in a 0.1-mm. cell showed bands at 3300, 1662, 1597, 1576, 1532, 1486 and 1454 cm.$^{-1}$.

Ozonolysis of Ethyl 1,2,3,4-Tetrahydro-1,6-diphenylpyridazin-4-one-3-carboxylate.—A solution of the pyridazinone (1 g.) in ethyl acetate (50 cc., AnalaR) was cooled in a Dry Ice–alcohol-bath and treated with ozonized oxygen (9 l./hr., 6–7%). After absorption was complete the suspension was allowed to reach room temperature, the solvent removed under reduced pressure and water added to the residue. The mixture was heated on the water-bath (effervescence) for 0.5 hr. and then distilled in steam. The distillate was extracted with ether and the solvent evaporated. The oily residue gave acetophenone 2,4-dinitrophenylhydrazone, m.p. 237–238°, on treatment with 2,4-dinitrophenylhydrazine. The melting point was undepressed on admixture with an authentic specimen but was depressed to 208–212° on admixture with benzaldehyde 2,4-dinitrophenylhydrazone (which also melts at 238°). Recrystallization of the 2,4-dinitrophenylhydrazone from glacial acetic acid gave needles, m.p. 244–245°, whose infrared absorption spectrum (Nujol mull) was identical with that of the authentic specimen.

Anal. Calcd. for $C_{14}H_{12}O_4N_4$: C, 56.0; H, 4.0. Found: C, 56.1; H, 4.2.

The residue from the steam distillation had a nitrobenzene-like smell though no product could be isolated from it.

Diacetyl monophenylhydrazone was prepared by the method of Benary[19] from ethyl methyl ketone and ethyl formate followed by reaction of the product with benzenediazonium chloride.

REHOVOTH, ISRAEL

[CONTRIBUTION NO. 2044 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY[1]]

On the Ultrasonic Cleavage of the Pyridine Ring

BY L. ZECHMEISTER AND EUGENE F. MAGOON

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On ultrasonic treatment of a solution of pyridine in aqueous silver nitrate roughly 5% of the ring atoms are precipitated as a mixture of silver acetylide, silver diacetylide and silver cyanide. The resolution of such mixtures and the estimation of the three components is described. Nicotine shows a similar behavior.

The exposure of bromobenzene in aqueous silver nitrate suspension to ultrasonic waves has been shown recently[2] to bring about partial cleavage of the aromatic ring. The resulting silver bromide precipitate was found to contain both silver acetylide and diacetylide, the quantities of which corresponded to about 10% of the original carbon atoms. This process may be considered as a reversal, at near room temperature, of Berthelot's pyrogenic synthesis of benzene from acetylene.[3]

We find that the analogous synthesis of pyridine from acetylene and hydrogen cyanide, as predicted by Dewar[4] and first realized by Ramsay,[5] can also be reversed ultrasonically. In this particular instance the presence of halogen is not required. Indeed, it has been observed that unsubstituted pyridine can be converted, to an extent of 5%, into a mixture of the silver salts of acetylene, diacetylene and hydrogen cyanide.

After the silver cyanide had been eliminated from the precipitate by extraction with ammonia, the remaining two explosive silver salts were determined either titrimetrically[2,6] or (after bromination in chloroform solution) gravimetrically.[2,7] The analysis was completed by a colorimetric estimation of the cyano group after its conversion into prussian blue.[8]

That the cleavage of the six-membered heterocyclic ring is not restricted to unsubstituted pyridine was demonstrated by the behavior of nicotine in aqueous silver nitrate solution which, upon ultrasonic treatment, deposited a slightly explosive mixture of silver salts. Some cyanide was also formed from nicotine, although in smaller yields than from pyridine. In these experiments about 2% of the ring atoms initially present in the pyridyl group of the nicotine molecule has been recovered.

Some of our results appear in Table I.

TABLE I

YIELDS OF ACETYLENE, DIACETYLENE AND CYANO GROUP OBTAINED BY ULTRASONIC TREATMENT FOR 20 HR. OF 1 ML. (980 MG.) OF PYRIDINE OR 1 ML. (1010 MG.) OF NICOTINE DISSOLVED IN 50 ML. OF AQUEOUS SILVER NITRATE

$AgNO_3$, mmoles	Wt. of ppt., mg.	Anal. meth. used for acetylene and diacetylene	C-Atoms of the pyridine ring recovered,[a] %, as			N-atoms of pyridine ring recvd. as CN,[a] %	Pyridine ring atoms recovd.,[a] %
			Acetylene[b]	Diacetylene	Cyano group		
			Pyridine				
5.0	412	Titr.[2,6]	2.7	..	0.9	4.7	3.8
1.25	620	Titr.	2.9	..	0.9	4.3	3.9
2.5	657	Titr.	4.0	..	1.7	8.2	5.6
2.5	638	Titr.	2.6	..	1.6	7.7	4.8
2.5	555	Grav.[2,7]	1.6	0.8	1.2	5.9	4.0
2.5	658	Grav.	1.5	.7	1.8	9.1	4.9
2.5	685	Grav.	1.0	.6	1.0	5.1	3.0
			Nicotine				
2.5	510	Titr.[2,6]	1.9	..	0.5	2.7	2.5
2.5	476	Grav.[2,7]	0.6	0.3	.4	2.1	1.5
2.5	366	Grav.	0.6	.2	.4	2.1	1.4

[a] "100% yield" would mean that the total carbon and nitrogen content of the pyridine ring had appeared in the form of acetylene + diacetylene + cyano group. [b] The titrimetric values are expressed as "acetylene" but represent the sum of acetylene and diacetylene (ratio, for example, 2:1).

