The Preparation and Properties of Aldehydes Containing Deuterium in the Functional Group[1]

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The only aldehyde that has been prepared with deuterium substituted for protium in the functional group is acetaldehyde-d_4 prepared by hydrolysis of deuteroacetylene by Zanetti and Sickman.[3]

Fig. 1a.

Fig. 1b.

This acetaldehyde-d_4 was prepared by a special method and there is available at present no description of a general method for obtaining aldehydes of the structure RCDO. This paper describes the preparation of C_6H_5CDO and p-

$C_6H_5C_6H_4CDO$ by the reduction of the corresponding acid chlorides with deuterium using Rosenmund's method.[4]

An apparatus was developed (Fig. 1) for carrying out the reductions with the minimum amount of deuterium repeatedly circulated through the reaction mixture, and good yields (up to 70%) of aldehyde were obtained based on the amount of deuterium consumed.

Unfortunately, it has not been possible to prepare pure specimens of deutero aldehydes in this manner. It has been shown[5] that the C–H bond in hydrocarbons is more or less labilized by noble metals at moderate temperatures, and this implies a certain admixture of protium with deuterium in the gaseous system after a period of time since xylene was used as solvent during the reaction. However, the deutero aldehydes admixed with some ordinary aldehyde may be used for certain exchange experiments involving the deuterium of the functional group, since it seems established that the C–H bond of hydrocarbons is not labile enough to exchange with water at room temperature. Moreover, the present experiments were planned so as to check this conclusion. Thus it was established that p-phenylbenzaldehyde-d_1, $pC_6H_5C_6H_4CDO$, in contact with conductivity water for four hundred hours caused no increase in density of the redistilled conductivity water. This was to be expected in view of the work of various investigators on the exchange of aldehyde hydrogen,[6] the behavior of aldehydes during the Cannizzaro reaction in heavy water[7] and during autoxidation reduction in heavy water.[8] In contrast, the bisulfite addition product of deutero benzaldehyde was found to exchange up to 0.765 equivalent of deuterium with
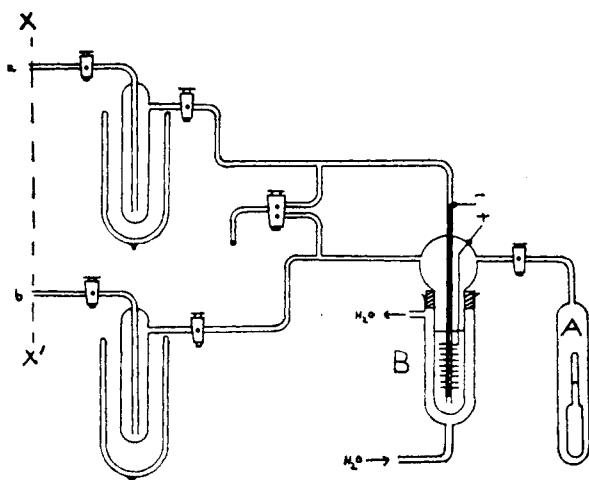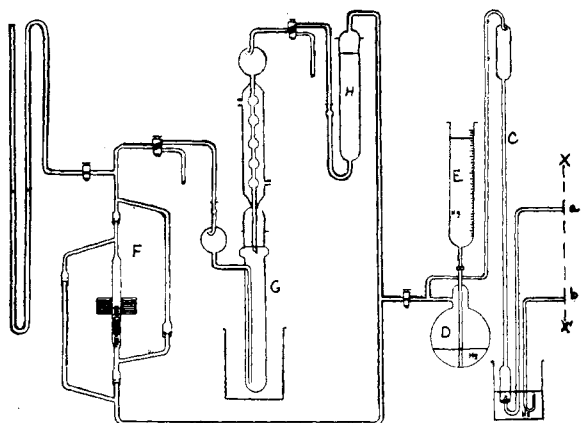
(1) Abstracted from the thesis of N. H. Cromwell submitted to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Master of Science.

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(3) Zanetti and Sickman, THIS JOURNAL, 58, 2034 (1936).

