quirements of the solvent and probably leads to a true value of accessible hydroxyl groups for a non-swelling reagent. In an aqueous medium, swelling takes place and a number of weak (van der Waals) bonds between hydroxyl groups of adjacent chains are opened and hitherto inaccessible areas are made penetrable by the reagent. One should, therefore, expect that all methods using aqueous systems should indicate higher degrees of accessibility, which is in fact the case. The highest proportions of disordered areas should be given by X-rays, by density considerations,[13] and by the heavy water exchange method; the figures deduced from these three methods should also agree numerically. Table VII contains the accessibilities as reported by all methods and shows, indeed, that the thallation method gives the lowest values whereas the two "destructive methods" in aqueous media, involving hydrolysis and oxidation, give higher figures for the disordered areas and agree with each other to a first approximation. Finally, the non-destructive methods of X-ray diffraction, density evaluation and heavy water exchange lead to the highest figures for the accessible domains; these methods, too, agree with one another reasonably well.

TABLE VII

ORDER OF ACCESSIBILITY FOUND BY DIFFERENT METHODS

Method	% Accessible or amorphous Cotton	Cotton linters	Wood pulp	Rayon
Thallation[3]	..	0.4[c]	..	...
Nickerson oxidation[5a]	..	5.3	10	24
Periodate oxidation[2]	1–2	6.0	..	7–19
Density[11]	40	...	50	75
Heavy water exchange[b]	21	46	46	66
X-Ray densitometry[5]	..	...	..	81

[a] Data supplied through courtesy of Drs. Conrad and Scroggie. [b] Values averaged from Table IV. [c] Unswollen samples.

Summary

It has been found that cellulose reacts very rapidly with heavy water, provided sufficient agitation is used; the rapid reaction is of limited extent, and is succeeded by a much slower reaction which persists for days. In none of the cases studied were all of the hydroxyls exchanged, even at the end of one week. The techniques used and the calculations involved are outlined.

The extent of the rapid reaction is a measure of the accessibility of the cellulose sample, and from the accessibility an estimate is made of the amount of amorphous material present in each of the samples studied. The average amounts found for different types of cellulose were as follows: 21% for cotton, 46% for wood pulp and 66% for rayon.

The different accessibility values found for the same cellulose sample when different methods are used are discussed and compared. These methods fall into three classes. In the first class is the thallation method, where a non-swelling solvent is used, and with which the lowest values are found. In the second class are the two hydrolytic, aqueous methods, which give intermediate values for accessibility. In the last class are the physical, non-destructive methods which give the highest values.

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n-Alkyl Diselenides

BY GEORGE G. STONER AND ROGER W. WILLIAMS

In connection with a program[1] of research on selenium and its compounds, it was of interest to examine a number of n-alkyl diselenides. Of this particular homologous series, methyl,[2,3] ethyl,[2,4] propyl,[2,3,5] butyl[3] and dodecyl[6] diselenides are known, having been prepared by a variety of methods.

A convenient method of synthesis, based on the following three reactions,[7] and not previously applied to this series, was used to prepare butyl, amyl, hexyl, heptyl, octyl, and nonyl diselenides.

$$\mathrm{Se} + \mathrm{K_2SO_3} = \mathrm{K_2SeSO_3}$$

$$\mathrm{RX} + \mathrm{K_2SeSO_3} = \mathrm{RSeSO_3K} + \mathrm{KX}$$

$$2\mathrm{RSeSO_3K} + \mathrm{I_2} + 2\mathrm{H_2O} = \mathrm{RSeSeR} + 2\mathrm{KHSO_4} + 2\mathrm{HI}$$

This sequence of reactions yields n-alkyl diselenides which are less likely to be contaminated than those prepared by the other methods,[2–6] and the yields are good (Table I). The offensive odors of the n-alkyl diselenides decrease considerably in intensity above hexyl in the homologous series.

