ency for coupling which results in a 95% yield of R·R compound. Directions are now available for the preparation of this unusual Grignard reagent in yields upwards of 70%. The coupling reaction is apparently due to the prior formation of free benzohydryl radicals, which are of red color and of short life.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MIDDLEBURY COLLEGE]

ALIPHATIC ACYLOINS. I. PREPARATION[1]

BY B. B. CORSON, W. L. BENSON AND T. T. GOODWIN

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The most promising method which has been described for the preparation of aliphatic acyloins involves the action of sodium on ethereal or benzene solutions of aliphatic esters. This reaction was first described by Bouveault and Locquin[2] and the following mechanism was assumed

$$\begin{aligned}2RCOOR' + 4Na &\longrightarrow 2NaOR' + RC(ONa){=}C(ONa)R\\ RC(ONa){=}C(ONa)R + 2H_2O &\longrightarrow RC(OH){=}C(OH)R + 2NaOH\\ RC(OH){=}C(OH)R &\longrightarrow RCHOHCOR\end{aligned}$$

Other mechanisms have been suggested.[3]

According to the original directions the reaction was run at 0° except in one case, pivaloin (2,2,5,5-tetramethylhexanol-3-one-4), where the reaction temperature was that of the room. The implication was that the acetoacetic ester condensation would result at higher temperatures and it was suggested that acyloins represented an intermediate step in the acetoacetic ester condensation.[4] Other investigators, however, have used higher temperatures, with equally good results.[5]

When the original directions are followed the reaction proceeds very slowly. In preparing pivaloin at room temperature Bouveault found it necessary to allow the reaction mixture to stand for eight to ten days. The use of a higher reaction temperature cuts down the time from days to hours. It has been suggested that the slowness of reaction in this particular case was due to the highly branched chain and the absence of enolizable hydrogen in the starting material, ethyl trimethylacetate.[5a] However, following the original directions the reaction also goes very slowly

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[1] Preliminary work was done by N. E. Sanborn and P. B. Smith in 1928–1929.

[2] Bouveault and Locquin, *Bull. soc. chim.*, [3] **35**, 629–643 (1906); *cf.* Bacon, *Am. Chem. J.*, **33**, 68 (1905), and Higley, *ibid.*, **37**, 293 (1907).

[3] (a) Scheibler and Voss, *Ber.*, **53**, 388 (1920); (b) Scheibler and Emden, *Ann.*, **434**, 265 (1923); (c) Egorova, *J. Russ. Phys.-Chem. Soc.*, **60**, 1199 (1928); *C. A.*, **23**, 2935 (1929); (d) *cf.* Gomberg and Bachmann, THIS JOURNAL, **50**, 2762 (1928).

[4] Bouveault and Locquin, *Ann. chim. phys.*, [8] **19**, 186 (1910).

[5] (a) Scheibler and Emden, *Ann.*, **434**, 265 (1923); (b) Feigl, *Ber.*, **58**, 2299 (1925); (c) *cf.* McElvain, THIS JOURNAL, **51**, 3124 (1929).

with straight chain esters such as ethyl butyrate. We have not applied the modified directions to the preparation of pivaloin but we have prepared a very similar substance, 3,3,6,6-tetramethyl-octanol-4-one-5 from ethyl dimethylethylacetate and, as far as we could see, the reaction proceeded as smoothly with the latter as with simpler esters. In the course of this work we have prepared propionoin, the two isomeric butyroins, two valeroins and four capronoins at the reflux temperature of the ether solutions.

For solvent, Bouveault used either dry ether or dry benzene, but from our experience, ether is much superior to benzene. Scheibler[3a] found the same to be true in a similar reaction, the preparation of ester enolates from aliphatic esters.

The yield of once-distilled product (25° boiling point range) is around 50% of the theoretical amount. The yield of pure product (1–3° boiling point range) is considerably smaller owing to the necessity of repeated vacuum fractionation. At least two substances are always obtained, the acyloin proper and a higher-boiling liquid of approximately twice the molecular weight and of unknown structure. Certainly, part of this second substance is formed during distillation and according to Bouveault the elevated temperature of distillation is responsible for all of it. A subsequent paper from this Laboratory will deal with this high-boiling by-product.