(4) Rosenmund, Ber., 54, 425 (1921).
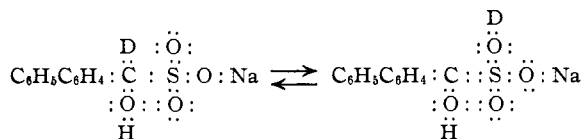
(5) (a) Farkas, Farkas and Rideal, Proc. Roy. Soc. (London), 146A, 630 (1934); (b) Horiuti and Polanyi, Nature, 134, 377 (1934); (c) Polanyi, Trans. Faraday Soc., 30, 663 (1934); (d) Bowman, Benedict and Taylor, THIS JOURNAL, 57, 960 (1935); (e) Farkas and Farkas, Trans. Faraday Soc., 33, 827 (1937).

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(8) Bonhoeffer and Fredenberg, Z. physik. Chem., A181, 379–391 (1938).

conductivity water during the same length of time. These results may be interpreted to indicate that the bisulfite compound may enolize in the sense

$$C_6H_5C_6H_4 : \overset{..}{C} : \overset{..}{\underset{..}{\overset{D}{\overset{..}{O}}}} : \overset{..}{\underset{H}{\overset{..}{\underset{O}{\overset{..}{\overset{..}{S}}}}}} : O : Na \; \rightleftharpoons \; C_6H_5C_6H_4 : C : : \overset{..}{\underset{H}{\overset{..}{\underset{O}{\overset{..}{\overset{D}{\overset{..}{\underset{..}{\overset{..}{S}}}}}}}} : \overset{..}{O} : Na$$

By this mechanism the great increase of mobility of the deuterium atom in the bisulfite compound can be explained. Alternatively, the sulfur can be regarded as having mobilized the deutero atom by withdrawing the electrons of the C:D bond slightly from the deuterium. The exact mechanism of the increased mobility of the deuterium atom in the bisulfite compound probably cannot be assigned.

Experimental

The deuterium oxide was obtained from the California Isotope Company and was labeled as follows: "99.8% D_2O; $D_{25°}^{0°}$ = 1.1077; batch No. 102."

p-Phenylbenzoic acid was prepared from p-bromobiphenyl by the Grignard reaction according to the "entrainment" technique of Grignard.

A mixture of 100 g. of p-$C_6H_5C_6H_4Br$, 47 g. of C_2H_5Br, and 25 g. of Mg was refluxed for ten hours. After carbonation and decomposition in the usual manner, a 50% yield of p-$C_6H_5C_6H_4COOH$ was obtained. It was recrystallized from glacial acetic acid, and melted at 218–221°.

p-Phenylbenzoyl chloride was obtained in a 90% yield by the action of $SOCl_2$ on the acid. The crude product was vacuum distilled and crystallized from high boiling ligroin, yielding white crystals, m. p. 113–114°.

Reducing Apparatus.—The reduction of the acid chlorides was carried out in the apparatus illustrated in Fig. 1 (a and b).

The commercial deuterium oxide was stored in the container A, whence it was distilled as needed into the electrolyzing cell B. Deuterium generated in the cell passed to the reducing apparatus through the tube C. C was over thirty inches (75 cm.) long and its lower end dipped beneath the same mercury layer as the oxygen outlet of the cell. This arrangement made evacuation of the reducing apparatus and filling with deuterium a comparatively simple matter. On evacuation of the reducing apparatus with a Hyvac pump a vacuum of 0.1 mm. or less was obtained in the apparatus and the mercury rose to the barometric level in C. The current was then applied to B and the apparatus filled with deuterium gas without further attention. Excess deuterium could be stored in the reservoir D. The amount of mercury from reservoir E required to restore original pressure conditions in the apparatus measured the volume of deuterium consumed during reduction.

The deuterium was circulated by means of a glass pump F as described by Livingston.[9] On leaving the reaction

flask G it passed through a trap H filled with sodium wire which reacted with the DCl formed in the reduction and restored the deuterium to the circulating gas. Trials showed this trap to be 100% efficient.

