NOTES

A Method of Estimating and Minimizing the Error of Measurement of the Rate of a Radioactive Exchange Reaction

By Norman Davidson and John H. Sullivan

It has been explicitly pointed out by several authors that for a radio-active exchange reaction between two components in chemical equilibrium, the activity of either component varies in a simple exponential manner with time.[1,2] We present here, as a consequence of this analysis, a method for: (a) the estimation of the error, due to the error of radioassay, in the rate constant for the exchange reaction, as a function of the extent of exchange; (b) the selection of the optimum degree of exchange to minimize this error.[3]

For the case where the rate is measured by the decrease in the activity of the component that initially contained all the activity, the integrated rate expression is

$$\ln\left[\left(\frac{a}{b}+1\right)\frac{x}{c}-\frac{a}{b}\right] = -R(a,b)\,\frac{a+b}{ab}\,t \qquad (1)$$

In this relation: a is concentration of component A that initially contained all the activity; b is concentration of initially inactive component B; c is initial activity of A; x is activity of A at time t and $R(a, b)$ is the rate of exchange.

For very short times of reaction x will be almost the same as c and the error in the rate large. For long times of reaction, the components will be almost in equilibrium with respect to the distribution of activity which will then change but little with time. It is often the case that the errors in a, b, t are small compared to the errors of radioassay in x and c. Set $z = x/c$ and $s = R((a + b)/ab)t$. The variable s is dimensionless and proportional to two factors: (1) Rt, the total number of concentration units (*i. e.*, atoms/cc. or moles/liter) that have undergone mutual exchange, and (2) the term $(a + b)/ab$. (Displayed in the form $s = Rt/b + Rt/a$, it is evident that s is the sum of the number of exchanges per atom of a, and the number of exchanges per atom of b). Then

$$-\frac{\mathrm{d}\ln s}{\mathrm{d}\ln z} = \frac{1+(a/b)\exp(s)}{s} = E(a/b,s) \qquad (2)$$

The relation $\sigma_s = |\mathrm{d}s/\mathrm{d}z|\sigma_z$ holds for the standard deviations, σ_s and σ_z, of s and z, because of the assumption that the error in s is due entirely to the error in z.[4] Then

$$\frac{\sigma_s}{s}\times\frac{z}{\sigma_z} = -\frac{\mathrm{d}\ln s}{\mathrm{d}\ln z} = E(a/b,s) \qquad (3)$$

For $\sigma_z,(\sigma_z/z)^2 = (\sigma_x/x)^2 + (\sigma_c/c)^2$; the standard deviations of the activities may be due to statistical counting errors or may be manipulative errors determined by reproducibility tests. It is often the case that the fractional error in $x,(\sigma_x/x)$, is a constant; this is roughly true, for example, if the error is principally a counting error and one counts all samples to the same number of counts, or if the error is a manipulative error in preparing chemically identical samples for radioassay. For such cases, the minimum of E locates the point for minimum error in s (and hence in the rate function R). Knowing the value of s corresponding to the minimum value of E and using a preliminary value of R, the optimum t may be chosen.

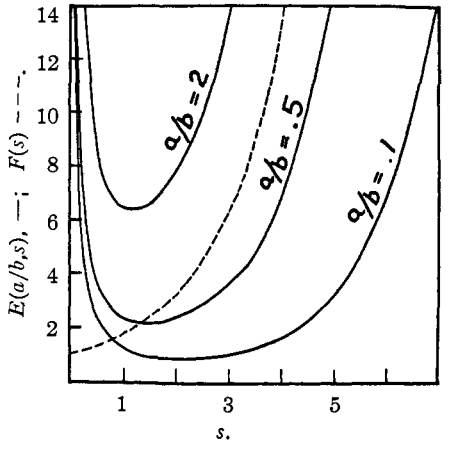

Fig. 1.—Error functions for exchange reactions.

The minimum of the error function, E, may be found by solution of the equation: $s - 1 = (b/a)\exp(-s)$. It will generally be more useful to construct a family of curves like those in the figure so that the error in s will be known for any s (or z). Estimates of the standard deviation in s obtained in this way are useful, for example as weighting factors in averaging data or in least squares treatments of data on the variation of rate of exchange with temperature or ionic strength. For such applications, the function E is useful even when the fractional error of radioassay is not constant. For these cases, knowing σ_x as a function of x and hence (for given a and b) as a function of s, one could construct the function, $E(s)\sigma_x(s)/x(s)$, and thus select the point of minimum error. For the usual case where σ_x/x does not change too rapidly with x, it may be sufficient to select by inspection a point in the region of the minimum of the $E(s)$ curve without making the more elaborate calculations required to select the optimum point.

(1) McKay, *Nature*, **142**, 997 (1938).

(2) Duffield and Calvin, This Journal, **68**, 557 (1946).

(3) Roseveare, *ibid.*, **53**, 1651 (1931), has applied similar arguments to the problem of estimating and minimizing the error in the rate constants for chemical reactions.

(4) See, for example, Margenau and Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., New York, N. Y., 1943. p. 498.

For the case where the rate of exchange is measured by the growth of activity, y, in B

$$y(t) = y(\infty)\ [1 - \exp(-s)] \quad (4)$$

$$\mathrm{d} \ln s/\mathrm{d} \ln (y/y(\infty)) = (\exp(s) - 1)/s = F(s) \quad (5)$$

The figure contains a plot of this function, too. In this case, of course, the fractional error in y cannot possibly be constant as y approaches zero; an estimate of σ_y as a function of y is needed for selecting an optimum reaction time or calculating the error of a particular determination.

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PASADENA 4, CALIFORNIA RECEIVED AUGUST 9, 1948

A Convenient Synthesis of N,N-Dimethyl-*p*-nitroaniline and N,N-Dimethyl-*o*-nitroaniline

BY TOD W. CAMPBELL

There are a number of methods in the literature for the preparation of N,N-dimethylnitroaniline[1]; but most of them are troublesome and result in low yields of a product which is usually of not too high purity. The methods in the literature[1g,i] which give acceptable or good yields involve a reaction in which a nitrohalobenzene is allowed to react with dimethylamine.

The author has found that this reaction is most conveniently brought about by refluxing a pyridine solution of nitrohalobenzene with a mixture of dimethylamine hydrochloride and sodium bicarbonate. The desired product is obtained in virtually quantitative yield; in the case of the para isomer, the product can be crystallized directly from the reaction solvent in a high state of purity. This procedure is therefore recommended for the preparation of these two substances.

Experimental Part

p-Nitrodimethylaniline.—A mixture of 42 g. of *p*-bromonitrobenzene, 300 cc. of pyridine, and 50 g. of sodium bicarbonate was placed in a 500-cc. round-bottom flask. To this mixture was added 30 g. of dimethylamine hydrochloride dissolved in about 10 cc. of warm water. The mixture was refluxed for ten hours. Mechanical stirring was not employed, since serious bumping did not occur. At the end of the reflux period, the hot solution was filtered free of inorganic salts, and the latter was extracted with 200 cc. of acetone, which was added to the pyridine solution. The mixed extracts were boiled, and water added to near the cloud point. On cooling, bright yellow needles of *p*-nitrodimethylaniline, 1–3 cm. in length, crystallized out. The melting point was observed to be 163.7–164.1° (lit. 163–166°) on a calibrated Anschütz thermometer in a Hershberg apparatus. The mother liquor on concentration to one third of its original volume gave an additional small yield of fine yellow needles, which had a melting point anywhere from 1–10 degrees low, for various experiments. One recrystallization from methanol raised the melting point to 163.5–164°. The over-all yield of pure product was 32.4–33.6 g. (94–97%).

o-Nitrodimethylaniline.—The above procedure was employed to prepare the ortho substituted derivative. Ten grams of *o*-nitrochlorobenzene gave 8.9 g. (85%) of product; b. p. 149 at 20 mm.; n^{25}D 1.6080.

Anal. Calcd. for $C_8H_{10}N_2O_2$; C, 57.81; H, 6.06. Found: C, 57.53; H, 6.21.