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(1) Sponsored by the Selenium Development Committee.

(2) Beilstein, "Handbuch der organischen Chemie," 4th ed., Vol. I, pp. 291, 349 and 360; and 2d supplement, pp. 278 and 357. Also, M. L. Bird and F. Challenger, *J. Chem. Soc.*, 570–574 (1942).

(3) H. J. Backer and W. van Dam, *Rec. trav. chim.*, **54**, 531–538 (1935).

(4) A. Baroni, *Atti accad. Lincei*, **14**, 28–32 (1931); *C. A.*, **26**, 1896 (1932).

(5) E. P. Painter, K. W. Franke and R. A. Gortner, *J. Org. Chem.*, **5**, 579–589 (1940).

(6) G. H. Denison, Jr., and P. C. Condit, U. S. Patents 2,398,414, 2,398,415, and 2,398,416 (April 16, 1946).

(7) This method was discovered by T. S. Price and L. M. Jones, *Proc. Chem. Soc.*, **24**, 134 (1908), and *J. Chem. Soc.*, **95**, 1729–1738 (1909), who used it in preparing benzyl and nitrobenzyl diselenides; *cf.* T. S. Price and D. F. Twiss, *J. Chem. Soc.*, **95**, 1489 (1909). Recently, H. P. Ward and I. L. O'Donnell, THIS JOURNAL, **67**, 883 (1945), used the same method to prepare two bis-(2-alkoxyethyl) diselenides, hydrogen peroxide having been used in place of iodine.

TABLE I

n-ALKYL DISELENIDES

Di-selenide	Distn. range, °C.[a]	Mm.	Distd. yield, %	M. p., °C.[a]	d^{20}_4	n^{20}_D	Exptl. MR_D	r_D[b]	Formula	Selenium, % Calcd.	Found[c]	
Butyl	113–119[d]	6–8	67	< −78	1.390	1.5399	61.41	11.14	$C_8H_{18}Se_2$	58.03	57.2	
Amyl	134–137	3	63	< −78	1.324	1.5343	70.51	11.06	$C_{10}H_{22}Se_2$	52.60	52.6	
Hexyl	150–152	3	83	−44	1.258	1.5246	79.91	11.14	$C_{12}H_{26}Se_2$	48.11	48.1	47.8
Heptyl	178–179	3	83	−11	1.211	1.5184	89.21	11.17	$C_{14}H_{30}Se_2$	44.32	45.3	45.5
Octyl	197–205	3	74	− 8	1.175	1.5142	98.53	11.22	$C_{16}H_{34}Se_2$	41.09	41.6	41.6
Nonyl	178–184	0.12	67	10	1.142	1.5092	107.89	11.28	$C_{18}H_{38}Se_2$	38.29	39.5	39.3

[a] Temperature readings were not corrected for emergent stem. [b] The atomic refraction of each Se in the diselenide calculated from the experimental molecular refraction (formula of Lorenz and Lorentz), assuming the atomic refraction for C and H to be 2.418 and 1.100 ml., respectively (sodium D light). [c] Selenium was determined by a method developed by Justin S. McNulty (to be published). Samples were decomposed and selenium was determined gravimetrically as elemental selenium. [d] Backer and van Dam (ref. 3) reported that butyl diselenide distilled in the range of 129–130° at 13 mm.

At room temperature these liquid diselenides are orange, but this coloration becomes weaker as the temperature is lowered. This is suggestive of a certain degree of dissociation into RSe radicals, increasing with temperature.[8]

From values obtained for d^{20}_4 and n^{20}_D, the atomic refraction of each selenium atom in these diselenides was 11.17 ± 0.11 ml. (sodium D light).[9]

Experimental

Materials.—The 1-bromoalkanes, each of which distilled within a two-degree range, were purchased from Columbia Organic Chemicals Co., Inc., Columbia, South Carolina. Powdered gray-black selenium, 99.5% pure, was obtained from Canadian Copper Refiners, Ltd., Montreal East, Quebec. The other compounds were chemically pure.

