melted at 210.5–213° (dec.). The two specimens were identical in appearance under the microscope.

Experiment with the Dihydriodide of Di-[α,α-dimethyl-β-(di-*n*-butylamino)-ethyl] Disulfide.—The oil which separated when 0.15 g. of the product (previously obtained[1] by the action of iodine on the mercaptan) was treated with aqueous sodium bicarbonate was collected in ether. The solution was dried and the solvent was removed and replaced by absolute ethanol. Addition of concentrated hydriodic acid and ether caused the separation of 0.1 g. of the dihydriodide, m. p. 167.5–170.5 (dec.). After two recrystallizations from absolute ethanol and ether the salt melted at 174–176° (dec.) alone or mixed with the original salt of m. p. 173.5–175° (dec.). The two specimens were identical in appearance under the microscope.

NOYES LABORATORY
THE UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED MAY 12, 1948

Apparent Molar Volume of Sodium in Liquid Ammonia

BY A. J. STOSICK[1] AND ELTON B. HUNT

In a series of communications Ogg[2] has reported the results of experiments with the unusual solutions of alkali metals in liquid ammonia. In one of his communications[2a] he reported that at a concentration of 3 × 10^{-3} molar, the molar volume of sodium was 700–1000 cc. These values are ten to fifteen times greater than the values reported by Kraus and co-workers[3] for more concentrated solutions. Since the data of Kraus, while indicating an abnormal molar volume, show no trend to larger values with increasing dilution, it seemed worth repeating measurements for dilute solutions. The error in our measurements is relatively large, since we designed our apparatus to accommodate the large effect reported by Ogg. However, our results definitely are not in accord with those of Ogg, but conform to those of Kraus. The experiments consisted in a direct measurement of the increase in volume of liquid ammonia when weighed amounts of sodium were added to form a uniform solution.

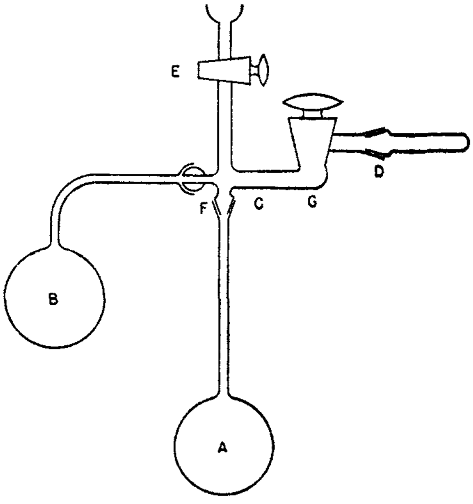

Fig. 1.

The apparatus (Fig. 1) consisted of two 100-cc. bulbs, with bulb A having a calibrated neck which served to measure the increase in volume. The whole unit was connected to a conventional vacuum line via stopcock E and a standard ball joint which permitted shaking the solution.

In the first experiment a freshly cut, massive piece of sodium (27.9 mg. in form of a cube with edge of about 3 mm.) was placed in the side-arm C and the system was quickly evacuated. Next ammonia from a concentrated sodium–ammonia solution contained in a trap on the vacuum line was distilled into bulb A. The stopcock E was then closed. The temperature of A was maintained at −44.5 ± 0.2° by means of an alcohol-bath in a large clear Dewar flask. After establishing constancy of the meniscus level, about half of the ammonia was distilled into B (previously at room temperature). This enabled the introduction of the sodium (by a magnetic pusher) to be made without splashing or "bumping" and permitted the solution to be stirred by shaking A. The ammonia in B was distilled back to A, B restored to room temperature, and A restored to −44.5°. The meniscus level was noted at intervals to be certain that constancy had been achieved. The observed rise of the meniscus, 3.0 ± 0.2 mm., the weight of the sodium, 27.9 mg., and the flask calibration lead to an apparent molar volume of 59 cc. for sodium, an excess of 36 cc. over 23 cc. for metallic sodium. The concentration of the solution was 1.1 × 10^{-2} molar. The precise measurements of Kraus indicate an excess volume of 41.0 to 43.5 cc. for concentrated solutions.

In the second experiment the side-arm at C was modified by the addition of an evacuable side chamber D to keep the sodium out of contact with ammonia gas until it was to be placed into solution. The side-arm had a large bore stopcock and an arrangement of magnetic pushers so that the sodium could be moved without touching stopcock grease. A second modification consisted in analyzing for the sodium remaining in A at the end of the experiment by means of a gasometric procedure. At the end of the experiment most of the ammonia was pumped from A, the temperature of A was raised to produce an ammonia pressure slightly over atmospheric. The flask A was detached at the joint F and transferred to a gasometric train where the remaining ammonia was pumped off. Dilute acid was introduced into A, the evolved hydrogen was flushed by means of carbon dioxide into a measuring vessel using concentrated potassium hydroxide as the confining fluid. Blank tests showed that this procedure introduced no gases which potassium hydroxide did not absorb.

