3. The properties of its triacetate, tri-*p*-toluenesulfonate, tri-*p*-nitrobenzoate, and trimethyl ether are described.

4. The glucosan contains a *trans*-glycol group which is not oxidized by periodic acid or lead tetraacetate under conditions used for the detection of adjacent hydroxyl groups.

PEORIA, ILLINOIS RECEIVED MARCH 6, 1946

NOTES

Preparation of Triethylchlorosilane from Ethyl Orthosilicate[1]

BY P. A. DI GIORGIO, W. A. STRONG, L. H. SOMMER AND F. C. WHITMORE

For studies on organosilicon compounds, large quantities of pure triethylchlorosilane and other trialkylchlorosilanes were needed. The preparation from silicon tetrachloride and ethylmagnesium bromide required a time-consuming fractional distillation to separate the desired compound (b. p. 144°) from diethyldichlorosilane (b. p. 128°). Moreover, the yield of triethylchlorosilane by this method is only 30–35%. The present method gives a 60% yield of pure product, diethyldichlorosilane not being formed.

Reaction of ethyl orthosilicate with three equivalents of ethylmagnesium bromide gave triethylethoxysilane which was converted to hexaethyldisiloxane by acid hydrolysis. Addition of ammonium chloride to a concentrated sulfuric acid solution of the disiloxane gave pure triethylchlorosilane.[2]

$$(EtO)_4Si \xrightarrow{EtMgBr} Et_3SiOEt \xrightarrow{Acid}$$

$$(Et_3Si)_2O \xrightarrow[H_2SO_4]{NH_4Cl} Et_3SiCl$$
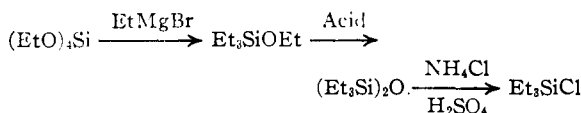
It is not necessary to isolate the disiloxane. The unpurified product from the reaction of ethyl orthosilicate and ethylmagnesium bromide can be dissolved directly in concentrated sulfuric acid and treated with ammonium chloride to give triethylchlorosilane. Diethyldichlorosilane and ethyltrichlorosilane are not formed in this step.

We have applied this method to the corresponding *n*-propyl and *n*-butyl compounds.

Experimental

Hexaethyldisiloxane from Ethyl Orthosilicate.—In a 12-liter three-necked flask, fitted with a mercury-sealed stirrer, reflux condenser and dropping funnel, there was prepared 22 equivalents of ethylmagnesium bromide in 10 liters of ether.[3] The flask was cooled with tap water and 1450 g. (7.0 moles) of ethyl orthosilicate was added during one hour. After stirring at room temperature for another hour, the ether was distilled and the product heated on the steam-bath for twelve hours. The ether was then returned

(1) Paper VI on Organosilicon Compounds; for V see Sommer, Goldberg, Dorfman and Whitmore, THIS JOURNAL, 68, 1083 (1946).

(2) Cf. Flood, ibid., 55, 1735 (1933).

(3) We now use copper lined reactors for all large Grignard reactions.

to the flask followed by hydrolysis of its contents with ice water and acid. After separation of the ether layer, the ether was distilled from the product; a small amount of ethanol was also removed by distillation. The product was then dissolved, with cooling, in 1.5 liters of concentrated sulfuric acid. This was then added to 6 liters of cold water and the organic layer separated, dried with calcium chloride, and fractionated. There was obtained 573 g. (2.5 moles) of hexaethyldisiloxane,[4] b. p. 233° (734 mm.), n^{20}D 1.4340, a yield of 66%.

Triethylchlorosilane from Hexaethyldisiloxane.—To 275 cc. of cold concentrated sulfuric acid there was added 265 g. (1.08 moles) of hexaethyldisiloxane. To this there was added, with stirring, 175 g. (3.1 moles) of ammonium chloride over a period of two hours. Stirring was continued for an additional hour, and the upper layer was then separated and fractionated in a column of 15 theoretical plates. All but 8 g. of this material proved to be triethylchlorosilane, 286 g. (1.9 moles), b. p. 144° (735 mm.), n^{20}D 1.4314, d^{20} 0.8967, a yield of 86%. Triethylchlorosilane was analyzed for chlorine content as follows: Weighed samples, about 0.5 g., were added to a mixture of 30 cc. of methanol and excess standard alkali, followed by titration with acid.

Anal. Calcd. for $C_6H_{15}SiCl$: Cl, 23.5. Found: Cl, 23.5, 23.6.

Isolation of the hexaethyldisiloxane is unnecessary; in other preparations, the undistilled reaction product from ethyl orthosilicate and ethylmagnesium bromide was dissolved in concentrated sulfuric acid and ammonium chloride was added. The yield of pure triethylchlorosilane by this shorter method was 60–70%.

The success of this shorter method depends on: (1) no tetraethylsilane (b. p. 154°) is formed from ethyl orthosilicate even with four or more equivalents of ethylmagnesium bromide under the conditions used. (2) Diethyldichlorosilane is not formed on treatment of the corresponding diethoxy compound with sulfuric acid and ammonium chloride.

(4) Ladenburg, Ann., 164, 325 (1872), first prepared this compound.

THE SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNA. RECEIVED NOVEMBER 12, 1945

The Purification of Thionyl Chloride

BY D. L. COTTLE

This substance is ordinarily purified by treatment with quinoline and linseed oil, a procedure that gives poor yields and difficult-to-handle residues. Pratt[1] modified the method by using a lower aliphatic ketone in place of quinoline and sulfur in place of the linseed oil. The latter procedure has been modified herein as follows: Nine hundred milliliters of crude technical thionyl

(1) H. R. C. Pratt, British Patent 538,028, July 17, 1941.

chloride was refluxed for four and one-half hours with 25 g. of flowers of sulfur and distilled rapidly through a 30-bulb Snyder column attached to an all-glass setup. A 94% yield of colored product was taken overhead. The distillate was fractionated through the 30-bulb column, about twelve hours being needed to remove the colored forerun. The colorless portion was taken overhead in about two hours and distilled over no range with a thermometer that was graduated in degrees. The yield in the second step was 88% making an 82% over-all yield. The product was colorless when viewed crossways in a liter graduate and very slightly yellow when viewed from the top. The still went to dryness and the residue was yellow with some black material reminiscent of organic matter. No attempts to improve the above procedure were made.

The sulfur probably aids in changing the sulfuryl chloride to sulfur dioxide and sulfur chlorides. The sulfur monochloride, b. p. 135.6°, presumably is left behind in the first distillation and sulfur dichloride, b. p. 69°, is the forerun of the fractionation which gives the colorless thionyl chloride, b. p. 78.8°. It is probably impractical to try removing both sulfur chlorides in one distillation because of the equilibrium between sulfur monochloride on the one hand and sulfur dichloride and sulfur on the other.

CONTRIBUTION FROM
THE SCHOOL OF CHEMISTRY
RUTGERS UNIVERSITY
NEW BRUNSWICK, N. J.   RECEIVED APRIL 5, 1946

The Molecular Refractions of the Higher Acetylenic Hydrocarbons[1]

BY G. F. HENNION AND T. F. BANIGAN, JR.

It is well known that the calculated molecular refractivities of organic compounds usually do not agree exactly with the observed values given by the Lorenz–Lorentz equation. In the absence of structural complications, e. g., conjugate unsaturation, the agreements are on the whole remarkably good for pure liquids. Notable exceptions to this fact are found among the higher acetylenic hydrocarbons. The treatises of organic chemistry uniformly cite the (D-line) value, 2.398, as the atomic correction factor for the triple bond, even though there is good evidence that this value is not entirely trustworthy. Auwers,[2] among others, called attention to this some years ago after examination of selected literature data. He suggested a triple bond correction of 2.325 for terminal acetylenes, R—C≡CH, and 2.573 for the non-terminal ones, R—C≡C—R′. Campbell and Eveslage[3] very recently showed that these values also are not fully reliable and recommended a new set of increments for 1-, 2-, 3-, 4-, and 5-

(1) Paper I. on the chemistry of the substituted acetylenes; previous paper. THIS JOURNAL. 68, 1202 (1946).