Also, a third substance is usually present, the 1,2-diketone (RCOCOR) corresponding to the acyloin (RCHOHCOR). Presumably autoxidation of the enediolate, RC(ONa)=C(ONa)R,[5a] accounts for the presence of the diketone, although some mechanisms of acyloin formation envisage the diketone as an intermediate step. The greater part of the diketone can be removed from the once-distilled product by shaking with saturated sodium bisulfite but the last traces must be removed by distillation. Since the diketones are deep yellow and the acyloins pale yellow, the depth of color in the distilling column is a useful guide as to the progress of fractionation.

It is our experience that acyloins as obtained by distillation are always slightly yellow. Butyroin was fractionated in a vacuum six times in succession in the attempt to obtain a colorless product. The film of liquid flowing down the column appeared to be colorless but the butyroin which collected in the receiver had a tinge of yellow. Although it seemed impossible to remove the last traces of yellow by distillation, we finally discovered that exposure to sunlight quickly brought about that result. Usually, a one-hour exposure was sufficient. In only one case, that of a sample of isobutyroin made from ethyl isobutyrate, were we unable to remove the color; on the other hand, a sample of isobutyroin made from isobutyl isobutyrate decolorized easily. When these colorless acyloins are kept in the dark or in diffused light, the yellow color returns in several days. This color change can be repeated several times by alternately exposing to sunlight and keeping in the dark.

Scheibler[3b] has recorded the extreme light sensitivity of an aromatic substituted aliphatic diketone, tetrabenzyldiacetyl, the photo-reaction being to some extent reversible.

$$(C_6H_5CH_2)_2CHCOCOCH(CH_2C_6H_5)_2 \rightleftharpoons (C_6H_5CH_2)_2CHCHOHCOCH(CH_2C_6H_5)_2$$

It has long been known that aromatic 1,2-diketones are light sensitive and the best known example of this reaction is the conversion of yellow benzil into colorless benzil-benzoin.

It may be that the yellow color of aliphatic acyloins is due to a small amount of the corresponding yellow diketone and by analogy with Scheibler's findings it may be that the reversible color change is due to the reversible reduction–oxidation of the diketone–hydroxyketone system. Further work is now in progress in this Laboratory on the photochemical decomposition products of aliphatic acyloins.

For some time we did not realize that this color change was indicative of alteration in composition, since the refractive index and the density were identical in colored and colorless samples. Finally, it was discovered that the colorless samples had a considerably different carbon–hydrogen composition. Up to this time exposure of the acyloins to light had never been avoided, with the result that after a few weeks in the laboratory the acyloins were far from pure. After this discovery all the acyloins were redistilled and a low-boiling fore-run was found in every case. There was very little, if any, high-boiling residue. With these acyloins, refractive index and density are merely rough criteria of purity, *e. g.*, a sample of *n*-valeroin which had been exposed to light still had the identical refractive index and density within 2 parts per 1000 although its carbon and hydrogen percentages had fallen 1.2 and 1.1%, respectively.

In the preparation of acyloins it is advisable to start with the methyl or ethyl ester of the acid in question. Although the reaction proceeds at least as fast and possibly faster[3a] with the higher esters such as iso-amyl, etc., it is difficult to obtain a pure product, due to contamination by the resulting high-boiling alcohol.

About 10% of the sodium becomes so thickly encrusted with sodium derivative that it is unable to react. Following these modified directions, satisfactory yields of acyloins are obtained with esters of acids from propionic up through caproic, but the limit has been reached in an acid of twelve carbons. With ethyl laurate and ethyl myristate only 20–30% of the sodium reacted in ten hours of heating followed by thirty-six hours of standing. The reaction was so incomplete that no attempt was made to isolate the products. Very likely potassium would extend the limits of the reaction. Acetoin cannot be prepared successfully by this method, due partly to its solubility in water and partly to its extreme sensitivity to alkali.

Aromatic acyloins have recently been prepared by Gomberg[3d] from both esters and acids by means of magnesious halide. With sodium, the free acid does not result in acyloin, the only product being the sodium salt of the acid. It may be that, under suitable conditions, the reaction would proceed, but at any rate, mere substitution of free acid for ester in the following directions results only in the sodium salt of the acid.