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(1) (a) Beilstein "Handbuch," Vol. XII, 690, 714, and first Supplement; (b) Le Fevre, *J. Chem. Soc.*, 147 (1930); (c) Davies, *Bull. soc. chim.*, [5] **2**, 295 (1935); (d) Donald and Reade, *J. Chem. Soc.*, 53 (1935); (e) Marsden and Sutton, *ibid.*, 599 (1936); (f) Shorygin, Topchier and Anan'ina, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 981 (1938); (g) Hodgson and Kershaw, *J. Chem. Soc.*, 280 (1930); (h) Evans and Williams, *ibid.*, 1199 (1939); (i) Senear, Rapport, Mead, Maynard and Koepfli, *J. Org. Chem.*, **11**, 378 (1946).

Vapor Density of Diborane[1]

BY E. M. CARR, J. T. CLARKE AND H. L. JOHNSTON

In connection with the process of adding diborane to a calorimeter it was necessary to determine its density at 275.16°K. The diborane was obtained from the Naval Research Laboratory, subjected to a two-plate distillation and shown by the cryoscopic method to have a purity of 99.95 mole per cent. The diborane was introduced into an evacuated, weighed and calibrated 1-liter Pyrex bulb immersed in a constant temperature water-bath at 275.16°K. and constant to 0.01° C. during the measurement. The pressure was read on a 15 mm. i. d. manometer using a Gaertner cathetometer and a standard meter bar in an insulated case; the readings were converted to standard conditions and meniscus corrections made according to Cawood and Patterson.[2] The bulb was then reweighed (using a similar bulb as tare) on a Troemner 4-kg. balance. One bulb had 1/8 inch Pyrex helices with a surface area 16.0 times that of the interior part of the bulb added to it. Since all density measurements were made at approximately atmospheric pressure the amount of adsorption was assumed to be constant.

The results were used to calculate the density and the second virial coefficient B in the equation

$$n - A = \frac{PV}{RT + PV}$$

where A equals moles of diborane adsorbed on the surface of a 1-liter bulb and was found to have a value of 2.4×10^{-5} mole. A summary of the data is

Pressure, atm., P	Temperature, °K., T	Moles in gas phase, $n - A$	Volume of bulb, ml., V	Second virial coef. B (ml.) 275.16° K.	Density g./l. 1 atm. 275.16°K.
0.98832	275.20	0.048232	1090.2	−247	1.2398
.98201	275.14	.047296	1076.4	−233	1.2393
.99445	275.16	.048488	1090.2	−223	1.2386
.94553	275.16	.046104	1090.2	−234	1.2393
.96219	275.17	.046314	1076.4	−227	1.2388
.97098	275.15	.046690	1076.4	−199	1.2374
		Average		−227	1.2389
		Av. deviation		±11	±0.0006

(1) This work was carried out under contract between the Office of Naval Research and The Ohio State University Research Foundation.

(2) Cawood and Patterson, *Trans. Faraday Soc.*, **29**, 514–523 (1933).

The value B equals -227, determined experimentally agrees very well with the value B equals -240 calculated from Berthelot's equation and the critical constants of A. E. Newkirk.[3]

(3) A. E. Newkirk, THIS JOURNAL, **70**, 1978 (1948).

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The Preparation of Xanthopterin

BY GERTRUDE B. ELION, AMOS E. LIGHT AND GEORGE H. HITCHINGS

The method of Totter[1] for the preparation of xanthopterin (2-amino-4,6-dihydroxypteridine) has several advantages with respect to the time involved, convenience and availability of starting materials, over those of Purrmann[2,3] and Koschara.[4] As will be shown, however, the product of this procedure is impure, as determined spectrographically. Moreover, such impure xanthopterin is shown to have a microbiological activity quite different from that of pure xanthopterin. The possibility exists that some of the reported biological activities of xanthopterin may be attributable to such impurities. This note describes modifications of the Totter procedure which result in their elimination.

Experimental: Preparation of Xanthopterin

Leucopterin.—The leucopterin was prepared by the method of Purrmann.[5] On standing, after neutralization, the acid filtrate from the crystallization of leucopterin deposited a red precipitate which had microbiological activity (Precipitate A, Expt. 9, Table I).

Dihydroxanthopterin.—Leucopterin (6 g., 0.03 mole) was suspended in 40 ml. of water and 4% sodium amalgam (88 g., 0.153 mole) was added in small portions with stirring, the temperature being maintained below about 50°. On completion of the reduction the mixture was decanted from the mercury and chilled in an ice-bath. The sodium salt of dihydroxanthopterin precipitated in shiny crystals which were filtered off, washed with 5 ml. of ice water and dried *in vacuo* (3.73 g., 60%). A small additional quantity of dihydroxanthopterin (0.46 g.) was obtained by acidification of the mother liquors. The filtrate from this fraction, on standing several days, deposited a red precipitate which had purine-like activity (Precipitate B, Expt. 10, Table I).

The sodium dihydroxanthopterin (3.73 g.) was dissolved in 300 ml. of hot water, with the aid of a small quantity of sodium hydroxide solution, filtered and acidified with acetic acid. Dihydroxanthopterin monohydrate precipitated as pale yellow microcrystals (3.4 g.); *cf.* Hitchings and Elion.[6]

Xanthopterin.—Dihydroxanthopterin monohydrate (2.5 g., 0.0125 mole) was dissolved at room temperature in 200 ml. of water containing 1.4 g. of potassium hydroxide. Potassium permanganate solution (84 ml. of 0.01 M) was added dropwise over the course of ten minutes. After coagulation of the manganese dioxide, the solution was separated by centrifugation. The manganese dioxide was extracted with 100 ml. of water; the combined supernatant fluids were filtered and acidified with acetic acid. The yellow-orange xanthopterin precipitate was collected by centrifugation, washed seven times with water, then with alcohol, finally with ether and dried *in vacuo*. The yield was 1.95 g. of xanthopterin monohydrate (79%). At *p*H 11.0 the monohydrate has an $E^{1\%}_{1\,cm.}$ of 0.92 at 255 mμ and 0.355 at 390 mμ.

(1) Totter, *J. Biol. Chem.*, **154**, 105 (1944).
(2) Purrmann, *Ann.*, **546**, 98 (1940).
(3) Purrmann, *ibid.*, **548**, 284 (1941).
(4) Koschara, *Z. physiol. Chem.*, **277**, 159 (1943).
(5) Purrmann, *Ann.*, **544**, 182 (1940).
(6) Hitchings and Elion, THIS JOURNAL, **71**, 467 (1949).

Microbiological

Each compound was tested for its ability to serve as a substitute for adenine in the growth of *Lactobacillus casei* with thymine as nutrilite at a concentration of 10 γ per ml.[7] It will be seen (Table I) that whereas pure xanthopterin (Expt. 1) and dihydroxanthopterin (Expt. 5) have only inhibitory effects, the product of the complete Totter procedure (Expt. 2) the product of further purification[8] of this material (Expt. 3) and that obtained by the oxidation of pure dihydroxanthopterin by silver oxide (Expt. 4) all possess purine-like activity. This activity is not due to the starting material (Expt. 6), the intermediate oxalyl derivative (Expt. 7) or leucopterin (Expt. 8). The activities appear to be properties of by-products which are formed in the various steps and in some instances deposit slowly on standing of the solutions (Expt. 9, Expt. 10). This finding demonstrates the necessity for the isolation and purification of the intermediates as a requisite for the preparation of pure xanthopterin.

TABLE I

PURINE-LIKE ACTIVITY OF XANTHOPTERIN AND INTERMEDIATES

Expt.	Compound	Titer: With compound I mg. per 10 ml.	Titer: Control
1	Xanthopterin I[a]	0.4	1.1
2	Xanthopterin II[b]	2.5	1.1
3	Xanthopterin III[c]	2.25	1.0
4	Xanthopterin IV[d]	1.9	1.3
5	Dihydroxanthopterin	0.3	0.6
6	2,4,5-Triamino-6-hydroxypyrimidine	0.5	0.5
7	2,4-Diamino-6-hydroxy-5-oxalamidopyrimidine	0.8	1.1
8	Leucopterin	0.4	0.6
9	Precipitate A	3.7	1.2
10	Precipitate B	5.0	1.2
11	Adenine sulfate (0.1 mg.)	7.1	1.2

[a] Permanganate oxidation of purified dihydroxanthopterin. [b] Silver oxide oxidation of crude dihydroxanthopterin. [c] Purified sample of II.[8] [d] Silver oxide oxidation of purified dihydroxanthopterin.