(2) Auwers, Ber., 68, 1635 (1935).

(3) Campbell and Eveslage, THIS JOURNAL, 67, 1851 (1945).

acetylenes, respectively. Actually none of these approaches are accurate. This was brought to our attention recently during a study of di-t-butylacetylene.[4] Using the accepted value for the triple bond, 2.398, the calculated and observed refractions were 46.378 and 47.641, respectively, thus showing an apparent exaltation of 1.263 units. Campbell's increment for 3-acetylenes, 2.696, improves the agreement insufficiently. A study has therefore been made of the refractions of twenty purified acetylenes reported in the literature (Table I). In order to obtain exact agreement between the calculated and observed refractions of these compounds, twenty different triple bond increments are needed. They range from 2.219 for 1-pentyne to 3.661 for 2,2,5,5-tetramethyl-3-hexyne (di-t-butylacetylene). The required correction increases with alkyl chain lengthening on each side of the triple linkage and with chain branching nearby. The triple bond increment therefore depends upon the number of carbon (?) atoms which come under the influence of the triple linkage and it seems impossible to assign any satisfactory value or values to the triple bond, per se.

In order to estimate the expected refractions more closely, an entirely different method of cal-

TABLE I

PHYSICAL CONSTANTS AND MOLECULAR REFRACTIONS OF HIGHER ACETYLENES

Compound	Formula	d^{20}	$n^{20}D$	MR_D obsd.	—MR_D calcd.— Present method	—MR_D calcd.— Old method
2-Butyne[a]	C_4H_6	0.6913	1.3921	18.637	18.638	18.670
1-Pentyne[a]	C_5H_8	.6908	1.3852	23.118	23.100	23.288
2-Pentyne[a]	C_5H_8	.7104	1.4039	23.444	23.443	23.288
1-Hexyne[a]	C_6H_{10}	.7156	1.3990	27.766	27.736	27.906
3-Hexyne[b]	C_6H_{10}	.7231	1.4110	28.204	28.248	27.906
3,3-Di-Me-1-butyne[c]	C_6H_{10}	.6686	1.3744	28.083	28.074	27.906
1-Heptyne[a]	C_7H_{12}	.7325	1.4088	32.444	32.336	32.524
5-Me-1-hexyne[a]	C_7H_{12}	.7274	1.4059	32.467	32.336	32.524
1-Octyne[a]	C_8H_{14}	.7460	1.4159	37.060	36.954	37.142
2-Octyne[a]	C_8H_{14}	.7596	1.4278	37.308	37.315	37.142
3-Octyne[a]	C_8H_{14}	.7522	1.4250	37.458	37.502	37.142
4-Octyne[a]	C_8H_{14}	.7509	1.4248	37.508	37.520	37.142
3-Nonyne[d]	C_9H_{16}	.7616	1.4295	42.090	42.120	41.760
3,3-Di-Me-4-heptyne[e]	C_9H_{16}	.7610	1.4360	42.679	42.494	41.760
5-Decyne[b]	$C_{10}H_{18}$	.7688	1.4332	46.746	46.756	46.378
3-Me-3-Et-4-heptyne[e]	$C_{10}H_{18}$	.7714	1.4386	47.104	47.130	46.378
2,2-Di-Me-3-octyne[e]	$C_{10}H_{18}$	.7491	1.4270	47.382	47.112	46.378
2,2,5,5-Tetra-Me-3-hexyne[f]	$C_{10}H_{18}$	.7120	1.4055	47.641	47.468	46.378
5-Undecyne[d]	$C_{11}H_{20}$	.7760	1.4360	51.306	51.374	50.996
3,3-Di-Me-4-nonyne[g]	$C_{11}H_{20}$	.7667	1.4317	51.480	51.748	50.996

[a] Henne and Greenlee, THIS JOURNAL, 67, 484 (1945). [b] Campbell and Eby, ibid., 63, 2684 (1941). [c] Egloff, "Physical Constants of Hydrocarbons," Reinhold Publishing Co., New York, N. Y., 1939, Vol. I, p. 367. [d] Campbell and O'Connor, THIS JOURNAL, 61, 2898 (1939). [e] Hennion and Eby, ibid., 62, 1800 (1940). [f] Hennion and Banigan, ibid., 68, 1202 (1946). [g] Eveslage, M.S. Dissertation, University of Notre Dame, 1945.

(4) Hennion and Banigan, previous paper, ref. 1.

culation was undertaken. From the numerous examples in Table I, it is possible to calculate approximate contributions of acetylenic carbon ($C^{\equiv}$) and of the α, β, γ, ..., ω carbon atoms combined thereto, assuming only that hydrogen is normal, *i. e.*, contributes 1.100 per atom. On this basis there is obviously no correction for the triple bond. The various calculations are best explained by the following examples. The observed refraction for 1-pentyne less 1.100 gives 22.018 as the value for the group CH_3—CH_2—CH_2—$C{\equiv}C$—; one-half the observed value for 4-octyne, 18.754, is the contribution of CH_3—CH_2—CH_2—$C{\equiv}$. Thus one $C^{\equiv}$ contributes 3.264, the difference between 22.018 and 18.754. Similar calculations made by comparison of 1-hexyne with 5-decyne and of 3,3-dimethyl-1-butyne with 2,2,5,5-tetramethyl-3-hexyne give $C^{\equiv}$ values of 3.293 and 3.163, respectively. The maximum deviation is only 0.130 and the average of the three values, 3.240, is now taken as the mean contribution of one acetylenic carbon atom, $C^{\equiv}$.

The value for *alpha* carbon atoms, C^{α}, was calculated from the data for 2-butyne: MR (obsd.), 18.637; $C^{\equiv}$, 3.240; H, 1.100; C^{α} (calcd.), 2.779.

In a similar way the average contribution of *beta* carbon atoms was obtained from the data for 2-pentyne, 3-hexyne, 3,3-dimethyl-1-butyne, and 2,2,5,5-tetramethyl-3-hexyne. The values so found are 2.606, 2.583, 2.608, and 2.624, respectively; average 2.605.

Using these average values, the increment for each C^{γ} was estimated from the observed refractions of 1-pentyne, 4-octyne, and 3-methyl-3-ethyl-4-heptyne. The agreement is again surprisingly good, the values being 2.454, 2.430, and 2.423, respectively; average, 2.436.

It is seen immediately that the succeeding carbon atoms rapidly approach the normal mean value, 2.418, and it may be assumed that the $C^{\delta \dots \omega}$ increments are, indeed, 2.418 units each. Not only is it likely that the atomic exaltations induced by the triple bond should be largely dissipated at the *delta* carbon atoms, it is possible to justify this assumption by noting the increments for succeeding methylene units in the symmetrical dialkylacetylenes: C_2H_5—$C{\equiv}$ > CH_3—$C{\equiv}$, 4.783; n-C_3H_7—$C{\equiv}$ > C_2H_5—$C{\equiv}$, 4.652; n-C_4H_9—$C{\equiv}$ > n-C_3H_7—$C{\equiv}$, 4.619; n-C_5H_{11}—$C{\equiv}$ > n-C_4H_9—$C{\equiv}$, 4.616; accepted, —CH_2—, 4.618.

The final atomic refractions recommended for alkyl and dialkylacetylenes are, therefore, $C^{\equiv}$ 3.240; C^{α}, 2.779; C^{β}, 2.605; C^{γ}, 2.436; $C^{\delta \dots \omega}$, 2.418; H, 1.100.

The comparison of molecular refractions, observed and calculated on the old and present basis, is made in Table I. The agreements for the present method are uniformly quite good, the maximum deviation being about 0.5%. The normal acetylenes check particularly well; the highly branched isomers deviate slightly in proportion to the extent of branching.

