A New and Simple Synthesis of Alkyl, Cycloalkyl, and Aralkyl Diselenides from Aliphatic and Aromatic Aldehydes. Aliphatic Ketones and Cyclo Ketones

Victor Israel Cohen

Organic Chemistry Laboratory, Faculty of Sciences, Ferdowsi University, Mashhad, Iran

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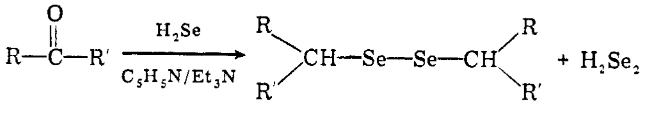
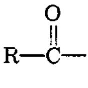
We recently described the preparation of symmetrical disulfides by the reaction of carbonyl compounds and H_2S.[1] The parallel formation of diselenides from ketones with H_2Se was reported by Margolis and Pittman,[2] but this reaction has apparently not had further application. Since diselenides are versatile intermediates for other organoselenium compounds we have extended this chemistry and have found that the reaction of H_2Se with aldehydes and ketones in the presence of triethylamine and pyridine provides a general method for preparing alkyl, cycloalkyl, and aralkyl diselenides.

The experiments showed (Table I) that the best contact time for obtaining diselenides from aldehydes and ketones and hydrogen selenide in the presence of triethylamine and pyridine at room temperature is 10 days.

Table I. Effects of Temperature and Time in Diselenide Formation

Compd	Time of passage of H_2Se and temp	Time of contact, days	Respective diselenide yield, %
Benzaldehyde	1 h/room temp	2	12
Benzaldehyde	1 h/room temp	4	13
Benzaldehyde	1 h/room temp	6	60
Benzaldehyde	1 h/room temp	8	70
Benzaldehyde	1 h/room temp	10	76
Benzaldehyde	2 h/reflux	4 h	36
Benzaldehyde	2 h/reflux	1	50
Benzaldehyde	2 h/reflux	3	72
Cyclohexanone	1 h/room temp	2	
Cyclohexanone	1 h/room temp	5	
Cyclohexanone	1 h/room temp	8	29
Cyclohexanone	1 h/room temp	10	38
Cyclohexanone	2 h/reflux		
Cyclohexanone	2 h/reflux	3	34





$R{-}\overset{O}{\overset{\|}{C}}{-}R'$ = aliphatic and aromatic aldehydes, aliphatic ketones, cyclo ketones

R = alkyl, aryl
R′ = H, alkyl

Previous preparations have involved the oxidation of selenoles,[3,4] or from other suitable compounds such as selenocyanates,[5] halides with sodium diselenide,[6-8] Grignard reagent with selenium bromide,[9,10] alkyl halides with $NaBH_4$ and Se,[11] and arylselenyl bromides with PPh_3.[12]

Of these methods, the best one for preparing diselenides is from selenols. In the first step of this procedure, selenols can be synthesized in a number of ways. Treatment of selenols with a mild oxidizing agent, such as air, provides diselenides. However, the present method is a simplified, one-step procedure, giving alkyl, cycloalkyl, and aralkyl diselenides in good yields.

The NMR spectrum of the diselenides shows a CH_2Se proton signal at δ 2.80–4.12 and a CHSe proton signal at δ 2.7–3.40.

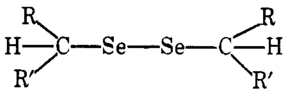
Experimental Section

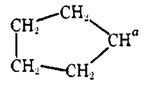
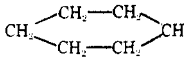
General. Proton magnetic resonance spectra were determined with a Varian T-60 spectrometer using tetramethylsilane as internal standard. Melting points were measured on a Kofler hot-bench apparatus. Elemental analyses were performed by CNRS (Service Central de Microanalyses, 2 rue Henry-Dunant, 94-Thiais, France).

All of the aliphatic and aromatic aldehydes, aliphatic ketones, and cyclo ketones were purchased from commercial sources.