Experimental Part

General Procedure.—In a three-necked 2-liter round-bottomed flask were placed 1000 cc. of dry ether and 92 g. of sodium cut into small slices. We did not find it practicable to convert such large quantities of sodium into wire; thin slices were found quite suitable. First, the sodium was cut into sticks 10–13 cm. long and about 2.5 sq. cm. in cross section and stored in wide-mouthed, rubber-stoppered bottles. Just before using, the sodium was freed from oxide, weighed and cut under dry ether with a thin knife, into 5-mm. slices (thinner if possible). The middle neck of the flask was fitted with a mechanical stirrer (propeller type) and mercury seal combination. In one of the side necks was placed a reflux condenser and in the other a 125-cc. dropping funnel. The stirrer was started and the ether heated to the reflux temperature by means of a jet of steam impinging on the bottom of the flask. A pan was placed under the flask to catch the drip. The heating necessary to keep the ether refluxing varied with the ester used—with ethyl *n*-caproate and ethyl propionate considerable steam heating was required, whereas with iso-amyl isovalerate and isobutyl isobutyrate very little heating was required. Two-gram molecules of the ester in question was added at the rate of two drops per second to the stirred, hot mixture. Addition required two hours. The mixture was then stirred and steam-heated for an additional hour. A yellowish (occasionally reddish to light brown) solid began to appear in fifteen to thirty minutes and gradually increased in amount until practically all of the sodium had been converted into it and the contents of the flask was a thick mush. With ethyl butyrate 1000 cc. of ether was sufficient but with ethyl valerate and iso-amyl isovalerate it was necessary to introduce another 500 cc. of ether after half the ester had been added in order to keep the mixture sufficiently liquid to stir.

After standing for twenty-four hours the sodium salt was ready to be decomposed. Longer standing does no harm. If the mixture is to be allowed to stand for several days, the flask should be stoppered to prevent evaporation of ether and also to exclude air. The reaction mixture was poured (small amount at a time) into a 2-liter battery jar containing about 8 cm. of water full of cracked ice and layered with 5 cm. of ordinary ether. Each portion was brought into solution by stirring with a rod before another addition; excess of ice was maintained throughout the process. Pieces of unreacted sodium were removed with a wire skimmer, rinsed in a small dish of ether and finally dropped into a beaker of alcohol. Sometimes the mixture was fluid and poured nicely; sometimes it was thick and had to be removed by means of a long spatula. The layer of ether prevents the sodium from igniting; most of the sodium pops up and down at the ether-water interface. Although this decomposition is surprisingly free from fire hazard it is advisable to have wet towels and fire extinguishers handy.

In several runs toluene was substituted for ether. The reaction proceeded nicely in the boiling toluene but it was impossible to work up the product in the usual manner by pouring into water without frequent fires. Possibly the excess sodium could have been decomposed with alcohol or acetic acid.

After the sodium salt had been added and both the water and ether had become clear, the ether was separated. The water layer was extracted with two 250-cc. portions of ether and then discarded. The discarded water contains about 6 g. of organic acid as sodium salt. In the preparation of butyroin the greater part of this acid was butyric but there was a certain amount of a higher-boiling liquid which seemed to be dipropylglycolic acid. The combined ether was washed twice with strong sodium chloride solution. The ether was then distilled through a 30-cm. column until the residue was about 250 cc., the temperature at the top of the column being 42–44°. The ether should be distilled rapidly with a free flame since prolonged heating increases the yield of the high-boiling product at the expense of the acyloin. The residue was distilled in a vacuum and collected over a wide range, the object being to remove ether. The distillate was thoroughly shaken (occasionally over a period of one hour) with 100 cc. of saturated bisulfite solution to remove diketone. In most cases a solid separated, necessitating suction filtration. Finally, the product was redistilled in a vacuum, the yield being about 50% of the theoretical amount.