An alternative method of calculation which has been employed commonly with other types of compounds is the use of alkyl group values determined from known compounds. The examples in Table I make possible the assignment of group values for methyl, ethyl, n-propyl, n-butyl, t-butyl, and a few others in the usual manner. Unfortunately, however, such group values taken from several examples frequently disagree. Thus the contribution for t-butyl calculated from t-butylacetylene is 19.749; taken from di-t-butylacetylene it is 20.204, both values based on 2.398 for the triple bond correction. It seems better, therefore, to calculate the expected molecular refraction by summation of the average contributions of the various types of atoms in the molecule.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA RECEIVED MARCH 29, 1946

The Preparation of Some Tertiary Alcohols by the Addition of Organic Acids to Grignard Reagents

BY RALPH C. HUSTON AND DONALD L. BAILEY

In 1904, Grignard[1] prepared 2-methyl-5-ethyl-5-heptanol by passing carbon dioxide into iso-amylmagnesium bromide and adding ethylmagnesium bromide to the reaction mixture. He also prepared 2,7-dimethyl-5-isobutyl-5-nonanol from isobutylmagnesium bromide and isoamylmagnesium bromide. Later Iwano[2] used the method to prepare 5-butyl-5-nonanol.

A patent[3] issued to Bayer and Company in 1906 covered the preparation of tertiary alcohols from organic acids (or their potassium salts) but gave little detail as to procedure or yield.

We have prepared the following sixteen tertiary alcohols in 40-60% yield by slowly adding one mole of organic acid in ether to 3,3 moles of primary Grignard reagent[4] and refluxing on a water-bath for two hours: 2-methyl-2-pentanol, 2-methyl-2-hexanol, 3-ethyl-3-hexanol, 2-methyl-3-ethyl-3-pentanol, 3-ethyl-3-heptanol, 3-ethyl-5-methyl-3-hexanol, 3-ethyl-3-octanol, 6-methyl-6-undecanol, 6-ethyl-6-undecanol, 6-propyl-6-undecanol, 6-isopropyl-6-undecanol,[5] 6-butyl-6-undecanol, 6-isobutyl-6-undecanol,[6] 6-amyl-6-undecanol and 5-butyl-5-nonanol. (The yield of 2-methyl-2-propanol was 4% and that of 3-methyl-3-pentanol was 32%.)

It was found that yields of the alcohols could be increased by adding the acid in benzene solution

(1) Grignard. *Compt. rend.*, **138**, 154 (1904).

(2) Iwano. *Bull. soc. chim.*, **32**, 244 (1925).

(3) German Patent 166,898-99 (1906).

(4) Whitmore and Badertscher. THIS JOURNAL, **55**, 1561 (1933).

(5) B. p. 104-106° (2 mm.); d^{20}_4 0.8425; n^{20}n 1.4477. Calcd. for $C_{14}O_{30}O$: C, 78.5; H, 14.02. Found: C, 78.41; H, 14.17.

(6) B. p. 116-118° (3 mm.); d^{20}_4 0.8367; n^{20}D 1.4464. Calcd. for $C_{15}H_{32}O$: C, 78.95; H, 14.04. Found: C, 78.63; H, 14.14.

(200 ml. per mole of acid), distilling off the ether until the temperature reached 83° and then refluxing for two hours. For example, when this method was used, the yield of 2-methyl-3-ethyl-3-pentanol was 70% instead of 53%.

The addition of the second molecule of alkylmagnesium halide to the salt and subsequent elimination of oxymagnesium halide was relatively slow. Less than fifteen per cent. of ketone was formed from butyric acid and s-butylmagnesium bromide, and less than two per cent. from the same acid and t-butylmagnesium bromide.

The addition of the final molecule of primary Grignard is more rapid but there was always a considerable amount (10–20%) of ketone in the reaction product. Attempts to prepare ketones by adding two moles of primary Grignard reagent to one of the acid gave, as the main product, the tertiary alcohol. This final step gave less than one per cent. of tertiary alcohol in the cases of secondary butyl and tertiary butyl Grignard reagents.

In all cases where primary Grignard reagents were used, the same colorless crystalline salt separated from the reaction mixture after most of the acid had been added. (It did not separate when acids were added to secondary or tertiary butylmagnesium bromide.) The ether was decanted off. The crystals were washed with anhydrous ether and dried in a vacuum desiccator over sulfuric acid. Analysis and reactivity shows a complex made up of one molecule and BrMgOMgBr, two molecules of $MgBr_2$ and four molecules of ether.

Anal. Calcd. for $C_{16}H_{40}O_5Mg_4Br_6$: Mg, 10.93; Br, 54.0; equiv. wt., 444.5. Found: Mg, 10.90; Br, 53.93; equiv. wt., 447.

When treated with water, the double salt decomposed rapidly and gave off ether. A sample was hydrolyzed. Concentration of the filtered solution gave $MgBr_2 \cdot 6H_2O$.

KEDZIE CHEMICAL LABORATORY
MICHIGAN STATE COLLEGE
EAST LANSING, MICHIGAN   RECEIVED MARCH 11, 1946

The Alcoholysis of Cellulose[1]

BY RICHARD E. REEVES, WILHELMINA M. SCHWARTZ, AND JOEL E. GIDDENS[2]

Although acid-catalyzed hydrolysis of cellulose has been the subject of numerous investigations, the alcoholysis of cellulose seems to have received less attention. Hibbert and co-workers,[3] Brown,

(1) From Southern Regional Research Laboratory. New Orleans, Louisiana. One of the laboratories of the Bureau of Agricultural and Industrial Chemistry. Agricultural Research Administration, U. S. Department of Agriculture. Not copyrighted.

(2) Resigned January 3, 1945.

(3) L. Brickman, W. L. Hawkins and H. Hibbert, THIS JOURNAL, 62, 2149–2154 (1940); W. B. Hewson, J. L. McCarthy and H. Hibbert, *ibid.*, 63, 3041–3045 (1941); 63, 3045-3048 (1941); E. West, W. S. MacGregor, T. H. Evans, I. Levi and H. Hibbert, *ibid.*, 65, 1176–1180 (1943); K. A. West, W. L. Hawkins and H. Hibbert, *ibid.*, 63, 3038-3041 (1941).

Heddle and Gardner,[4] and unpublished investigations by Ambler[5] have been concerned chiefly with the non-cellulosic substances which pass into solution upon alcoholysis of wood or other cellulosic materials. Pulping with alcohols has been studied,[6] but the conditions were unfavorable for acid-catalyzed alcoholysis and the products did not resemble those described below. Mark and Siggia[7] encountered the alcoholysis of modified "carboxy cellulose," but their interest was principally concerned with the esterification of carboxyl groups, not in the cleavage of the glucosidic linkages.

In hydrolysis of cellulose certain glucose–glucose linkages are ruptured with addition of a molecule of water. It was anticipated that alcoholysis would result in rupture of glucose-glucose bonds with the addition of a molecule of alcohol. This conception of the reaction seems to receive confirmation in the experiments described below.

Alcoholyzed cellulose differs from hydrocellulose in a number of ways: It is stable toward hot aqueous alkali, is non-reducing by the copper number determination, and it contains measurable amounts of alkoxyl groups attached by glycosidic (acid labile) linkages. Although degradation of cellulose appears to be more rapid by alcoholysis than by hydrolysis, it is found that approximately the same upper limit of fluidity is reached in each instance.

Experimental

Rate of Alcoholysis.—Parallel experiments were set up employing 0.5 *N* hydrochloric acid in methanol, ethanol, methanol–water (9:1 by volume), and water. Commercial grades of absolute methanol and ethanol were used without further purification. Samples of cotton fiber[8] were placed in glass-stoppered flasks containing 30 volumes of one of the acid solutions. After having been allowed to stand various lengths of time in a thermostat at 20°, the samples were removed, filtered on sintered glass filters, rinsed with water until free from acid, and allowed to dry in air. The recovery of fiber was greater than 95% in all instances. The results of fluidity measurements[9] on the products from the experiments with absolute methanol, 90% methanol, and water are shown in Fig. 1. Inspection of this figure shows that the rate of degradation is greatest for absolute methanol, intermediate for the

(4) J. S. Brown, R. D. Heddle and J. A. F. Gardner, *ibid.*, 62, 3251–3252 (1940).

(5) J. A. Ambler, private communication.

(6) S. I. Aronovsky and R. A. Gortner, *Ind. Eng. Chem.*, 28, 1270–1276 (1936); 29, 1431–1434 (1937); H. Y. Charbonnier, *Paper Trade J.*, 114, No. 11, 31–36 (1942).