The reductions were carried out according to Rosenmund's directions[4] using xylene as a solvent, Pd·BaSO₄ as a catalyst, and sulfur–quinoline as inhibitor.

p-Phenylbenzaldehyde-d_1, Bisulfite Addition Compound, p-$C_6H_5C_6H_4CDO$:NaHSO₃.—A mixture of 6 g. of p-phenylbenzoyl chloride, 3 g. of 5% Pd·BaSO₄, and 10 mg. of Rosenmund sulfur–quinoline was placed in 30 cc. of xylene and deuterium was passed through the mixture for eleven hours at 140°. The total deuterium consumption was 165 cc. The catalyst was filtered off, and the mixture shaken with saturated sodium bisulfite solution for thirty minutes. The mixture was centrifuged and the bisulfite compound separated and dried as quickly as possible. About 2 g. of bisulfite compound was obtained, a yield of 47% based on the deuterium used.

p-Phenylbenzaldehyde-d_1, p-$C_6H_5C_6H_4CDO$.—The bisulfite compound was treated with 3% sodium carbonate and 1 g. of the aldehyde was obtained after recrystallizing from ligroin. Its m. p., 55–56°, was the same as that of p-$C_6H_5C_6H_4CHO$, which would be expected. The substance was prepared several times and the isotopic analysis of two samples follows. A modification of Erlenmeyer's method[10] was used. The density was determined in a pycnometer[11] instead of with a float and this necessitated the combustion of large amounts of material to obtain sufficient accuracy.

Aldehyde sample, g.	1.2473	0.9344
D_2O–H_2O obtained, g.	0.6196	0.4644
H_2O added, g.	0.6314	0.8327
Total H_2O–D_2O sample, g.	1.2510	1.2971
Increase in density over density of conductivity H_2O	0.00416	0.00356
D in sample, g. Found	0.009652	0.008562
Theoretical	0.013739	0.010289
% of 1 D atom found	70.2	83.2

The low and variable deuterium content may be laid to exchange between the deuterium gas and the xylene used as solvent. This resulted in an admixture of protium with the deuterium in the reducing system. However, the rate of exchange with Rosenmund's inhibited catalyst is evidently slow compared to the rate of reduction and so a deuterium content as high as 83.2 atom % could be obtained.

Benzaldehyde-d_1, Bisulfite Addition Compound, C_6H_5CDO·NaHSO₃.—A mixture of 6 g. of benzoyl chloride, 25 cc. of xylene, 10 mg. of Rosenmund's sulfur–quinoline and 2 g. of 5% Pd·BaSO₄ was heated to 145° and D_2 gas was passed through it for nine hours. Total D_2 consumed was 150 cc. After filtering, the mixture was shaken for fifteen minutes with sodium bisulfite, the addition compound was separated in the centrifuge, washed with ether, and dried; yield, 1.87 g., or 66% of the theoretical based on deuterium consumed.

(9) Livingston, *J. Phys. Chem.*, **33**, 955 (1929).

(10) Erlenmeyer and Gartner, *Helv. Chim. Acta*, **19**, 129 (1936).

(11) Yuster and Reyerson, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 61 (1936).

TABLE I

Expt.	Time, hrs.	W_{H_2O} g.	W_S, g.	M_S	W_A, g.	W_B, g.	$W_B - W_A$, g.	ΔD	X	Y	% interchange
1	3	1.5551	1.8400	0.00874	0.87376	0.87389	0.00013	......	....	.....	..
2	144	1.4814	1.8645	.00885	.94707	.94843	.00136	0.001437	0.0133	0.00192	21.7
3	254	1.8486	1.823	.00865	.93213	.93327	.00114	.001223	.0113	.00208	24.0
4	412	1.8347	1.937	.00918	.93213	.93597	.00384	.004120	.0382	.00702	76.5
5	412	1.8391	1.619	.00880	.93213	.93216	.00003	......	....	.....	..

Interchange Experiments.—p-Phenylbenzaldehyde-d_1, was used for the aldehyde interchange reactions since it is a solid and can be isolated easily in a pure condition. For the interchange reactions of the bisulfite addition compounds, the addition compound of benzaldehyde was used since the lower molecular weight makes possible a more favorable proportion of deuterium.

