Tetrahedron. 1964, Vol. 20, pp. 427 to 436. Pergamon Press Ltd. Printed in Northern Ireland

3d-ORBITAL RESONANCE IN DIVALENT SULPHIDES—V

ACTIVITY OF α-HYDROGEN ATOM OF CYCLIC MERCAPTALS[1,2]

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Abstract—Previously,[1] it was found that the base-catalysed hydrogen exchange reactions of sulphides is effected by 3d orbital resonance involving uncharged sulphur groups. This investigation now extended to several cyclic mercaptals, reveals that ring size and conformation affect the exchange rates substantially. Unsubstituted cyclic mercaptals are more reactive than the open chain compounds, the relative rates of open chain, five- and six-membered ring compounds being 39·9, 516 and 214 respectively. Alkyl substituents reduce the rates substantially in both open chain and cyclic mercaptals; the relative rates of ethyl substituted compounds being 1·00 for acyclic, 19·1 for five-, 1·55 for six- and 5·37 for seven-membered cyclic compounds. This rate reduction is greater by a factor of about 4–5 for six-membered cyclic compounds (214/1·55 = 138) than for the other compounds. These results are interpreted in terms of conformational changes, solvation and the 3d orbital resonance of sulphur atoms.

THE 3d orbital resonance in positively charged sulphur compounds is the principal factor responsible for the increased acidity of the α-hydrogen atom attached to sulphur groups and for the acidity of substituted phenols or anilines with sulphur groups in either *o*- or *p*-position.[4] More recently, attention has been focussed on the possible aromaticity of the sulphur containing ring systems,[5] and on the stereochemical capability and the stability of the sulphone stabilized carbanions,[6] and many interesting features in the chemistry of positively charged sulphur compounds have been revealed. In uncharged divalent sulphur compounds, although there are many indications of the importance of 3d orbital resonance of sulphur groups when the sulphur atom is attached to a carbanion or an unsaturated group,[7] most of the work is either uncritical or only qualitative in nature explaining a certain reaction pathway in terms of 3d orbital resonance. Therefore, quantitative and critical investigations with well defined systems are necessary in order to elucidate the role of the 3d orbital resonance in divalent sulphur groups.

In the preceding paper,[1] it was shown that 3d orbital resonance is the major

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[1] Part IV: S. Oae, W. Tagaki and A. Ohno, *Tetrahedron* the preceding paper.

[2] This work has been supported by the Petroleum Research Fund, administered by the American Chemical Society.

[3] Present address, Department of Chemistry, Massachusetts Institute of Technology.

[4] [a] G. Cilento, *Chem. Revs.* **60**, 147 (1960); [b] C. C. Price and S. Oae, *Sulfur Bonding* Ronald Press, New York (1962).

[5] R. Breslow and E. Mohacsi, *J. Amer. Chem. Soc.* **85**, 431 (1961), and the preceding papers.

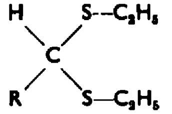
[6] [a] D. J. Cram and A. S. Wingrove, *J. Amer. Chem. Soc.* **85**, 1100 (1963), and the preceding papers; [b] E. J. Corey, H. Koenig and T. H. Lowry, *Tetrahedron Letters* 515 (1962); [c] C. Y. Meyers, *Ibid.* 1125 (1962).

[7] Part III of this series: S. Oae, 3*d Orbital Resonance Involving the Sulfur Atoms in Organic Sulfides*, in *Organic Sulfur Compounds* (Edited by N. Kharasch) Vol. IV. Pergamon Press, in publication.

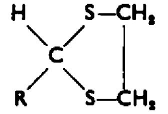
contributing factor for the facile base-catalysed isotopic hydrogen exchange reactions of α-deuterated mercaptals and orthothioformates. The unusual reactivity of the bicyclic compound, VI, as compared to the open chain counterpart, V, has prompted the suggestion that an effective 3d orbital resonance may be associated with certain ring structures. The present investigation was undertaken in order to find how and to what extent various cyclic structures of mercaptals affect the rates of base-catalysed T–H exchange reactions of the cyclic mercaptals.