(7) H. F. Mark and S. Siggia, U. S. Patent 2,379,917, July 10, 1945.

(8) The cotton fiber used in this work had been mechanically cleaned in a Shirley Analyzer. It was extracted in a Soxhlet extractor for four hours with alcohol and boiled for eight hours with water. The cotton linters used in some experiments had been purified by a commercial firm. The fibers and linters were used in the air-dried condition, it having been found in separate experiments that the small amount of moisture introduced with the sample did not cause a detectable change in the course of the reaction.

(9) Fluidity measurements were made at 25° in British Fabrics Research Committee type viscometers (see "The viscosity of cellulose solutions," H. M. Stationery Office, London, 1932). The cuprammonium solvent contained 15 ± 0.1 g. of copper and 240 ± 5 g. of NH₃ per liter. The dispersions contained 0.5 g. anh. fiber per 100 ml. and the results are expressed in rhes.

methanol containing water, and least for aqueous solutions of acid. This finding recalls earlier work in which it has been shown that, under equal conditions of temperature and acid concentration,[10] alcoholysis of simple glucosides proceeds as much as one hundred times more rapidly than hydrolysis. The curve obtained from the ethanolysis experiment not shown in Fig. 1 was slightly lower than that of methanolysis (Curve A in Fig. 1) during the early stages of the alcoholysis, but it appeared to reach the same ultimate value.
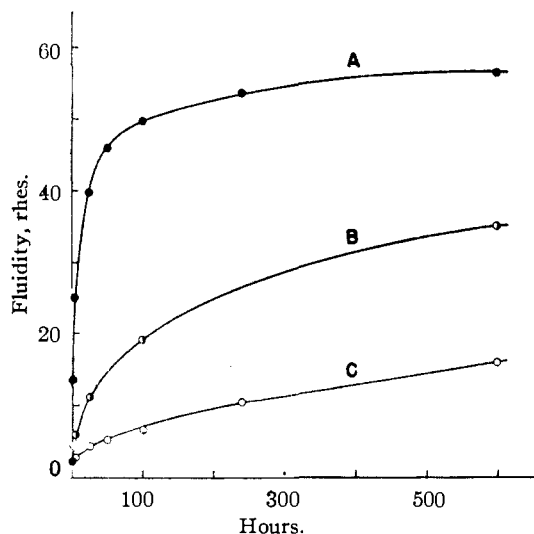

Fig. 1.—The cuprammonium fluidity of cellulose previously treated at 20° for various lengths of time with 0.5 N HCl in absolute methanol (Curve A); 0.5 N HCl in 90% methanol (Curve B); and 0.5 N HCl in water (Curve C).

Copper Number of Alcoholyzed Cellulose.—In contrast with hydrolysis, degradation by alcoholysis does not produce an increase in the copper number[11] of cellulosic material. This finding is to be expected if the conception of the alcoholysis reaction expressed above is correct. Cleavage of the glucose–glucose chain and simultaneous introduction of an alcohol molecule should lead to glucoside formation and not to the production of aldehydic reducing groups. In Fig. 2 is presented the copper number vs. fluidity relationship for cotton cellulose degraded by acid-catalyzed methanolysis or hydrolysis. The high-fluidity-methanolyzed samples were usually prepared by autoclaving the linters with methanol containing an initial concentration of 1 to 2% anhydrous hydrochloric acid. The temperatures employed were 100 to 120°. At these temperatures a rapid loss of acid occurred, but since the products did not contain chlorine it is assumed that the loss of acid was due to formation of methyl chloride. The highly degraded hydrolyzed samples were obtained by refluxing or autoclaving linters with 1 to 3% solutions of hydrochloric acid or sulfuric acid in water.

The Limiting Fluidity and Methoxyl Content of Alcoholyzed Cellulose.—Davidson[12] has recently emphasized the fact that, on long-continued hydrolysis, cellulose approaches a maximum or limiting cuprammonium fluidity value which is well below the fluidity of the cuprammonium solvent. Although cellulosic material disappears on drastic hydrolysis, the fluidity of that part which remains undissolved in the aqueous acid does not exceed the limiting value. A higher limiting fluidity has been found for mercerized cellulose than for native cellulose. A similar
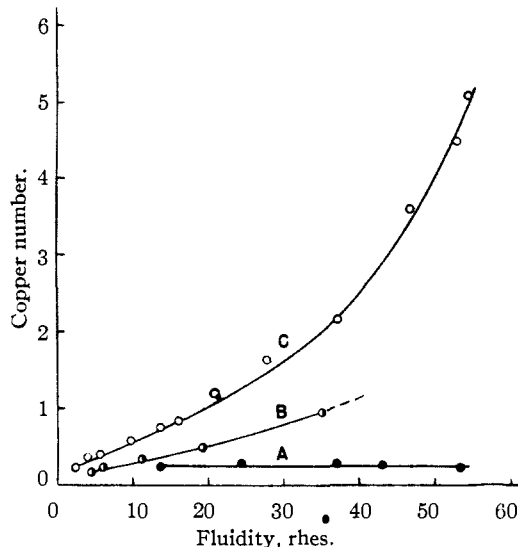
(10) W. Voss and W. Wachs, Ann., **522**, 240–261 (1936).

(11) Copper numbers were determined by the micro method described by T. F. Heyes, J. Soc. Chem. Ind., **47T**, 90 (1920).

(12) G. F. Davidson, J. Textile Inst., **34T**, 87–96 (1943).

Fig. 2.—The copper number–fluidity relationship for cellulose degraded by acid in absolute methanol (Curve A); 90% methanol (Curve B); and water (Curve C).

situation is encountered upon alcoholysis of cotton cellulose; and furthermore the limiting fluidity values correspond very closely with those obtained upon hydrolysis. Under the conditions employed for measurement of fluidity,[9] the limiting values upon methanolysis appear to be approximately 60 rhes for native cellulose and approximately 70 rhes for mercerized cellulose. The corresponding values for hydrolyzed celluloses are 59 and 69 rhes, respectively.

The material which has been methanolyzed to maximum fluidity has been found to yield measurable amounts of methoxyl when subjected to standard methoxyl analyses.[13] Methanolyzed native cotton linters yield approximately 0.58% and methanolyzed mercerized linters, 0.87% methoxyl. By the same technique purified cotton linters, starch, sucrose, and National Bureau of Standards glucose all yield low but fairly reproducible methoxyl values of approximately 0.2 to 0.34%. The methoxyl value of methanolyzed cellulose is thus definitely above that of non-methanolyzed cellulose. Long-continued extraction of methanolyzed linters with water in a Soxhlet apparatus failed to remove any methoxyl from the cellulose, but hydrolysis for 24 hours with 0.5 N hydrochloric acid reduced the methoxyl content from 0.54 to 0.25%, and at the same time increased the copper number from 0.24 to 8.6. This is the type of behavior which would be expected if glucosidic methoxyl groups were replaced by hydroxyl groups by hydrolysis.

TABLE I

COMPARISON OF THE ALKALI-SOLUBILITY OF METHANOLYZED AND HYDROLYZED COTTON FIBER

	Fluidity[a] rhes	% Alkali soluble[b]
Methanolyzed cotton fiber	56.5	2.4
Hydrolyzed cotton fiber	56.8	45.6

[a] See footnote 9. [b] The sample was placed with 100 parts of 1% NaOH in a test-tube immersed in a boiling water bath for six hours. The undissolved residue was collected on a sintered glass filter, rinsed with water, dilute acid, water, and dried to constant weight.

(13) The methoxyl analyses were made by Alva Faust, employing Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, 5th ed., 1940, pp. 647–648. The phenol was omitted and samples were weighed directly into glass micro beakers.

Alkali Solubility of Alcoholyzed Cellulose.—Hydrolyzed cellulose is known to undergo extensive degradation by hot aqueous alkalies. Data given in Table I show that methanolyzed cotton cellulose does not undergo such an effect. This finding provides support for the view expressed by others that the loss of weight suffered by hydrocellulose in hot, dilute alkali is a function of reactivity, and not of solubility.[12] Alkaline solutions heated with hydrocellulose become discolored, whereas when heated with alcoholyzed cellulose they show no discoloration.

