brown, and the coloring matter (hemin?) had precipitated during the growth test. Comparison of the turbidity in this case with that in a control tube containing the same amounts of hydrolyzed hemoglobin and medium but to which no yeast seeding had been added, showed that the turbidity was due almost entirely to the precipitated coloring matter. The difference between the two turbidities corresponded to 0.07 microgram of β-alanine per four mg. of original hemoglobin, which is much less than the minimum figure of 5.3 micrograms per 4 mg. which would be required by the presence of one β-alanyl unit in the hemoglobin molecule (molecular weight 66,700).

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The Preparation of Desoxycholic Acid from Cholic Acid

ALEXANDER W. SCHNEIDER[1] AND WILLARD M. HOEHN

In a recent publication by Haslewood[2] the preparation of desoxycholic acid from cholic acid was presented. The details of the method were not given. It was stated the cholic acid was preferentially oxidized by means of chromic acid to 3,12-dihydroxy-7-ketocholanic acid and this product converted to the corresponding semicarbazone. We assume the semicarbazone was reduced according to the Wolff–Kishner technique to yield desoxycholic acid.

More than two years ago we carried out these particular reactions not only with cholic acid but also with derivatives of it. The data obtained from these investigations enabled Schmidt, Hughes and one of us (W. M. H.) to ascertain the course of the bacterial oxidation of cholic acid.[3] Cholic acid, methyl cholate, methyl 3-benzoxy-7,12-dihydroxycholanate[4] were some of the derivatives used. The compound was dissolved in either acetic acid or a mixture of acetic acid, benzene and water, and a solution of chromic acid in dilute acetic acid added. The mixture of oxidation products was converted to semicarbazones or hydrazones, which were then reduced according to the method of Wolff and Kishner (*cf.* ref. (3)). It was found that concentrated solutions of potassium or sodium hydroxide in methanol could be used instead of an alcoholic sodium alkoxide solution. The desoxycholic acid was isolated from the mixture of reduction products in accordance with known methods.

The controlled oxidation of methyl 3-benzoxy-7,12-dihydroxycholanate gave a mixture of products. From this mixture a monosemicarbazone was isolated by virtue of its solubility in methanol. The monosemicarbazone was heated with sodium methoxide in methanol (10 g. of sodium in 100 cc. of methanol) or with sodium or potassium hydroxide in methanol (10% solutions), to a temperature of 170–200° for periods up to six hours. The crude desoxycholic acid prepared by these reactions may be crystallized directly from acetic acid to yield the acetic-choleic acid. Desoxycholic acid is obtained from this complex in the usual manner.[5] The melting point[6] for the pure acid was 174–176°. The desoxycholic acid prepared by this procedure still gave a positive Gregory–Pascoe reaction[7] which is indicative of the presence of cholic acid. The melting point of a mixture of a sample of desoxycholic acid (m. p. 172–173°) (Gane and Ingram, N. Y.) and that prepared by the above method was 172–174°. The $[\alpha]^{26}\text{D}$ of a methanol solution of the desoxycholic acid was observed to be +57 ± 1°.

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[1] Present address: Central Soya Company, Decatur, Ind.

[2] Haslewood, *Nature*, **150**, 211 (1942); also *cf. C. A.*, **36**, 7029 (1942).

[3] The results of this investigation were presented at the A. C. S. meeting in Memphis, April, 1942.

[4] Hoehn and Mason, THIS JOURNAL, **62**, 569 (1940).

[5] Sobotka, "Chemistry of Sterids," Williams and Wilkins Co., Baltimore, Md., 1938, p. 77.

[6] Melting points were observed on the Johns melting point block.

[7] L. H. Schmidt, *Am. J. Physiol.*, **120**, 75 (1937).

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Total and Partial Pressures of Binary Mixtures of Dioxane in Benzene at 25°

BY PEYTON C. TEAGUE[1] WITH W. A. FELSING

In an investigation with dioxane, it became necessary to know the partial vapor pressure of a solution of dioxane (diethylene dioxide) in benzene. Since the similarity in structure and polarity indicated solutions approaching ideality, it was decided to cover the entire composition range.

The method used was the differential method of Parks and Schwench[2] as modified by Olsen and Washburn[3] and by Allen, Lingo and Felsing.[4] The benzene was purified as described previously[4] and the dioxane was purified by the method of

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[2] Parks and Schwenck, *J. Phys. Chem.*, **28**, 720 (1924).

[3] Olsen and Washburn, *ibid.*, **41**, 457 (1937).

[4] Allen, Lingo and Felsing, *ibid.*, **43**, 425 (1939).

Eigenberger,[5] followed by repeated fractional freezing. The final products had the following characteristic constants

	B. p. (750 mm.), °C.	F. p., °C.	$n^{25}D$	d^{25} (g./cc.)
Benzene	79.7	5.5	1.4980	0.8732
Dioxane	101.0	11.8	1.4202	1.0280

All solutions were made by weight using weight burets; the exact compositions approximated 20, 35, 50, 65 and 80%. Moisture was excluded.