RESULTS

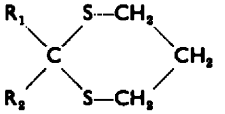
The compounds studied were five- (II), six- (III) and seven-membered cyclic mercaptals (IV). The tritiation of the hydrogen atom for alkylated compounds was carried out by the method previously used: α-tritiated acetals were prepared from α-tritiated triethyl orthoformate, and converted to the cyclic mercaptals by a catalysed reaction with the corresponding dithiols. These synthetic procedures do not change the positions of α-tritium as verified by previous experiments[1] in which similar α-deuterated compounds were shown by their NMR spectra not to isomerize during the reactions. The unsubstituted dihydrogen compounds were tritiated by the base-catalysed exchange reactions of the protium compounds in t-butanol-t_1 at 100–120°. Although there is a possibility of the tritiation of the ring protons other than those of the α-carbon atoms, such an exchange should be very small as there is a tremendous rate drop in passing from the three mercapto compound (V) to the two mercapto compound (Ib). In the case of the α,α-dimethyl compound (IIIf), T–H exchange reactions took place only after prolonged heating (~140°/40–70 hr) resulting in very low tritium incorporation. Thus, it is clear that the T–H exchange reaction of the unsubstituted dihydrogen compounds occurs exclusively at the α-carbon atom.



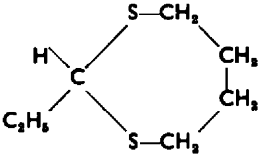
Ia, R = H
Ib, $R = C_2H_5$



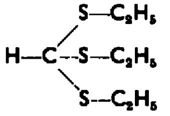
IIa, R = H
IIb, $R = C_2H_5$



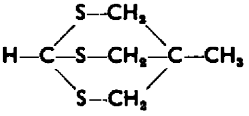
IIIa, $R_1 = R_2 = H$
IIIb, $R_1 = H$, $R_2 = CH_3$
IIIc, $R_1 = H$, $R_2 = C_2H_5$
IIId, $R_1 = H$, $R_2 = i$—C_3H_4
IIIe, $R_1 = H$, $R_2 = t$—C_4H_9
IIIf, $R_1 = R_2 = CH_3$



IV



V



VI

The exchange reactions were carried out in t-butanol using potassium t-butoxide as the base, usually at 120° except for very reactive compounds (at 50°), and the kinetic experiments were followed by measuring the loss of tritium activity using a Packard Tri-carb liquid scintillation counter. The pseudo first order rate constants thus obtained are listed in Table 1 together with the previous data for comparison. A few typical kinetic examples are shown in Table 2. The relative rates in Table 1 are calculated from the rates of propionaldehyde diethylmercaptal (Ib), assuming that the

Table 1. Kinetics for the base-catalysed tritium-hydrogen exchange reactions in potassium t-butoxide-t-butanol and the ultraviolet absorption maxima[a]

Compound	Temp., °C	First order reaction rate constants, $k_1 \times 10^6$	Relative rate	UV maxima λ_{max} (mμ)	ε
Ia	120	125[b]	39·9	237	553
Ib	120	3·13	1·00	231	834
IIa	50	5·40[b]	516[c]	246	285
IIb	120	59·90	19·1	246	314
IIIa	50	2·24[b]	214[c]	250	469
IIIb	120	1·23	0·393	252	449
IIIc	120	4·84	1·55	250	619
IIId	120	4·06	1·30	249	690
IIIe	120	3·75	1·20	249	767
IV	120	16·8	5·37	245	428
V			$1{\cdot}48 \times 10^4$ [d]	235	954
VI			$1{\cdot}78 \times 10^7$ [d]	251	1,242

[a] See the ref. 8. [b] One half of the empirical rate constant. [c] Calc. from the previous results. [d] Previous results.[1]

temperature dependency of the rate is not very different in the range of 50–120° for all the compounds. For additional information concerning the nature of the α-C–H bond, the NMR spectra of six-membered cyclic compounds were recorded in carbon tetrachloride solutions as shown in Table 3.

DISCUSSIONS

Effects of ring size and conformation. As can be seen in Table 1, unsubstituted cyclic compounds react faster than the corresponding acyclic compounds, the relative rates of acyclic (Ia), five- (IIa) and six-membered cyclic compounds (IIIa) being 39·9, 516 and 214 respectively. These rate changes are undoubtedly ascribed to steric or conformational effects rather than the inductive effects of the ring which should not be very different in each of these compounds.