RECEIVED APRIL 11, 1946

Dehydrogenation of 1,4-Pentanediol

BY L. P. KYRIDES AND F. B. ZIENTY

The availability of 1,4-pentanediol (I) prompted the study of the dehydrogenation[1] of this glycol. Using a typical copper chromite hydrogenation catalyst,[2] and operating in the liquid phase under reflux, two moles of hydrogen were evolved and γ-valerolactone (II) was produced in 80% yield (an unexpected result). When the reaction mixture was slightly acidified with an organic acid and a downward condenser was used, as much as 30% of γ-acetopropanol[3] (III) was produced together with some (II).

Anal. Calcd. for $C_5H_8O_2$: mol. wt., 100.1; MR, 24.7. Found: mol. wt., 100.0; MR, 24.6.

Addition of a small amount of potassium hydroxide, monobasic sodium phosphate, alundum or decolorizing charcoal (Darco) to the reaction mixture produced an 87–90% yield of (II).

(b) In Presence of Organic Acids.—Under slightly acid conditions, such as could be attained by the addition of 0.003–0.005 mole per cent. of a non-volatile fatty acid like stearic acid,[1] to the reaction mixture, water and a low-boiling organic material could be distilled off and condensed in appreciable amounts. The mechanism in this reaction probably involves dehydrogenation of the secondary alcohol group in (I) to form (III), which, in its cyclic form,[5] dissociates into water and 2-methyl-4,5-dihydrofuran[6] (IV) which distil over and subsequently recombine to form (III).[7] The reaction of (IV) with water is slow (24–48 hours) and may be accelerated by stirring, but will proceed instantly, and even with violence, in the presence of a small amount of mineral acid, such as hydrochloric acid.

In order to separate the (III) from the (II) formed in the reaction, the crude reaction products were distilled slowly at atmospheric pressure using a short column. The volatile dissociation products of (III) distilled over, leaving the (II) behind in the still. (II) and (III) have similar boiling points under atmospheric pressure.

Reaction in an atmosphere of hydrogen was without benefit in producing (III). Activated copper made by decomposition of cupric carbonate in (I) caused some dehydrogenation to (II), but no (III) was obtained. A nickel

TABLE I

Derivative		Recrystn. solvent	M. p.,[a] °C.	Formula	% Nitrogen[b]	
					Calcd.	Found
(I)	Bis-*p*-nitrobenzoate	Me$_2$CO-EtOH	150–151	$C_{19}H_{18}N_2O_8$	7.0	6.8
(III)	Semicarbazone	EtOH	154–155[c]	$C_6H_{13}N_3O_2$	26.4	26.5
(III)	Thiosemicarbazone	H$_2$O	102–103	$C_6H_{13}N_3OS$	24.0	23.9
(III)	Acetate semicarbazone[d]	H$_2$O	125–126	$C_8H_{15}N_3O_3$	20.9	21.0
(III)	Acetate thiosemicarbazone[d]	MeOH	117–118	$C_8H_{15}N_3O_2S$	19.3	19.3

[a] All melting points are corrected. [b] The analyses were performed by Mrs. J. D. Nevins of the Monsanto Analytical Laboratory. [c] Paul, *Bull. soc. chim.*, **53**, 426 (1933), reported 155–157°. [d] Prepared from (III) acetate, b. p. 88–89° (7 mm.). Slobodin, Zigel and Yanishevskaya, *C. A.*, **39**, 702 (1945), reported b. p. 100–115° (22 mm.). Palomaa, *Chem. Zentr.*, **84**, II, 1959 (1913), reported 211–213°. Bergel, U. S. Patent 2,358,618 (September 19, 1944), reported b. p. 96–99° (12 mm.), 103–104° (14 mm.) and 110–112° (17 mm.).

Several derivatives of (III) were prepared (Table I).

Experimental

Dehydrogenation of (I). (a) In Absence of Organic Acids.—A mixture of 104 g. (1 mole) of (I), 4 g. of copper chromite catalyst[2] and 0.15 g. of powdered reagent sodium hydroxide was stirred vigorously and heated under reflux. At 200° a lively evolution of hydrogen occurred and the temperature soon dropped to 190–192° where the dehydrogenation proceeded smoothly. The evolution of gas (39 liters or two moles on the (I) reacted) ceased in about three hours. The reaction mixture was cooled to about 30°, filtered from the catalyst and distilled under reduced pressure, producing 79 g. (87%) of (II), b. p. 90–92° (16 mm.), n^{26}D 1.4290, d^{25}_4 1.047^4, and 12 g. of unreacted (I), b. p. 124–126° (16 mm.) or 120–121° (14 mm.). The (II) was analyzed by titration with alkali.

hydrogenation catalyst caused extensive dehydration of (I), and produced only about 15% of (III).

(1) Kyrides and Zienty, U. S. Patent 2,382,071 (August 14, 1945); *C. A.*, **40**, 90 (1946).

(2) Calingaert and Edgar, *Ind. Eng. Chem.*, **26**, 878 (1934).

(3) Several other examples of the formation of keto alcohols by dehydrogenation of glycols are described in the literature: McNamee and Blair, U. S. Patent 2,143,383 (January 10, 1939), *Chem. Zentr.*, 110, I, 4842 (1939); Hilger, U. S. Patent 1,955,882 (April 24, 1934), see *Chem. Zentr.*, 104, 1, 2172 (1933); Neish, *Can. J. Research.*, **23B**, 67 (1945); Holmes, U. S. Patent 2,036,940 (April 7, 1936), *Chem. Zentr.*, **107**, II, 402 (1936).

(4) Schuette and Sah, THIS JOURNAL, 48, 3165 (1926), reported n^{25}D 1.4301 and d^{25} 1.04608.

(5) Buchman, THIS JOURNAL, **58**, 1804 (1936).

(6) Lipp, *Ber.*, **22**, 1199 (1889).

(7) Marshall and Perkin, *J. Chem. Soc.*, **59**, 882 (1891). Paul, *Bull. soc. chim.*, **53**, 419 (1933), produced γ-acetopropanol by addition of water to 2-methylene-tetrahydrofuran in the presence of sulfuric acid. Knunyantz, Chelintzev, and Osetrova, *C. A.*, **28**, 4382 (1934), reported b. p. 115–116° (30 mm.) for γ-acetopropanol, while we found b. p. 85–86° (10 mm.)

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Solubility Product of Silver Selenocyanate at 25°

BY G. R. WAITKINS AND C. R. McCROSKY

Subsequent to studies dealing with selenocyanic acid and the gravimetric analysis of SeCN$^-$ as silver selenocyanate (AgSeCN)[1] it became of interest to determine the solubility of this silver salt.

A solubility product of 6.9×10^{-15} (K_{sp} average of four determinations) was found for silver selenocyanate at 25 ± 0.1° using the cell: Ag/

(1) Waitkins, M. S. Thesis, Syracuse University, 1934.

AgSeCN, KSeCN/KNO₃/AgNO₃/Ag. The cell was permitted to attain equilibrium in the dark in ten to fifteen hours with the salt-bridge removed. Upon insertion of the salt-bridge, the immediate potentiometer reading was taken as the final equilibrium point owing to the rapid deposition of selenium on the silver electrode and the resultant lowering in e.m.f. Table I lists e.m.f. values observed for this cell at several concentrations of potassium selenocyanate near 0.1 M and the K_{sp} values that were obtained by solving the Nernst equation. The activity coefficients of potassium selenocyanate required for these calculations were taken as the mean of values for the activity coefficients of potassium bromide and iodide.[2,3] The K_{sp} values appear to be in fair agreement considering the difficulty of measurement arising from the drift in potentiometer readings as noted above.

