a]	Time/temp[b]	Product ratio[c] of imide:bis amide
1	4:1	THF	5% aq NaOH	0.5 hr/RT	80%[c]
2	3:1	C_6H_6	NaH[d]	0.5 hr/Δ	56%[c]
3	4:1	$(CH_3O)_3B$		2 hr/Δ	56%[c]
4	1:1	C_6H_6	$BF_3 \cdot Et_2O$ (4) + C_5H_5N (4)	4 hr/Δ	1:3
5	1:1	C_6H_6	Et_3N	5 min/RT	1:1
6	1:1[e]	C_6H_6	C_5H_5N	1 hr/RT	1:4
7	1:1	CH_2Cl_2	Et_3N (1)[f]	0.5 hr/RT	3:2
8	1:1[e]	*t*-BuOH	*t*-BuO^- (2)	3 hr/RT	1:1
9	1:1[e]	*t*-BuOH	*t*-BuO^- (2)	4 hr/Δ	1:1

[a] Excess base, except (no./equiv) in parentheses. [b] RT = room temp; Δ = reflux. [c] Isolated yield of bis amide noted. [d] Amine added first to NaH. [e] Slow addition of amine last, over 0.5–1 hr. [f] 1 equiv of base first (with chloride), then slow addition of amine followed by excess base.

cooled. 42 mg (36%) crystalline ZCH_2CH_2Ph sublimed to colorless crystals, mp 112–3°. Ir: 7.40, 8.42, 8.62 μ. Nmr: τ 2.05 (d, 4 H), 2.68 (s, 5 H), 5.89–6.92 (m, 4 H). Second crop 17 mg (14%) ZCH_2CH_2Ph (total yield 50%).

Reactions of ZCH_2CH_2Ph.—84% recovery from 24 hr/100°/C_5H_5N + 1 equiv Et_3N. At 170°/N_2/2 hr in 1,5-diazabicyclo-[4.3.0]-5-nonene, ZCH_2CH_2Ph was destroyed. Residue + Br_2 yielded 5% $PhCHBrCH_2Br$.

161 mg (0.5 mmol) ZCH_2CH_2Ph + 112 mg (2 mmol) KOH ground + Δ/N_2/180°/80 mm/2 hr. Distillate + $Br_2/CHCl_3$ → 14 mg (11%) $PhCHBrCH_2Br$, recryst/aq EtOH to mp 72–3° (lit.[13] 74°).

***o*-Benzenedisulfonhydrazide.**—0.30 g 95% NH_2NH_2/8 ml EtOH. Added disulfonyl chloride (0.8 g)/15 ml C_6H_6/0°. After 5 min filtered crystals, washed/H_2O + C_6H_6. 0.45 g (67%), mp 123–6°; recryst/THF–petrol ether, mp 126–8°. Ir: 2.92, 3.03, 7.50, 8.58 μ. Nmr: τ 1.8–2.4 (m, 4 H), 6.3 (m, ~5 H), disappears/D_2O).

Anal. Calcd for $C_6H_{10}S_2O_4N_4$: C, 27.05; H, 3.77; N, 21.05; S, 24.05. Found: C, 27.32; H, 3.80; N, 21.23; S, 23.81.

Suspension/hydrazide (50 mg)/H_2O slowly bubbles + soln overnight. Evap/vac/RT to 42 mg (98%) white solid, mp ~70° (bubbles), insol/$CHCl_3$. Ir: 3–4 (br), 7.5, 8.6, 9.9, 10.5 μ. Solid goes gummy in 2 days or on recryst. Hydrazide/H_2O + Br_2: bubbles, decolorizes. Evap to crystals, ir identical with *o*-benzenedisulfonic acid.

22 mg white solid/CH_3OH + 13 mg *p*-$MeOC_6H_4CHO$ → 19 mg (76%) azine (*p*-$MeOC_6H_4CH{=}N)_2$ identified with authentic sample.

***o*-Benzenedisulfonyl Azide.**—30 mg hydrazide + 5 ml/20% aq H_2SO_4. Added 50 mg $NaNO_2/H_2O$. Ppt 25 mg, mp 112–4°, identical with authentic sample from disulfonyl Cl with NaN_3. Ir: 4.60, 7.24, 7.32, 8.5 μ. Ms: 246 (p − 42) but no parent at 288.

Anal. Calcd for $C_6H_4S_2O_4N_6$: C, 25.05; H, 139; N, 29.21; S, 22.22. Found: C, 24.79; H, 1.41; N, 29.03; S, 22.51.

Registry No.—ZH, 4482-01-3; Z-Cl, 21691-08-7; Z-Br, 21691-09-8; Z-OCH_3, 21691-10-1; Z-$OCOCH_3$, 21691-11-2; ZCH_2Ph, 21748-37-8; ZCH_2CH_2Ph, 21691-12-3; Z-Cl, cyclohexene adduct, 21691-13-4; *o*-benzenedisulfinic acid, 21691-14-5; N,N′-dibenzyl-*o*-benzenedisulfonamide, 21691-15-6; *o*-benzenedisulfonhydrazide, 21691-16-7; *o*-benzenedisulfonyl azide, 21691-17-8.

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(13) C. Glaser, *Ann. Chem.*, **154**, 154 (1870).

The Preparation and Reactions of Perfluoro-β-oxa-δ-valerolactone

JAMES R. THROCKMORTON

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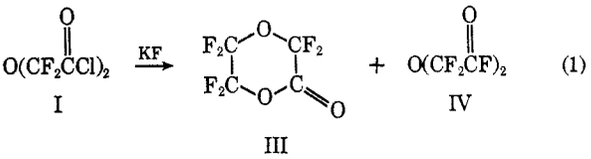
The preparation of perfluoro-β-oxa-δ-valerolactone (III) from perfluorooxydiacetyl chloride (I) and fluoride (IV) and metal fluorides is described. Reaction of III with excess water, methanol, and ammonia gives perfluorooxydiacetic acid, dimethylperfluorooxy diacetate, and perfluorooxydiacetamide, respectively. Ultraviolet irradiation of III gives perfluoro-1,3-dioxolane (V).

In a study of the chemistry of certain perfluoroacyl halides, it has been found that perfluoro-β-oxa-δ-valerolactone is formed when perfluorooxydiacetyl chloride or fluoride is allowed to react with metal fluorides. It is the purpose of this paper to describe the preparation and some chemical reactions of perfluoro-β-oxa-δ-valerolactone, and to describe the formation of perfluoro-1,3-dioxolane from the photolytic decarbonylation of this new lactone.

The reaction of perfluorooxydiacetyl chloride (I) with anhydrous potassium fluoride (eq 1) proceeded smoothly giving a 90% yield of perfluorinated product which was found to contain 44% perfluoro-β-oxa-δ-valerolactone (III) and 56% perfluorooxydiacetyl fluoride[1] (IV). Fractional distillation afforded pure



I III IV (1)

samples of the two isomeric products which were readily differentiated by spectroscopic analyses, and further characterized by elemental analysis.

(1) J. L. Warnell, U. S. Patent 3,250,806 (1966).