The method used in this and all other exchange reactions was as follows. The dry solid substance was accurately weighed and placed in one arm of a U-tube, A, Fig. 2.
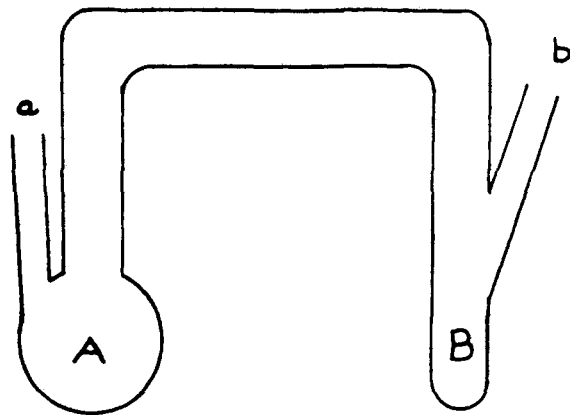

Fig. 2.

This tube was then chilled with solid carbon dioxide and a known weight of conductivity water was introduced. The delivery tube (a) was then sealed off and the apparatus thoroughly evacuated through a delivery tube (b) on the other arm of the U. After complete evacuation this second tube (b) was also sealed and the apparatus allowed to stand evacuated at about 25°. The solid substance was shaken with the water until the whole was intimately mixed. At the end of the experiment the empty arm of the tube, B, was chilled until all the water had collected there. The apparatus was then carefully opened and an aliquot portion of the water removed through (b) and its density determined. From the density of this aliquot portion the amount of D_2O in it and in the whole sample was calculated.

Table I summarizes the results obtained.

The columns of Table I contain the following data: column 1, the experiment number; column 2, the hours duration of the interchange experiment; column 3, W_{H_2O} weight of water used in the interchange experiment; column 4, W_S = weight of substance taken for the interchange experiment; column 5, M_S = moles substance taken; column 6, W_A = weight of conductivity water contained in a pycnometer at 25°,[9] column 7, W_B = weight of water from the interchange experiment contained in the same pycnometer at 25°; column 8, the difference

between these weights, corresponding to the increase in the density of the conductivity water due to interchange; column 9, ΔD = the difference in the density of the two water samples; column 10, the fraction of D_2O in the interchange water equal X; $\Delta D/X$ = 0.1079, where 0.1079 is the difference in density between H_2O and D_2O at 25°; column 11, y = atoms of deuterium exchanged, calculated from the formula

$$y = \frac{2W_{H_2O}X}{M_D - X(M_D - M_H)}$$

where W_{H_2O} = g. of water taken, y = atoms of deuterium exchanging into the water, M_D and M_H refer to the molecular weights of deuterium oxide and water, respectively; column 12, % interchange calculated from columns 5 and 11 by comparison of the amount of deuterium actually exchanged with the amount that was actually present in the substance being investigated. Experiments 1–4 refer to the bisulfite compound, experiment 5, to the free aldehyde.

The data in Table I are self-explanatory.

Experiment 1 shows that in three hours the bisulfite compound in contact with water loses a negligible amount of deuterium. After 251 hours more the same sample lost 24.0% of its deuterium (expt. 3) by exchange with the conductivity water. These results show that the amount of deuterium exchanged during the period of working up the reaction mixtures must be negligible. Experiments 2, 3, and 4 bear out the contention that the bisulfite compound exchanges with water. In experiment 4, 76.5% exchange was observed. This value seems high, but a large molar excess of water was present in these experiments. Experiment 5 shows that no deuterium is lost to the water from the aldehyde even after four hundred and twelve hours. It should be emphasized that no claim of great quantitative accuracy is made for these data. Only the qualitative facts are meant to be established. For this purpose the accuracy of the data is adequate.

Summary

Two aldehydes have been prepared with deuterium substituted for hydrogen in the functional group. The deutero aldehydes were prepared by reduction of the corresponding acid chlorides with deuterium according to the method of Rosenmund using a special apparatus. The bisulfite compound of such an aldehyde has been found to exchange hydrogen with water although the corresponding deutero aldehyde does not exchange. This may be interpreted as evidence for the sulfonic acid structure of aldehyde bisulfite addition products.