TABLE I

	Compounds	B. p., °C., 760 mm.	n^{D}	Temp., °C.	dn/dt
C_1	CH_3Cl	−23.7	1.3830	−42.5	
	CH_3Br	+ 4.5	1.4631	−50.0	0.00066
			1.4432	−20.0	
C_2	$C_2H_5F^a$	−37.7	1.3057	−40.0	
	C_2H_5Cl	+13.1	1.4085	−50.0	.00057
			1.3913	−20.0	
	$(CH_3)_2O$	−24.9	1.3441	−42.5	
C_3	C_3H_6 (Cyclopropane)	−32.9	1.3799	−42.5	
	C_3H_8	−42.2	1.3395	−42.5	
	n-$C_3H_7F^b$	− 3.2	1.3496	−50.0	.00057
			1.3326	−20.0	
	i-$C_3H_7F^a$	−10.1	1.3406	−50.0	.00055
			1.3240	−20.0	
C_4	C_4H_6 (1,3 Butadiene)	− 2.6	1.4293	−25.0	
	C_4H_8 (Butene-1)	− 6.1	1.3803	−25.0	
	C_4H_8 (i-Butylene)	− 6.6	1.3814	−25.0	
	C_4H_{10} (n-Butane)	− 0.5	1.3621	−25.0	.00059
			1.3562	−15.0	
	C_4H_{10} (i-Butane)	−10.2	1.3514	−25.0	
C_7	C_7H_{16} (n-Heptane)	+98.4	1.4141	−25.0	.00060
			1.3870	+20.0	

[a] Prepared by Carl B. Linn and the author by direct addition of hydrogen fluoride to the corresponding olefin.

[b] Prepared by Carl B. Linn and the author by direct addition of hydrogen fluoride to cyclopropane.

Attention may be drawn to the fact that the refractive index of ethyl fluoride is, so far as we know, the lowest yet recorded for any liquid or solid compound.[8,9]

In the field of inorganic chemistry it would be very worth-while, particularly for analytical purposes, to obtain refractometric data on the volatile simple compounds of the metalloids, such as ammonia, hydrogen chloride, hydrogen bromide, hydrogen fluoride, hydrogen sulfide, sulfur dioxide, nitric oxide, nitrous oxide, chlorine and others.

It is hoped that the manufacturers of Abbé refractometers will be in a position to make a few minor mechanical changes and adjustments in the present model to make it more adaptable for low temperature measurements.

(8) See "International Critical Tables," Vol. I, p. 276.

(9) Theoretically the *compound* with the lowest possible refractive index, n_D 1.16 at +19.0°, should be *hydrogen fluoride*, since its constituents, hydrogen and fluorine, have the lowest atomic refractions of all elements (AR_D = 1.100 and 0.997, respectively) and it has the lowest value for the expression Mol. ref./(Mol. vol. − mol. ref.), which should have a minimum for the lowest "n" according to the Lorenz–Lorentz formula. The *element* with the lowest index should be *fluorine*: the calculated value for n_D at −187.0° (= b. p. at 760 mm.) is approximately 1.09.

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Yellow and Colorless Modifications of Benzal- and N-3-Methylbenzal-hydantoin

BY DOROTHY A. HAHN AND MARGARET M. ENDICOTT

In view of the fact that benzalhydantoin recently has been obtained in the form of a white crystalline compound,[1] instead of a deep yellow compound as previously reported,[2] it may be of interest to state that both benzalhydantoin and N-3-methylbenzalhydantoin have been observed to exist in two crystalline modifications, one yellow and the other white. In both cases the difference between these two modifications appears to be limited to a difference in color, since the yellow and white varieties possess the same melting point (dec.) and exhibit the same chemical properties. Each of the two modifications of benzalhydantoin yields benzylhydantoin on reduction with hydrogen iodide and red phosphorus and each of the two modifications of N-3-methylbenzalhydantoin yields a corresponding single reduction product.

In both cases the yellow and white crystals may readily be transformed into each other. For example, if the yellow modification is dissolved in aqueous alkali and the solution neutralized immediately by the addition of a mineral acid, a *white* crystalline compound is precipitated. If, on the other hand, the latter is heated for some time in a boiling concentrated solution of glacial acetic acid, *yellow* crystals are deposited on cooling.

The fact that benzalhydantoin has been commonly described in the literature as a quite definitely yellow compound, would seem to be due to the accident that it was originally prepared by condensing hydantoin with benzaldehyde in an acid medium.[2] When the same condensation occurs in an alkaline medium, the product is white.[1] The synthesis of N-3-methylbenzalhydantoin, on the other hand, takes place in an alkaline solution[3] and the product is therefore commonly described as white. Under the conditions of the experiment as performed in this Laboratory, N-3-methylbenzalhydantoin separates in long, fine, soft, white needles, interlacing to form a mesh of fiber-like strands, which completely fill the space occupied by the solution. The product separates in much the same manner when recrystallized from boiling glacial acetic acid—provided that care is taken to see that the solution is not too concentrated. When, however, concentrated solutions of the reaction product in glacial acetic acid are boiled for more than a very short period of time, they deposit a heavy deep yellow precipitate which forms on the bot-

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(1) Boyd and Robson, *Biochem. J.*, **29**, 543, 545 (1935).