An open chain compound is not held in a fixed rigid geometry but the most stable form will assume a conformation in which the two mercapto groups twist the two C–S–C planes out of symmetry which is presumably quite important for an efficient hybridization of 2p, 3p and 3d orbitals to form a non-classical structure described later. In a cyclic compound, the two sulphur atoms are held in a fixed rigid geometry and the α-C–H bond is confined to the symmetry planes which bisect the S–C_α–S plane. Thus the carbanions formed from the cyclic compounds could be stabilized by two sulphur atoms, while in the open chain compounds there is steric hindrance. These differences in symmetry and conformation are considered responsible for the difference in rates between the acyclic and the cyclic compounds. Similar differences are revealed in the near UV spectra (Table 1) in which the absorption maxima of cyclic compounds are found at longer wavelength than those of the open chain compounds, suggesting that the bathochromic shift of cyclic mercaptals is due to a direct interaction between the non-bonded sulphur atoms involving their 3p (of lone electron pair) and vacant 3d orbitals.[7,8]

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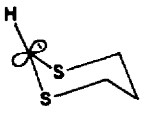
[8] Part VI; S. Oae, W. Tagaki and A. Ohno, *Tetrahedron* forthcoming paper.

Recently it has been suggested that ring strain in four and five-membered cyclic sulphones causes structural rupture of the corresponding sulphonyl carbanions.[9] A similar ring strain was also suggested as being responsible for the transformation of 2-methyl-2,3-dihydrothianaphthalene into thiachroman by a ring enlargement from a five to a six-membered structure when refluxed with quinoline.[10] Even the enhanced reactivity of the cage compound (VI) was ascribed to ring strain.[6c] However, it has recently been shown that the stability of cyclic carbanions, such as cyclobutyl and cyclopentyl, is even less than that of the open chain analogues except for the cyclopropyl carbanion which is very stable.[11] Therefore, the ring strain alone cannot account for the present results, even if it is partly responsible for the enhanced acidity of the five-membered compounds.

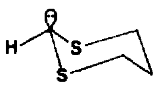
Another interesting observation is that the rate of exchange reactions of the unsubstituted six-membered compound (IIIa) is 138 times greater than that of the ethyl substituted compound (IIIc), and this rate reduction by ethyl substitution is much greater than that of the open chain (39·9) and five-membered compounds (27·0) by a factor of about 4–5. This observation can be accounted for by the following explanations.

The first is based on the assumption that the carbanion is better stabilized in the sp^2 configuration (VIIa) and the rehybridization of sp^3 to sp^2 in the ethyl substituted six-membered compounds (IIIc) will require more energy than that of open chain and five-membered compounds (Ib and IIb). This conception is essentially the same as "I-strain"[12] and is supported by the fact that the rates of ethyl substituted compounds are in the decreasing order of $5 > 7 > 6$, identical with that observed in the acidity sequence of alicyclic compounds, where sp^2 configuration has been assumed for the carbanions.[13] However, the "I-strain" theory cannot offer any quantitative estimation of the difference of strains between the dihydrogen and the ethyl substituted compounds of the same ring structure, and it is difficult to understand why such a rate reduction is greater for six-membered than for the five-membered compounds and that this rate reduction is further reduced by ethyl substitution.

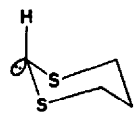
The second explanation is that the carbanion has a pyramidal sp^3 configuration and 3d orbital resonance operates most effectively when the non-bonded lobe assumes an equatorial position (structure VIIc), the axial conformation (VIIb) contributing little to the resonance. This idea may be supported by the high reactivity of the cage compound (VI) in which the α-carbanion would assume sp^3 pyramidal configuration and the non-bonded lobe is coplanar with the three C–S–C planes. When normal



sp^2, VII a



sp^3-axial, VII b



sp^3-equatorial, VII c

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[9] C. Y. Meyers, C. Rinaldi and L. Bonoli, *Abstracts of* 144th *ACS Meeting* 4M. Los Angeles, April 1–5 (1963).

[10] C. Y. Meyers, C. Rinaldi and L. Bonoli, *J. Org. Chem.* in press, private communication.

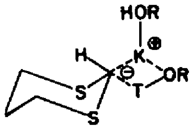
[11] D. E. Applequist and D. F. O'brien, *J. Amer. Chem. Soc.* **85**, 743 (1963).

[12] H. C. Brown, R. S. Fletcher and R. B. Johanessen, *J. Amer. Chem. Soc.* **73**, 212 (1951).