Table I

Analytical Data

Freshly distilled acyloin[a]	Wt. taken, mg.	CO_2, mg.	H_2O, mg.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Propionoin[b]	26.38	60.75	23.79	62.02	62.81	10.42	10.09
$C_6H_{12}O_2$	23.41	54.06	21.39		62.98		10.22
	27.67	63.92	26.16		62.99		10.58
n-Butyroin[c]	20.55	50.22	20.52	66.61	66.63	11.18	11.17
$C_8H_{16}O_2$	18.54	45.45	18.39		66.86		11.10
Isobutyroin[d]	24.44	59.43	24.36	66.61	66.32	11.18	11.15
$C_8H_{16}O_2$							
n-Valeroin[e]	21.75	55.76	23.04	69.70	69.92	11.71	11.85
$C_{10}H_{20}O_2$	22.43	57.68	23.39		70.13		11.67
Isovaleroin[f]	19.98	51.39	20.86	69.70	70.13	11.71	11.68
$C_{10}H_{20}O_2$	16.26	41.70	16.58		69.93		11.41
n-Capronoin[g]	19.97	52.95	21.75	71.93	72.30	12.08	12.18
$C_{12}H_{24}O_2$	18.25	48.38	19.07		72.28		11.69
	17.90	47.66	19.09		72.59		11.93
Isocapronoin	21.66	57.13	23.35	71.93	71.92	12.08	12.06
$C_{12}H_{24}O_2$							
3,8-Dimethyldecanol-5-one-6, $C_{12}H_{24}O_2$	19.49	51.33	20.70	71.93	71.83	12.08	11.88
3,3,6,6-Tetramethyloctanol-4-one-5, $C_{12}H_{24}O_2$	18.81	49.70	19.86	71.93	72.06	12.08	11.81

[a] The ethyl butyrate used in the preparation of *n*-butyroin was kindly furnished by the Waukegan Chemical Co. The ethyl esters of isobutyric, *n*-valeric, isovaleric, *n*-caproic, isocaproic and β-methylvaleric acids were obtained by the oxidation of the corresponding primary alcohols [Robertson, "Organic Syntheses," John Wiley and Sons, Inc., New York, 1925, Vol. V, p. 23]. The resulting esters (isobutyl isobutyrate, *n*-amyl *n*-valerate, etc.) were saponified. The free acids were liberated, purified by distillation and finally esterified with ethyl alcohol. The ethyl ester of dimethylethylacetic acid was prepared from *tert.*-amyl magnesium chloride plus carbon dioxide [Corson, Thomas and Waugh, This Journal, 51, 1950 (1929)]. The amyl alcohols used in the synthesis of the four caproic acids were generously furnished by the Sharples Solvent Co. [b] Anderlini, *Gazz. chim. ital.*, **25**, II, 51, 128 (1895). [c] Schmitz, *Ber.*, **24**, 1273 (1891). [d] Basse and Klinger, *ibid.*, **31**, 1218 (1898). [e] Basse and Klinger, *ibid.*, **31**, 1221 (1898). [f] Feigl, *ibid.*, **58**, 2299 (1925). [g] Bouveault and Locquin, *Bull. soc. chim.*, [3] **35**, 641 (1906).

TABLE II

PHYSICAL CONSTANTS

	B. p., °C. (corr.)	$n_D^{26.6}$	$d_4^{26.6}$	$M_D(n^2)$ Calcd.	$M_D(n^2)$ Found	$M_D(n)$ Calcd.	$M_D(n)$ Found
Propionoin	50–53 (3 mm.)	1.4183	0.9310	31.26	31.39	51.8	52.1
n-Butyroin	80–82 (10 mm.)	1.4242	.9160	40.40	40.12	67.0	66.7
Isobutyroin	55–57 (3 mm.)	1.4159	.8990	40.40	40.16	67.0	66.6
n-Valeroin	90–92 (3 mm.)	1.4298	.9000	49.54	49.38	82.2	82.2
Isovaleroin	94–97 (12 mm.)	1.4260	.8930	49.54	49.32	82.2	82.0
n-Capronoin	105–107 (3 mm.)	1.4339	.8900	58.69	58.51	97.4	97.5
Isocapronoin	101–103 (3 mm.)	1.4326	.8865	58.69	58.60	97.4	97.6
3,8-Dimethyldecanol-5-one-6	102–104 (3 mm.)	1.4330	.8880	58.69	58.51	97.4	97.5
3,3,6,6-Tetramethyloctanol-4-one-5[a]	96–97 (3 mm.) (m. p., ±12°)	1.4471	.9300	58.69	57.58	97.4	96.2

[a] In this one case it should be noted that the actual molecular refraction did not check the theoretical. The carbon–hydrogen analysis, however, was satisfactory.