TABLE I

K_{sp} VALUES FOR SILVER SELENOCYANATE AT 25 ± 0.1°

Expt.	M, KSeCN	M, AgNO₃	E.m.f., volt	K_{sp} × 10⁻¹⁵
1	0.0894	0.1363	0.7081	7.1
2	.0935	.0856	.7008	6.5
3	.0958	.3183	.7288	6.6
4	.0644	.1340	.6988	7.4

A comparison of the K_{sp} values for silver halides and halogenoids (thiocyanate and selenocyanate) as shown in Table II reveals the interesting fact that these values decrease progressively with increase in ionic weight of the anion attached to the silver ion. Points obtained by plotting ionic weights against the log of the reciprocal of K_{sp} values will be found to lie very nearly along a straight line. This would seem to be further evidence for the assumption that halide and halogenoid ions are structurally similar. The fluoride and cyanide ion which form complexes with silver ion fall outside this classification. The K_{sp} value for silver cyanate (AgOCN) is not known but might be predicted to lie between that of silver chloride and silver thiocyanate.

TABLE II

COMPARISON OF K_{sp} VALUES FOR SILVER HALIDES AND HALOGENOIDS

Anion combined with Ag⁺	Ionic weight	K_{sp} value at 25°
Cl⁻	35.46	1.95 × 10⁻¹⁰ [4]
OCN⁻	42.02	....
SCN⁻	58.08	1.34 × 10⁻¹² [5]
Br⁻	79.92	6.3 × 10⁻¹³ [4]
SeCN⁻	104.98	6.9 × 10⁻¹⁵
I⁻	126.92	9.7 × 10⁻¹⁷ [4]

Experimental.—The concentration cell, held in a constant-temperature bath and away from

(2) Harned, THIS JOURNAL, **51**, 416 (1929).

(3) Robinson, *ibid.*, **57**, 1161 (1935).

(4) Hess and Jellinek, Z. *physik. Chem.*, **A162**, 153 (1932).

(5) (Average of four determinations) Vol. 11, p. 1182, Landolt-Börnstein "Physikalisch-chemische Tabellen," Julius Springer, Berlin, 1923.

light in a dark-room, was connected with a Type K potentiometer (Leeds and Northrup), a standard cell, a 2-volt battery, and a galvanometer. One arm of the concentration cell consisted of a standard silver nitrate solution (50 ml.) in a 100-ml. glass weighing bottle. The other side of the cell was formed in a similar fashion by dissolving a weighed sample of pure potassium selenocyanate (thrice recrystallized from absolute ethanol and dried at 100-105°) in 50 ml. of water. Silver nitrate (one drop of 0.1 M) was then added to the potassium selenocyanate solution and the mixture was allowed to reach equilibrium after ten to fifteen hours in the dark with occasional stirring by hand for a few minutes after every two to three hours. A thin layer of silver was flashed over the surface of the silver electrodes[6] prior to immersion in the two arms of the cell and the electrical circuit was completed by immediately setting the salt-bridge in place (saturated potassium nitrate in agar). Potentiometer readings were made within ten to fifteen seconds thereafter since the selenocyanate polarized the silver electrode in a few minutes by electrochemical deposition of an observable layer of red selenium, with the probable formation of cyanide ion and possibly some free cyanogen. In any case it is not believed that these side reactions could have seriously affected the final e.m.f. values during the short interval required for taking the readings. In the last determination (Table I) the procedure was varied by adding silver nitrate (10 ml. of 0.001 M) to the potassium selenocyanate solution. In this case the solubility was increased somewhat possibly owing to the colloidal nature of the precipitated silver selenocyanate.

The solubility product of silver chloride determined by the use of the above apparatus under the same experimental conditions was found to be 1.93 × 10⁻¹⁰ which compares favorably with the value of 1.95 × 10⁻¹⁰ determined by Hess and Jellinek.

(6) Hoyt, J. *Chem. Ed.*, **14**, 185 (1937).

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Synthesis of Methyl Ketones from Diethyl Acylmalonates

BY HOWARD G. WALKER AND CHARLES R. HAUSER

A convenient method for preparing certain methyl ketones consists in the acylation of the sodium or, preferably, the magnesiumethoxy derivative of diethyl malonate with the appropriate acid chloride, followed by hydrolysis and decarboxylation of the two ester groups of the resulting diethyl acylmalonate in the presence of acid, thus
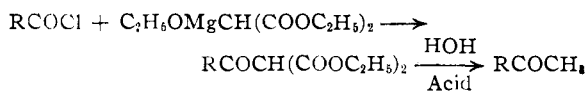
$$RCOCl + C_2H_5OMgCH(COOC_2H_5)_2 \longrightarrow$$
$$RCOCH(COOC_2H_5)_2 \xrightarrow[\text{Acid}]{\text{HOH}} RCOCH_3$$

TABLE I

SYNTHESIS OF METHYL KETONES FROM DIETHYL MALONATE AND VARIOUS ACID CHLORIDES

Acid chloride	Ketone	B. p. or m. p., °C.	Over-all[a] yield, %
o-Chlorobenzoyl	o-Chloroacetophenone	85-87.5, 5.5 mm. 227-228 atm.[b]	81
o-Nitrobenzoyl	o-Nitroacetophenone	158.5-159, 16 mm.[c]	85
p-Nitrobenzoyl	p-Nitroacetophenone	78.5-80°(m. p.)[d]	61
Phenylacetyl	Phenylacetone	97-98.5, 13 mm. 214-215, (cor.) atm.[e]	71
2,4,6-Trimethylphenylacetic	Mesitylacetone	59.5-60.0 (m. p.)[f]	83
Hexahydrobenzoyl	Hexahydroacetophenone	64-65.5, 12 mm. 178-179 (uncor.) atm.[g]	66
Caproyl	Methyl n-amyl ketone	[h]	

[a] Yield of ketone is based on the acid chloride. [b] Thorpe and Brunskill, THIS JOURNAL, 31, 1260 (1915). Oxime, m. p. 105-106°. These authors report m. p. of 104°, for oxime. [c] Camps, Ber., 32, 3232 (1899). [d] Drewsen (ref. 6) reported m. p. of 80-81°. Oxime, m. p. 170-171° (uncor.); Posner [Ann., 389, 43 (1912)] reported 172-173°. [e] Fourneau and Tiffeneau, Compt. rend., 141, 663 (1905). Semicarbazone, m. p. 187-190° (Tiffeneau and Cahnmann, Bull. soc. chim., [5] 3, 1880-1881 (1935)). [f] Anal. Calcd. for C₁₂H₁₆O: C, 81.77; H, 9.16. Found: C, 81.58; H, 9.25. Holmberg [Svensk Kem. Tid., 40, 304-305 (1928)] reported the preparation of the semicarbazone (m.p. 198-199°), but was unable to isolate the free ketone. We prepared a semicarbazone m. p. 204-205° (uncor.). Anal. Calcd. for C₁₃H₁₉N₃: N, 18.00. Found: N, 18.22. (Microanalyses by Arlington Laboratories, Fairfax, Virginia.) [g] B. p. 179-180°, Darzens, Compt. rend., 144, 1124 (1907). Semicarbazone, m. p. 175-176°. Bouveault, Bull. soc. chim., [3] 29, 1051 (1903). [h] No appreciable amount of methyl n-amyl ketone could be isolated; instead, higher boiling products were obtained along with a considerable residue which appeared to have resulted from aldol condensations.

The method has previously been employed by several workers,[1] but its usefulness does not appear to have been widely recognized.

In the present investigation, satisfactory yields (Table I) have been obtained for o-chloroacetophenone, o- and p-nitroacetophenones, phenyl[2] and mesityl acetones, and hexahydroacetophenone, but not for methyl n-amyl ketone. We have chosen the magnesium ethoxy derivative of diethyl malonate[3] rather than the sodium derivative because we believe the former is prepared more conveniently. Although the acid chloride does not appear to react appreciably with the excess alcohol[3] used in the preparation of the magnesium-ethoxy derivative, we have employed a 10% excess of the latter in order to minimize this possible side reaction. The crude diethyl acylmalonates were hydrolyzed and decarboxylated in the presence of aqueous acetic and sulfuric acids according to the method previously employed for the ketonic cleavage of certain β-keto esters.[4]

The present method appears to be one of the best for the preparation of certain higher aliphatic or aliphatic-aromatic[5] methyl ketones, and especially for certain substituted acetophenones. Methods involving Grignard, Friedel–Crafts, or nitration reactions do not appear to be applicable to the preparation of o- or p-nitroacetophenones,[6]

while the Friedel–Crafts reaction is not applicable to o-chloroacetophenone. These and other substituted acetophenones have been prepared by the acylation of acetoacetic ester, followed by hydrolysis and decarboxylation of the ester group and cleavage of the acetyl group. However there appears to be a greater tendency for o-acylation to occur with acetoacetic ester[7] than with malonic ester; moreover, in the acetoacetic ester method cleavage might occur at either acyl group, whereas, in the malonic ester method, cleavage of the two ester groups may usually be effected without appreciable cleavage of the acyl group.