The refractive indices and densities at 25° are represented by the relations

$$n^{25}D = 1.4980 - 0.0743x - 0.035x^2$$

and

$$d^{25}(\text{g./cc.}) = 0.8732 + 0.1514x + 0.0034x^2$$

where x is the mole fraction of the dioxane in the mixture.

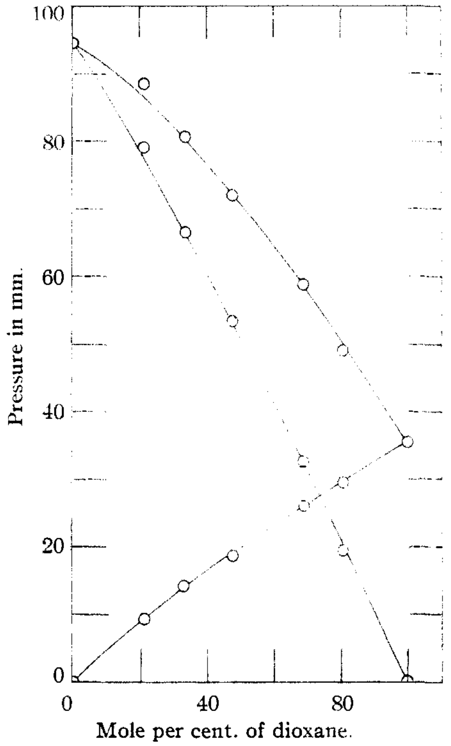

Fig. 1.

The partial pressure data are presented in the following table and in the figure.

Mole fraction of dioxane in solution	Total press., mm.	Mole fraction of dioxane in condensate	Partial pressures, mm. Dioxane	Benzene
0.000	94.4	0.000	..	94.4
.212	88.5	.106	9.4	79.1
.334	80.7	.176	14.2	66.5
.478	72.0	.259	18.6	53.4
.689	58.7	.445	26.1	32.6
.806	49.0	.602	29.5	19.5
1.000	35.5	1.000	35.5	..

The deviation from ideality is slight as was anticipated; this is shown in the figure.

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[5] Eigenberger, *J. prakt. Chem.*, **75**, 130 (1931).

The Addition of Triphenylmethyl to 2-Methyl-buten-1-yne-3

BY A. F. THOMPSON, JR., AND DOUGLAS M. SURGENOR

Some years ago, Conant[1] and two co-workers showed that triphenylmethyl, and other free radicals, entered into addition reactions with unsaturated substances, including conjugated dienes, pyrrole, and maleic anhydride. It seemed of interest to study the application of this reaction to enynes, and the interaction of triphenylmethyl with 2-methyl-buten-1-yne-3 was accordingly investigated.

2-Methyl-buten-1-yne-3 was prepared according to Thompson and Shaw.[2]

Triphenylmethyl chloride was recrystallized from benzene and acetyl chloride to give a product melting at 112-113°.[3] Addition of the free radical to the enyne was carried out by shaking together 14 g. (0.05 mole) of triphenylmethyl chloride, 50 g. of pure mercury, 12 g. (0.18 mole) of 2-methyl-buten-1-yne-3 (b. p. 34-35°) and 18 g. of dry, thiophene-free benzene at room temperature for five days in an atmosphere of dry nitrogen. The reaction mixture was then evaporated to dryness under reduced pressure, and the residue extracted with ether. From the ether solution, 6.5 g. of crystalline addition product was obtained, m. p. 182-184°, yield 47%. On recrystallization from benzene-petroleum ether, a melting point of 184-185.5° was obtained.

Anal.[4] Calcd. for $C_{43}H_{36}$: C, 93.47; H, 6.53. Found: C, 93.5, 93.0; H, 6.88, 6.78.

The addition product, in ethyl acetate solution, was hydrogenated with platinum oxide catalyst. The absorption by 0.340 g. (0.61 millimole) of the compound was 26.9 cc., corresponding to 1.97 double bonds, and indicating that the reaction stopped after addition of two triphenylmethyl radicals to the conjugated enyne system.

Ozonolysis of 3.8 g. (6.9 millimoles) of addition product was carried out by passing ozone through a solution in 70 cc. of dry ethyl acetate at 0°, during twelve hours. The ozonide solution was then hydrogenated according to F. G. Fischer,[5] using 0.75 g. of 5% Pd-$CaCO_3$ catalyst. On oxidation with silver oxide, and separation of the neutral and acid fractions with sodium carbonate, two substances were obtained.

From the acid fraction 24 mg. (0.083 millimole) of tri-

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[1] (a) Conant and Scherp, THIS JOURNAL, **53**, 1959 (1931); (b) Conant and Chow, *ibid.*, **55**, 3475 (1933).

[2] Thompson and Shaw, *ibid.*, **64**, 365 (1942).

[3] All melting points in this paper are corrected.

[4] The authors wish to acknowledge the courtesy of Malcolm Brown, who carried out the semi-micro combustion analyses.

[5] F. G. Fischer, Düll and Ertel, *Ber.*, **65**, 1467 (1932).