General Procedure for Synthesis of Alkyl, Cycloalkyl, and Aralkyl Diselenides. Method A. Solid Diselenides. The following preparation of dibenzyl diselenide (Table II, expt 1) will serve as an example of the procedure used to prepare the solid diselenides listed in Table II. In this case, a solution of 10.6 g (0.1 mol) of benzaldehyde and 25 mL of dry pyridine and 10 mL of triethylamine in a 100-mL

Table II. Diselenides



No.	RR′CH	Mp, °C	Bp, °C	Yield, %	Registry no.
1	$C_6H_5CH_2$	92		76	1482-82-2
2	$p\text{-}ClC_6H_4CH_2$	76		85	56344-11-7
3	$p\text{-}CH_3OC_6H_4CH_2$	72		78	62212-22-0
4	$p\text{-}C_2H_5OC_6H_4CH_2$	78		68	62212-23-1
5	$\alpha\text{-}C_{10}H_7CH_2$	102		72	53391-04-1
6	$CH_3(CH_2)_2$		92^{10}	48	7361-89-9
7	$(CH_3)_2CH$		58^{5}	25	37826-18-9
8	$CH_3(CH_2)_3$		108^{8}	80	20333-40-8
9	$CH_3(CH_2)_4$[a]		126^{10}	85	52056-07-2
10	$(C_2H_5)_2CH$[a]		100^{12}	30	62212-24-2
11	$CH_3(CH_2)_5$		148^{11}	70	52056-08-3
12	$(C_2H_5)_2CHCH_2$[a]		119^{4}	28	62212-25-3
13			138^{5}	43	62212-26-4
14			158^{3}	38	56592-97-3

[a] New compound.

round-bottom flask was chilled in an ice bath. About 20 g (0.25 mol) of dry hydrogen selenide (hydrogen selenide was generated from aluminum selenide by addition of water and passed through the calcium chloride tube) was passed through the solution. In the course of time the elemental selenium precipitated at the bottom of the flask. After 10 days at room temperature, the elemental selenium was removed by filtration. The filtrate was poured into cold water and diselenide was collected by filtration, treated with dilute hydrochloric acid, and washed with water. Recrystallization from ethanol provided **1** (76%), mp 92 °C. The solid diselenides listed in Table II were recrystallized from absolute alcohol to afford analytically pure products.

Method B. Liquid Diselenides. The following synthesis of dipropyl diselenide (Table II, expt 6) will serve as general procedure for the preparation of liquid diselenides. Following the general procedure described above (method A) with the slight modification, a mixture of 5.8 g (0.1 mol) of propionaldehyde, 25 mL of anhydrous pyridine, and 10 mL of triethylamine in a 100-mL flask was chilled in an ice bath. About 20 g (0.25 mol) of dry hydrogen selenide was passed through the solution. After 10 days at room temperature, and elimination of elemental selenium as described in method A, the solution was poured into cold water and extracted with three 50-mL portions of diethyl ether. The extracts were combined, treated with dilute hydrochloric acid, and washed with water. The ether solution was dried over anhydrous sodium sulfate. Evaporation of the solvent left a liquid which on distillation gave 5.8 g (48%) of **6**, bp 92 °C (10 mm).

Registry No.—Benzaldehyde, 100-52-7; 4-chlorobenzaldehyde, 104-88-1; 4-methoxybenzaldehyde, 123-11-5; 4-ethoxybenzaldehyde, 10031-82-0; 1-naphthalenecarboxaldehyde, 66-77-3; propanal, 123-38-6; 2-propanone, 67-64-1; butanal, 123-72-8; pentanal, 110-62-3; 3-pentanone, 96-22-0; hexanal, 66-25-1; 2-ethylbutanal, 97-96-1; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; hydrogen selenide, 7783-07-5.