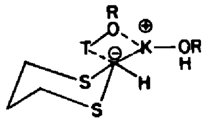
[13] H. C. Brown, *Rec. Chem. Progr. Kresge-Hooker, Sci., lib.* **14**, 83 (1953).

bond lengths and bond angles (C–C, 1·54 Å; C–S, 1·81 Å; C–H, 1·09 Å; ∠C–C–C, 109°28′; ∠C–S–C, 100°), and the chair conformation are assumed for the six-membered compound, IIIa, then a simple calculation[14] reveals that the equatorial α-C–H bond or the non-bonded lobe on the pyramidal α-carbon atom is nearly coplanar with the two C–S–C planes, and this coplanarity is maximum for six-membered rings. Whereas the preferred conformation of the corresponding ethyl substituted compound, IIIc, would have an axial α-C–H bond and an equatorial ethyl group, the resulting carbanion would not receive resonance stabilization as much as that of the unsubstituted compound, IIIa. However, the stabilization of carbanion by p–d overlap has been known to have neither strict configurational nor conformational requirement,[6b,15,4b] and hence this explanation also has some shortcomings.

The third possibility is that the solvation in the transition state plays an important role in determining the rate of H–T exchange reaction of these mercaptals just it does in the determination of both the steric course and the rate of the similar carbanion reactions stabilized by sulphonyl, sulphinyl or phosphinoxy groups.[6a] If the solvation is important in lowering the transition state energy, then non-dissociating and bulky solvents such as t-butanol[6a] may produce large steric effects on the rate. Thus, the solvation of an equatorial carbanion (structure, VIIIa) is more favoured than that of an axial one (structure, VIIIb). Since the alkyl substituted compound will have an axial α-C–H bond and an equatorial alkyl group, the solvation of the resulting carbanion is less favoured than that of the unsubstituted compound which has two α-C–H bonds in the equatorial and axial directions. Although this explanation is the most reasonable, further investigations leading to more concrete evidence are necessary.

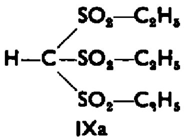


VIII a



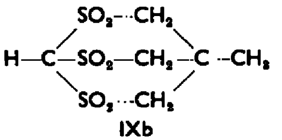
VIII b

Meanwhile, it is interesting to compare the results obtained for divalent sulphides with those for the corresponding sulphones. The open chain trisulphone, IXa, is known to be a stronger acid than the bicyclic trisulphone, IXb,[15c] while the situation is quite contrary in the corresponding trisulphides, V and VI (Table 1). In the case of disulphones, the acidity of the open chain compound, Xa, is comparable with that of the six-membered compound, Xb (n = 3),[6b] while in the mercaptals the cyclic

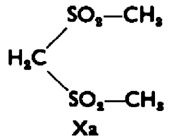


$$H\text{—}C(SO_2\text{—}C_2H_5)_3$$

IXa

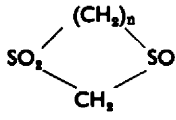


IXb



$$H_2C(SO_2\text{—}CH_3)_2$$

Xa



Xb, n = 2,3,4,5

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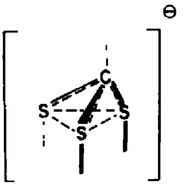
[14] E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.* 77, 2505 (1955).

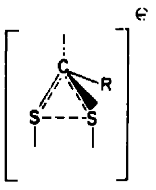
[15] [a] G. E. Kimball, *J. Chem. Phys.* 3, 188 (1944); [b] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.* 332 (1954); [c] W. E. von Doering and L. K. Levy, *J. Chem. Soc.* 77, 509 (1955); [d] H. E. Zimmerman and B. S. Thyagarajan, *Ibid*, 82, 2505 (1960); [e] T. Jordan, W. Smith and N. N. Lipscomb, *Tetrahedron Letters* 2, 37 (1962).

compound, IIIa, is more acidic than the open chain compound, Ia. On the other hand, the acid strength of Xb increases as n increases, the five-membered compound (n = 2) being the weakest acid and the eight-membered compound (n = 5) the strongest,[6b] while in the mercaptals the most acidic one is the five-membered compound, IIa.

