water, the reaction would be second order; but heretofore this has never been actually demonstrated. By using acetone as a solvent and having present only enough water to react with the methyl acetate, we were able to demonstrate the second order course of the reaction under these conditions.

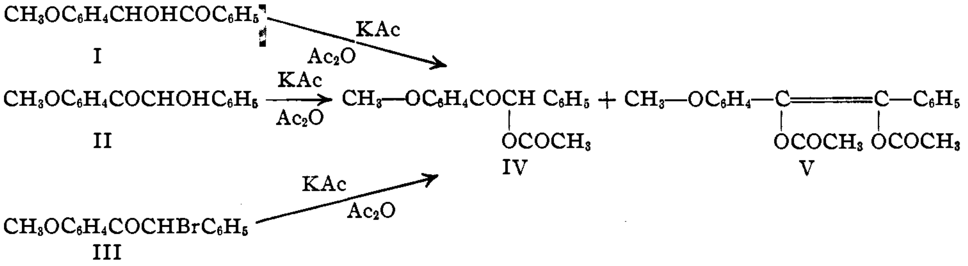
ATLANTA, GA. RECEIVED OCTOBER 31, 1940

NOTES

Interconversion of Mixed Benzoins

BY R. P. BARNES AND V. J. TULANE

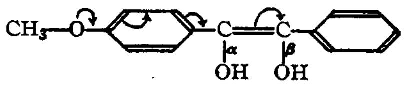
In view of the ease with which it has been found possible to prepare diacetates of ene-diols from benzoin and non-enolic α-bromo ketones,[1,2] we made pure anisbenzoin (I), benzanisoin (II) and anisoyl phenyl bromo-methane (III), and acetylated[1] each of these compounds. In each instance there was obtained a mixture of the monoacetate (IV) and the diacetate (V). The anisbenzoin melted sharply at 89°, the benzanisoin at 106°. Since the mono-acetate was the same in each instance and since it hydrolyzed to benzanisoin, it is reasonable to conclude that it resulted by way of a partial hydrolysis of the diacetate.



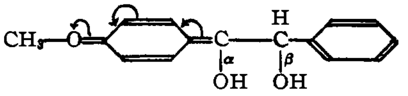
$$CH_3OC_6H_4COCHOHC_6H_5 \xrightarrow[Ac_2O]{KAc} CH_3{-}OC_6H_4\underset{\substack{|\\OCOCH_3}}{COCH}\,C_6H_5 + CH_3{-}OC_6H_4{-}\underset{\substack{|\\OCOCH_3}}{C}{=}\underset{\substack{|\\OCOCH_3}}{C}{-}C_6H_5$$

When an alcoholic solution of the diacetate was boiled for a few minutes with a few cubic centimeters of concd. hydrochloric acid an odor of ethyl acetate was produced and on cooling, the 106°-melting benzoin separated out. Thus the diacetate upon hydrolysis goes by way of the unstable ene-diol to the more stable high-melting benzanisoin in acid solution.

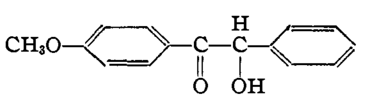
In this case of the ene-diol of anisbenzoin or benzanisoin there is obviously a directing influence. We believe that this influence can be explained in terms of the CH_3O- group. This ene-diolic modification contains a completely conjugated system, and since the CH_3O- group possesses a strong tendency toward electron release,[3,4] its mesomeric effect will give rise to a condition of electronic strain in the attached aromatic nucleus with the result that the para-carbon atom will be negatively charged and the two intermediate carbon atoms (α and β) charged positively and negatively, respectively. Thus there is created a seat for a proton on the β-carbon from the anisyl group



This molecule combines with a proton at the β-carbon



with subsequent ejection of a proton from the α-hydroxyl and regeneration of the stable benzanisoin



This mechanism lends support to the view that benzanisoin must be the stabler isomer (lower

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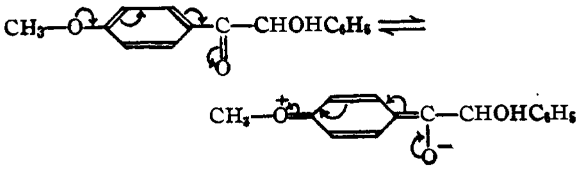
[1] R. P. Barnes and Victor J. Tulane, THIS JOURNAL, **62**, 894 (1940).

[2] R. P. Barnes, Charles I. Pierce and Chappelle C. Cochrane, *ibid.*, **62**, 1084 (1940).

[3] R. Robinson and co-workers, *J. Chem. Soc.*, 401 (1926).

[4] C. K. and E. H. Ingold, *ibid.*, 1310 (1926).

energy content) since it gives rise to benzanisoin and since there is the possibility for resonance between the CH_3O- group and the carbonyl in this molecule whereas anisbenzoin does not have this possibility



Experimental Part

Acetylation Products (IV) and (V).—Separate solutions of 5 0 g. each of anisbenzoin, benzanisoin, and anisoylphenylbromomethane in 25 cc. of acetic anhydride are refluxed gently with equal weights of freshly fused potassium acetate for thirty minutes. Each solution turns slightly yellow. After cooling they are worked up as described,[1] producing a cream-colored granular solid. Repeated fractional crystallizations from methyl alcohol yield in each case approximately 1.0 g. of the monoacetate, melting sharply at 83°, and 1.0 g. of the diacetate, melting at 127°.

Anal. Calcd. for $C_{17}H_{16}O_4$: $—OCH_3$, 10.9. Found: 11.2. Calcd. for $C_{19}H_{18}O_5$: $—OCH_3$, 9.5. Found: 9.7.

Both the mono and the diacetate on dissolving in alcohol and on gentle refluxing with concd. hydrochloric acid hydrolyze completely in thirty minutes to benzanisoin, melting and mix melting sharply with an authentic sample at 106°. The odor of ethyl acetate is observed.

DEPARTMENT OF CHEMISTRY
HOWARD UNIVERSITY
WASHINGTON, D. C.

RECEIVED NOVEMBER 14, 1940

The Photolysis of the Aliphatic Aldehydes. IX. Glyoxal and Acetaldehyde

BY F. E. BLACET AND ROBERT W. MOULTON

A study of vapor phase mixtures of glyoxal and acetaldehyde has been made in an attempt to throw light on the primary photochemical process for glyoxal, as well as on the reaction

$$CH_3CHO + HCO \longrightarrow H_2 + CO + CH_3CO \quad (1)$$

which has been postulated as a part of the mechanism of acetaldehyde decomposition.[1]

Experimental Method

The photochemical technique was very similar to that previously described.[2] In a number of experiments glyoxal was mixed with carbon dioxide instead of with acetaldehyde. λ 3660 Å. was the principal radiation employed, since it is absorbed by glyoxal but not by acetaldehyde. The gaseous products were analyzed by well-known micro methods. Glyoxal was prepared by oxidizing ethylene with selenium dioxide in the presence of phosphorus pentoxide in a manner similar to that described by Riley and Friend.[3]

Experimental Results

Experiments with pure glyoxal gave a gaseous product which consisted of 97% CO and 3% H_2. This is in very good agreement with 97% CO, 2.5% H_2 and 0.5% unsaturated compounds reported by Norrish and Griffiths.[4] No unsaturated hydrocarbons were detected in our work. The percentages of carbon monoxide reported in the accompanying tables are based upon the sum of the two gases found, hence the per cent. of hydrogen in each case is the difference between 100 and the figure given for carbon monoxide.

Table I gives the percentages of carbon monoxide obtained in the photolysis of a series of glyoxal and acetaldehyde mixtures in which the ratio of these two substances was varied. Since it was evident that some polymerization was taking place during the runs, the reporting of ratios and percentages beyond two significant figures would not be justified.

Table II gives the results of a similar study in which carbon dioxide was substituted for acetaldehyde. In Fig. 1 the carbon monoxide to hy-

TABLE I

DATA OBTAINED FROM GLYOXAL-ACETALDEHYDE MIXTURES

Pressure, mm. $(CHO)_2$	CH_3CHO	$CH_3CHO/(CHO)_2$	% CO	Ratio CO/H_2
75	0	0	97	32
64	210	3.3	90	9.0
60	600	10	73	2.7
36	440	12	66	2.0
50	650	14	79	3.8
45	705	16	88	7.3

TABLE II

DATA OBTAINED FROM GLYOXAL-CARBON DIOXIDE MIXTURES

Pressure, mm. $(CHO)_2$	CO_2	Ratio $CO_2/(CHO)_2$	% CO	Ratio CO/H_2
75	0	0	97	32
100	216	2.2	89	8.1
75	465	6.2	79	3.8
56	555	10	66	2.0
40	510	13	77	3.3
50	685	14	86	6.1
40	555	14	90	9.0
40	630	16	90	9.0

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[1] (a) Blacet and Volman, THIS JOURNAL, **60**, 1243 (1938). (b) Leighton, *J. Phys. Chem.*, **42**, 749 (1938). (c) Gorin, *J. Chem. Phys.*, **7**, 256 (1939).

[2] Blacet and Taurog, THIS JOURNAL, **61**, 3024 (1939).

[3] Riley and Friend, *J. Chem. Soc.*, 2342 (1932).

[4] Norrish and Griffiths, *ibid.*, 2829 (1928).

drogen ratios are plotted against the respective ratios of acetaldehyde and carbon dioxide with glyoxal.

Although many tests were made, no methane was found in the photolysis products of glyoxal and acetaldehyde mixtures.

A small amount of exploratory work was done at shorter wave lengths as shown in Table III, where is given the percentage of carbon monoxide obtained in the photolysis of pure glyoxal at λ 3660, 3130 and 2537.

