

TABLE I
 CHLORO-(PERFLUOROALKYL)-BENZENES

Compound	B. p., °C. 748 mm.	M. p., °C.	n_D^{20}	d_4^{25}	Analyses, %						
					Obs.		Calcd.		Mol. wt.		
					Cl	F	Cl	F	Cl	F	
bis-(Trifluoromethyl)-benzenes											
5-Chloro-1,3-	137.3-137.5	-22.2 to -22.0	1.4043	1.484	14.1	45.6	245	14.3	45.7	248.5	
Dichloro-1,3- ^a	173.0-173.2	-36 to -35	1.4372	1.609	25.0	40.9	281	25.1	40.4	283	
Trichloro-1,3- ^a	209.2-209.4	-2 to -1	1.4704	1.713	33.2	36.0	319	33.6	36.0	317.5	
2,3,5-Trichloro-1,4-	209.6-209.8	-12 to -11	1.4711	1.711	33.4	35.8	314	33.6	36.0	317.5	
2,5-Dichloro-1,4-	174.4-174.6	34.6 to 34.9	25.1	40.9	286	25.1	40.4	283	
Tetrachloro-1,4-	245.5-245.8	48.3 to 48.6	40.6	31.9	350	40.4	32.4	352	
1-(Pentafluoroethyl)-4-(trifluoromethyl)-benzenes											
2,5-Dichloro-	180.9-181.0	Sets to glass	1.4250	1.648	21.4	46.0	332	21.6	45.6	333	
Trichloro- ^a	213.8-214.0	29.3	41.7	366	29.0	41.4	367.5	
Tetrachloro-	247.6-248	50.4 to 51.2	33.6	37.9	403	35.4	37.8	402	
bis-(Pentafluoroethyl)-benzenes											
5-Chloro-1,3-	153.3-153.6	-22.5 to -22.0	1.3791	1.568	9.9	..	346	10.2	54.7	348.5	
2-Chloro-1,4-	164.8-164.9	-21.0 to -20.5	1.3871	1.601	10.0	..	349	10.2	54.7	348.5	
2,5-Dichloro-1,4-	187.8-188.1	39.0 to 39.5	18.9	50.0	320	18.6	49.6	383	
Tetrachloro-1,4-	250.0-252.4	97.5 to 98.3	31.2	42.4	445	31.4	42.0	452	

^a These materials are probably mixtures.

Summary

A procedure generally applicable to the preparation of chloro-bis-(perfluoroalkyl)-benzenes has been devised which involves vapor-phase chlorination of a bis-(perfluoroalkyl)-benzene in contact

with activated carbon catalyst impregnated with an inorganic chloride. Iron(III) chloride was found to be the most satisfactory of the catalysts studied.

RECEIVED¹⁰ JANUARY 5, 1949

(10) Original manuscript received November 28, 1947.

NOTES

Concerning the Structure of D-Glucosone

BY CHARLES E. BECKER¹ AND CLARENCE E. MAY

The structure of D-glucosone has not been definitely established.

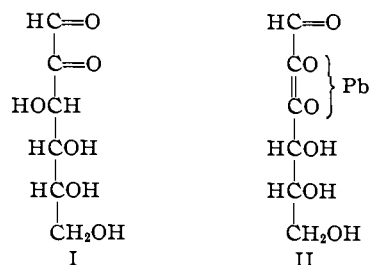
Since it reacted in the cold with various hydrazines, particularly methyl phenylhydrazine, Fischer² believed that D-glucosone existed as the keto-aldehyde, I.

Since it reacted with Schiff reagent in the cold and was bound by sodium sulfite, Dixon and Harrison³ concluded that D-glucosone contained a free carbonyl group.

Because of the selective absorption shown by its aqueous solutions in ultraviolet light, Bednarczyk and Marchlewski⁴ felt that D-glucosone, like D-

fructose and D-sorbose, possessed a free carbonyl group.