Carbon-hydrogen Analysis of Acyloins.—Aliphatic acyloins are difficult substances to burn properly. In order to obtain consistent analytical results the combustion must be slow and more oxygen than usual must be passed through the combustion tube. These substances are too volatile to be weighed in the usual combustion boat. Using Pregl's method of weighing the substance in small tubes containing a little potassium chlorate and ending in capillary tips, there were often small explosions during the combustion and finally one explosion was so violent that it wrecked the combustion tube. These explosions were due to the fact that the liquid did not vaporize from the tip but was forced out in drops by the pressure within. Finally, small ground-glass stoppered pyrex tubes (50 × 9 mm.) were used. These were ignited, cooled in a desiccator and weighed in a little wire frame which sat on the balance pan. The tube was then transferred to another wire frame and two drops of liquid were dropped into the tube from a small pipet. The tube was then half filled with previously ignited copper oxide powder, the ground-glass stopper was inserted and the tube was re-weighed. These tubes are easily handled by means of steel tweezers with curved tips.

Sodium Bisulfite Addition Product of Diketones.—Usually the amount of solid obtained on treatment of the crude acyloin with sodium bisulfite was small and was not further investigated. Bouveault removed diketone by means of bisulfite solution but he did not observe the formation of any solid product. Incidentally, we substantiated Bouveault's finding that ether interferes with the removal of diketone by means of bisulfite. With one run of isovaleroin which had stood for two weeks before it was worked up, bisulfite occasioned an appreciable warming and a considerable quantity of solid was obtained. The air-dried salt was analyzed and almost the theoretical figure was obtained for the sodium bisulfite addition product of the diketone. Later, the solids from *n*-capronoin and isobutyroin were analyzed and about twice the theoretical sodium percentage found; but there was this difference in procedure—the first salt was merely air-dried, whereas the last two were dried at 100° in a vacuum over concentrated sulfuric acid. The first analysis was therefore repeated on a sample which had been thoroughly dried, and the sodium percentage was then found to be about twice the theoretical. During the drying of the isovaleroin product considerable yellow oil came out of the solid and slowly evaporated into the sulfuric acid which was the drying agent. No oil was noticed in the drying of the other two salts.

Solid from Crude Isovaleroin.—*Anal.* Calcd. for $C_{10}H_{20}O_8Na_2S_2$: Na, 12.4. Found: Na, 12.8 (air-dried); 28.5 (dried at 100°).

Solid from Crude *n*-Capronoin.—*Anal.* Calcd. for $C_{12}H_{24}O_8S_2Na_2$: Na, 11.3. Found: Na, 24.4.

Solid from Crude Isobutyroin.—*Anal.* Calcd. for $C_8H_{16}O_8S_2Na_2$: Na, 13.1. Found: Na, 24.8.

These values are very close to that of sodium bisulfite (Na, 22.1) and sodium pyrosulfite (Na, 24.2). Possibly these addition products decompose at 100° into diketone and bisulfite.

Photochemical Decomposition.—Many analyses were made on acyloins which had been exposed to light for various lengths of time but in Table III are listed only those values which are farthest from the percentages of the original acyloins. The acyloins whose analyses are recorded below were exposed to sunlight for about two weeks. However, a much shorter exposure causes a decided change in the carbon and hydrogen percentages. This change seems to be least with the two capronoins, 3,8-dimethyl-decanol-5-one-6 and 3,3,6,6-tetramethyl-octanol-4-one-5. In every case the percentage of carbon and hydrogen dropped except with isocapronoin, where exposure to light resulted in raising the figures for both carbon and hydrogen.