TABLE III

PER CENT. CARBON MONOXIDE OBTAINED AT DIFFERENT WAVE LENGTHS

λ, Å.	Glyoxal pressure, mm.	CO, %
3660	75	97
3130	90	93
2537	85	88

Discussion of Results

The absorption by glyoxal at λ 3660 is of the predissociation type[5] and some form of dissociation, although not required, is to be expected. A consideration of the energetics involved leads to the conclusion that a primary dissociation into two formyl radicals

$$\mathrm{CHOCHO} + h\nu \longrightarrow 2\mathrm{HCO} \qquad (2)$$

probably would not occur at this wave length. This is substantiated by electron diffraction measurements which have shown that resonance in the conjugated system has shortened the C–C bond distance in glyoxal.[6] The absence of methane from the gases formed in the photolysis of glyoxal–acetaldehyde mixtures is additional evidence that formyl is not a primary product, since otherwise reaction 1, followed by methane producing reactions,[1] would be expected to occur under some of the experimental conditions employed. Methane formation would have been evidence of both reactions 1 and 2.

Norrish and Griffiths[4] have suggested that in the primary process activated molecules are formed which dissociate according to the equations

$$\mathrm{CHOCHO'} + \mathrm{CHOCHO} \longrightarrow \mathrm{CO} + \mathrm{C_3H_4O_3} \qquad (3)$$

$$\mathrm{CHOCHO'} \longrightarrow 2\mathrm{CO} + \mathrm{H_2} \qquad (4)$$

It is evident that glyoxal does not induce the decomposition of acetaldehyde and that in the glyoxal–acetaldehyde mixtures the acetaldehyde was acting merely as an inert gas. Since reaction 3 is bimolecular while reaction 4 is unimolecular, the presence of a foreign gas would be expected to hinder reaction 3 much more than 4, and a decrease in the percentage of carbon monoxide would be anticipated with an increase of the ratio of foreign gas to glyoxal. Such a decrease was first observed with an acetaldehyde–glyoxal mixture, but since it is conceivable that acetaldehyde might have contributed in some other way to this change in ratio, mixtures of glyoxal and carbon dioxide were studied also. As shown in Fig. 1, the effects of acetaldehyde and carbon dioxide on the carbon monoxide to hydrogen ratio are very similar if not identical within the limits of experimental error in determining the average glyoxal pressure during an exposure.

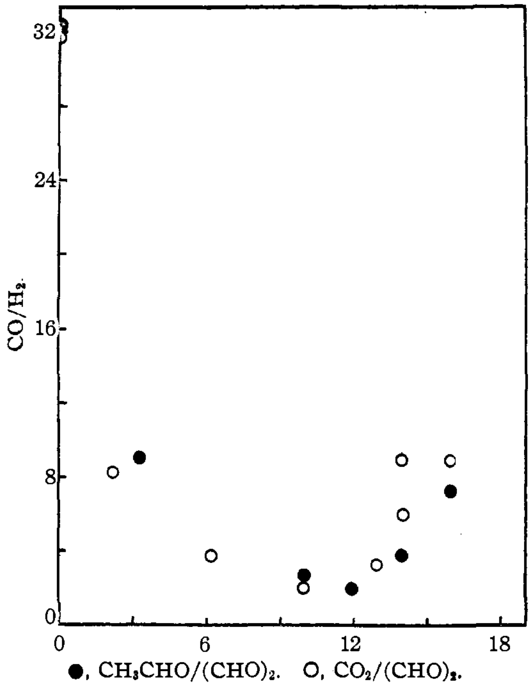

Fig. 1.—The carbon monoxide to hydrogen ratios plotted against the ratios of acetaldehyde and of carbon dioxide to glyoxal.

It was thought that by increasing the ratio of inert gas to glyoxal, reaction 4 could be made to predominate over 3 and the CO/H_2 ratio might be reduced to a value of 2 and would remain there with further increase of the first named ratio. Figure 1 shows a drop in CO/H_2 to a value of 2 at a foreign gas to glyoxal ratio of from 10 to 12, but contrary to expectations CO/H_2 does not remain constant beyond this point but rapidly increases again. This fact lends credence to reaction 4, but implies that some process other

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[5] Luthy, *Z. physik. Chem.*, **107**, 285 (1923).

[6] LuValle and Schomaker, THIS JOURNAL, **61**, 3520 (1939).

than reaction 3 must account for the high percentage of carbon monoxide found in experiments having a relatively high concentration of foreign gas. A reaction such as

$$\mathrm{CHOCHO'} \longrightarrow \mathrm{CO} + \mathrm{HCHO}$$

would meet the requirements but why it would predominate only at high pressures is not obvious. However, it is evident from the large variation of gaseous products that the primary process for glyoxal is the formation of an activated molecule which does not spontaneously dissociate into formyl radicals.

From the limited results obtained, it appears that the same chemical processes occur at λ 3660, 3130 and 2537, the variation being only one of degree.

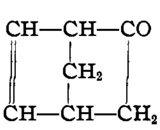
DEPARTMENTS OF CHEMISTRY
STANFORD UNIVERSITY AND
UNIVERSITY OF CALIFORNIA AT LOS ANGELES
LOS ANGELES, CALIF.
RECEIVED OCTOBER 9, 1940

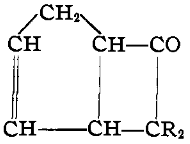
The Reaction of Cyclopentadiene and Ketene

BY BENJAMIN T. BROOKS AND GODFREY WILBERT

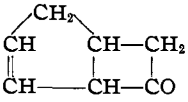
The now well-known Diels–Alder reaction was discovered by these authors[1] in a study of the reactions of cyclopentadiene with acrolein, acrylic acid and the anhydrides of maleic, citraconic and itaconic acids. All of these reactions give endomethylene products, acrolein giving endomethylene tetrahydrobenzaldehyde. It is obvious that ketene and cyclopentadiene would give an unsaturated ketone (1) which upon hydrogenation would give norcamphor, if the reaction follows the type Diels–Alder reaction. Norcamphor has been synthesized by Hinticka and Komppa[2] and by Diels and Alder[3] by other methods.

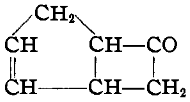
None of the ketenes appear to react with cyclopentadiene in the Diels–Alder fashion. Diphenylketene with cyclopentadiene gives a product (2) having the cyclobutanone structure[4,5] as originally suggested by Staudinger[6] and his co-workers. In view of these results, it appeared desirable to study the reaction of ketene itself upon cyclopentadiene.

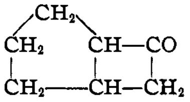

(1)


(2)

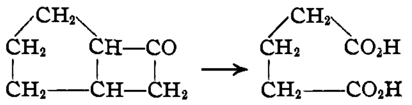
Recently Smith, Agre, Leekley and Prichard[5] were unable to obtain a reaction product of ketene and cyclopentadiene. We have found that ketene reacts with cyclopentadiene in a manner analogous to the reaction with diphenylketene, and not to give the product (1) to be expected from the Diels–Alder reaction. The resulting unsaturated ketone (3) or (4) was hydrogenated to the saturated ketone (5) which proved to be not identical with norcamphor.


(3)


(4)


(5)

The unsaturated ketones (3) and (4) obviously give the same hydrogenated product. That the saturated ketone (5) is not identical with norcamphor is indicative of this structure which was further confirmed by oxidation to glutaric acid.



All attempts to isolate the intermediate product cyclopentane-1,2-dicarboxylic acid were negative.

Experimental

Ketene.—This was prepared in the customary manner, passing acetone vapor rapidly through a $^{1}/_{4}''$ (6-mm.) copper tube maintained at about 700°. Unchanged acetone was condensed and the ketene absorbed from the gas stream by passing through toluene cooled to about −70° by solid carbon dioxide in isopropyl alcohol.

Cyclopentadiene.—This was prepared as needed by slowly distilling dicyclopentadiene through a packed four-foot (122-cm.) glass column, all of the product used distilling at 39–41°.

Reaction between Cyclopentadiene and Ketene.—Ketene was absorbed in two wash-bottles in series, each containing 300 g. of toluene, cooled as described. When the ketene dissolved in the toluene amounted to about 75 g., the toluene solutions were combined and 145 g. of freshly distilled cyclopentadiene were added and the solution placed in two small steel cylinders. The solution of ketene and cyclopentadiene in toluene was then heated under pressure at about 100° for one hour. The product was separated by fractional distillation, the material distilling at 150–160° being retained as the crude ketone. The crude unsaturated ketone, yield 78 g., a nearly colorless oil, thus obtained contained some cyclopentadiene

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[1] O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

[2] Hinticka and Komppa, *Chem. Zentr.*, **89**, II, 369 (1918).

[3] O. Diels and K. Alder, *Ann.*, **470**, 98 (1928).

[4] J. R. Lewis, G. R. Remage, J. L. Simonsen and W. G. Wainwright, *J. Chem. Soc.*, 1837 (1937).

[5] L. I. Smith, P. L. Agre, R. M. Leekley and W. W. Prichard, THIS JOURNAL, **61**, 9 (1939).

[6] H. Staudinger, "Die Ketene," Stuttgart, p. 59, 1912; *Ann.*, **356**, 51 (1907).

resulting from breakdown of the dimer. It was further purified by redistilling, and through the sodium bisulfite compound, made in a minimum of aqueous methyl alcohol solution. The washed bisulfite compound in water was treated with sodium bicarbonate and gently warmed to regenerate the ketone. Thus purified the unsaturated ketone distilled at 157.5–159°, sp. gr. (20°C.) 0.9813, analysis C, 77.62; H, 7.51; calcd. C, 77.74; H, 7.46. The semicarbazone recrystallized from alcohol melted at 222° and showed N, 24.76; calcd., N, 25.45.

Bicyclo-(0,2,3)-heptanone-7.—The unsaturated ketone was reduced, in dilute alcohol solution, by colloidal palladium and hydrogen at substantially atmospheric pressure. The saturated ketone distills at 164–165°, sp. gr. 0.9958 (20°C.), n^{20}_{D} 1.5030. It forms a semicarbazone melting at 216° (semicarbazone of norcamphor melts at 196.5–197.5°).

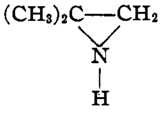
Oxidation of Bicyclo-(0,2,3)-heptanone-7.—The ketone was oxidized by refluxing for three hours with dilute nitric acid, equal parts of concentrated nitric and water. On gently evaporating the resulting solution nearly to dryness, the product crystallized on cooling and on purification proved to be glutaric acid, melting point 98°.