In the cases of sulphones, it has been suggested that the stability of the carbanion of its stereochemical form is largely dependent on the electrostatic interactions between the negative charge of carbanion and the dipole, the negative charge on the sulphone–oxygen atom[6a,b] or the negative field of RSO_2 group.[6c] The unfavourable solvation was also suggested for the weaker acidity of the bicyclic sulphone (IXb).[6c] The electrostatic interaction due to the ion dipoles, important in the RSO_2 group, is undoubtedly small for the divalent sulphides. Previously,[1] we suggested that the enhanced acidity of the bicyclic compound (VI), as compared with its acyclic counterpart (V), is due to the contribution of a non-classical pyramidal resonance structure (XIa) to the stabilization of the incipient carbanion of VI where the 2p–3d overlapping between the non-bonded lobe and the three sulphur atoms is cooperating with the 3p–3d overlapping between the three non-bonded sulphur atoms. In the case of cyclic mercaptals, at least for five- and six-membered compounds, one may also safely presume the contribution of a similar structure, XIb, to the carbanion stability in view of the foregoing discussions on the possible configurations of carbanions together with the UV data. The sulphones having no unbonded 3p electrons on the sulphur atom are incapable of forming similar structures.



XI a



XI b

Effects of alkyl substituents. As can be seen in Table 1, the substitution of unsubstituted mercaptals with one ethyl group substantially reduces the rate regardless of open chain or cyclic structures.

There are a number of other examples in which the substitution of an alkyl group reduces the rate or equilibration constant in carbanion reactions, such as in enolizations, metalation and aci-nitro interconversion reactions.[16] It was also shown that the rate of the base-catalysed deuterium–hydrogen exchange reactions of toluene-α-d_1 was substantially reduced by the substitution of an electron releasing group by either inductive or resonance effects or by both effects.[17] The recent work in which the relative stabilities of several aliphatic carbanions were determined by equilibration reactions of alkyl lithium compounds with alkyl halides is closely related to the present investigations. It was found that the successive replacement of an hydrogen

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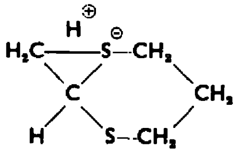
[16] [a] G. S. Hammond in M. S. Newman's *Steric Effects in Organic Chemistry* Chap. 9. John Wiley, New York (1959); [b] P. B. Bell, *The Proton in Chemistry* Chap. 10. Cornell Univ. Press, Ithaca, New York (1959) [c] J. Hine, *Physical Organic Chemistry* (2nd Edition) Chap. 10. McGraw-Hill, New York (1962).

[17] A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* Chap. 14. John Wiley, New York (1961); A. Streitwieser, Jr., *Abstract of ACS Meeting* Sept. 9–14 (1962).

atom by a methyl group, i.e., changing from a methyl to a t-butyl group, reduced the equilibrium constants in a regular fashion.[11] This tendency it was suggested is due to the destabilization of the carbanion by electron releasing inductive effects of alkyl groups.

The results of the present investigation indicate that, the rate variation in the alkyl substituted six-membered mercaptals follows the usual order of inductive effect, although the changes are rather small. However, the rate of the methyl compound, IIIb, is unusually small by a factor of about three as compared to those of the other alkylated compounds (see Table 3). In addition to the above inductive effect, the steric effects may also be responsible for the reduced acidities of the alkylated compounds. However, both these steric and inductive effects should be smaller for the methyl group than for the other alkyl groups, and hence the rates of the methyl compounds should be larger, although the actual effect observed was smaller. In fact, this anomaly was not observed in the halogen-metal interconversion reaction.[11]

The abnormal behaviour of the methyl compounds was also observed in the UV and NMR spectra. As can be seen in Tables 1 and 3, the absorption maxima of near UV spectra of the methyl substituted compounds are found at about 2–3 mμ longer wavelength than those of the other alkyl substituted compounds.[18] Although small, this red shift is opposite to that expected from the generally observed order of the inductive effects of alkyl groups in the photoexcitation. On the other hand, the NMR spectra of the six-membered compounds shown in Table 3 indicate that both the peaks of α-proton and methyl protons of α-monomethyl compound (IIIb) are found at lower field than those of the other alkylated compounds. The less shielding for α-protons of the methyl compound does not seem to be due to the smaller inductive effect of the methyl group because there is practically no difference between the peaks of ethyl and t-butyl compounds as would be expected if the inductive effects of the alkyl group are important for the shielding of α-protons. Although no satisfactory explanation is available at present, the abnormal behaviour of the methyl compound could be caused partly by a non-bonding hyper-conjugation between the methyl group and the sulphur atom involving either of its 3p or vacant 3d orbitals, or both orbitals as represented by a structure, XII. The contribution of XII would weaken the abilities of sulphur atoms to delocalize the negative charge developed on the α-carbon atom during the base-catalysed exchange reaction and also would lower the energy of the photoexcitation.