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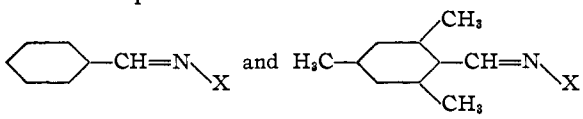
(7) Hitchings, Falco and Sherwood, *Science*, **102**, 251 (1945).

(8) Crude xanthopterin prepared by Totter's method was dissolved in N sulfuric acid, treated with norite and filtered. The product was precipitated with ammonium hydroxide, washed, dried, rewashed and redried. This treatment increased the $E^{1\%}_{1\,cm.}$ at 390 mμ in glycine buffer of *p*H 11.0 from a value of 0.31 to 0.35, the latter indicating approximate purity. The greater part of the microbiological activity remained, however.

Absorption Spectra of Some Benzal and Mesitylal Schiff Bases

By Lloyd N. Ferguson and John K. Robinson

When considering the relative light absorptions of two compounds such as



where X is any simple group, it is difficult to predict whether the steric effect of the *ortho* methyl groups in the mesityl compound will decrease absorption from that of the simple phenyl compound or whether there will be an increase in absorption due to hyperconjugation of the methyl groups. For this reason, the spectra of several Schiff bases of benzaldehyde and mesitylaldehyde were measured. The spectral characteristics are listed in Table I.

Table I

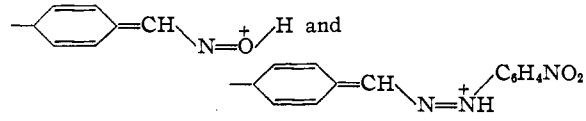
Spectral Characteristics of Some Benzal and Mesitylal Schiff Bases

Compound	Oxime λ_m (mμ)	Oxime ϵ_m	*p*-Nitrophenylhydrazone λ_m (mμ)	*p*-Nitrophenylhydrazone ϵ_m	Ethylenediamine λ_m (mμ)	Ethylenediamine ϵ_m
Benzal	252	14,300	407	34,200	247[1]	29,000[1]
Mesitylal	252	9,400	411	31,700	264	8,100
Difference	0	4,900	4	2,500	17	20,900

From these results, it is observed that there are no significant differences between the wave lengths of maximum absorption of the two oximes or of the two *p*-nitrophenylhydrazones. In going from dibenzalethylenediamine to dimesitylalethylenediamine there is a bathochromic effect. This, perhaps, is due to the hyperconjugation of the methyl groups becoming more prominent since the chromophoric system is double. Actually upon constructing the Fisher–Hirschfelder models of these three classes of compounds there appears to be only a small steric hindrance between the mesityl methyl groups and the group X.[2]

It has been observed before[3] that small steric hindrances have little effect upon $\lambda_{max.}$ but do decrease $\epsilon_{max.}$. This is illustrated in the present case by the oximes and the ethylenediamines. It is noted that this effect is very small in the case of the nitrophenylhydrazones; however, this is understandable. The nitrophenylhydrazones have absorption bands near 400 mu[4] without the aid of the phenyl or mesityl groups at the other end of the molecule, and consequently steric hindrance does not affect appreciably the molecular extinction.

The only explanation offered at this time for the trend in the differences of $\lambda_{max.}$ is to say that forms such as



contribute to the resonances of benzaldoxime and benzal-*p*-nitrophenylhydrazone. Such forms would be opposed by the hyperconjugation of the methyl groups in the mesityl nucleus. It may be that the two effects just cancel one another in the mesitylaldoxime, that the hyperconjugation is slightly more effective than the opposing resonance in the mesitylal-*p*-nitrophenylhydrazone and that in the ethylenediamine compounds, where the corresponding resonant forms cannot exist and the chromophoric system is double, the hyperconjugation causes a much larger bathochromic effect.

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(1) Taken from Ferguson and Branch, This Journal, **66**, 1467 (1944).

(2) O'Shaughnessy and Rodebush found the steric interference between the *ortho* methyl groups and the carbonyl oxygen of 2,4,6-trimethylacetophenone to be hardly strong enough to prevent a coplanar configuration, *ibid.*, **62**, 2910 (1940).

(3) O'Shaughnessy and Rodebush, *ibid.*, **62**, 2910 (1940).

(4) Ferguson and Battle, Report presented before the Organic Division of the Washington Chemical Society, Oct., 1948, at Washington, D. C.

Comparison of Age with the Relative Abundance of Argon and Potassium in Rocks

By R. L. Farrar, Jr., and George H. Cady

The study reported in this communication was done as a test of the proposal of Thompson and Rowlands[1] that the accumulation of argon resulting from decay by K electron capture of K^{40} should serve as a measure of the age of rocks containing potassium. For this study solid rocks of known geologic age were kindly furnished by G. E. Goodspeed of our Department of Geology.

The analytical procedure involved the following steps: (1) A 60-g. sample of sodium carbonate was freed of argon by pumping away gas for three hours from the molten salt held in a stainless steel vessel at about 950°. (2) Argon and other gases were removed from the surface of a 10-g. sample of rock composed of pea-sized pieces by allowing the material to stand for about an hour at room temperature in a vacuum. (3) The rock was then dissolved in the sodium carbonate at 950 to 1000°. This process was allowed to continue for a twenty-four-hour period to secure complete liberation of rare gases. (4) He + Ne and A + Kr + Xe were determined in the gas, using methods previously described by Cady and Cady.[2] Since spectroscopic tests showed that not more than traces of Ne, Kr or Xe could have been present in each case, the results of the analyses are reported in the table as helium and argon, respectively. (5) Potassium was determined in the mass resulting from the sodium carbonate fusion.

Conclusions: (1) These analyses indicate no regular increase of the A/K ratio with age. (2) The range in argon content is much less than that of helium. (3) Most of the argon in at least the first two samples probably originated from a source, perhaps the atmosphere, other than the

(1) F. C. Thompson and S. Rowlands, *Nature*, **152**, 103 (1943).

(2) G. H. Cady and H. P. Cady, *Ind. Eng. Chem., Anal. Ed.*, **17**, 760 (1945).

TABLE I

COMPARISON OF AGE WITH THE RATIO A/K IN ROCKS

Description of sample	Location from which obtained	He, cc./g. at S. T. P.	A, cc./g. at S. T. P.	K, %	G. ats. A / G. ats. K	Approximate age in millions of years
Quartz, Cornucopia formation	Cornucopia, N. E. Oregon	0.022×10^{-4}	1.3×10^{-4}	0.027	8.4×10^{-4}	100 (Late Mesozoic)
Soda feldspar	Ohanepecosh Hot Springs, Washington	0.062×10^{-4}	1.9×10^{-4}	0.43	7.7×10^{-5}	30 (Tertiary)
Potash feldspar, Cornucopia formation	Cornucopia, N. E. Oregon	0.19×10^{-4}	3.25×10^{-4}	12.8	4.4×10^{-6}	100 (Late Mesozoic)
Bostonite	Marblehead, Massachusetts	$<0.005 \times 10^{-4}$	0.81×10^{-4}	2.08	6.8×10^{-6}	300 (Carboniferous)
Granite, Silver Plume Formation	Silver Plume, Colorado	2.4×10^{-4}	1.4×10^{-4}	1.91	1.3×10^{-5}	940[3]
Granite	Sudbury, Ont.	0.65×10^{-4}	4.5×10^{-4}	3.33	2.4×10^{-5}	700 (Keweenawan)
Granite gneiss	Sudbury, Ont.	0.51×10^{-4}	5.2×10^{-4}	1.05	8.6×10^{-5}	1050 (Laurentian)

decay of potassium-40 in the existing minerals. (4) A careful isotopic analysis would be required to establish the relative proportions of "atmospheric" argon and that formed by the decay of K^{40} in the rock. (5) Without such an analysis, the ratio, A/K, appears not to be a good measure of the age of a rock.[4]

(3) Age by U, Th, Pb method: E. N. Goddard and J. J. Glass, *Am. Mineralogist*, **21**, 199 (1936).