NEW YORK, N. Y. RECEIVED DECEMBER 5, 1940

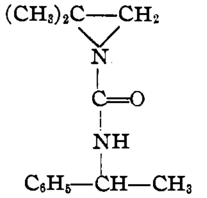
The Preparation and Attempted Resolution of 2,2-Dimethylethyleneimine

BY THEODORE L. CAIRNS

Previous investigations[1] of the possible asymmetry of the nitrogen atom in substituted ethyleneimines have all failed because it was not possible to synthesize the desired compounds. A method for the preparation of 2,2-dimethylethyleneimine (I) has now been developed. This compound gave a sulfonamide, insoluble in alkali, identical with one previously prepared[1a] by a different method. Compound I did not reduce permanganate and when treated with dilute sulfuric acid the ring opened to give 1-amino-2-methyl-2-propanol.



I



II

The substituted urea derivative (II) derived from compound I and *l*-α-phenylethylisocyanate was subjected to fractional crystallization, but no evidence of separation into diastereoisomers was obtained. Compound II exhibited mutarotation in boiling benzene, but the change in rotation could always be accounted for by decomposition.

There are certain objections to a compound having a carbonyl group directly attached to the nitrogen atom.[2] However, the whole problem is provided with a theoretical basis by the calculations of Kincaid and Henriques[3] and the synthesis of more suitable derivatives is now being investigated.

Experimental[4]

2,2-Dimethylethyleneimine.—To a solution of 100 g. of 2-methyl-2-amino-1-propanol (Commercial Solvents Corporation) in 200 cc. of water was added with shaking 110 g. of sulfuric acid in 200 cc. of water. The solution was distilled at atmospheric pressure until the temperature of the reaction mixture reached 115°, and then at 25–30 mm. and a temperature of 150–170° for one hour. The flask was cooled and broken and the brown crystalline mass crushed. This was treated with an excess of 40% aqueous sodium hydroxide and the mixture distilled until about 120 g. of distillate was obtained. The distillate was saturated with potassium hydroxide and the organic layer separated and dried with potassium hydroxide and finally with sodium. Distillation gave 30–40 g. of a mobile, colorless liquid of ammoniacal odor; b. p. 69–70°, n^{25}_{D} 1.4052.

Anal. Calcd. for C_4H_9N: C, 67.55; H, 12.76. Found: C, 67.59; H, 12.70.

***l*-α-Phenylethyl Isocyanate.**—A solution of 20 g. *d*-α-phenylethylamine[5] in 200 cc. of toluene was saturated with dry hydrogen chloride. A heavy white precipitate was formed. An additional 100 cc. of toluene was added and phosgene passed into the mixture for a few minutes. The mixture was then heated to boiling and phosgene bubbled through for four hours. The solution was cooled to room temperature, decanted from a very small amount of a white crystalline solid, and fractionated under reduced pressure; yield 16.5 g.; b. p. 82–83° at 12–14 mm.

Rotation. 0.3541 g. made up to 10 cc. with benzene gave α^{24}_{D} −0.09°, l = 1, $[\alpha]^{24}_{D}$ −2°.

***d*-N-(α-Phenylethyl)-urea.**—Treatment of a few drops of *l*-α-phenylethyl isocyanate in benzene solution with anhydrous ammonia gave white crystals, which, after crystallization from water, had m. p. 121–122°.

Rotation. 0.2225 g. made up to 10 cc. in absolute alcohol gave α^{25}_{D} 1.086, l = 1, $[\alpha]^{25}_{D}$ +48.8°.

Anal. Calcd. for $C_9H_{12}ON_2$: C, 65.83; H, 7.31. Found: C, 65.75; H, 7.16.

The literature[6] gives m. p. 122–123° and $[\alpha]_{D}$ 46.2.

***d*-(1-α-Phenylethylcarbamyl)-2,2-dimethylethyleneimine.**—A solution of 10.35 g. *l*-α-phenylethyl isocyanate

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[1] (a) Adams and Cairns, THIS JOURNAL, **61**, 2464 (1939). (b) Meisenheimer and Chou, *Ann.*, **539**, 70 (1939). (c) Mole and Turner, *Chem. and Ind.*, 582 (1939). (d) Maitland, *Ann. Repts. Chem. Soc.*, **36**, 243 (1939).

[2] Gilman, "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1938, Vol. I, p. 334.

[3] Kincaid and Henriques, THIS JOURNAL, **62**, 1474 (1940).

[4] Analyses by Dr. L. Weisler.

[5] "Organic Syntheses," Vol. XVII, 1937, p. 80.

[6] Marckwald and Methe, *Ber.*, **38**, 801 (1905).

in 20 cc. of dry benzene was added slowly to 5.0 g. of 2,2-dimethylethyleneimine in 50 cc. of dry benzene. Some heat was evolved; the temperature of the solution was 50° after the addition of all the isocyanate. The solution was allowed to stand for two to three days and then poured into 400 cc. of petroleum ether (60–70°). A slight cloudiness developed and after the walls of the flask were scratched, crystallization began and continued for ten to fifteen minutes. The white microcrystalline powder was removed by filtration; yield 9.8 g., m. p. 100–102.5°. Recrystallization from benzene–petroleum ether mixture (2.5:10 parts by volume) gave long needles; m. p. 104–105°.

Rotation. 0.1104 g. made up to 10 cc. in dry benzene gave α^{25}_{D} +0.532, l = 1, $[\alpha]^{25}_{D}$ +48°.

Anal. Calcd. for $C_{11}H_{15}ON_2$: C, 71.52; H, 8.31. Found: C, 71.44; H, 8.15.

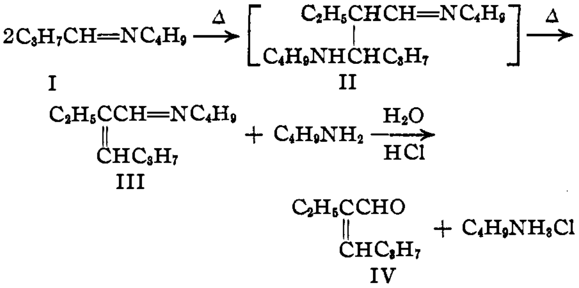
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROCHESTER
ROCHESTER, NEW YORK
RECEIVED JULY 30, 1940

Aldol Condensations with Aliphatic Schiff Bases

BY WILLIAM S. EMERSON, S. M. HESS AND F. C. UHLE

Several investigators[1] have mentioned the readiness with which aliphatic Schiff bases polymerize without examining the products of the reaction. Picon[2] showed that when ethylidene ethylamine was treated with sodium in liquid ammonia, a condensation of the aldol type took place. Hydrogenation of this product gave a 60% yield of 1,3-di-(ethylamino)-butane. Likewise Strain[3] postulated an aldol condensation as the first step in the thermal polymerization of aliphatic imines to pyridine derivatives, and Kharasch, Richlin and Mayo[4] have isolated the aldol condensation product of butylidene aniline.

We have found that the purely aliphatic Schiff base, *n*-butylidene-*n*-butylamine (I) is converted to 2-ethyl-2-hexenal-butylamine (III) by merely heating at 140–150° for three hours.



$$2C_3H_7CH{=}NC_4H_9 \xrightarrow{\Delta} \left[\begin{array}{l} \quad C_2H_5CHCH{=}NC_4H_9 \\ C_4H_9NHCHC_3H_7 \end{array}\right] \xrightarrow{\Delta}$$

$$\underset{\text{III}}{\begin{array}{l} C_2H_5CCH{=}NC_4H_9 \\ \quad \| \\ \quad CHC_3H_7 \end{array}} + C_4H_9NH_2 \xrightarrow[HCl]{H_2O} \underset{\text{IV}}{\begin{array}{l} C_2H_5CCHO \\ \quad \| \\ \quad CHC_3H_7 \end{array}} + C_4H_9NH_3Cl$$

When 48.8 g. (0.67 mole) of *n*-butylamine and 48.2 g. (0.67 mole) of *n*-butyraldehyde were heated at 20 mm. in a Claisen flask, *n*-butylidene-*n*-butylamine (I) distilled at 45–50° in the course of thirty-five minutes. It was then separated from the water and redistilled, b. p. 140–150°; yield 72.5 g. (85%). A sample which was again distilled boiled at 140–145°; d^{20}_{20} 0.764; n^{20}_{D} 1.4211; M^{20}_{D} calcd. 42.4; M^{20}_{D} found 42.2.

Anal. Calcd. for $C_8H_{17}N$: N, 11.02. Found: N, 10.93.

2-Ethyl-2-hexenalbutylamine (III) was prepared by refluxing 72.5 g. of *n*-butylidene-*n*-butylamine for three hours. This product was dried over sodium sulfate and then distilled, b. p. 213–235°; yield 33.9 g. (65%). A sample was redistilled at 217–220°; d^{20}_{20} 0.847; n^{20}_{D} 1.4745; M^{20}_{D} calcd. 60.5; M^{20}_{D} found 60.4.

Anal. Calcd. for $C_{12}H_{23}N$: N, 7.74. Found: N, 7.70.

The structure of III was established by refluxing 10 g. with 25 cc. of 6 *N* hydrochloric acid for thirty-five minutes. The upper layer was then separated and distilled giving 3 g. of the known unsaturated aldehyde, 2-ethyl-2-hexenal (IV), b. p. 170–171° (173–174°),[5] whose 2,4-dinitrophenylhydrazone melted at 122° (122°).[6]

The production of III easily can be accounted for by an initial condensation of the aldol type leading to II which then loses butylamine to produce III.

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[1] Schiff, *Ann.*, **140**, 92 (1866); Chancel, *Bull. soc. chim.*, [3] **11**, 933 (1894); Henry, *Compt. rend.*, **120**, 839 (1895); Mailhe, *Bull. soc. chim.*, [4] **25**, 321 (1919).