XII

EXPERIMENTAL

All the m.ps and the b.ps were uncorrected. The IR spectra were recorded with Perkin-Elmer Model 221 IR Spectrophotometer. The NMR spectra were recorded with Varian NMR Spectrophotometer at 60 Mc, and the spectra of six-membered mercaptals are shown in Table 3. The

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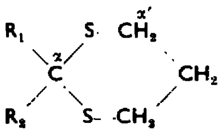
[18] Even more larger red shift by methyl substitution was observed for the acyclic compounds, see the Ref. 8.

TABLE 2. KINETICS FOR THE BASE-CATALYSED T–H EXCHANGE REACTIONS[a]

Time, sec.	$X \times 10^4$, d.p.m.	$X/X_0 \times 100$	$k_1 \times 10^6$
	A. *Propionaldehyde diethylmercaptal*-α-t_1 (Ib), Temp. 120°		
0	1·502	100·00	—
9,000	1·460	97·20	3·17
16,200	1·429	95·14	3·07
19,800	1·412	94·01	3·13
			av. 3·13
	B. 2-*Ethyl*-1,3-*dithian*-α-t_1 (IIIb), temp. 120°		
0	1·688	100·00	—
1,800	1·673	99·11	4·99
7,200	1·631	96·22	4·77
14,400	1·576	93·36	4·77
			av. 4·84
	C. 1,3-*Dithian*-α-t_1 (IIIa), temp. 50°		
	$X \times 10^5$, d.p.m.		
0	1·117	100·00	—
7,200	1·082	96·84	4·46
14,400	1·047	93·76	4·48
21,600	1·014	90·80	4·48
			av. 4·47

[a] See Table 1.

TABLE 3. PROTON CHEMICAL SHIFTS AND ULTRAVIOLET SPECTRA OF SUBSTITUTED SIX-MEMBERED MERCAPTALS



R_1	R_2	$\mathcal{T}$-values of the NMR peaks in carbon tetrachloride αH (R_1)	α'H	CH_3(in R_2)	UV maxima in ethanol λ_{max} (mμ)	ε	relative rates of T–H exchange
H	H	6·31 (singlet)	7·21	—	250	469	544
H	CH_3	5·97 (quartet)	7·21	8·60	252	449	1·00
CH_3	CH_3	—	7·18	8·36	252	657	—
H	C_2H_5	6·11 (triplet)	7·22	8·94	250	619	3·94
H	i-C_3H_7	6·07 (doublet)	7·20	8·94	249	690	3·31
H	t-C_4H_9	6·10 (singlet)	7·18	8·92	249	767	3·05

TABLE 4. PROPERTIES, YIELDS AND ELEMENTAL ANALYSES OF SULPHUR H-COMPOUNDS

Compound	b.p. (m.p.), °C	yield, %	Found C%	Found H%	Calc. C%	Calc. H%
Ia	182–183	65	43·66	8·05	44·12	8·82
Ib	106/36 mm	70	51·41	9·82	51·22	9·76
IIa	76/23 mm	68	33·54	5·61	33·96	5·66
IIb	68/10 mm	72	44·68	7·53	44·78	7·46
IIIa	95/17 mm (53)	70	39·50	6·53	40·00	6·66
IIIb	108/42 mm	60	51·12	9·56	51·22	9·76
IIIc	112/21 mm	76	48·03	7·68	48·65	8·11
IIId	134/35 mm	70	51·29	8·36	51·85	8·64
IIIe	129/22 mm	50[a]	54·09	8·79	54·45	9·09
IIIf	102/24 mm	75	48·30	8·07	48·65	8·11
IV	94/7 mm	25[b]	51·75	8·42	51·85	8·64

[a] Starting aldehyde was crude. [b] The main product was a high-boiling solid.

tritium-activities were measured with Packard Model 314 A Tri-carb liquid scintillation counter. The properties, yield and the elemental analyses of the sulphur H-compounds are shown in Table 4.