(4) Aldrich and Nier (*Phys. Rev.*, **74**, 876 (1948)) have reported since the date of submission of this note, that the ratio A^{40}/A^{36} is higher in potassium minerals than in air. Their analyses of four samples indicate an increase in the ratio Radio A/K with age.

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RECEIVED SEPTEMBER 22, 1948

[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Some New Polyhalogenated Phenyl Isocyanates

BY LOUIS W. GEORGES[2] AND CARL HAMALAINEN

Previously reported work on the reaction of organic isocyanates with cellulose has been concerned with (1) the preparation of new cellulose derivatives of possible utility in the plastics field, and (2) the production of a more or less superficial esterification of cotton textiles to impart new properties. Thus, cellulose carbamate and cellulose acetate carbamate,[3] soluble in common organic solvents, and chlorophenyl carbamate of methyl cellulose with as much as 12% chlorine have been obtained.[4] By the preparation of carbamates, cotton textiles have been rendered water repellent,[5] their dyeing characteristics have been modified,[6] and the softening point and solubility properties of cellulose acetate rayon have been altered.[7]

The object of the present study was to investigate the possibility of providing a fire-resistant cotton textile by chemical combination of a fire-retarding agent with the cellulose molecule yet preserving the fibrous character of the cotton. Halogen-containing organic compounds are either not combustible or, in general, burn with difficulty. It seemed likely that partial carbamylation of cellulose with a polyhalogenated phenyl isocyanate would introduce sufficient halogen (27–31%) in cellulose to achieve fire-proofness and still retain the fiber structure. Such partial carbamylations could be successfully effected in a manner similar to that described by Hearon, Hiatt and Fordyce[3c] in which phenyl isocyanate was used. A patent covering the fireproofing of lint cotton has been issued.[8]

It is believed that the polyhalogenated phenyl isocyanates used in the reaction with cotton in the manner described in the patent are new compounds. The preparation of these compounds is given in the experimental section below.

Experimental

2,5-Dichlorophenyl Isocyanate.—Forty-five grams of 2,5-dichloroaniline hydrochloride was suspended in 500 ml. of chlorobenzene and phosgene[9] was passed through the suspension in a steady stream with stirring until complete solution of the hydrochloride was effected. During the

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Present address: Firestone Tire and Rubber Company, Akron, Ohio.

(3) (a) P. E. C. Goissedet, U. S. Patent 1,357,450 (November 2, 1920); (b) C. J. Malm and G. F. Nadeau, U. S. Patent 1,991,107 (February 12, 1935); (c) W. M. Hearon, G. D. Hiatt and C. R. Fordyce, THIS JOURNAL, **65**, 829 (1943); (d) W. M. Hearon and J. L. Lobsitz, *ibid.*, **70**, 296 (1948).

(4) E. Dyer and K. L. McCormick, *ibid.*, **68**, 986 (1946).

(5) (a) E. Schirm, U. S. Patent 2,303,364 (December 1, 1942); (b) W. Kaase, U. S. Patent 2,370,405 (February 27, 1945); (c) R. W. Maxwell, U. S. Patent 2,343,920 (March 14, 1944); (d) I. G. Farbenindustrie, A.-G., British Patent 461,179 (February 8, 1937); (e) British Patent 474,403 (November 1, 1937).

(6) P. S. Pinkney, U. S. Patent 2,350,188 (May 30, 1944).

(7) D. D. Coffman and J. S. Reese, British Patent 548,807 (December 25, 1942).

(8) L. W. Georges and C. Hamalainen, U. S. Patent 2,428,843 (October 14, 1947).

(9) (a) D. V. N. Hardy, *J. Chem. Soc.*, 2011 (1934); (b) J. Hilger, U. S. Patent 1,916,314 (July 4, 1933); (c) W. Hentrich and H. J. Engelbrecht, U. S. Patent 2,261,156 (November 4, 1941).

course of the reaction the temperature was raised gradually until there was a gentle refluxing of the solvent. After concentrating the clear chlorobenzene solution under reduced pressure the product was distilled and 26.3 g. (62%) of colorless 2,5-dichlorophenyl isocyanate was obtained; b. p. 83–84° at 3–4 mm. The isocyanate was identified by means of the crystalline di-(2,5-dichlorophenyl)-urea; m. p. 289° (cor.).

Anal. Calcd. for $(C_6H_3Cl_2)_2(NH)_2CO$: N, 8.0; Cl, 40.1. Found: N, 7.9; Cl, 40.0.

2,4,6-Trichlorophenyl Isocyanate.—Phosgene was passed through a suspension of 50 g. of 2,4,6-trichloraniline hydrochloride in 500 ml. of chlorobenzene. The temperature was raised gradually to the reflux point. The bulk of the suspended material dissolved. The small amount of crystalline compound that was separated by filtration proved to be the disubstituted urea derivative. The clear filtrate was concentrated under reduced pressure until free of chlorobenzene. The hot residue was transferred to a crystallizing dish and stored in a vacuum desiccator in which upon cooling the product crystallized. The yield of crude 2,4,6-trichlorophenyl isocyanate was 29.2 g. (61%). Pure material was obtained on recrystallization from petroleum ether; m. p. 64–65°.

Anal. Calcd. for $C_6H_2Cl_3NCO$: N, 6.3; Cl, 47.9. Found: N, 5.9; Cl, 47.3.

The crystalline di-(2,4,6-trichlorophenyl)-urea was prepared; m. p. 295° (cor.).

2,4,6-Tribromophenyl Isocyanate.—Dry hydrogen chloride was passed into a solution of 107 g. of 2,4,6-tribromoaniline in 500 ml. of chlorobenzene until a voluminous precipitate of the hydrochloride was formed. Phosgene was then passed into the reaction mixture in a steady stream with continuous stirring until solution of the 2,4,6-tribromoaniline hydrochloride was effected. The reaction mixture was heated gradually during the course of the reaction to the reflux temperature of the solvent. An appreciable amount of the crystalline disubstituted urea was formed and this product was separated by filtration. The clear filtrate was concentrated under reduced pressure until free of solvent and the hot liquid residue transferred to a crystallizing dish. After cooling in a vacuum desiccator a crystalline mass was obtained. The yield of crude 2,4,6-tribromophenyl isocyanate was 44.6 g. (39%). Pure material was obtained on recrystallization from petroleum ether; m. p. 92–94°.

Anal. Calcd. for $C_6H_2Br_3NCO$: N, 3.9; Br, 67.5. Found: N, 3.9; Br, 66.8.

The addition of water to a pyridine solution of the isocyanate yielded the di-(2,4,6-tribromophenyl)-urea; m. p. 323° (cor.).

Acknowledgment.—We are indebted to Miss Alva Faust and Mr. Richard H. Robinson for the chemical analyses, and to Mr. Frank C. Magne for the melting point determinations.

SOUTHERN REGIONAL RESEARCH LABORATORY
NEW ORLEANS, LOUISIANA RECEIVED AUGUST 30, 1948

The Chloromethylation of Veratrole[1]

BY OSCAR GAWRON

In connection with a synthesis of a compound of pharmaceutical interest, a large supply of 4-chloromethyl-veratrole was needed. Recourse to the literature showed several unsuccessful attempts[2,3] at chloromethylation of veratrole by the usual procedures and a successful attempt[4] by a two phase chloromethylation. The unsuccessful attempts yielded 2,3,6,7-tetramethoxy-9,10-dihydroanthracene as a condensation product.[3,4]

The successful Bide and Wilkinson[4] procedure was tried and found to give somewhat erratic results, probably due to the critical conditions involved, −2 to +2°, rate of stirring, and rate of passage of the hydrogen chloride. In addition, temperature control of large scale laboratory preparations was difficult, although this was partially solved by the direct addition of dry ice to the reaction mixture from time to time.

Since the above procedure did not prove entirely satisfactory, several chloromethylation experiments were run with chloromethyl ether in glacial acetic acid. These were found to be satisfactory. The conditions used were essentially those employed by Vavon, Bolle and Calin[5] in their study of the influence of substituents on rates of chloromethylation of aromatic compounds.