[2] Picon, *Compt. rend.*, **175**, 695 (1922).

[3] Strain, THIS JOURNAL, **54**, 1221 (1932).

[4] Kharasch, Richlin and Mayo, *ibid.*, **62**, 494 (1940).

[5] Gorhan, *Monatsh.*, **26**, 73 (1905).

[6] Backes, *Compt. rend.*, **196**, 277 (1933).

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS
RECEIVED DECEMBER 2, 1940

Some Alkyl Nitrophenols

BY WALTER H. HARTUNG[1] AND HARRY F. KOEHLER

p-Nitrophenol has been reported to be beneficial in the treatment of fungus disease of the skin.[2] In view of the well-known fact that the germicidal activity of a phenol is increased by the introduction of an alkyl group, it was believed worth while to synthesize analogous alkyl nitrophenols, hoping that the alkyl group might have a corresponding effect also on the fungicidal activity of nitrophenol. Two such compounds were therefore synthesized by direct nitration of alkyl phenols prepared by the condensation of the alcohol with phenol in the presence of zinc chloride. The position of the nitro group in the alkylphenol was not determined.

***s*-Hexylnitrophenol.**—To a stirred solution of 71.2 g. of *s*-hexylphenol (0.4 mole) in 175 ml. of benzene in a three-necked, round-bottom flask, equipped with a stirrer, reflux condenser and dropping funnel, cooled by means of an ice-salt-bath to below +5°, 125 g. of dilute nitric acid (1:1)

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[1] Present address: School of Pharmacy, University of Maryland, Baltimore, Maryland.

[2] Robertson, *Brit. Med. J.*, 1339 (1935); Marriatt and Robertson, *ibid.*, 136 (1935).

was slowly added during a period of about fifty minutes, being careful not to let the temperature rise above +5°. Stirring was continued for an additional two hours, during which the temperature was allowed to rise to 15°. The mixture was then washed with three 100-ml. portions of water and the benzene distilled off on a steam-bath. The residue was then distilled at lowest possible pressures. The product distilled at 165–185° at 2 mm.; yield, 70.6 g., 79%. Found: N (Kjeldahl), 6.26; calcd. N for $C_{12}H_{17}O_3N$, 6.28.

_t_-Octylnitrophenol.—This was prepared from *t*-octylphenol in a similar manner. The product distilled at 157–168° at 1 mm.; 97% yield. Found: N, 5.58; calcd. N for $C_{14}H_{21}O_3N$, 5.61.

The nitration of *s*-hexyl-*m*-cresol was carried out similarly and every evidence indicated that the reaction proceeded normally. However, at the distillation temperature, the product began to decompose, and the decomposition progressed spontaneously and could not be stopped by cooling the distillation flask.

Neither compound showed any decided fungicidal activity when tested against a mold culture by the Agar Cup Plate Method.[3]

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[3] These tests were made by S. R. Pence and W. A. Feirer, to whom the authors acknowledge their thanks.

MEDICAL-RESEARCH DIVISION
SHARPE AND DOHME, INC.
GLENOLDEN, PENNSYLVANIA RECEIVED OCTOBER 23, 1940

The Qualitative Determination of Cadmium in the Presence of Copper

BY ALBERT C. HOLLER

This paper describes a qualitative determination of cadmium in the presence of copper. The principle is that described by Sachs,[1] who states that a number of insoluble hydroxides are colored by a 1% alcoholic solution of phenolphthalein. He ascribes this to the activated adsorption of phenolphthalein on the hydroxide.

The procedure was worked out to fit into the method used to analyze group II as described by Engelder,[2] but may be applicable to other schemes.

The copper and cadmium were present in approximately equal amounts (about 30 mg. of each). It has been determined that cadmium can be detected in the presence of copper when the copper–cadmium ratio is as large as 10 to 1.

Procedure.—The filtrate from the lead separation is neutralized with ammonium hydroxide and the bismuth hydroxide is filtered off in the usual way.[2] If copper is present the filtrate will be colored deep blue. The solution is neutralized with nitric acid and 5 cc. of concd. nitric acid added. The solution is evaporated to dryness and the residue ignited below a dull red heat until the volatilization of ammonium salts is complete. The baked residue is then dissolved in 1.5 cc. of dilute nitric acid and the volume adjusted with water to 25 cc. Twelve cc. of 0.5 *N* sodium hydroxide is added to the solution. The hydroxides of cadmium and copper are filtered off and washed once with water. The hydroxides are then spotted with a 1% alcoholic solution of phenolphthalein and moistened with a few drops of water.

A crimson color indicates the presence of cadmium.

Copper hydroxide does not adsorb phenolphthalein when the hydroxide is prepared using a 10% excess of the salt (cupric nitrate) and thus does not form a colored compound.

I wish to express my appreciation to Mr. H. R. Heiple who helped me prepare this paper.

DEPARTMENT OF CHEMISTRY
ERIE CENTER, UNIVERSITY OF PITTSBURGH
ERIE, PENNSYLVANIA RECEIVED JANUARY 14, 1941

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[1] Sachs, THIS JOURNAL, **62**, 3514 (1940).

[2] Engelder, "Elementary Qualitative Analysis," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1933, pp. 119 and 124.

The Exchange of Sulfate Ion with Water

BY JAMES L. HYDE

The oxygen exchange of sulfate ion has been studied in acid, neutral and alkaline solutions. Heavy oxygen water, prepared by fractional distillation,[1] was obtained through the courtesy of Professor Merle Randall, and was distilled from alkaline permanganate before use. Analysis of the water[2] was performed with a mass spectrometer. After placing each sample, whose composition is shown in the table below, in a sealed tube in a thermostated bath for the indicated time, two cubic centimeters of water was distilled off *in vacuo*, and this water analyzed in the same way. The precision of analysis was ± 1%.

The alkaline exchange experiment was performed in a sealed platinum bulb similar to the silver one used by Winter, Carlton and Briscoe[3] in order to avoid any possible interference by glass. The results are tabulated below.

In a recent publication Hall and Alexander,[4] who used solutions containing lower concentrations of hydrogen ion and hydroxyl ion, respectively, reported results which were similar except for the fact that their exchange in acid solution was incomplete.

Our results are also in agreement with those of all other observers[3,5,6] for the neutral solution.

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[1] Randall and Webb, *Ind. Eng. Chem.*, **31**, 227 (1939).

[2] Cohn and Urey, THIS JOURNAL, **60**, 679 (1938).

[3] Winter, Carlton and Briscoe, *J. Chem. Soc.*, 131 (1940).

[4] Hall and Alexander, THIS JOURNAL, **62**, 3455 (1940).

[5] Datta, Day and Ingold, *J. Chem. Soc.*, 1968 (1937).

[6] Titani and Goto, *Bull. Chem. Soc. Japan*, **13**, 667 (1938); **14**, 77 (1939).

TABLE I

	H_2SO_4 (96%)	Na_2SO_4	NaOH	Na_2SO_4
Solutes, g.	9.125	2.10	2.84	1.68
Water, g.	9.93	5.00	4.00	
% O^{18} in water	0.79	0.79	0.84	
% O^{18} in water of orig. soln. (calcd.)	0.77	0.79	0.675	
Temp., °C.	100	100	100	
Time (hrs.)	59	87	84	
Vessel	Pyrex	Pyrex	Platinum	
% O^{18} in water recovered	0.55	0.79	0.67	
Obsd. decr. in % O^{18}	0.22	0.00	0.005	
% decr. calcd. for compl. exch.	0.22	0.11	0.06	
Amt. of exch.	Complete	None	None	

We also agree with Winter, Carlton and Briscoe for alkaline solution, but disagree with Datta, Day and Ingold.

Partial exchange has been observed for potassium acid sulfate by Titani and Goto and by Mills.[7] Winter, Carlton and Briscoe observed no exchange of sulfate in acid solution, but we must disagree with this observation.

Our results, coupled with those of Mills for potassium acid sulfate, lead us to postulate, as the mechanism for the exchange of sulfate, the same type of reversible anhydride formation which has satisfactorily accounted for the exchange of carbonate under all conditions of acidity.[8] The difference in the rates appears to be chiefly due to the fact that sulfuric acid is a stronger acid than carbonic, and that a much smaller quantity of the anhydride is present in solution.

(7) Mills, THIS JOURNAL, **62**, 2833 (1940).

(8) Mills and Urey, *ibid.*, **62**, 1019 (1940).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF.

RECEIVED DECEMBER 31, 1940

Density of Perchloric Acid Solutions

BY AARON E. MARKHAM

Data in the literature on the density of perchloric acid cover only a limited range of concentration. In this work, the density at 25° has been determined over the range up to 65% concentration. Measurements were in a 25-cc. pycnometer, the volume found by weighing filled with water, weights reduced to vacuum. The solutions were made from a stock solution of C. P. acid, meeting A. C. S. specifications. Its concentration was found by density and the data of Smith and Goehler[1] to be 71.209%. Titration confirmed this concentration.

The estimated maximum error, based on the differences of duplicate determinations, is about five in the last figure.

Measurements at 30° at intervals of 10% give a basis for estimating the temperature coefficient of density, over the range 25° to 30°. Empirically, $\Delta d/\Delta t = -(28 + 1.4x)10^{-5}$ in which x is the per cent. of acid.