In the second experiment the weighed amount of sodium, 5.3 mg., was placed in D and, after evacuation, was isolated by stopcock G. The subsequent steps were similar to the first experiment except for the final analysis for sodium. The temperature of A was maintained at −42.9 ± 0.1°, and no change (±0.2 mm.) was noted in the level of the meniscus. When correction is made for the ammonia gas which entered the evacuated chamber D, the meniscus rise is 0.5 ± 0.2 mm. The analysis for sodium indicated 3.0 mg., which must be taken as a minimum since no allowance was made for solubility loss of hydrogen in the gasometer. These data lead to an apparent molar volume of 52 cc. (5.3 mg. of sodium by weighing) or 92 cc. (3.0 mg. of sodium by analysis). The concentration of the solution was 2.1 × 10^{-3} molar or 1.2 × 10^{-3} molar, respectively.

It is clear that these results are not in accord with those of Ogg and conform to those of Kraus. Assuming the solutions to have the same coefficient of expansion as

---

[1] Present address: Department of Chemistry, University of Southern California, Los Angeles 7, California.

[2] Richard A. Ogg, Jr., (a) THIS JOURNAL, 68, 155 (1946); (b) *J. Chem. Phys.*, 14, 114, 295, 399 (1946); (c) *Phys. Rev.*, 69, 668 (1946).

[3] Kraus, Carney, and Johnson, THIS JOURNAL, 49, 2206 (1927).

ammonia itself, it can easily be seen that temperature variations cannot account for the difference from Ogg's result. To agree with his results the elevation of the meniscus would have had to be about ten times the values (3.0 and 0.5 mm.) we observed.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED APRIL 7, 1948

The Preparation of Some Cyclic Acetals

BY M. SULZBACHER, E. BERGMANN AND E. R. PARISER

The present investigation of cyclic acetal derivatives of ethylene glycol (1,3-dioxolanes) was undertaken because of their possible convertibility, by hydrogenolysis, into ethylene glycol monoalkyl ethers,[1] not always available by the usual methods. It was known that aldehydes condense with ethylene glycol without catalyst[2] and that acidic substances accelerate the reaction.[3] It was also known that ketones which cannot easily be acetalated by monohydric alcohols, are capable of such catalyzed condensation with glycols; *p*-toluenesulfonic acid has proved to be an efficient catalyst.[4] Without catalyst, the reaction is extremely slow: in the same period in which cyclohexanone, *e.g.*, reacts completely with glycol in presence of the above acid, the reaction proceeds only to an extent of 10% in its absence.

The most convenient method for the preparation of the acetals consists in the azeotropic distillation of the mixture of the components with benzene in presence of the catalyst.[4,5,6] The time required for the liberation of the theoretically expected quantity of water gives an at least qualitative indication of the reactivity of the carbonyl compounds. From Table I in which our results are briefly summarized, the following conclusions can be drawn: Benzaldehyde has approximately the same reactivity as heptaldehyde. As in many other instances,[7] a 4-methoxy group decreases, while halogen, even in ortho-position, increases the activity of the carbonyl group. Among the ketones, those containing the $—CH_2 — CO — CH_2 —$ group, are most active, and in the case of cyclohexanone, even an ortho-methyl group does not affect the activity. Bulky radicals, as in the case of pinacolone, acetophenone and benzophenone deactivate the carbonyl group. Methyl isobutyl ketone shows an unexpectedly slow reaction, although it contains the group $—CH_2—CO—CH_2$. This recalls the inactivity of that ketone in other instances, *e.g.* in the condensation with chloroform.[8] Mesityl oxide behaves in a manner similar to that of its hydrogenation product, methyl isobutyl ketone.