The procedure finally adopted was as follows: In a one-liter, three-necked, round-bottom flask, equipped with a thermometer, a mercury seal stirrer, and a calcium chloride tube, were placed 282 g. of glacial acetic acid, 247 g. of veratrole (1.8 moles) and 288 g. of chloromethyl ether (3.6 moles). The stirrer was started and the initial temperature was noted. If below 20°, the reaction mixture was gently warmed to 20 to 21°. The reaction was then allowed to proceed for seven hours. In four to six hours the temperature rose to 30° and subsequently the reaction mixture was kept below 30° by means of a cold water-bath. The reaction, which had proceeded to almost 50% completion (analytical method of Vavon, Bolle and Calin[5]) at the end of seven hours was then stopped by pouring with stirring, onto 800 g. of cracked ice and 400 ml. of chloroform. Stirring was continued until most of the ice had melted. The chloroform layer was then separated and the water layer extracted twice with 100-ml. portions of chloroform. The combined chloroform extracts were washed once with 50 ml. of water and then dried over anhydrous sodium sulfate. The chloroform was removed *in vacuo* and the residue distilled at less than 1 mm. The fore run was unchanged veratrole and then the 4-chloromethylveratrole distilled at 100–103°. It crystallized on cooling the receiver; m. p. 48–50°; yield, 62 g. (54%), based on recovered veratrole.

Further preparatory studies and kinetic studies on the mechanism of the general chloromethylation reaction are in progress.

(1) Work done at the New York Quinine and Chemical Works, Inc., Brooklyn, N. Y.

(2) Carré and Liberman, *Compt. rend.*, **199**, 791 (1934).

(3) Fitscher and Bogert, *J. Org. Chem.*, **4**, 71 (1939).

(4) Bide and Wilkinson, *J. Chem. Soc.*, 84 (1945).

(5) Vavon, Bolle and Calin, *Bull. soc. chim.*, [5] **6**, 1025 (1939).

DUQUESNE UNIVERSITY
PITTSBURGH 19, PA. RECEIVED OCTOBER 11, 1948

Substituted Quinolyl Dodecyl Sulfides

BY HENRY GILMAN AND SAMUEL P. MASSIE

The therapeutic activities of some quinoline ethers and the germicidal activities of some aryl sulfides[1] suggested the preparation of some quinoline sulfides for pharmacological testing. It was also considered desirable to incorporate a fat-soluble group into the molecule, so as to increase the possibility of absorption of the drug by the animal body. These considerations initiated the preparation of some high-molecular weight alkyl quinolyl sulfides for therapeutic investigation.

(1) Foss, Dunning and Jenkins, THIS JOURNAL, **56**, 1978 (1934).

TABLE I

QUINOLYL DODECYL SULFIDES

Haloquinoline	Dodecyl sulfide	Yield, %	M. p., °C.	Color	Formula	S Analyses, % Calcd.	Found
5-Nitro-6-chloro-	5-Nitro-6-quinolyl	80	44–5°	Yellow	$C_{21}H_{30}O_2N_2S$	8.56	8.50
5-Nitro-6-chloro-8-acetamido-	8-Amino-5-nitro-6-quinolyl	93	89.5–90.5	Orange	$C_{21}H_{31}O_2N_3S$	8.23	8.30
6-Methoxy-2-chloro-4-methyl-	6-Methoxy-4-methyl-2-quinolyl	70	71–72	Cream	$C_{23}H_{35}ONS$	8.58	8.70
4,7-Dichloro-	7-Chloro-4-quinolyl	87	59–60	White	$C_{22}H_{30}NSCl$	8.80	8.90

TABLE II

AMINOQUINOLYL DODECYL SULFIDES

Nitro derivative	Amino derivative	Yield, %	M. p., °C.	Formula	S Analyses, % Calcd.	Found
5-Nitro-6-quinolyl	5-Amino-6-quinolyl[a,b]	76	59–60	$C_{21}H_{32}N_2S$	9.30	9.02
8-Acetamido-5-nitro-6-quinolyl	8-Acetamido-5-amino-6-quinolyl	80	77–78	$C_{23}H_{35}ON_3S$	7.98	6.97[c]

TABLE III

ACETAMIDOQUINOLYL DODECYL SULFIDES

Amine	Acetamide	M. p., °C.	Color	Formula	S Analyses, % Calcd.	Found
5-Amino-6-quinolyl	5-Acetamido-6-quinolyl	121–122	White	$C_{23}H_{34}ON_2S$	8.29	8.21
8-Amino-5-nitro-6-quinolyl	8-Acetamido-5-nitro-6-quinolyl	67–68	Yellow	$C_{23}H_{33}O_3N_3S$	7.42	7.29
8-Acetamido-5-amino-6-quinolyl	5,8-Diacetamido-6-quinolyl	126–127	Cream	$C_{25}H_{37}O_2N_3S$	..[d]	..

[a] This amine would not form a derivative with salicylaldehyde or acetonylacetone. [b] The dihydrochloride melted at 156–157°. Calcd. for $C_{21}H_{34}N_2Cl_2S$: S, 7.67. Found: S, 7.67. [c] This amine could not be purified, but the acetamido derivative gave the correct analysis. [d] Calcd. for $C_{25}H_{37}O_2N_3S$: N, 9.48. Found: N, 9.48.

A series of substituted quinolyl dodecyl sulfides was prepared from activated chloroquinolines and sodium dodecyl mercaptide in methyl cellosolve. The quinoline compounds used were 5-nitro-6-chloroquinoline,[2] 5-nitro-6-chloro-8-acetamidoquinoline,[3] 4,7-dichloroquinoline[4] and 6-methoxy-2-chlorolepidine.[5] The nitroquinolyl sulfides were then reduced to the amino derivatives and these, in turn, were acetylated to the acetamido derivatives.

These compounds were tested against tuberculosis; reports on their activities will be published elsewhere. The authors are grateful to Parke, Davis and Co. for arranging for the tests, and to William Meikle for assistance.

Experimental

Quinolyl Dodecyl Sulfides.—The general method of preparation was to add a solution of sodium dodecyl mercaptide in methyl cellosolve to the chloroquinoline in hot methyl cellosolve.[6] The mixture was refluxed for an hour, cooled, poured into 200 ml. of water, acidified with acetic acid, filtered, and the precipitate recrystallized from methanol.

Aminoquinolyl Dodecyl Sulfides.—The nitroquinolyl dodecyl sulfides were reduced with hydrogen and Raney nickel in absolute ethanol. Recrystallization was not necessary. The amines were yellow solids.

Acetamidoquinolyl Dodecyl Sulfides.—The acetamido derivatives were prepared by heating the amine and acetic anhydride in glacial acetic acid. The mixture was poured into water, filtered and recrystallized from absolute ethanol.

The results are given in Tables I, II and III.

CHEMICAL LABORATORY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED OCTOBER 11, 1948

(2) Kindly furnished by Mrs. Martha Mackin.

(3) Gilman and co-workers, THIS JOURNAL, **68**, 1577 (1946).

(4) Surrey and Hammer, *ibid.*, **68**, 115 (1946).

(5) Prepared by directions of Dr. K. N. Campbell, The University of Notre Dame, South Bend, Indiana.

(6) 5-Nitro-6-chloroquinoline yielded only a small amount of the sulfide by this procedure. It was found desirable to stir the solution of the reactants at room temperature for two hours or more before heating.

A New Synthesis of 2,4-Dihydroxyquinoline

BY E. H. HUNTRESS AND J. BORNSTEIN

A recent review[1] of 4-hydroxyquinolines prompts us to report a synthesis of 2,4-dihydroxyquinoline from isatin, giving better results by simpler procedure than prior methods.

The most widely used method for the preparation of 2,4-dihydroxyquinoline has been the treatment of the esters of N-acetylanthranilic acid with sodium metal in toluene or xylene.[2,3,4] Although Camps[2] reported 60% crude yield, subsequent investigators[2,3,4] (including ourselves) have been unable to obtain more than 28–40%.

Reaction of isatin with chloroacetyl chloride gave N-(chloroacetyl)-isatin which on refluxing with aqueous potassium hydroxide, followed by acidification of the reaction mixture with hydrochloric acid, precipitated 2,4-dihydroxyquinoline with the simultaneous evolution of carbon dioxide.