Evans, *et al.*,⁵ have speculated that Fischer's lead-glucosone complex might be the salt of a 2,3-enediol



Hynd⁶ retained Fischer's formula for D-glucosone but considered it possible that the compound might later be proved to contain one, or perhaps two, oxidic rings.

Since, in his opinion, the osones showed none of the characteristic reactions of the aldehydes

(1) Taken in part from a thesis submitted by Charles E. Becker to the Faculty of the Graduate School in partial fulfillment of the requirements for the degree Master of Arts in the Department of Chemistry, Indiana University, 1948.

(2) E. Fischer, *Ber.*, **21**, 2631 (1888); **22**, 87 (1889); **23**, 2114 (1890).

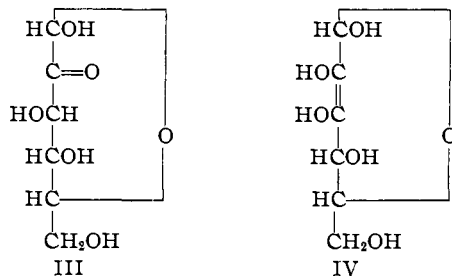
(3) K. Dixon and K. Harrison, *Biochem. J.*, **26**, 1954 (1932).

(4) W. Bednarczyk and L. Marchlewski, *Biochem. Z.*, **300**, 42 (1938); *Bull. intern. acad. polon. sci., Classe sci. math. nat.*, **A**, 524 (1938).

(5) W. Evans, W. Nicoll, G. Strauss and C. Waring, *THIS JOURNAL*, **50**, 2267 (1928).

(6) A. Hynd, *Proc. Roy. Soc. (London)*, **B101**, 244 (1927).

(bisulfite addition, hydroxamic acid reaction, Doebner's reaction) but did show a complete analogy with the reductones, Brüll⁷ felt that D-glucosone must not have a structure corresponding to the formula assigned by Fischer but would exist rather as the hemiacetal form in equilibrium with the tautomeric enediol form



Angeli and Marchetti⁸ have reported that D-glucosone gives a positive hydroxamic acid reaction.

In view of Criegee's⁹ observation that, in contrast to periodic acid, lead tetraacetate does not break ring structure if that structure is present, we felt that oxidation of D-glucosone with lead tetraacetate under the conditions set up by Hockett, *et al.*,¹⁰ for such oxidations would furnish evidence as to the structure of D-glucosone.

It was found that oxidation of D-glucosone with lead tetraacetate produced no significant amount of formaldehyde. Figure 1 shows the kinetics of this oxidation. It was noted that D-glucosone does not consume iodine in acetic acid solution and that aqueous solutions of D-glucosone show slight mutarotation.

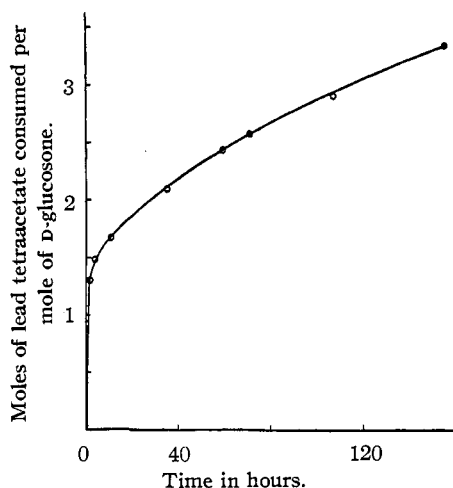


Fig. 1.—Oxidation of D-glucosone by lead tetraacetate.

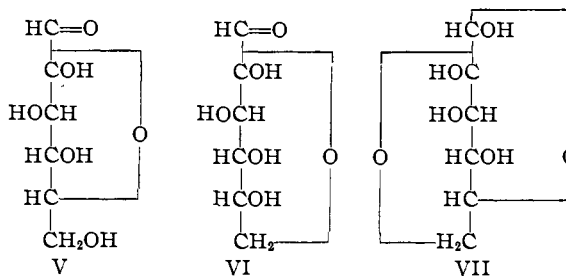
(7) L. Brüll, *Ricerca sci.*, **8**, I, 527 (1937).