An attempt to extend the malonic ester method using diethyl α-n-butylmalonate and p-nitrobenzoyl chloride has not been satisfactory under the conditions which were employed for the preparation of methyl ketones.

Experimental

General Procedure.—Diethyl acylmalonates were prepared by a modification of the procedure of Lund.[3,8] In a 500-ml. three-necked flask equipped with a mercury-sealed stirrer, dropping funnel, and reflux condenser protected by a drying tube, was placed 5.35 g. (0.22 mole) of magnesium. Five ml. of absolute ethanol and 0.5 ml. of carbon tetrachloride were added. The reaction, which started almost immediately, was allowed to proceed for a few minutes and 75 ml. of absolute ether was then added cautiously. The resulting mixture was placed on the steam bath and a solution of 35.2 g. (0.22 mole) of diethyl malonate, 20 ml. of absolute ethanol and 25 ml. of absolute ether was added at such a rate that rapid refluxing was maintained, heat being applied when necessary. The mixture was refluxed for three hours, or until the magnesium had dissolved. To the clear solution was added with vigorous

(1) For example, Adickes [J. prakt. Chem., 161, 271-279 (1943)] prepared methyl pentadecyl ketone; Wilds and co-workers, [THIS JOURNAL, 66, 1688 (1944), and 68, 89 (1946)] and Johnson and Offenhauer, [ibid., 67, 1045 (1945)] have synthesized certain rather complex methyl ketones.

(2) Metzner [Ann., 298, 378 (1897)] prepared phenyl acetone by this method, but no yield is reported.

(3) Lund, Ber., 67B, 935 (1934).

(4) Hudson and Hauser, THIS JOURNAL, 63, 3136 (1941).

(5) We believe that the malonic ester method is more convenient for phenylacetone than those described in "Organic Syntheses," Coll. Vol. II, 389, 391 (1943).

(6) p-Nitroacetophenone has been prepared from p-nitrocinnamic

acid [Drewsen, Ann., 212, 160 (1882)], but the method does not appear to be any more convenient than the malonic ester method.

(7) See Bouveault and Bongert, Bull. soc. chim.,[3] 27, 1039 (1902).

(8) The present procedure is similar to that of Breslow, Baumgarten, and Hauser [THIS JOURNAL, 66, 1286 (1944)] for the preparation of ethyl-t-butyl acylmalonates.

stirring[9] an ethereal solution of 0.20 mole of the acid chloride and the mixture refluxed for one-half hour. The reaction mixture was cooled and acidified with dilute sulfuric acid. The ether phase, with which an ether extract of the aqueous phase was combined, was washed with water and the solvent distilled.

To the crude diethyl acylmalonate was added a solution of 60 ml. of glacial acetic acid, 7.5 ml. of concentrated sulfuric acid and 40 ml. of water, and the mixture refluxed for four or five hours until the decarboxylation was complete. The reaction mixture was chilled in an ice-bath, made alkaline with 20% sodium hydroxide solution, and extracted with several portions of ether. The combined ethereal extracts were washed with water, dried with sodium sulfate followed by Drierite, and the solvent distilled. The residue containing the ketone was distilled *in vacuo* or recrystallized. The results are summarized in Table I.

(9) In certain cases a viscous mixture was formed and unless it was stirred vigorously, lower yields were obtained.

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DURHAM, NORTH CAROLINA   RECEIVED MARCH 11, 1946

Cyclic Thioureas

BY F. B. ZIENTY

A number of monoformyl-diamines were prepared and cyclized to the cyclic thioureas by reaction with sulfur.[1] The by-products obtained in the preparation of two N,N'-dialkyl-alkylenediamines were identified.

Experimental[2]

N,N'-Dibutyl-ethylenediamine (I).—In the preparation of this product, b. p. 110–111° (8 mm.),[3] yield, 64%, from five moles of butylamine and one mole of ethylene dichloride,[4] the high-boiling by-product obtained was identified as N,N',N''-tributyldiethylenetriamine (II),[5] b. p. 163–165° (8 mm.). Upon titration in acetone solution with aqueous hydrochloric acid using brom phenol blue indicator, only two nitrogens of (II) were titrated.

(I) forms an insoluble monohydrate, m. p. 48–49°, recrystallized from hexane.[6]

N,N'-Dibutyl-trimethylenediamine (III).—Prepared by the method under (I), this product boiled at 120–121° (14 mm.); yield, 72%. The linear amine, N,N',N''-tributyl-di-(trimethylene)-triamine, b. p. 164–165° (3 mm.), obtained as a by-product, behaves as a triatomic base on titration in acetone solution with aqueous hydrochloric acid, using brom phenol blue indicator.

(III) hydrate melts at 44–45°, after pressing on absorbent paper.

Formylation of Ethylenediamine (IV).—Condensation of (IV) with 85% formic acid at reflux did not produce appreciable amounts of formyl derivatives. A 30% yield of crude N-formyl-(IV),[7] b. range 90–110° (14 mm.), was obtained by the ester acylation method.[8]

(1) Zienty and Thielke, THIS JOURNAL, **67**, 1040 (1945).

(2) All melting points are corrected.

(3) Sebrell and Clifford, U. S. Patent 1,948,317 (February 20, 1934); *Chem. Zentr.*, **105**, II, 1695 (1934), reported the b. p. to be 185–187° (3 mm.), which obviously is in error.

(4) Kyrides, U. S. Patent 2,126,560 (August 9, 1938); *Chem. Zentr.*, **110**, I, 1107 (1939).

(5) Sebrell and Clifford, ref. 3, reported the formation of N,N'-dibutylpiperazine as the by-product when two moles of butylamine reacted with one mole of ethylene dichloride.

(6) Sebrell and Clifford, ref. 3, reported 40°.

(7) This material, heated with sulfur at 130–135°, gave ethylenethiourea, m. p. 195–196°. Ruiz and Libenson, *C. A.*, **24**, 5726 (1930), reported m. p. 195° (uncor.).

(8) Hill and Aspinall, THIS JOURNAL, **61**, 822 (1939).

TABLE I

Derivative	Formula	Nitrogen, % Calcd.	Found
N,N'-Dibutyl-ethylenediamine (I)	$C_{10}H_{24}N_2$	16.3	16.1
Hydrate of I	$C_{10}H_{26}N_2O$	14.7	14.5
N,N',N''-Tributyl-diethylenetriamine (II)	$C_{16}H_{37}N_3$	15.5	15.3
N-Formyl-(I)	$C_{11}H_{24}N_2O$	14.0	13.7
N,N'-Diformyl-(I)	$C_{12}H_{24}N_2O_2$	12.3	12.6
(I)-Dithiocarbamate[a]	$C_{11}H_{24}N_2S_2$	11.3	11.2
1,3-Dibutyl-ethylenethiourea (VI)	$C_{11}H_{22}N_2S$	13.1	13.1[b]
N,N'-Dibutyl-trimethylenediamine (III)	$C_{11}H_{26}N_2$	15.0	14.9
Hydrate of III	$C_{11}H_{28}N_2O$	13.7	13.7
N,N',N''-Tributyl-di-(trimethylene)-triamine	$C_{18}H_{41}N_3$	14.0	13.9
N-Formyl-(III)	$C_{12}H_{26}N_2O$	13.1	13.1
N,N'-Diformyl-(III)	$C_{13}H_{26}N_2O_2$	11.6	11.9
1,3-Dibutyl-trimethylenethiourea (VII)	$C_{12}H_{24}N_2S$	12.3	12.3
N-Formyl-(V)	$C_{15}H_{16}N_2O$	11.7	11.9
N,N'-Diformyl-(V)	$C_{16}H_{16}N_2O_2$	10.4	10.2
1,3-Diphenyl-ethylenethiourea[c]	$C_{15}H_{14}N_2S$	11.0	10.9

[a] M. p. 135–136° with effervescence. Sebrell and Clifford, ref. 3, reported 134–136°. [b] Calcd.: S, 15.0. Found: S, 14.8. [c] Recrystallized from methanol, m. p. 189–190°.