TABLE III

ANALYTICAL DATA

Acyloin exposed to sunlight	Taken, mg.	CO_2, mg.	H_2O, mg.	Carbon, %		Hydrogen, %	
				Calcd.	Found	Calcd.	Found
Propionoin	21.66	46.63	18.13	62.02	58.71	10.42	9.36
n-Butyroin	22.07	49.75	19.73	66.61	61.48	11.18	10.00
Isobutyroin	18.43	43.33	17.53	66.61	64.12	11.18	10.64
n-Valeroin	21.20	53.14	20.14	69.70	68.36	11.71	10.63
Isovaleroin	17.65	44.59	17.45	69.70	68.90	11.71	11.06
n-Capronoin	22.34	56.58	22.35	71.93	69.07	12.08	11.19
Isocapronoin	18.60	49.48	20.60	71.93	72.55	12.08	12.39
3,8-Dimethyldecanol-5-one-6	17.43	45.83	17.17	71.93	71.70	12.08	11.03
3,3,6,6-Tetramethyl-octanol-4-one-5	22.49	58.62	23.43	71.93	71.09	12.08	11.66

Identification of Butyroin.—At first erratic analyses forced us to doubt that these substances were really acyloins. At this time we did not realize that aliphatic acyloins are difficult substances to burn and that they also undergo photochemical decomposition. Two derivatives of butyroin were prepared following Bouveault's directions.

Butyroin Acetate.—The boiling point was 113–115° (21 mm.), which is in agreement with Bouveault's figures, 117–118° at 21 mm.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.47; H, 9.75. Found: C, 65.06; H, 10.11.

Butyroin Osazone.—A good yield of yellow crystalline solid resulted. The compound melted at 140.5–141° (corr.), which agrees as well as can be expected with the uncorrected values given in the literature, 135°,[6] and 138°.[7]

Reaction between Sodium and *n*-Valeric Acid.—The reaction was carried out in the usual manner except that free acid was substituted for ester. A white solid quickly appeared which did not turn yellow or red as is the case when the reactant is ester. After standing for the usual length of time, a sample of this solid was removed, washed with dry ether, dried between filter paper and analyzed. The product was sodium valerate.

Anal. Calcd. for $C_5H_9O_2Na$: Na, 18.6. Found: Na, 16.9.

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[6] Klinger and Schmitz, *Ber.*, **24**, 1271 (1891).

[7] Basse and Klinger, *ibid.*, **31**, 1219 (1898).

When the run was worked up in the usual manner no valeroin was found. On the other hand, 50% of the valeric acid was recovered from the alkaline water layer.

Summary

Detailed directions are given for the preparation of aliphatic acyloins. Approximately 50% yields of the following acyloins were obtained: propionoin, *n*-butyroin, isobutyroin, *n*-valeroin, isovaleroin, *n*-capronoin, isocapronoin, 3,8-dimethyldecanol-5-one-6 and 3,3,6,6-tetramethyl-octanol-4-one-5. The last three substances are new.

Aliphatic acyloins easily undergo photochemical decomposition.

MIDDLEBURY, VERMONT

[COMMUNICATION FROM THE DEPARTMENT OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES. XXX. THE COMPARATIVE HYDROLYSIS OF SOME DISACCHARIDES AND POLYSACCHARIDES

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Introduction

The problem of the relative ease of hydrolysis of disaccharides and of polysaccharides such as starch and cellulose is an important one, not only from the scientific, but also from the industrial standpoint. Thus its solution is of great importance for a thorough understanding not only of the role played by starch as a "reserve material" in the vegetable kingdom but also of the close inter-relationship existing between starch and cellulose in plant metabolism. Also since it may be assumed that the structure of cellulose as a long chain of cellobiose units is now established on a reasonably firm basis, and that starch is presumably derived in a similar manner from maltose, the inter-relation of the reactions involving both analysis and synthesis of these products is of considerable interest.

It would also seem that a more intimate knowledge of the relative ease of hydrolysis of these products into glucose might throw some light on their relative stability and the bearing of the latter on the mode of linkage in the long-chain polysaccharides. Many of these hydrolytic changes, as shown in other researches to be published later, can be readily brought about under the influence of bacterial action as well as by the enzyme isolated from such organisms. There thus exists the possibility of co-relating two widely different types of hydrolytic agents.

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