General Procedure.—In an atmosphere of nitrogen, 40 g. (0.50 g.-atom) of selenium was allowed to react for two hours with a mechanically stirred, hot solution of 119 g. (0.75 mole) of anhydrous potassium sulfite in 1200 ml. of 50% aqueous ethanol. Some undissolved matter was filtered from the hot mixture, and the filtrate was transferred immediately into a 5-liter, 3-neck flask. Without delay, 0.40 mole of the appropriate 1-bromoalkane was added portionwise during a period of one-half hour, while the mixture was kept refluxing in an atmosphere of nitrogen and mechanically stirred. An additional period of two hours under these conditions was allowed for the reaction. The solution of potassium alkylselenosulfate was cooled to room temperature and oxidized to the *n*-alkyl diselenide by iodine added portionwise until the color of the iodine persisted. The small excess of iodine was reduced by bubbling sulfur dioxide into the solution. The diselenide separated out as an orange oil.

In each case, the oil was washed with water and distilled at reduced pressure. Experimental data are given in Table I. Practically no unreacted 1-bromoalkanes were recovered in the purification of butyl, amyl, hexyl and heptyl diselenides. However, in the cases of octyl and nonyl diselenides, 10% of the original 1-bromoöctane and 27% of the original 1-bromononane were recovered. Hence, a period of reaction longer than two hours is indicated in the case of these higher 1-bromoalkanes.

All the diselenides had offensive odors, but those of heptyl, octyl, and nonyl diselenides were much less pronounced. All six of these compounds were orange at room temperature. Butyl and amyl diselenides remained liquid at −78°, at which temperature they were straw-colored. The higher diselenides formed yellow crystals below their melting points (Table I).

For the purpose of comparison, amyl diselenide also was prepared from 1-chloropentane (Sharples Chemicals, Inc., Philadelphia, Pa.). The period allowed for reaction was extended to twelve hours. In other respects the conditions were the same as those described above. After distillation, the yield of amyl diselenide was 65%, which is practically identical with the yield of 63% resulting from the use of 1-bromopentane (Table I).

Acknowledgment.—The authors are grateful to Phyllis K. Distelhorst and Justin S. McNulty, who performed the determinations of selenium.

Summary

Potassium alkylselenosulfates were used as intermediate compounds in conveniently preparing five new *n*-alkyl diselenides (amyl through nonyl). Several properties characterizing these homologs were determined. The value of the atomic refraction for each atom of selenium in such diselenides was found to be 11.17 ± 0.11 ml. (sodium D light).

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(8) Analogous to radicals containing univalent sulfur, discussed by W. E. Bachmann in H. Gilman's "Organic Chemistry, an Advanced Treatise," Vol. I, 1st ed., John Wiley & Sons, Inc., New York, N. Y., p. 528.

(9) G. R. Levi and A. Baroni, ***Atti accad. Lincei***, [6] **9**, 1022 (1929), according to Beilstein, *op. cit.*, Vol. I, p. 357, reported that d^{18} and $n^{12.8}_D$ for ethyl diselenide were, respectively, 1.6962 g. per ml. and 1.5885, from which the experimental molecular refraction is 42.89 ml. and the atomic refraction for each selenium atom is 11.11 ml. L. Chugaev, *Ber.*, **42B**, 53 (1909), reported that $d^{22.2}$, $n^{22.2}_D$, MR_D, and r_D (Se) were, respectively, 1.4991 grams per ml., 1.55535, 52.20 ml., and 11.33 ml. for propyl diselenide. A recalculation gave 52.29 and 11.19, respectively, for MR_D and r_D (Se), when 1.008, 12.010, and 78.96 were used as the atomic weights for H, C, and Se, and 1.100 and 2.418 were used as the respective atomic refractions (sodium D light) for H and C.