The empirical equation which most nearly fits these data is:

$$d^{25}_4 = 0.99707 + 0.00562796x + 0.0000230045x^2 + 0.00000049593x^3$$

The maximum deviations of this equation over portions of the concentration range are:

Range	Maximum error in d^{25}_4	Maximum error in x
0 – 20%	0.00027	0.045
20 – 40	0.00006	0.006
40 – 65	0.00298	0.222

Wt. per cent. acid	d^{25}_4	d^{30}_4
0	(0.99707)	(0.99568)
1	1.00265	
2	1.00828	
4	1.01975	
6	1.03154	
8	1.04355	
10	1.05591	1.05388
12	1.06862	
14	1.08163	
16	1.09498	
18	1.10866	
20	1.12280	1.11999
22	1.13734	
24	1.15224	
26	1.16761	
28	1.18359	
30	1.20002	1.19651
32	1.21697	
34	1.23446	
36	1.25259	
38	1.27130	
40	1.29073	1.28658
45	1.34252	
50	1.39937	1.39435
55	1.46134	
60	1.52766	1.52177
65	1.59628	

The value which Smith and Goehler gave for the density at 65% concentration was 1.59665. This value was found by interpolation between two points at some distance apart, using a straight line. Since the analysis of the acid used depends on their data, closer agreement than this with

(1) Smith and Goehler, *Ind. Eng. Chem., Anal. Ed.*, **3**, 61 (1931).

their other points should be expected. Their use of a straight line over the range 63–70% seems poorly justified, since there were no experimental points in this range. In the range 70–75% the straight line they used is supported by a number of points. The stock acid used in this work was in this range of concentration. It should be noted that while the difference in density figures at 65% is rather large, it corresponds to a difference in acid concentration of about 0.027%.

DEPARTMENT OF CHEMICAL ENGINEERING
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON RECEIVED DECEMBER 10, 1940

A Note on the Phase Rule Diagram for a Mixture of Sodium Palmitate and Sodium Laurate with Water

BY J. W. MCBAIN AND S. A. JOHNSTON

The temperatures above which mixtures of soap and water in various proportions form isotropic solutions, T_i, and the temperatures below which they contain soap curd, T_c, have been determined for most of the single pure soaps. It is therefore of interest to see how these are affected when two such soaps are mixed. For this purpose a constant mixture of equal weights of sodium palmitate and sodium laurate has been examined with different percentages of water, using the materials and technique of previous communications.[1]

Briefly, this consisted in preparing sealed Pyrex tubes containing the mixture with varying amounts of water. The contents of the tubes were homogenized by heating to a high temperature, around 300° in this case. If the tube was then cooled slowly a temperature was reached at which another phase separated. This phase is frequently anisotropic and may be recognized even in minute quantities by observing the solution through crossed Polaroids. These points form the T_i curve. The tubes were then cooled to room temperature and heated slowly. The temperature at which the white curdiness disappeared was noted and these temperatures form what is usually called the T_c curve.

The results are given in Fig. 1 for the mixture where also the positions of middle soap, neat soap and curd are indicated. Figure 1 also compares these results with those of the separate single soaps, represented by faint lines. A comparison of the curves shows that the mixture tends to follow a behavior which would be an average of the individual curves. Probably the outstanding difference is that the peak for middle soap is higher than either of the individual peaks and if anything is nearer the peak for sodium palmitate. The T_c curve, on the other hand, adheres more closely to the curve for sodium laurate, as might be expected from previous experience.[1a,1c] Mixed micelles of smaller size, less orientation and greater solubility, must be produced by the occurrence of the shorter laurate molecules amongst the longer homologs, an example of mutual solubilization.

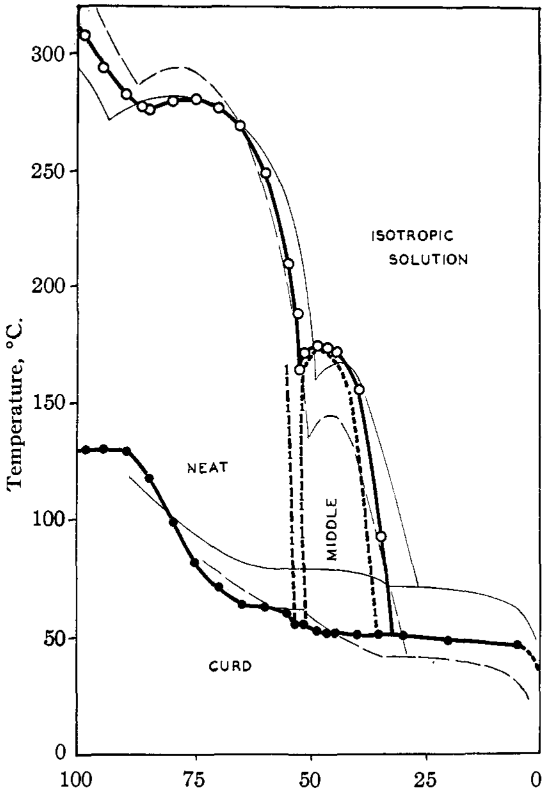

Fig. 1.—○, T_i curve; ●, T_c curve; ——, NaP; - - -, NaL.

STANFORD UNIVERSITY
STANFORD UNIVERSITY, CALIFORNIA RECEIVED NOVEMBER 12, 1940

The Effect of Potassium Oleate upon the Solubility of Hydrocarbon Vapors in Water

BY J. W. MCBAIN AND J. J. O'CONNOR

Solubilization by colloidal electrolytes and other detergents is best studied in systems where there

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[1] (a) McBain, Lazarus and Pitter, *Z. physik. Chem.*, **A147**, 87, 116 (1930); (b) McBain, Brock, Vold and Vold, THIS JOURNAL, **60**, 1870 (1938); (c) McBain, Vold and Jameson, *ibid.*, **61**, 30 (1939); (d) Vold, *J. Phys. Chem.*, **43**, 1213 (1939).

is no possibility of competing effects, such as mere emulsification or suspension. Likewise all possibility of salt formation should be excluded since we have found that base exchange may be an important factor in detergent action.[1]

We have therefore studied the solubility of the indifferent hydrocarbons, isobutane, butadiene and propylene in water and in solutions of potassium oleate.

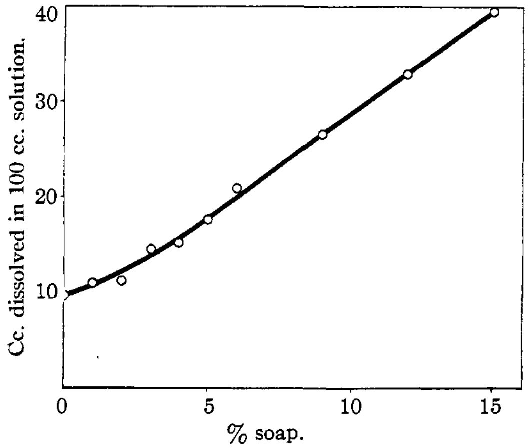

Fig. 1.

Experimental

The following simple but effective method was employed. The liquid was placed in a weighed tube sealed at one end and closed with a stopcock at the other. The liquid is degassed by evacuation and the tube reweighed. The connection between the tube and a gas buret containing the hydrocarbon vapor was evacuated and then opened to the hydrocarbon vapor. After admitting a suitable volume of hydrocarbon vapor, the tube was shaken in a thermostat at 25.0° for several hours. Thereupon an ordinary buret filled with mercury was attached through an evacuated connection to the stopcock, the tube being held vertically with stopcock underneath. Mercury was admitted to establish atmospheric pressure and the tube weighed to determine its amount and therefore the volume of gas remaining undissolved. From this, making all corrections for hydrostatic and vapor pressure, etc., the equilibrium pressure was calculated together with the amount of hydrocarbon dissolved.

Soap solution does not froth at all when evacuated and degassed.

The hydrocarbons were supplied through the kindness of the Shell Development Company. The propylene was made by dehydrogenation of isopropyl alcohol with subsequent fractionation. A similar sample, a portion of whose vapor was analyzed, contained 0.3% propane. However, it is probable that the liquid contained more propane and that appreciable fractionation occurred between first and last use of the cylinder as was shown by definitely decreased solubility.

The potassium oleate was made from Merck oleic acid of molecular weight 288.4 and iodine value 93, by neutralizing in 80% ethyl alcohol with Baker's stick potash containing about 4% carbonate; however, before use, half of each stick was first washed away and discarded.

The results may be presented in graphical form, plotting the total volume of hydrocarbon, corrected to 0° and 760 mm., which was dissolved in 100 g. of liquid, against the equilibrium pressure.

Figure 1 shows the effect of the addition of soap to water in enhancing the solubility of propylene when the final equilibrium pressure is adjusted in every case to 400 mm. It is seen that the solubility which in water was 9.8 cc./100 cc. is raised to 39 cc. by the presence of 15% potassium oleate.

Figure 2 shows that isobutane is about as soluble in 1% potassium oleate as was propylene in water. The work was broken off through call to duty as Ordnance Officer of one of us (J. J. O'C.) before the solubility of the isobutane in water was determined. Figure 2 also shows the enhancement of the solubility of butadiene by 1% potassium oleate.

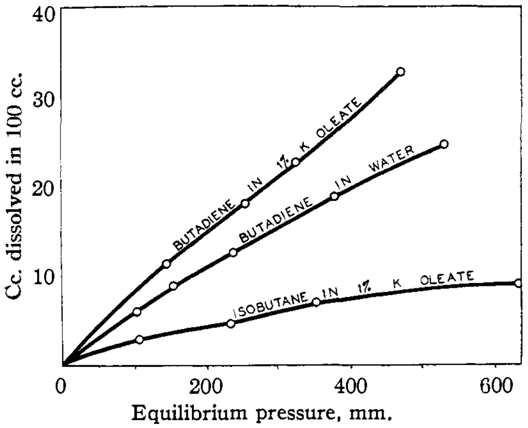

Fig. 2.

Figure 3 shows, first, by points marked in circles, the solubility of propylene in water and the increased solubility due to 1% and 5% of potassium oleate. An earlier series of measurements with the freshly opened cylinder of propylene is marked with crosses, showing a distinctly higher solubility, and also its enhancement by 1% potassium oleate.

Since McBain and Woo[2] had obtained a pronounced effect upon 5% sodium oleate solutions by the addition of 0.2% of silica in the form of

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(1) McBain, Lee, Merrill and O'Connor, *Chem. Prod.* (*London*), communicated October, 1940.

(2) McBain and Woo, *Kolloid-Z.*, **87**, 76 (1939).