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A Reinvestigation of Nitration in Aqueous Sulfuric Acid of Benzene and Halogenobenzenes

N. C. Marziano,* A. Zingales, and V. Ferlito

Facoltà di Chimica Industriale, Università, Dorsoduro 2137, 30123 Venezia, Italy

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The nitration of benzene in aqueous sulfuric acid is a matter of interest because its reaction mechanism appears to be affected by an encounter rate-determining step.[1,2] Evidence for this circumstance comes from the estimated rate coefficient at 68% H_2SO_4. The value appears to be close to the rate coefficient for encounter between two species, under the same conditions.[1,2] Also a limiting rate of nitration, reached with sufficiently reactive aromatics, has been regarded as an important source of information, in connection with the influence of encounter upon the benzene.[1,2]

Concerning the acidity dependence of the rate profile, two different slope values have been observed in the range 63–82% H_2SO_4 on the plot log $k_{2(\mathrm{obsd})}$ vs. $(H_R + \log a_w)$.[1,2] The behavior of the rate profile prompted us to extend previous kinetic data for benzene.[2,3] This was during the attempt to determine whether the observed deviation from linearity is significant evidence of the interference of different rate-determining steps upon the benzene. For comparative purposes, the nitration of some deactivated compounds, such as halogenobenzenes, has been reinvestigated.[3,4]

Table I. Second-Order Rate Coefficients for Nitration in Aqueous Sulfuric Acid at 25 °C

H_2SO_4, %[a]	$[HNO_3]$, mol/L	[AcOH], mol/L	Log $k_{2(\mathrm{obsd})}$, L $\mathrm{mol^{-1}\,s^{-1}}$ [c]
	Benzene[b]		
71.77	4.24×10^{-3}		0.24
70.97	3.72×10^{-3}		−0.328
70.97	3.26×10^{-3}		−0.328
69.87	3.47×10^{-3}		−0.775
69.87	3.76×10^{-3}		−0.787
69.87	3.98×10^{-3}		−0.779
69.87	4.15×10^{-3}		−0.791
69.87	4.39×10^{-3}	3.80×10^{-4}	−0.810
69.20	4.12×10^{-3}		−0.997
68.22	5.74×10^{-3}		−1.335
68.18	2.37×10^{-3}		−1.369
67.71	4.06×10^{-3}		−1.577
66.95	4.57×10^{-3}		−1.775
66.95	3.53×10^{-3}	1.69×10^{-3}	−1.793
66.78	2.37×10^{-2}		−1.849
66.08	4.25×10^{-3}		−2.096
66.04	2.37×10^{-2}		−2.173
65.41	1.02×10^{-2}		−2.364
64.79	3.33×10^{-3}		−2.587
64.68	1.69×10^{-2}		−2.534
64.68	1.69×10^{-2}	5.12×10^{-4}	−2.553
63.91	3.07×10^{-3}		−2.848
62.37	9.43×10^{-3}	6.01×10^{-4}	−3.422
	Fluorobenzene[b]		
69.91	1.08×10^{-2}		−1.613
69.43	4.27×10^{-2}	3.99×10^{-3}	−1.801
67.69	1.31×10^{-2}		−2.409
67.11	1.94×10^{-2}		−2.609
65.76	1.27×10^{-1}		−3.049
	Chlorobenzene[b]		
73.37	7.71×10^{-3}		−0.497
71.42	6.73×10^{-3}		−1.259
69.43	1.39×10^{-2}		−2.060
69.43	8.86×10^{-2}	3.52×10^{-3}	−2.064
67.11	8.93×10^{-2}		−2.902
65.76	1.099×10^{-1}		−3.378
	Bromobenzene[b]		
73.37	5.201×10^{-3}		−0.576
71.42	1.67×10^{-2}		−1.296
69.43	1.13×10^{-1}		−2.087
69.43	1.07×10^{-1}	3.99×10^{-3}	−2.105
67.11	7.66×10^{-2}		−2.981
65.76	1.62×10^{-1}		−3.567
	Iodobenzene[b]		
73.37	4.586×10^{-3}	1.998×10^{-3}	−0.097
71.21	1.691×10^{-3}	1.998×10^{-3}	−0.970
70.57	4.722×10^{-3}	1.998×10^{-3}	−1.150
67.65	1.173×10^{-1}	1.998×10^{-3}	−2.153
67.11	7.687×10^{-2}		−2.343
65.81	2.873×10^{-1}	1.998×10^{-3}	−2.698

[a] ±0.1%. [b] [Aromatic] = $10^{-4}/10^{-5}$ mol L^{-1}. [c] Estimated percentage of standard error of the mean ±2.5%.

Results and Discussion

Rate coefficients for the nitration of benzene and halogenobenzenes in the range 62–74% sulfuric acid are in Table I.