Experimental

N-(Chloroacetyl)-isatin.—Isatin (10 g., 0.068 mole) was vigorously refluxed with chloroacetyl chloride (70 ml., 100 g., 0.89 mole) for five hours. The dark brown reaction mixture was cooled for two hours in an ice-bath

(1) Reitsema, *Chem. Revs.*, **43**, 43 (1948).

(2) Camps, *Arch. Pharm.*, **237**, 689–691 (1899).

(3) Ashley, Perkin and Robinson, *J. Chem. Soc.*, 388 (1930).

(4) Brooker and Smith, THIS JOURNAL, **59**, 72 (1937).

and the precipitate filtered. The filtrate was saved and the solid washed twice with 20 ml. portions of ether and air-dried. The N-(chloroacetyl)-isatin (10.0 g., 66%) consisted of fine-golden-yellow needles, m. p. 210–211° cor., suitable for use without additional purification. The reaction filtrate was replenished with fresh chloroacetyl chloride (10 ml.) and the run repeated with additional isatin (10 g.) giving more equally pure product (12.0 g., 78%). For analysis the N-(chloroacetyl)-isatin was recrystallized from ethyl acetate.

Anal. Calcd. for $C_{10}H_6O_3NCl$: C, 53.71; H, 2.71; N, 6.26; Cl, 15.85. Found: C, 53.32; H, 2.91; N, 6.41; Cl, 15.79.

On recrystallization from methanol the yellow N-(chloroacetyl)-isatin separated with one mole of solvent as fine, *colorless* needles, m. p. 83.0–83.5° cor.

Anal. Calcd. for $C_{11}H_{10}O_4NCl$: C, 51.68; H, 3.95; N, 5.48; Cl, 13.88. Found: C, 51.52; H, 4.09; N, 5.46; Cl, 14.02.

2,4-Dihydroxyquinoline.—Into 150 ml. of an aqueous boiling solution of potassium hydroxide (5.0 g., 0.09 mole) was added all at once 5.0 g. (0.022 mole) of yellow N-(chloroacetyl)-isatin. The straw-colored solution was refluxed for two hours and then cooled to room temperature. On acidification of the reaction mixture with concentrated hydrochloric acid a cream-colored solid separated which was filtered and washed three times with 10-ml. portions of cold water. The crude yield was 2.0–2.5 g., 56–70%. From the filtrate small amounts of isatin were isolated. The 2,4-dihydroxyquinoline was purified by dissolving in the minimum amount of 10% sodium carbonate solution, filtering, boiling the filtrate with Darco for five minutes, filtering, and then reacidifying. On recrystallizing from methanol the compound separated as fine, colorless needles; m. p. 352–354° cor., recorded m. p. 355°.[5]

Anal. Calcd. for $C_9H_7O_2N$: C, 67.08; H, 4.38; N, 8.69. Found: C, 67.21; H, 4.63; N, 8.65.

The identity of the 2,4-dihydroxyquinoline was confirmed by means of its nitroso derivative, m. p. 208° dec., uncor. (recorded 208°[6]), which melted at the same temperature when mixed with an authentic sample. In addition, the (mono) acetyl derivative was prepared; m. p. 215.0–215.5° uncor. (recorded 214–215°[6]), mixed melting point with authentic sample was 215.0–215.5° uncor.

(5) Niementowski, *Ber.*, **40**, 4289 (1907).

(6) Baeyer and Homolka, *ibid.*, **16**, 2216 (1883); *cf.* Meyer, Heimann, *Compt. rend.*, **203**, 335-337 (1936).

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

RECEIVED NOVEMBER 3, 1948

The Synthesis of Boron Trichloride

BY DALLAS T. HURD

A well known and convenient method for preparing small amounts of boron trichloride or boron tribromide comprises passing boron trifluoride gas over aluminum chloride or aluminum bromide.[1] I recently have found that a reaction may occur at elevated temperatures between aluminum chloride and boric oxide to produce boron trichloride.

Experimental.—120 grams of anhydrous boric acid and 440 g. of aluminum chloride were ground together and placed in a steel pressure vessel. The reaction mixture was heated at 350° for sixteen hours. The bomb then was cooled and the gaseous reaction product was bled off and caught in a trap held at −80°. The collected product was a clear colorless liquid boiling at 12° (reported boiling point of boron trichloride +12.5°). This material fumed in moist air, reacting with the moisture to produce white solid boric acid. A small amount of the liquid was dissolved in water to give a solution which, when tested with silver nitrate, gave a strong test for chloride.

The total amount of product collected was 30 g. or about 7.5% yield based on a complete conversion of boric oxide to boron trichloride.

It also was observed that a molten mixture of boric oxide and calcium chloride at 800–900° evolved boron trichloride very slowly and became more viscous, precipitating an infusible residue in the magma. This solid residue was treated with water after it was cool and a strongly alkaline solution resulted, indicating a conversion of some of the calcium chloride to calcium oxide.

Discussion.—The low yields of boron trichloride are ascribed to: (1) the reaction between aluminum chloride and boric oxide to form aluminum oxide and boron trichloride may be an equilibrium reaction which did not go to completion in the sealed bomb; and/or (2) part of the boric oxide may become bound chemically as aluminum borate by reaction with the aluminum oxide as this material is formed. It is noteworthy that attempts to prepare boron trichloride by a reaction of sodium borate or tetraborate with aluminum chloride were unsuccessful at reaction temperatures up to 350°.

(1) Gamble, Gilmont and Stiff, THIS JOURNAL, **62**, 1257 (1940).

GENERAL ELECTRIC RESEARCH LABORATORY
SCHENECTADY, N. Y. RECEIVED OCTOBER 25, 1948

Reactions of Polyhaloparaffins with Grignard Reagents. 1,1,1-Trichloropentane

BY CORLISS R. KINNEY AND WILLIAM L. SPLIETHOFF

Binaghi[1] has shown that chloroform and carbon tetrachloride react readily with ethylmagnesium bromide, but that gaseous reduction products are formed for the most part. We have reëxamined the reaction from the point of view of controlling its course for the production of tri- and tetrasubstituted paraffins. However, even at −78°, using the less reactive *n*-butylmagnesium chloride, and carrying the halide into the reaction flask vaporized in a stream of dry nitrogen, a vigorous reaction occurs and the products are largely gaseous.

On the other hand, the reaction may be controlled to a certain extent by using the inverse Grignard technique. Thus, adding *n*-butylmagnesium chloride to a solution of carbon tetrachloride in ether gives a small yield of the first step in the reaction, 1,1,1-trichloropentane. The new compound loses hydrogen chloride at about 140° but could be vacuum distilled without decomposition. This thermal instability further indicates activity of the vicinal chlorine atoms. No attempt was made to treat this compound with additional Grignard reagent, but instead the more available 1,1,1-trichloroethane was investigated. This compound, like chloroform, gave largely

(1) Binaghi, *Gass. chim. ital.*, **52**, II, 132-138 (1922); **53**, 879 (1923).

gaseous products and the reaction appeared to be unsuited as a synthetic method. To complete the series, methylene chloride also was tried but did not react at the boiling point of ether. These results indicate a marked difference in the reactivity of vicinal chlorides at the trichloro level. This is of interest in connection with the behavior of chloral for which only reduction at the carbonyl group with aliphatic Grignard reagents containing β-hydrogen atoms has been reported[2] and the behavior of monochloroacetone which was found to react with isoamylmagnesium bromide at the chlorine atom as well as adding on the reagent at the carbonyl group.[3]

Considering the violence of the reaction of carbon tetrachloride, even at −78°, carbon tetrafluoride was also treated with *n*-butylmagnesium chloride at the boiling point of ether. However, no reaction was observed.

Experimental

1,1,1-Trichloropentane.—*n*-Butylmagnesium chloride was prepared from one mole of *n*-butyl chloride, one gram atom of magnesium and 300 ml. of dry ether. The solution was forced by means of dry nitrogen under pressure, into a stirred mixture of 2 moles of carbon tetrachloride and 300 ml. of dry ether cooled in a bath of Dry Ice and acetone. A vigorous reaction occurred with the formation of a white precipitate and a gas which decolorized bromine in carbon tetrachloride. White fumes were also formed which settled on the walls of the flask as a white solid. Since this was very soluble in water it was concluded that it was magnesium chloride. After the reagent had been added the cooling bath was removed and the mixture allowed to come to room temperature and stand for two hours. It was then refluxed gently for forty-five minutes and after cooling was decomposed with ice-water. Some basic magnesium precipitate was filtered out with suction and the organic layer separated, dried with calcium chloride and distilled to 100° to remove ether and excess carbon tetrachloride. The residue weighed about 30 g. and constituted a crude yield of 16.5%. On continuing the distillation, hydrogen chloride was evolved copiously at about 140°; consequently, the residue was vacuum distilled. Refractionation at 20 mm. through a 10-plate column packed with glass helices gave a heart-cut boiling at 56–57°. The index of refraction was $n^{20}D$ 1.4540.