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[1] This research was supported by the United States Air Force, through the Office of Scientific Research of the Air Research and Development Command.

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Experimental

The generator was a Hypersonic Transducer Model BU 305A-600 (Brush Electronic Co., 8 amp., estimated power input 200 watts at 550–600 kilocycles). A barium titanate transducer element with a glazed finish was used.

Treatment of Pyridine.—A solution of 1 ml. of pyridine in 50 ml. of 0.05 *N* silver nitrate darkened after a few minutes of ultrasonic treatment and began to deposit a heavy precipitate. The treatment was continued for a total of 20 hr. At 5-hr. intervals the precipitate was removed by centrifugation, washed successively with water, alcohol, ether, then dried and weighed. The amount of the silver eliminated from the liquid phase was then determined approximately (the precipitates contained about 85% silver) and replaced by adding silver nitrate crystals. The four precipitate fractions were combined. (The aqueous filtrate was yellow and slightly acid.)

Treatment of Nicotine.—A freshly prepared solution of 1 ml. of nicotine in 50 ml. of 0.05 *N* silver nitrate was filtered after standing for 30 min. to remove a negligible amount of a black precipitate (1–2 mg.). The filtrate was then treated ultrasonically and the precipitate worked up in the manner described for pyridine.

Estimation of Cyanide.—The brownish-black precipitate was extracted thrice with 10-ml. portions of concentrated ammonia while vigorously shaking for 30 min. each time. After centrifugation[9] and washing, the brownish extract was diluted to 50 ml. in a volumetric flask. A 1-ml. or 2-ml. sample was then pipetted into a 15-ml. conical centrifuge tube and a 10% potassium iodide solution (about 5 drops) was added in slight excess in order to precipitate the silver. The suspension was made weakly acid with dilute nitric acid and the silver iodide was removed by centrifugation. The resulting solution was made basic with a few drops of 5% potassium hydroxide. Finally, 0.5 ml. of freshly prepared 3% ferrous sulfate was added, followed by the introduction of a small potassium fluoride crystal (about 50 mg.).[8] The liquid (the ferrous hydroxide precipitate included) was shaken to mix the reactants and was allowed to stand for 10 min. (in case of very small amounts of cyanide, for 25 min.). After acidification with dilute nitric acid, dilution with water to 10 ml. and vigorous shaking, the extinction of the (semi-colloidal) prussian blue was estimated at 750 mμ in a Beckman spectrophotometer, model DU. The values were compared with a calibration curve obtained by carrying out the operations described with known amounts of cyanide.

Estimation of Acetylene and Diacetylene.—The fraction that remained undissolved after the extraction of the silver precipitate with ammonia was converted into a mixture of cuprous acetylide and diacetylide as described earlier.[2] This was dissolved in acid ferric sulfate and titrated according to Willstätter and Maschmann.[6]

Details of the separation of acetylene tetrabromide and diacetylene hexabromide were given in our first report.[2] After recrystallization from chloroform (rather than from alcohol) the diacetylene hexabromide crystals melted at 182–183° (cor.) and did not give a depression with an authentic sample.

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[9] Some difficulty was encountered in the centrifugation of these basic solutions; small losses of precipitate were observed.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Some Colorado Shale-oil Bases[1]

BY H. L. LOCHTE AND H. W. H. MEYER[2,3]

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A combination of fractionation by distillation, by chloroform extraction of aqueous solutions of hydrochlorides, and by systematic fractional neutralization yielded Colorado shale-oil base fractions from which quinoline and isoquinoline and a series of methyl homologs were isolated and identified from material boiling from 227 to 239°, while similar separations of bases boiling from 264–290° yielded large amounts of 2,3,8-trimethylquinoline and a series of unidentified picrates but none of the very stable $C_{16}H_{25}N$ base found in high concentration in California petroleum bases. In general these shale-oil bases formed much larger amounts of tar than did corresponding California petroleum base fractions.

A number of investigators have studied the nitrogen compounds in various shale oils and shale-oil fractions. They have found that a considerable fraction of the compounds cannot be extracted with dilute acids and that these compounds, including pyrroles, seem to be responsible for the much greater tendency toward tar formation in various separation procedures than has been observed in working with petroleum bases. In this respect the shale-oil bases show greater similarity to low temperature coal tar bases than to petroleum bases.

A considerable amount of work has been done on the lower boiling shale-oil bases[4-10] and these studies have led to the identification of a number of simple alkylpyridines. Quinolines and isoquinolines have been mentioned and recently the U. S. Bureau of Mines workers[10] have reported the presence of quinoline and 2-methylquinoline on the basis of boiling point, index of refraction and ultraviolet absorption spectra. This group also isolated two pyrroles and three benzonitriles.

Quite recently Fushizaki[11] reported the isolation and identification of a series of alkylpyridines, quinoline, isoquinoline, 2-methyl- and 3-methylquinoline and probably several others from Manchurian shale-oil.

None of the higher boiling alkylquinolines, the alkylcyclohexylpyridine identified by Bailey[12,13]

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[1] Presented before the Petroleum Division at the American Chemical Society Meeting in Cincinnati, Ohio, March, 1955.

[2] General Aniline and Film Corporation Fellow, 1950–1952.

[3] From the Ph.D. Dissertation of H. W. H. Meyer, The University of Texas, 1953.

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