"O" brand, originally containing 29.4% SiO_2 and 9.3% Na_2O, ratio 3.15, a similar addition was made to the 5% potassium oleate here. This made no influence upon the result, as shown by the three triangles which fall upon the original curve in Fig. 3. In Woo's experiments the oleate was not only solubilizing Yellow AB, but to a still greater extent was suspending and protecting colloidal particles of Yellow AB, and we have since shown that solubilizing and protective or suspending actions are wholly separate processes. The present experiments are designed to exclude the protective factor. The foam in 1 atmosphere of propylene with and without silicate was not very different; possibly the one containing silicate was creamier after standing a short time. The effect of the silicate upon the solubility in water was not measured for lack of time. However, in such dilution it would have been negligible.

The soap is exerting its expected action, namely, definite solubilization, overriding other factors. Electrolytes as such would be expected slightly to reduce the solubility by salting out. An additional small influence in the same direction would be caused by hydration of the soap. This is illustrated by the slight but distinct negative sorption of propylene on cotton thread. One gram of cotton thread added to 50 g. of water (the two square points on Fig. 3, corresponding to the crosses for pure water) caused this small decrease in the apparent solubility of the propylene, showing that the cotton preferentially sorbed the water.

In the previous work with the less volatile hexane and methylcyclopentane the amount taken up from the saturated vapor was approximately one mol of hydrocarbon to one mol of soap. It is quite possible that the solubility of the present hydrocarbons would be of comparable magnitude if measured at similarly high relative vapor pressures. It is thought that if the excess solubility above that in water alone were plotted against relative vapor pressure of hydrocarbon, the general curve would be sigmoid in character. The first part would, as here, be concave downward, and pass through a point of inflection before rising to much higher values. The isobutane and propylene are here studied only at the left-hand part of the curve; the butadiene extends further and indicates a further stage of the S-shaped curve, whereas the previous less volatile hydrocarbons were studied on the right-hand portion near saturation. According to this working hypothesis, the soap itself is strongly modified by the larger amounts of solubilized hydrocarbon.

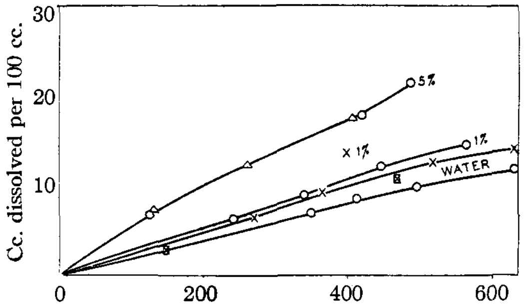

Fig. 3.

Comparing the amount of extra hydrocarbon dissolving in the presence of soap with that dissolving in an equal amount of olein, the only comparable material for which we have data,[3] we find that the potassium oleate dissolves only about one quarter as much as would an equal weight of olein. In general, solubilization appears to involve several factors other than mere solution in hydrocarbon groups, if any.

The most extensive series of studies of the solubility of gases as affected by other dissolved substances are those of Findlay and collaborators, 1910–1915. They found that proteins sometimes increased the solubility of gases such as carbon dioxide, and that polysaccharides did not. They likewise observed departures from Henry's law similar to those found here.

Summing up, the solubility of the hydrocarbons, propylene, isobutane and butadiene, is enhanced by presence of potassium oleate acting as solubilizer. This is one, but only one, of the important factors in detergent action.

(3) Berthelot, *Ann. chim. phys.*, **43**, 276 (1855).

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
CALIFORNIA

RECEIVED DECEMBER 10, 1940

Heavy Oxygen (O^{18}) as a Tracer in the Study of Photosynthesis

BY SAMUEL RUBEN, MERLE RANDALL, MARTIN KAMEN AND JAMES LOGAN HYDE

It is generally agreed that the net reaction for green plant photosynthesis can be represented by the equation

$$CO_2 + H_2O + h\nu \xrightarrow{\text{Chlorophyll}} O_2 + (1/n)(C{\cdot}H_2O)n \qquad (1)$$

and also that very little is known about the actual mechanism. It would be of considerable interest to know how and from what substance the oxygen is produced. Using O^{18} as a tracer we have found that the oxygen evolved in photosynthesis comes from water rather than from the carbon dioxide.

The heavy oxygen water used in these experiments was prepared by fractional distillation[1] and was distilled from alkaline permanganate before use. The isotopic oxygen content was determined by the method of Cohn and Urey[2] using carbon dioxide and a mass spectrometer. Heavy oxygen carbonate was prepared by allowing a solution of potassium acid carbonate ($KHCO_3$) in heavy oxygen water to come to approximate isotopic equilibrium, adding a nearly equivalent quantity of potassium hydroxide and distilling off the water, finally drying in an oven at 120°. Isotopic analysis of this carbonate or of the carbonate in a solution, was performed by rendering the solution sufficiently alkaline to prevent exchange[3] and precipitating calcium carbonate. The calcium carbonate after filtering, washing and drying at 120°, was calcined at red heat in an evacuated platinum bulb connected to the gas handling system of the mass spectrometer, and the evolved carbon dioxide analyzed for heavy oxygen.

Young active *Chlorella* cells were suspended in heavy oxygen water (0.85% O^{18}) containing ordinary potassium bicarbonate and carbonate. Under these conditions the oxygen exchange between the water and bicarbonate ion is slow and readily measurable.[3] The isotopic ratio in the evolved oxygen was measured with a mass spectrometer. In other experiments the algae were allowed to carry on photosynthesis in ordinary water and heavy oxygen potassium bicarbonate and carbonate. The results of these experiments are summarized in Table I.

TABLE I

ISOTOPIC RATIO IN OXYGEN EVOLVED IN PHOTOSYNTHESIS BY *Chlorella*[a]

Expt.	Substrate	Time between dissolving $KHCO_3$ + K_2CO_3 and start of O_2 collection, minutes	Time at end of O_2 collection, minutes	Percent. O^{18} in— H_2O	HCO_3^- + $CO_3^=$	O_2
1	0.09 *M*	0		0.85	0.20	..
	$KHCO_3$	45	110	.85	.41[b]	0.84
	+0.09 *M*	110	225	.85	.55[b]	.85
	K_2CO_3	225	350	.85	.61	.86
2	0.14 *M*	0		.20		..
	$KHCO_3$	40	110	.20	.50	.20
	+0.06 *M*	110	185	.20	.40	.20
	K_2CO_3					
3	0.06 *M*	0		.20	.68	..
	$KHCO_3$	10	50	.20		.21
	+0.14 *M*	50	165	.20	.57	.20
	K_2CO_3					

[a] The volume of evolved oxygen was large compared to the amount of atmospheric oxygen present at the beginning of the experiment. [b] These are calculated values.

It is apparent that the O^{18}/O^{16} ratio of the evolved oxygen is identical with that of the water. Since the oxygen in OH, COOH, O—O, C=O, etc., groups exchanges but very slowly[4] with water at room temperature and moderate *p*H, it seems reasonable to conclude that the oxygen originates solely from the water. While this conclusion makes it possible to reject many of the suggestions proposed in the past[5] it does not enable a choice to be made between the several more recent hypotheses. However it is of interest to note that van Niel[6] has specifically suggested that the oxygen may arise by a dehydrogenation of water.

We have also attempted to ascertain whether the evolution of oxygen was a reversible reaction. The algae were suspended in ordinary potassium bicarbonate and carbonate solution and photosynthesis allowed to proceed in the presence of heavy oxygen. In other experiments the algae evolved heavy oxygen in the presence of light oxygen. The results are shown in Table II.

TABLE II

ISOTROPIC RATIO IN OXYGEN EVOLVED IN PHOTOSYNTHESIS BY *Chlorella* IN PRESENCE OF OXYGEN

O_2 present in gas space at beginning, ml.	O_2 produced in photosynthesis by 200 mm.[3] algae, ml.	Per cent. O^{18} at end of experiment Obsd.	Calcd. for no exchange
2.29 (O^{18} = 0.20%)	1.55 (O^{18} = 0.85%)	0.43	0.46
3.64 (O^{18} = .20%)	1.18 (O^{18} = .85%)	.34	.36
1.44 (O^{18} = .85%)	0.73 (O^{18} = .20%)	.59	.62
4.81 (O^{18} = .85%)	1.22 (O^{18} = .20%)	.69	.71

There is no indication of exchange reactions involving oxygen. The experimental errors are such that an exchange involving less than $5 \cdot 10^{-8}$ mol of oxygen with each cu. mm. of algae would not be detected.

Similar experiments with *Chlorella* and yeast were performed in order to determine whether the oxidation (respiration) reactions utilizing oxygen

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(1) Randall and Webb, *Ind. Eng. Chem.*, **31**, 227 (1939).

(2) Cohn and Urey, THIS JOURNAL, **60**, 679 (1938).

(3) Mills and Urey, *ibid.*, **62**, 1019 (1940).

(4) For a review of oxygen exchange reactions see Reitz, *Z. Elektrochem.*, **45**, 100 (1939).

(5) For an excellent review of this subject up to 1926 see H. A. Spoehr "Photosynthesis," Chem. Cat. Co., New York, N. Y., 1926.

(6) Van Niel, *Cold Spring Harbor Symposia on Quant. Biol.*, **3**, 138 (1935).

were reversible. The results are summarized in Table III.

TABLE III

ISOTOPIC OXYGEN RATIO IN RESPIRATION WITH *Chlorella* AND YEAST

Respiring system	O_2 (O^{18} = 0.85%) present at start of expt., ml.	O_2 utilized in respiration, ml.	Per cent. O^{18} in O_2 at end of experiment	
			Obsd.	For no exchange
Chlorella cells in dark for 90 minutes	0.82	0.11	0.85	0.85
Yeast cells for 60 minutes	4.5	2.4	.84	.85

Here also there is no indication for an exchange reaction involving molecular oxygen.

The authors wish to thank the National Research Council for a grant made to Merle Randall for the purchase of materials used in the study of heavy water; also the Works Progress Administration for assistance, O. P. No. 165-1-08-73 (Unit C-2).