Triethylorthoformate-α-t$_1$ was used as the starting compound for the preparation of α-tritiated acetals and mercaptals, and was prepared from tritium cyanide, tritium chloride and tritiated ethanol through the ethanolysis of tritiated formiminoester hydrochloride.[1]

α-*Tritiated acetals* were prepared by the Grignard reactions of triethylorthoformate-α-t$_1$ with alkylmagnesium iodides or bromides in anhydrous ether.[1]

Acetaldehyde diethylacetal-α-t$_1$, b.p. 101–103°, yield 47%; propionaldehyde diethylacetal-α-t$_1$, b.p. 123–125°, yield 58%; Isobutyraldehyde diethylacetal-α-t$_1$, b.p. 133–136°, yield 81%.

ω,ω'-*Alkanedithiols* were prepared by the reaction of ω,ω'-dibromoalkanes with thiourea and the subsequent hydrolysis of the salts.[19]

1,2-Ethanedithiol, b.p. 61–63°/45 mm, yie.d 45%; 1,3-propanedithiol, b.p. 72°/24 mm, yield 70%; 1,4-butanedithiol, b.p. 54°/3 mm, yield 40%.

α-*Tritiated mercaptals* were prepared by the reactions of α-tritiated acetals with the corresponding dithiols using either fused anhydrous zinc chloride or *p*-toluenesulphonic acid as the catalysts.

Propionaldehyde diethylacetal-α-t$_1$, 10 g, 1,3-propanedithiol, 8 g and *p*-toluenesulphonic acid, 1 g, were dissolved in anhydrous benzene and refluxed for 16 hr. The reaction mixture was washed (with water, 5% Na_2CO_3 and finally with water) and the benzene layer dried ($CaCl_2$). The dried benzene solution was concentrated and the residue was distilled under a stream of nitrogen to give a pale yellow oil, b.p. 112°/21 mm, yield 7·8 g (70%), tritium activity 9·45 μc/mM.

The b.ps and the yield for the other tritiated mercaptals were similar with those of H-compounds listed in Table 4. The tritium activities were in a range of 9·45 ± 0·02 μc/mM.

α-*Dihydrogen compounds* were prepared by the reactions of formaldehyde and the corresponding dithiols by saturating the reaction mixture with hydrogen chloride. The b.ps and the yields are shown in Table 4.

2-t-*Butyl*-1,3-*dithian*. Since attempted reactions of t-butylmagnesium chloride with triethyl orthoformate were all unsuccessful resulting in the recovery of triethyl orthoformate, this mercaptal was prepared from the corresponding aldehyde and 1,3-propanedithiol by the procedure employed for the preparation of the unsubstituted 1,3-dithian, and the α-tritiation was done by the T–H exchange reactions as described below. The aldehyde was prepared by the Grignard reaction of t-butylmagnesium chloride with ethyl formate in anhydrous ether.[20]

Tritiation by T–H *exchange reactions*. Two grams of 1,3-dithian (0·099 mole) was dissolved in 10 ml 0·1 N t-butanol-t$_1$–potassium t-butoxide (10·35 μc/mM) and sealed in high vacuum line and

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[19] *Organic Synthesis*, Coll. Vol. IV, p. 35.

[20] K. N. Campbell, *J. Amer. Chem. Soc.* 59, 1980 (1937).

reacted for 24 hr at 120°. The reaction mixture was neutralized with 0·1 N methanolic hydrogen chloride, concentrated, and the residue extracted into ether, washed repeatedly with water, dried ($CaCl_2$), concentrated and distilled twice to give the α-tritiated product, yield 1·8 g (90%), 1·4 μc/mM.

Tritiation of the other compounds was carried out by similar procedures: 1,3-dithian, yield 70%, 1·95 uc/mM; diethylthioformal, yield 70%, 1·89 μc/mM; 2-t-butyl-1,3-dithian, yield 85%, 1·50 μc/mM.

Tritium-hydrogen exchange kinetics were carried out by the procedures described in the previous paper[1], and the results are shown in Tables 1 and 2. The tritiated compounds described above were diluted with H-compounds before the exchange kinetics, so that the tritium activities fall in a range of 10^4–10^5 d.p.m.

Since the isolation of products was not done during these kinetic experiments, in separate experiments using H-components it was shown that the starting compounds could be recovered quantitatively without any detectable decomposition or side reactions under the conditions of the exchange kinetics listed in Tables 1 and 2.

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