(2) Wheeler and Hoffman, *Am. Chem. J.*, **45**, 371 (1911).

(3) Litzinger, THIS JOURNAL, **56**, 673 (1934).

tom of the containing vessel and consists of small glistening crystals.[4] Neither the crystalline structure nor other of the physical properties of these two modifications has been studied in any detail.

The fact that in the case of both benzalhydantoin and N-3-methylhydantoin, the white modification seems to be stable in alkaline solutions while the yellow modification is stable in an acid medium, suggests the possibility that they may represent, respectively, lactim, and lactam forms of the hydantoin molecule.

[4] This observation was made several years ago but was not reported at the time. It was disconcerting until the fact was established that the yellow compound could be substituted for the white in reduction and alkylation reactions without apparent loss in the percentage yields.

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The Condensation of Aldol with Dimedon

BY ISAKU KASUYA

In the course of another investigation it became necessary to obtain for comparison an authentic sample of the condensation product of aldol with dimedon.

The preparation of this compound has been reported previously by Fricke[1] who obtained a product which after crystallization from 50% ethanol melted at 170–172°. He reported further that crystallization of this substance from 96% ethanol gave rise to the formation of crotonaldimedon, m. p. 183°.

The condensation product obtained by us melted at 146–148° and could be crystallized repeatedly from 96% ethanol without appreciable change.

In view of the disparity existing between these results, it seemed of interest to reinvestigate the nature of the condensation product obtained under the conditions specified by Fricke. In the light of our investigation it seems probable that the product obtained by him was an impure sample of crotonaldimedon. This result is not surprising when we consider that the reaction mixture of alcohol, aldol and dimedon is allowed to stand for several days in the presence of sodium chloride giving ample opportunity for dehydration to take place.

The author wishes to express his gratitude to Mr. Konomu Matsumura for his assistance in this investigation.

Experimental

Aldol was prepared from acetaldehyde by the method of Claisen[2] and the portion which distilled at 63–66° (6 mm.) was taken. By this method aldol was obtained as a colorless viscous liquid with a fragrant odor at room temperature, but odorless at 0°.

Condensation of Aldol with Dimedon.—A solution of aldol (0.4 g.) with dimedon (2 g.) in methanol (20 cc.) was refluxed for an hour, poured into water (500 cc.), and allowed to stand for two days. The solid which separated was crystallized from dilute (30%) methanol giving colorless prisms, m. p. 146–148°. This product was soluble in dilute sodium hydroxide.

Anal. Calcd. for $C_{20}H_{30}O_5$: C, 68.57; H, 8.57. Found: C, 68.36; H, 8.59.

Crotonaldehyde was obtained by repeated distillation of aldol. The fraction taken boiled at 100–105°.

Condensation of Crotonaldehyde with Dimedon.—A solution of dimedon (1.6 g.) in ethanol (16 cc.) was added with stirring to a suspension of crotonaldehyde (0.5 g.) in water (400 cc.). Upon standing for two days the product separated as colorless prisms, m. p. 182–186°. Upon recrystallization from ethanol it formed colorless prisms which were soluble in dilute alkali and melted at 185–186°.

Anal. Calcd. for $C_{20}H_{28}O_4 \cdot 0.5C_2H_5OH$: C, 70.99; H, 8.73. Found: C, 71.14, 70.77; H, 8.98, 8.75.

Condensation of Aldol with Dimedon by the Method of Fricke.[1]—The experiment was carried out under the conditions recorded by Fricke.

The crude product melted at 160–170° with previous softening at 140°. On recrystallization from 50% ethanol it gave colorless prisms, m. p. 170–173° with preliminary softening at 160°. This product shows no depression of melting point when mixed with an authentic sample of crotonaldimedon (m. p. 185–186°). It is soluble in dilute sodium hydroxide solution.

Anal. Calcd. for $C_{20}H_{28}O_4$: C, 72.29; H, 8.43. Found: C, 72.19; H, 8.33.

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[1] Fricke, *Z. physiol. Chem.*, **116**, 129 (1921).

[2] Claisen, *Ann.*, **306**, 323 (1899).

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The Isolation of Glutathione from Wheat Germ

BY B. SULLIVAN AND MARJORIE HOWE

In a previous contribution from this Laboratory[1] it has been shown that the harmful effect of wheat germ on the baking quality of flour is due to some compound exhibiting a very strong nitroprusside test present in the water extract of the germ. Qualitative tests indicated that this compound was glutathione and it was obtained in an impure state from the germ.

We have now succeeded in isolating glutathione from wheat germ in yields of from 0.1–0.2 g. by

[1] Sullivan, Howe and Schmalz, *Cereal Chem.*, **13**, 665 (1936).