TABLE I

CONDENSATION PRODUCTS WITH ETHYLENE GLYCOL

Carbonyl compound	Time required, hr.	Yield, %	B. p. °C.	B. p. Mm.	Formula	Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Dioxolanes d^{20}_4	Dioxolanes n^{20}_D	Dioxolanes Mol. refraction Calcd.	Dioxolanes Mol. refraction Found
Heptaldehyde[2]	2.5	81.0	94	20	$C_9H_{18}O_2$	..	..	..	...	0.9077[a]	1.43060[a]	44.85	44.70
Benzaldehyde[9]	2.5	82.7	101	10	$C_9H_{10}O_2$	..	..	..	...	1.1156[a]	1.52696[a,b]	41.25	41.53
4-Methoxybenzaldehyde	3.25	84.4	158–60	17	$C_{10}H_{12}O_3$	66.7	66.8	6.7	6.9	1.1776[a]	1.53622[a]	47.51	47.79
2-Chlorobenzaldehyde[10]	1.00	83.5	150–52	16	$C_9H_9O_2Cl$	58.7	58.5	4.9	5.1[c]	1.2639[i]	1.2631[i]	56.11[i]	45.99[i]
Methyl isobutyl ketone	4.0	84.0	48	10	$C_8H_{16}O_2$	66.7	66.9	11.5	11.5	0.908	1.4180	40.23	40.00
Mesityl oxide[11,d]	5.5	66.9	156	760	$C_8H_{14}O_2$	67.6	67.3	9.9	9.8	.9471[j]	1.43963[j]	39.76[j]	39.52[j]
Pinacolone[12]	4.5	80.5	139	760	$C_8H_{16}O_2$	66.7	66.9	11.1	11.4	.9239	1.42356	40.23	39.77
Cyclohexanone[13]	1.5	84.5	65	10	$C_8H_{14}O_2$	..	..	..	...	1.026[e]	1.4580[e,f]	38.07	37.67
2-Methylcyclohexanone	1.4	83.3	82	15	$C_9H_{16}O_2$	69.2	69.3	10.3	10.1	1.0000[a]	1.45579[a]	42.65	42.41
Acetophenone	3.5	85.3	110	30	$C_{10}H_{12}O_2$	73.2	73.5	7.3	7.6	......	....	....	....
Methyl benzyl ketone[14]	1.5	78.5	133–34	40	$C_{11}H_{14}O_2$	74.2	73.9	7.9	7.7	1.0520[a]	1.51028[a]	50.49	50.62
Dibenzyl ketone[h]	1.15	85.8	200–202	18	$C_{12}H_{18}O_2$	80.3	80.6	7.1	7.3	.....	....	....	....
Benzophenone	5.0	81.4	168	10	$C_{15}H_{14}O_2$	79.6	80.0	6.2	6.1	1.1794[a]	1.59013[a]	65.36	65.53

[a] Temperature, 19.5°. [b] Salmi and Louhenkurru (ref. 11) give d^{20}_4 1.1116; n^{20}_D 1.52513. [c] Calcd.: Cl, 19.2. Found: Cl, 19.0. [d] The bromine addition product, b. p. 80–90° (30 mm.), was a purple-colored liquid which gradually split off hydrobromic acid, upon standing. [e] Temperature, 21°. [f] Salmi (ref. 4) gives d^{20}_4 1.0280; n^{20}_D 1.45828. [g] The acetal crystallized and had, after recrystallization from alcohol, m. p. 60°. It was described recently by Salmi, Tamminen and Louhenkurru.[15] [h] The acetal crystallized: m. p. 69° (from methanol). [i] Data by Salmi and Kyriki (ref. 4). [j] Data by Salmi and Rannikko, *Ber.*, **72**, 600 (1939).

---

[1] Hydrogenolysis of 2-phenyl-1,3-dioxolane and of furfural diethylacetal: Adkins, Covert and Connor, THIS JOURNAL, **54**, 1651 (1932), of ethylenimine derivatives: Karabinos and Serijan, *ibid.*, **67**, 1856 (1945); Campbell, Sommers and Campbell, *ibid.*, **68**, 140 (1946).

[2] Lochert, *Ann.*, [6] **16**, 26 (1889).

[3] Delépine, *Bull. Soc. Chim.*, [3] **23**, 915 (1900); Verley, *ibid.*, **21**, 275 (1899); Trillat and Cambier, *Compt. rend.*, **118**, 1277 (1894).

[4] Salmi, *Ber.*, **71**, 1803 (1938); Salmi and Kyrki, *C. A.*, **41**, 5480 (1947); see also Fourneau and Chantalou, *Bull. Soc. Chim.*, [5] **12**, 845 (1945).

[5] Meerwein in Houben-Weyl, Vol. 3, 3rd edition, Leipzig, 1930, p. 191.

[6] Haworth and Lapworth, *J. Chem. Soc.*, **121**, 81 (1922); see also Senkus, U. S. Patent 2,419,505 (*C. A.*, **42**, 616 (1948)).

[7] Compare, *e. g.*, Petrenko-Kritschenko, *Ann.*, **341**, 165 (1905).

[8] Ch. Weizmann, E. Bergmann and Sulzbacher, THIS JOURNAL, **70**, 1189 (1948).

[9] Hibbert and Timm, *ibid.*, **46**, 1283 (1924).

[10] Salmi and Kyrki (ref. 4).

[11] Salmi, *Ber.*, **72**, 600 (1939). The normal acetal formation of unsaturated aldehydes has already been observed by Leopold and Michael, German Patent 434,989 (*Chem. Zentr.*, **97**, II, 2846 (1926); by Senkus, U. S. Patent 2,383,622 (*C. A.*, **40**, 898 (1946), and by Fourneau and Chantalou (ref. 4). See also Salmi and Louhenkurru, *C. A.*, **42**, 537 (1948).

[12] Salmi and Rannikko (ref. 11).

[13] Salmi (ref. 4).

[14] Preparation by hydrolysis of phenylacetoacetonitrile, prepared according to "Organic Syntheses," Coll. Vol. II, p. 487.

[15] Salmi, Tamminen and Louhenkurru, *C. A.*, **42**, 537 (1948).