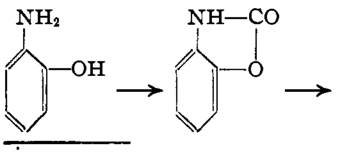
CHEMICAL LABORATORY, AND
RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

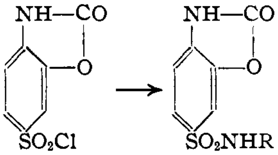
RECEIVED JANUARY 23, 1941

A Stable Derivative of 1-Amino-2-hydroxybenzene-4-sulfonamides

BY JOHN V. SCUDI AND R. P. BUHS

The urinary elimination of oxidation products of the sulfonamide drugs has been definitely established.[1,2] Certain oxidation products have been shown to be of importance in relation to the incidence of acetylsulfapyridine urolithiasis in experimental animals.[3] Since such oxidation products are of interest in connection with theories of the mode of action of these drugs, much attention has been devoted to 1-hydroxylaminobenzene-4-sulfonamide.[4] Another oxidation product which may have physiological significance is the 1-amino-2-hydroxybenzene-4-sulfonamide. The stable benzoxazolone analog of this compound has been prepared as follows





The method appears to be general for the preparation of benzoxazolone-5-sulfonamides.

The benzoxazolone-sulfonamide was administered in aqueous suspension by stomach tube to a series of mice infected with cultures of hemolytic streptococci. Subsequent examination of the urine showed that the oxazolone ring had not been cleaved in passage through the animal. The compound was not effective in protecting the infected mice.

Experimental

Benzoxazolone.—*o*-Hydroxyaniline in dry pyridine was treated with phosgene according to the method of von Meyer.[5] The benzoxazolone, crystallized from acidulated water, melted at 138–139°, cor. It was obtained in 50% yields. In our hands this method failed to give the yields previously reported.

Benzoxazolone-5-sulfonyl Chloride.—One-half mole of the benzoxazolone was added slowly with stirring to 2.5 mole of chlorosulfonic acid at 10–15°. The reaction mixture was stirred for fifteen minutes after all the benzoxazolone was added. The temperature was then raised to 60° and maintained at this temperature for two hours. The reaction mixture was poured onto ice. The product was removed by filtration and dissolved in ether. The ethereal solution was washed free of acid and dried with anhydrous sodium sulfate. The product was precipitated in good crystalline form by the addition of petroleum ether, m. p. 182–183° cor. The yields were 50 to 60%.

Anal. Calcd. for $C_7H_4O_4NSCl$: C, 35.96; H, 1.72. Found: C, 35.79, 35.66; H, 2.07, 2.08.

Benzoxazolone-5-sulfonamide.—9.0 g. of benzoxazolone-5-sulfonylchloride was added to 100 cc. of cold concentrated ammonium hydroxide, and the mixture was warmed to solution. On cooling the ammonium salt of the benzoxazolone-5-sulfonamide separated. This was removed by filtration and converted to the free sulfonamide by crystallization from 300 cc. of acidulated water. The product, melting at 269–270° (decompn.), was obtained in 60% yields.

Anal. Calcd. for $C_7H_6O_4N_2S$: C, 39.23; H, 2.82; N, 13.08. Found: C, 39.33; H, 3.02; N, 13.01, 12.91.

Benzoxazolone-5-sulfonanilide.—150 mg. of the benzoxazolone-5-sulfonyl chloride and 1 cc. of freshly distilled aniline in 3 cc. of dry dioxane were refluxed for fifteen minutes. The reaction mixture was cooled, acidified with hydrochloric acid and diluted to 10 cc. with water. The oil which separated crystallized on standing. The product, obtained in approximately 50% yields, melted at 215–216° cor. after crystallization from water.

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(1) J. V. Scudi, *Science*, **91**, 486 (1940).

(2) W. V. Thorpe and R. T. Williams, *Nature*, **146**, 686 (1940).

(3) J. V. Scudi and H. J. Robinson, *Am. J. Med. Sci.*, in press.

(4) For bibliography see A. C. Bratton, H. J. White and E. K. Marshall, Jr., *Proc. Soc. Exptl. Biol. Med.*, **42**, 847 (1939).

(5) E. von Meyer, *J. prakt. Chem.*, **92**, 256 (1915).

Anal. Calcd. for $C_{13}H_{10}O_4N_2S$: C, 53.77; H, 3.47; N, 9.65. Found: C, 53.52; H, 3.86; N, 9.75.

MERCK & CO., INC.
RAHWAY, N. J.
RECEIVED JANUARY 11, 1941

Hydrogen Fluoride as a Condensing Agent. XIV. Alkylation Studies[1]

BY J. H. SIMONS AND G. C. BASSLER

As a condensing agent hydrogen fluoride is related to both the metallic halide and the acidic agents. It promotes reactions with alkyl halides, with olefins, and also with hydroxy compounds. For the metallic halide promoted reactions an alkyl halide–metallic halide complex may be postulated as the reactive intermediate. With the acidic agents a complex between the olefin and the acid can be postulated. With hydrogen fluoride the mechanism is obscure, but because of its relationships to the other types of agents, information obtained which aids in the interpretation of its reactions may be of general value. The following experiments were performed to obtain such information.

It seemed desirable to answer three questions concerning alkylations promoted by hydrogen fluoride. First, does hydrogen fluoride act by forming the alkyl fluoride, which then reacts and regenerates the hydrogen fluoride? It is known that hydrogen fluoride is readily removed from aliphatic compounds, *i. e.*, alkyl fluorides lose hydrogen fluoride readily to form olefins. It is also known that olefins, alkyl chlorides, and alcohols react with hydrogen fluoride under certain conditions to form fluorides. Second, what is the relative ease of reaction of olefins and alkyl fluorides with aromatic compounds in the presence of hydrogen fluoride? Third, what is the relative ease of reaction of alcohols and other alkyl halides? Three different sets of experiments were performed to answer these questions.

A sample of pure tertiary amyl fluoride was desired but it was found that this compound would not undergo distillation even at reduced pressure and at −12° without partial decomposition into the olefins and hydrogen fluoride. This was independent of whether the initial substance was prepared from tertiary amyl alcohol and aqueous hydrogen fluoride or the olefin and anhydrous hydrogen fluoride. A mixture of olefin and fluoride was made by adding to 200 cc. of amylenes (prepared by the dehydration of *t*-amyl alcohol) dry-ice and 17 g. of anhydrous hydrogen fluoride. Dry sodium carbonate was added in excess, and the mixture was filtered through a Büchner funnel packed with dry-ice. This procedure should produce a mixture of olefins and tertiary amyl fluoride.[2] Three reaction mixtures were prepared: (1) 60 cc. of amylenes, 21 g. of HF and 50 cc. of benzene; (2) 60 cc. of *t*-amyl fluoride and olefin mixture, 15 g. of HF, and 50 cc. of benzene; (3) 60 cc. of *t*-amyl fluoride and olefin mixture and 50 cc. of benzene. These were allowed to stand in ice for one hour and then an iced solution of sodium carbonate was added. The organic layers were removed, washed, and dried over potassium carbonate. From number 1 about 27 g. of high boiling material was obtained which consisted chiefly of polyalkylated benzene. From number two about 4 g. of high boiling material was obtained and of this it is estimated that perhaps half was aliphatic polymers. From number 3 less than 2 g. of high boiling residue was obtained which probably was chiefly aliphatic polymer.

The following substances were then used for reaction with toluene under similar conditions and for a time short of complete reaction for the most rapid reaction: (1) cyclohexene, (2) cyclohexyl fluoride, (3) cyclohexanol, (4) cyclohexyl chloride, (5) cyclohexyl bromide, and (6) cyclohexyl iodide; 1.5 moles of toluene was added to 3.2 to 3.3 moles of hydrogen fluoride and 0.33 mole of the cyclohexyl compound then added. The mixture was allowed to stand for two hours at room temperature and then the flask was again placed in ice and water carefully added. The organic materials were separated, neutralized, dried, and distilled. The yields of *p*-cyclohexyltoluene obtained were as follows: (1) 74%; (2) 75.6%; (3) 45%; (4) 8%; (5) 0%, and (6) 0%.

The above experiments were then repeated using the following aliphatic compounds in the same molar proportions: (1) octene-1, (2) a mixture made by adding hydrogen fluoride to octene-1 at low temperature (2-fluorooöctane apparently cannot be distilled without decomposition), (3) octanol-2, (4) 2-chlorooöctane, and (5) 2-bromooöctane. Yields of 2-*p*-octyltoluene were as follows: (1) 73%; (2) 13.5%, (3) 42%, (4) 0%, and (5) 0%. In number two a considerable residue was found which is probably aliphatic polymer.

These experiments strongly indicate that the aliphatic fluoride alone is not reactive but that the presence of hydrogen fluoride is also necessary. It also appears that an olefin reacts as readily or more readily than the fluoride. In the second series of experiments the yields are about the same but in the first and third the yield is less when the fluoride is used. This however, is complicated by the difficulties of obtaining the pure fluoride and the polymerization of the aliphatic compounds. The high yield obtained when the alcohol is used is interesting in view of the fact that water is a product of the reaction and remains to dilute the hydrogen fluoride. The decreasing yields as the atomic weight of the halide increases may be correlated in two ways. The reaction produces the hydrogen halide and the order of decreasing

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[1] For the previous paper of this series see Simons, Passino and Archer, THIS JOURNAL, **63**, 608 (1941).

[2] Grosse and Linn, *J. Org. Chem.*, **3**, 26 (1938).

yields is the order of increasing boiling point or decreasing ease of removal from the reaction zone. The order is also the order of decreasing ease of ionization, should an ionic mechanism be postulated.

CHEMICAL LABORATORY
PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNSYLVANIA
RECEIVED DECEMBER 27, 1940

The Preparation of 2,2- and 3,3-Dimethylpentane

BY HAROLD SOROOS AND H. B. WILLIS

Wibaut and co-workers[1] have stated that they were unable to prepare 2,2- and 3,3-dimethylpentane by the condensation of tertiary alkyl halides with Grignard reagents, as reported by Edgar and co-workers.[2] Because of the attractiveness of this one-step reaction for the preparation of branched-chain paraffins, it seemed of interest to us to retest the method.