Formylation of N,N'-Dibutyl-ethylenediamine (I).—Technical 85% formic acid (108 g. or 2 moles) and 86 g. (0.5 mole) of (I) reacted by the procedure described.[1] The mixture was quenched with water, alkalinized strongly, and the water-insoluble product was separated with the aid of benzene and distilled. N-Formyl-(I), 47 g., was obtained at 153–165° (7 mm.); on redistillation, the fraction boiling at 134–135° (4 mm.) was collected. N,N'-Diformyl-(I), 40 g., was recovered at 197–199° (7 mm.).

Formylation of N,N'-Dibutyl-trimethylenediamine (III).—From the reaction of 108 g. of 85% formic acid and 93 g. (0.5 mole) of (III), N-formyl-(III) was collected at 146–155° (4 mm.), and on redistillation yielded 41.6 g. (39%) of product at 148–149° (4 mm.). N,N'-Diformyl-(III), 41.3 g. (34%), was obtained at 200–201° (4 mm.).

Formylation of N,N'-Diphenyl-ethylenediamine[9] (V).—The reaction mixture from 108 g. of 85% formic acid and 106 g. (0.5 mole) of (V) was poured into 500 cc. of water, precipitating a thick oil which hardened to a semi-solid mass on standing. The supernatant liquid was decanted, the semi-solid was air-dried for 24 hours and then treated with 150 cc. of methanol at 25°. The crystals were filtered from the methanol mother liquor, washed with 50 cc. of methanol and air-dried; yield, 54 g. (45%) of N,N'-diformyl-(V), which, after crystallization from methanol, melted at 121–122°.

The aqueous supernatant liquid obtained above was filtered, alkalinized with 80 g. of 50% sodium hydroxide solution, and cooled to 25°. The solid N-formyl-(V) precipitated was filtered off, washed with water and air-dried; yield, 19 g. (14%); m. p. 65–66°, recrystallized from methanol. The monoformyl derivative is somewhat soluble in hot water and in aqueous acids.[10]

1,3-Dibutyl-ethylenethiourea (VI).—(1) A mixture of 20 g. (0.1 mole) of N-formyl-(I) and 4.0 g. of sulfur heated

(9) Prepared by the method of Bennett, *J. Chem. Soc.*, **115**, 577 (1919).

(10) These properties are similar to those of N-acetyl-N,N'-diphenyl-ethylenediamine described by Bischoff and Nastvogel, *Ber.*, **22**, 1784 (1889).

at 135–140° for two hours produced 17.3 g. (80.8%) of (VI), a yellow liquid, at 183–185° (8 mm.).

(2) Twenty-nine grams of N,N'-dibutyl-ethylenediamine dithiocarbamate heated at 130–135° for about two hours gave 21.5 g. (85%) of (VI) at 183–184° (8 mm.).

1,3-Dibutyl-trimethylenethiourea (VII).[11]—(1) Starting with 21.4 g.[*] (0.1 mole) of N-formyl-(III) and 4.0 g. of sulfur and heating at 145–150° for two hours and at 175° for one-half hour, 9.2 g. of unconverted N-formyl-(III) was recovered, and 5.8 g. (25%) of (VII) was obtained as a yellow liquid, b. p. 177–178° (3 mm.).

(2) A stirred solution of 37.2 g. (0.2 mole) of (III) in 50 cc. of methanol was treated with a solution of 15.2 g. (0.2 mole) of carbon disulfide in 40 cc. of methanol in the course of fifteen minutes. The solvent was evaporated from the resulting solution and the remaining thick liquid, the dithi-

(11) N-Monosubstituted-trimethylenethioureas have been made by pyrolysis of the dithiocarbamates of the corresponding N-substituted-trimethylenediamines; Goldenring, *Ber.*, **23**, 1171 (1890); Fränkel, *ibid.*, **30**, 2501 (1897).

ocarbamate, was heated at 150–155° until the evolution of gas ceased (about two hours).; The reaction mixture then was distilled, yielding 12.4 g. of recovered (III), b. p. 107° (7 mm.), and 14.6 g. (31%) of (VII), b. p. 177–178° (3 mm.).

1,3-Diphenyl-ethylenethiourea.—This product was prepared in 71% yield by heating N-formyl-(V) with sulfur, but in this case little reaction was observed below 195°. (V) did not form a dithiocarbamate on treatment with carbon disulfide and water under reflux at atmospheric pressure for twenty hours.

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RESEARCH LABORATORIES
MONSANTO CHEMICAL CO.
ST. LOUIS 4, MISSOURI RECEIVED JANUARY 17, 1946

COMMUNICATIONS TO THE EDITOR

CRYSTALLINE VITAMIN A METHYL ETHER

Sir:

In recent years much interest has been shown in the synthesis of vitamin A ethers. However, since no data are available concerning the biological activity of these ethers, we have undertaken the preparation of vitamin A methyl ether from the natural vitamin.

The methyl ether was prepared by the action of dimethyl sulfate on the lithium derivative of the vitamin, which was formed by the reaction of n-butyl lithium[1] and crystalline vitamin A alcohol.[2] It was purified by chromatography on activated alumina[3] and was obtained as an orange oil, which crystallized from methanol after several months at −70°, m. p. 31–33°. After three recrystallizations from methanol and two from a 65–70° hydrocarbon fraction [Purified Skelly Solve B],[4] vitamin A methyl ether was obtained as light yellow crystals melting at 33–34°. *Anal.* Calcd. for $C_{21}H_{32}O$: C, 83.95; H, 10.74; OCH$_3$, 10.34. Found: C, 83.76; H, 11.07; OCH$_3$, 9.94.

The spectrophotometric curve for crystalline vitamin A methyl ether is identical in all respects with that of vitamin A alcohol, both having absorption maxima at 326 mμ on the Beckman spectrophotometer. The extinction coefficient $(E_{1\ cm}^{1\%})$ in isopropanol at 326 mμ is 1660. This corresponds to an equivalent extinction coefficient of 1742 for vitamin A alcohol.

Vitamin A methyl ether possesses a biological potency greater than 3,000,000 U. S. P. XII units

(1) Gilman, Langham and Moore, THIS JOURNAL, **62**, 2327 (1940).

(2) Distillation Products, Inc., Rochester, N. Y.

(3) Aluminum Ore Co., East St. Louis, Illinois.

(4) Purified by treatment with concentrated sulfuric acid and distillation.

per gram and is of the same order of activity as crystalline vitamin A alcohol.

The experimental details and complete biological data will appear in a forthcoming paper.

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RECEIVED JUNE 17, 1946

AMINOMETHYLATION OF THIOPHENE

Sir:

During the course of formylation studies with thiophene it was noted that in the presence of ammonium chloride and formaldehyde thiophene appeared to undergo a reaction to give water-soluble amine hydrochlorides. From the reaction mixture was isolated 2-thenylamine (2-aminomethylthiophene) (I), b. 58° (5 mm.), n^{20}D 1.5589; secondary di-(2-thenyl)-amine, b. p. 150–152° (10 mm.), n^{22}D 1.5914; and a third amine (III). Amine III is polymeric in nature and is believed to contain methylol groups. The hydroxyl number of III produced by the reaction of one mole of thiophene with four moles of 37% formaldehyde and one mole of ammonium chloride at the reflux was 475, indicating that methylol groups may be substituted around the thiophene in all remaining positions. Other analysis obtained on the product were as follows: 20.6% sulfur and 7.3% nitrogen. With the use of aqueous 37% formaldehyde in excess III is obtained exclusively and molecular weights of 600–750 are the usual order. The use of trioxymethylene with a few per cent. by weight acetic acid (to promote depolymerization at lower temperatures) gave