(8) A. Angeli and G. Marchetti, *Atti. reale accad. Lincei*, [v] **17**, ii, 360 (1908).

(9) R. Criegee, *Ann.*, **494**, 211 (1932); *Angew. Chem.*, **53**, 321 (1940).

(10) (a) R. Hockett, M. Dienes and H. Ramsden, *THIS JOURNAL*, **65**, 1474 (1943); (b) R. Hockett, M. Zief and R. Goepf, Jr., *ibid.*, **68**, 935 (1946).

Structure III and the following structures for D-glucosone are not eliminated by these observations but, as yet, no selection can be made from amongst them.



Experimental

Materials.—D-Glucosone was prepared by splitting D-glucose phenylsazone¹¹ with pyruvic acid according to Brüll,¹² purified from absolute alcohol, and had a specific rotation of -1.40^{13} at equilibrium (c , 0.550; l , 4; H_2O). It was hygroscopic, rapidly reduced Fehling solution, and gave an immediate precipitate with 2,4-dinitrophenylhydrazine at room temperature. This precipitate melted at 252° (capillary tube, rapid heating).

Lead tetraacetate¹⁴ and aldehyde-free, specially dried acetic acid^{10a} were prepared according to McClenahan, Hockett, *et al.*

Resublimed iodine, approximately 437 mg. (0.00172 mole), was dissolved in 25 ml. of special acetic acid containing 564 mg. (0.00376 mole) of sodium iodide; 5.5 ml. of 0.1 *N* sodium thiosulfate was equivalent to 4.0 ml. of this iodine solution.

Methods.—D-Glucosone, 52.7 mg. (0.000296 mole) in 50 ml. of acetic acid, was oxidized with 2.4 g. (0.00540 mole) of lead tetraacetate under the conditions set forth by Hockett, *et al.*,^{10b} except that the reaction set-up was swept out with tank nitrogen instead of air. No significant amount of formaldehyde was formed.

D-Glucosone, 44.5 mg. (0.000250 mole) in 42 ml. of acetic acid, was oxidized with 57.45 ml. of 0.1323 *N* (0.00380 mole) of lead tetraacetate under the conditions set forth by Hockett, *et al.*^{10a} (Fig. 1).

D-Glucosone, 24.8 mg. (0.000139 mole), was dissolved in 60 ml. of acetic acid. Four ml. of the iodine solution was added. After standing in the dark at room temperature for sixty minutes, the solution was diluted with 150 ml. of water, and titrated with 0.1 *N* sodium thiosulfate. It was found that no iodine had been consumed. This experiment was repeated, except that the D-glucosone was dissolved in water instead of acetic acid, with the same results.

Mutarotation of D-Glucosone.—An ice-cold aqueous D-glucosone solution containing lead acetate was treated with cold saturated barium hydroxide added dropwise with good stirring. The precipitated lead-glucosone complex was filtered off, washed well with ice-water, sucked as dry as possible, and resuspended in ice-water. Just enough cold 20% sulfuric acid was added dropwise with good stirring to break up the complex. The mixture was neutralized with a paste of barium carbonate, filtered rapidly, and the filtrate examined immediately in the polarimeter. After, 20, 26, 31, 35, 41 and 50 minutes the observed specific rotations were -2.55 , -2.18 , -1.95 , -1.73 , -1.40 and -1.40° , respectively.

CHEMICAL LABORATORIES

INDIANA UNIVERSITY

BLOOMINGTON, INDIANA

RECEIVED OCTOBER 16, 1948

(11) E. Fischer, *Ber.*, **19**, 1921 (1886).

(12) L. Brüll, *Ann. chim. applicata*, **26**, 415 (1936).

(13) All rotations quoted in this paper represent specific rotations of the D line of sodium at 21° ; c is concentration in grams per 100 ml. of solution; and l is the tube length in decimeters.

(14) W. McClenahan and R. Hockett, *THIS JOURNAL*, **60**, 2061 (1938).