Anal. Calcd. for $C_5H_9Cl_3$: Cl, 60.5. Found: Cl, 60.2, 60.1.

Acknowledgments—The authors are indebted to Mr. H. L. Lovell for the analysis reported above and to the Fluorine Laboratories of The Pennsylvania State College for the sample of carbon tetrafluoride used.

(2) Gilman and Abbott, *J. Org. Chem.*, **8**, 224 (1945); Floutz, THIS JOURNAL, **67**, 1615 (1945).

(3) Kinney and Splieth off, to be published in the *Journal of Organic Chemistry*.

DIVISION OF FUEL TECHNOLOGY
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RECEIVED OCTOBER 4, 1948

Decomposition of Aliphatic Azo Compounds

BY FREDERICK M. LEWIS AND MAX S. MATHESON

Certain aliphatic azo compounds have several properties which make them especially suitable as sources of free radicals for kinetic investigations. These properties include stability, clean first order decompositions nearly independent of reaction media, and the ability to act as efficient photosensitizers in the near ultraviolet.

The decomposition rates (Table I) as measured by nitrogen evolution, were in all cases first order after a short induction period, probably due to a thermal adjustment after sample addition and to the disappearance of oxygen traces introduced with the sample. Thiele and Heuser[1] and Dox[2] have described the method of preparation of these compounds. Further, it has been shown that 2-azo-bis-isobutyronitrile heated at 110° in high boiling petroleum ether quantitatively splits out nitrogen, tetramethyl succinonitrile being formed in 50% yield.[1] Of course such fragments of the azo compound as initiate polymerization in the presence of monomer will not appear as tetramethyl succinonitrile.

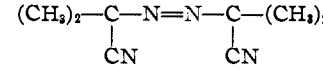
TABLE I

DECOMPOSITION OF AZO COMPOUNDS IN XYLENE AT 80°

Material, 0.1–0.3 mole/l.	k, min.$^{-1}$	Ea, kcal.
2-Azo-bis-isobutyronitrile	0.0092	31.3
2-Azo-bis-2-methylbutyronitrile	.00598	29.4
2-Azo-bis-2-methylheptonitrile	.0107	30.2
1-Azo-bis-1-cyclohexanecarbonitrile	.000282	39.9
Dimethyl-2-azo-bis-isobutyrate	.00653	35.8
4-Azo-bis-4-cyanopentanoic acid	.00538[a]	34.0

[a] In water, insoluble in xylene.

Table II shows that there is little change in rate for 2-azo-bis-isobutyronitrile (sold as Porofor N by Naugatuck Chemical Division of U. S. Rubber Co.) with widely different reaction solvents, and



even a powerful inhibitor (tetrachloroquinone) has little effect. Accordingly these materials offer several advantages over peroxides as free radical sources when a constant rate of production of radicals is desired. (As an example of free radical activity 0.096 g./l. of Porofor N in purified vinyl acetate induces 4.7% polymerization per hour at 50°.) Several authors[3] have shown that

TABLE II

SOLVENT EFFECT IN THE DECOMPOSITION OF 2-AZO-BIS-ISOBUTYRONITRILE (~0.3 mole/l.) AT 80°

Solvent	k, min.$^{-1}$
Xylene	0.0092
Xylene contg. 0.012 mole/l. tetrachloroquinone	.00898
Glacial acetic acid	.00914
N-Dimethylaniline	.011
Dodecyl mercaptan	.00875
Carbon tetrachloride	.00725 (77°)

(1) Thiele and Heuser, *Ann.*, **290**, 1 (1896).

(2) Dox, THIS JOURNAL, **47**, 1473 (1925).

(3) Nozaki and Bartlett, *ibid.*, **68**, 1686 (1946); Cass, *ibid.*, **68**, 1976 (1946).

the rate of decomposition of benzoyl peroxide varies widely with solvent and concentration.

These compounds are highly efficient photosensitizers as well as thermal initiators for free radical reactions. An absorption band has its peak at 3500 Å. (measurements on 2-azo-bis-isobutyronitrile) so that the compounds are especially suited for work using the 3660 Å. line of the mercury arc. Table III illustrates some results obtained in irradiations with Type A Hanovia mercury arc light filtered through Pyrex. Because of the characteristics of the absorption, the absorbed light is >80% 3660 Å. Slightly smaller values than those given in the Table have been found for 2-azo-bis-isobutyronitrile using monochromatic 3660 Å. radiation. The quantum yields show the aliphatic azo nitriles to be superior in efficiency to such a photosensitizer as biacetyl.[4] The first six compounds in the table vary little in efficiency in styrene, and the variations in vinyl acetate are probably less than shown, as it is believed the reactions with vinyl acetate overheated several degrees. These polymerizations were carried out *in vacuo* to eliminate the effects of oxygen. Light intensities were measured with the uranyl oxalate actinometer.

TABLE III

PHOTOPOLYMERIZATION WITH AZO SENSITIZERS AT 3660 Å.[a] AND 30°

Sensitizer (~0.038 m./l.)	Quantum yield polymerization[b] Vinyl acetate	Styrene
2-Azo-bis-isobutyronitrile	360	55
2-Azo-bis-propionitrile (unstable)	...	50
Dimethyl-2-azo-bis-isobutyrate	>600	50
1-Azo-bis-1-cyclohexanecarbonitrile	600	50
2-Azo-bis-2-methylheptonitrile	230	55
2-Azo-bis-2-methylbutyronitrile	255	60
4-Azo-bis-4-cyanopentanoic acid	284	...
2-Azo-bis-propane[c]	80	2.80
Biacetyl	10.3	1.4[d]

[a] λ>3000 Å. but largely 3660 Å. absorbed so quantum yield calculated on basis of 3660 radiation absorbed. [b] Molecules monomer polymerized per quantum of 3660 Å. radiation absorbed by sensitizer. Quantum yield cor. to 3.94×10^{-5} einstein/hr./cc. ~50% of 3660 Å. light absorbed in 1 cm. with sensitizer concentrations used. [c] This azo compound does not initiate polymerizations at room temperature in the absence of light. [d] With monochromatic 3660 Å.

(4) C. L. Agre (U. S. Patent 2,367,660, Jan. 23, 1945, to du Pont.)

CONTRIBUTION 80 FROM THE
UNITED STATES RUBBER CO.
PASSAIC, NEW JERSEY RECEIVED OCTOBER 11, 1948

Reaction of Hydrogen Bromide with Di-*t*-butyl Peroxide

BY NICHOLAS A. MILAS AND CHARLES N. WINNICK[1]

Vaughan and Rust[2] claimed the preparation of di-*t*-butyl peroxide by the vapor oxidation of isobutane in the presence of hydrogen bromide. More recently Raley, Rust and Vaughan[3] reported that hydrogen chloride sensitizes the vapor phase decomposition of di-*t*-butyl peroxide, but that under comparable conditions hydrogen bromide has little effect on this decomposition. However, the behavior of hydrogen bromide with liquid di-*t*-butyl peroxide is different. We have found recently that at 0° it reacts rapidly and exothermically with di-*t*-butyl peroxide in accordance with the equations

$$(CH_3)_3COOC(CH_3)_3 + 4HBr \longrightarrow 2(CH_3)_3CBr + Br_2 + 2H_2O \quad (1)$$

$$(CH_3)_3CBr + Br_2\ (\text{peroxide}) \longrightarrow (CH_3)_2CBrCH_2Br + HBr \quad (2)$$

The validity of the second reaction was determined experimentally by allowing *t*-butyl bromide to react with bromine in the presence of di-*t*-butyl peroxide as a catalyst. A yield of 64% of isobutylene dibromide was obtained.