In order to remove any uncertainty that may still exist regarding the workability of the process, an exact description is given below of the method as applied by us.

Grignard Reagents.—All the Grignard reagents were prepared in the conventional manner, using 6.0 gram atoms of magnesium turnings (the magnesium used should be of a good grade, free of slag, and, preferably, from extruded bar rather than castings), 6.6 moles of alkyl halide, and 1500 cc. of anhydrous ether. Because of its high volatility, a larger excess (about 25%) of ethyl chloride was used in preparing the ethylmagnesium chloride, and when the magnesium had practically all dissolved, the excess was removed by refluxing the ether for a short time. After allowing the Grignard reagents to stand overnight, and after samples of the clear reagents had been analyzed by titration, they were transferred under nitrogen to graduated separatory funnels, where their volumes were noted. Care was taken to see that only the clear reagent and none of the sludge was transferred. Each was then transferred, under nitrogen, to a 5-liter 3-neck round-bottom flask, equipped with a separatory funnel, reflux condenser and vapor-proof mechanical stirrer for addition of the *t*-alkyl chlorides.

The Coupling of RMgX with RX.—To each of the Grignard reagents was added an equivalent amount (based on the volume and titration of an aliquot of each Grignard reagent) of the appropriate *t*-alkyl chloride. Mercuric chloride was not used in these tests since recent work in this Laboratory has shown that it has little or no effect on the yield. In the case of the Grignard reagents prepared from alkyl chlorides, the *t*-alkyl chloride was added rapidly and the reaction mixture was allowed to stand in a cooling bath at 25–30° without further attention. Reaction started in four to ten hours.

In the case of the Grignard reagents prepared from alkyl bromides, it was first necessary to start the reaction by the addition of only a small portion of the tertiary chloride. When the reaction had definitely started, as evidenced by the liberation of heat and the precipitation of magnesium bromide etherate, the remainder of the halide was added at such a rate that the temperature of the reaction could be maintained at 33–39° by slight cooling with an ice–water-bath. Failure to follow this procedure results in a very vigorous reaction which is difficult to control.

All the reaction mixtures were allowed to stand in cooling baths at 23–30° for six days. The condensers were then set for distillation, water was added slowly to the mixtures, and the ether and hydrocarbons were steam distilled. The ether solutions of the products were washed with water and dried over anhydrous sodium carbonate. The hydrocarbons were recovered from their ether solutions by fractionation. The yields of crude products were as follows: 2,2-dimethylpentane, 27% from *t*-BuCl with *n*-PrMgCl and 29% with *n*-PrMgBr; 3,3-dimethylpentane, 43% from *t*-AmCl with EtMgCl and 41% with EtMgBr.

Purification of Hydrocarbons.—The respective crude hydrocarbons from two runs were combined, were washed successively with concentrated sulfuric acid and 5% sodium bicarbonate solution, were refluxed and distilled from sodium–potassium alloy, and, finally, were fractionated carefully through an efficient column packed with crushed carborundum. The properties and yields of the finished products were as follows: 2,2-dimethylpentane, b. p. (760 mm.) 78.7–79°, d^{20}_4 0.6736, $n^{20}\mathrm{D}$ 1.3822, yield 20%; 3,3-dimethylpentane, b. p. (760 mm.) 85.7–86.0°, d^{20}_4 0.6931, $n^{20}\mathrm{D}$ 1.3910, yield 31%.

THE RESEARCH LABORATORIES OF
THE ETHYL GASOLINE CORPORATION
DETROIT, MICHIGAN
RECEIVED DECEMBER 28, 1940

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[1] Wibaut, Hoog, Langedijk, Overhoff and Smittenberg, *Rec. trav. chim.*, **58**, 329 (1939).

[2] Edgar, Calingaert and Marker, THIS JOURNAL, **51**, 1483 (1929).

NEW COMPOUNDS

Glycyl-*l*-methionine

Chloroacetyl-*l*-methionine was prepared from *l*-methionine by the method described by Fischer and Suzuki[1] for the preparation of diglycyl-*l*-cystine. Five grams of *l*-methionine was dissolved in 20 ml. of *N* sodium hydroxide. While the methionine solution was being vigorously stirred there was added simultaneously, from two dropping funnels, 4.52 g. of chloroacetyl chloride and 40 ml. of *N* sodium hydroxide. The addition required thirty minutes. The solution was then acidified with 90 ml. of *N* hydrochloric acid and the acidified solution was extracted five times with 150-ml. portions of ethyl ether. After removal of the ether by distillation the sirupy residue was crystallized by rubbing with petroleum ether and ethyl ether. The yield varied in several preparations from 5.0 g. to 5.4 g. (65–71% of theoretical). The melting point of the several preparations of chloroacetyl-*l*-methionine was 105–107°.

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[1] Fischer and Suzuki, *Ber.*, **37**, 4575 (1904).

The chloroacetyl-*l*-methionine was converted into glycyl-*l*-methionine by dissolving 5 g. of the compound in 20 ml. of 25% ammonium hydroxide. The solution, in a pressure flask, was heated for one hour in a water-bath maintained at 70°. The solution was then treated with silver carbonate or silver sulfate to remove the ammonium chloride. The resulting solution, after the removal of silver with hydrogen sulfide, was gently boiled with 100 mg. of Norit A and the slightly yellow filtrate was placed in a vacuum desiccator over sulfuric acid until sirupy. The glycyl-*l*-methionine was obtained as a white solid by rubbing the gummy residue with absolute alcohol. In several preparations the yield varied from 2.6 g. to 2.9 g. (57–64% yield based on the chloroacetyl-*l*-methionine used) and the melting point was 140–145°.

Anal. Calcd. for $C_7H_{14}N_2O_3S$: S, 15.54. Found: S, 15.52.

CHEMO-MEDICAL RESEARCH INSTITUTE
GEORGETOWN UNIVERSITY W. C. HESS
WASHINGTON, D. C. M. X. SULLIVAN

RECEIVED DECEMBER 20, 1940

14-Bromo-2,6,10-trimethylpentadecane

6,10,14-Trimethyl-2-pentadecanone[1] was prepared by ozonizing phytol. Reduction of this ketone was accomplished by dissolving 11.1 g. (0.0414 mole) of it in 100 ml. of anhydrous isopropyl alcohol and adding 6.9 g. (0.30 equiv.) of sodium, in small pieces, to the boiling mixture over a two-hour period. After the reaction mixture had been neutralized, it was extracted with ether and this extract was washed and dried. On distillation, the fraction which boiled at 146–148° at 1 mm. was collected. The yield of 6,10,14-trimethyl-2-pentadecanol, a colorless, practically odorless, mobile liquid, was 9.2 g. (82%). Although this alcohol is a new compound, it was not further characterized, but was converted directly into its bromide.

By the ordinary phosphorus tribromide method, 9.2 g. (0.0341 mole) of the above alcohol, dissolved in 80 ml. of anhydrous petroleum ether, was treated with 3.5 g. (0.0129 mole) of the reagent which converted it to the bromide. Upon distillation of the reaction products, two fractions were obtained neither of which was analytically pure. The more promising fraction which weighed 3.2 g., and which represented approximately 50% of the total distillate, was dissolved in petroleum ether, extracted with concentrated sulfuric acid and redistilled. This acid treatment should have been employed before the first distillation. The 14-bromo-2,6,10-trimethylpentadecane boiled at 138–140° at 1 mm. The yield of 2.8 g. (25%) which was obtained could no doubt be substantially improved. The bromide is a bright, colorless, odorless, mobile liquid; n^{20} 1.4614; d^{20}_{20} 0.9726. *Anal.* Calcd. for $C_{18}H_{37}Br$: Br, 23.97. Found: Br, 23.75.

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY PERRIN G. SMITH
EVANSTON, ILLINOIS CARL E. SCHWEITZER

RECEIVED JANUARY 20, 1941

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[1] Fischer and Löwenberg, *Ann.*, **464**, 69 (1928).

2-Methyl-1,4-naphthohydroquinone Hydrogen Succinate

Incidental to some other work, 2-methyl-1,4-naphthohydroquinone hydrogen succinate was prepared, by heating 2-methyl-1,4-naphthohydroquinone with 4 moles of succinic anhydride in a bomb tube (nitrogen atmosphere) for six hours at 140°. The acidic product was then isolated via the sodium salt. Recrystallized from benzene, then from aqueous alcohol, the compound forms faintly tan-colored small prisms, melting at 176–178°. It is readily soluble in sodium bicarbonate solution.

Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.66; H, 5.15. Found: C, 65.91; H, 5.45.

The compound showed, in 2 γ doses, a clotting time of two minutes, five hours after injection (chicks on Ansbacher diet, with a clotting time of more than sixty minutes). The same result was obtained with 1 γ doses of 2-methyl-1,4-naphthoquinone.

THE BURROUGHS WELLCOME & CO. U. S. A.
EXPERIMENTAL RESEARCH LABORATORIES
TUCKAHOE, N. Y. RICHARD BALTZLY
JOHANNES S. BUCK

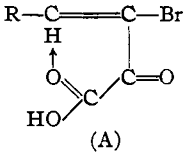
RECEIVED JANUARY 8, 1941

COMMUNICATIONS TO THE EDITOR

HYDROGEN BRIDGES AND ISOMERISM

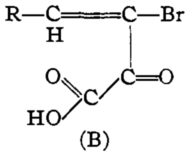
Sir:

In recent issues of THIS JOURNAL there have appeared two articles [Reimer and Tobin, THIS JOURNAL, **62**, 2515 (1940); Reimer and Morrison, *ibid.*, **63**, 236 (1941)] in which a new type of isomerism is postulated in order to account for the existence of certain pairs of separable isomers. Although the two isomers differ markedly in their physical and chemical properties, the only difference in the structures of the two forms is stated to be the presence of a hydrogen bridge in the one (A) and its absence in the other (B).



(A)

and



(B)

[R = *p*-BrC_6H_4—, *p*-$C_2H_5OC_6H_4$—]

The separation and independent existence of isomers at ordinary temperatures implies an energy barrier amounting to at least 20 kcal.