Experimental

Reaction of Di-*t*-butyl Peroxide with Hydrogen Bromide.—A sample (16.4 g., 0.181 mole) of di-*t*-butyl peroxide prepared and purified according to directions given elsewhere[4] was cooled to 0° and a slow stream of hydrogen bromide (Dow Chemical Co.) from a tank was allowed to come in contact with the peroxide. The reaction, which was immediate and exothermic, was continued for three hours, the temperature being kept as close to 0° as possible. At the end of this period the mixture separated into two distinct layers which were separated and weighed. The bromine was estimated in each layer iodimetrically and the hydrogen bromide plus bromine by titration against standard alkali. The water in the aqueous layer was estimated by difference. The remainder of the non-aqueous layer was washed with concentrated sodium bisulfite solution, dried over anhydrous magnesium sulfate, then fractionated. A fraction (24 g.) boiling at 72–73° was collected; $n^{25}D$ 1.426. This was identified as *t*-butyl bromide. Another fraction (21.4 g.) was collected at 143–145° which was refractionated through a six-plate Podbielniak column; b. p. 145–148°; $n^{25}D$ 1.5050; d^{25}_{25} 1.7426. From the analysis and physical constants, this fraction was identified as isobutylene dibromide. *Anal.* Calcd. for $C_4H_8Br_2$: C, 22.22; H, 3.70; Br, 74.07. Found: C, 22.44; H, 3.87; Br, 74.62. In addition to the two bromides, a black residue remained in the distillation flask.

From 26.4 g. (0.181 mole) of di-*t*-butyl peroxide and excess hydrogen bromide, we obtained 0.1685 mole (92.2%) of bromine (free 0.0695 mole; reacted, 0.099 mole), 0.35 mole of water (96.6%), and 0.274 mole of *t*-butyl bromide (0.175 mole) plus isobutylene dibromide (0.099 mole).

Catalyzed Bromination of *t*-Butyl Bromide.—A mixture of 50 g. of *t*-butyl bromide and 5 g. of di-*t*-butyl peroxide was cooled to 0° and to it was added slowly with frequent shaking 58 g. of liquid bromine. No apparent reaction was noticed during the first few minutes of bromine addition, then a vigorous reaction set in with copious evolution of hydrogen bromide. The reaction mixture was allowed to stand overnight at 0°, then shaken with anhydrous potassium carbonate and distilled. Only 7 g. distilled below 90°, 76 g. between 90–160° and a small tarry residue remained in the distilling flask. The main product was fractionated and the fraction (51 g., 64%) boiling at 148–151° collected and identified as isobutylene dibromide; $n^{26}D$ 1.5075.

CAMBRIDGE, MASSACHUSETTS RECEIVED SEPTEMBER 14, 1948

(1) Research Assistant under a special grant from the Union Bay State Chemical Company; present address, Department of Chemistry, University of Illinois.

(2) Vaughan and Rust, U. S. Patent 2,403,771, July 9 (1946).

(3) Raley, Rust and Vaughan, THIS JOURNAL, **70**, 2767 (1948).

(4) Milas and Surgenor, *ibid.*, **68**, 205 (1946).

Base Strength of Urea and Thiourea in Methanol

BY RALPH G. PEARSON AND JAMES TUCKER

In some work with solutions containing thiourea and strong acids dissolved in methanol it became apparent that salt formation was appreciable even though thiourea is generally considered too weak a base to form salts stable in solution. The explanation lies in the inherent weak basicity of methanol which causes other bases to appear abnormally strong in this solvent.[1]

The hydrolysis constants for thiourea and urea in dry methanol were determined by a conductimetric method essentially the same as that used by Goldschmidt and Dahlls[1a] to find the base strength of water in methanol. β-Naphthalenesulfonic acid was recrystallized from water and dried to the composition of the monohydrate in a vacuum oven at 60°. Methanol was dried by the use of magnesium turnings.[2] C. P. thiourea and urea were used.

Resistances were measured at 25.0 ± 0.03° on a Jones bridge of solutions containing a fixed amount of acid and varying amounts of base. If R_0 is the resistance of the solution containing only acid and R the resistance of a solution with added base, then $R/(R - R_0)$ plotted against the reciprocal of the base concentration[3] gave straight lines which could be extrapolated to infinite base concentration. From this a value of R_∞ could be found corresponding to the resistance of a solution completely converted to the salt of the base. From R_0, R_∞ and R the fraction of acid converted to salt could be found for each solution and the concentration equilibrium constant, K_h, for the reaction could be determined.

$$BH^+ + CH_3OH \rightleftarrows B + CH_3OH_2^+ \qquad (1)$$

Table I shows the experimental results, the calculated values of R_∞ and the average value of K_h for each base. The effect of urea and thiourea on the resistances of methanolic solutions of lithium acetate and potassium chloride was checked and found to be negligible except for the more concentrated urea solutions. Assuming the effect here to be due to viscosity, an equivalent correction was made on the measured conductances of the acid solutions before any calculations were made.

TABLE I

THIOUREA

Thiourea, molar	Resistance, ohms
0.00556 *M* β-Naphthalene Sulfonic Acid	
0.0000	3111[a]
.0314	3709
.0628	4164
.1257	4643
.2514	5103
∞	5942

$K_h = 5.46 \pm 0.1 \times 10^{-2}$

Urea, 0.00525 *M* Acid

Urea, molar	Resistance, ohms
0.00000	2764[a]
.00271	3552
.00525	4370
.01080	5108
.0314	5331[b]
.0627	5447[b]
∞	5447

$K_h = 4.37 \pm 0.2 \times 10^{-4}$

0.00592 *M* Potassium Chloride

0.0000	3974
.0314	3986
.0627	4002

[a] Different conductivity cells were used. [b] Not corrected for viscosity.

The basic ionization constant can be obtained by dividing the hydrolysis constant into the ion product for methanol, 2.0×10^{-17} at 25°.[1b] The corresponding hydrolysis constants in water are 9.0 for thiourea and 0.67 for urea.[4] The stability of the salts is thus increased several hundred-fold in methanol.

(1) (a) Goldschmidt and Dahlls, *Z. physik. Chem.*, **108**, 121 (1924); (b) Unmack, *ibid.*, **133**, 45 (1928).

(2) Lund and Bjerrum, *Ber.*, **64B**, 210 (1931).

(3) The concentration of free base must be used, correcting for that used up in salt formation. Successive approximations as to the magnitude of K_h are needed to bring the solutions of low base concentration into line.

(4) Walker, *J. Chem. Soc.*, **67**, 576 (1895).

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RECEIVED SEPTEMBER 9, 1948

Isomerization of Saturated Hydrocarbons. VI.[1] Effect of Benzene upon the Isomerization of Methylcyclopentane

BY HERMAN PINES, EUGENE ARISTOFF[2] AND V. N. IPATIEFF

The study of the isomerization of *n*-butane[3] and cyclohexane and methylcyclopentane[1] in the presence of aluminum bromide–hydrogen bromide catalyst using a high vacuum technique and highly purified materials has been reported recently. This work has shown that under certain carefully controlled conditions the isomerization of saturated hydrocarbons does not proceed unless a small amount of an olefin or an alkyl or cycloalkyl halide is present.

In the study of isomerization of methylcyclopentane it was found that small amounts of impurities which are present commonly in this hydrocarbon, such as benzene, have a profound effect upon the rate of isomerization. By fractional distillation it is difficult to eliminate the last traces of benzene; this can, however, be accom-

(1) For paper V of this series see H. Pines, B. M. Abraham and V. N. Ipatieff, THIS JOURNAL, **70**, 1742 (1948).

(2) Universal Oil Products Company Research Fellow 1947–1948.

(3) H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 595 (1946), **68**, 2518 (1946).

plished by passing methylcyclopentane over silica gel.[4]

The following table shows the inhibiting effect of benzene upon the isomerization of methylcyclopentane promoted by *s*-butyl bromide. The experiments were carried out by a general procedure described previously[3]; the reaction temperature was 25° and the duration of each experiment was two hours. On the average about 0.04 mole of methylcyclopentane was used in each experiment.

TABLE I

EFFECT OF BENZENE UPON THE ISOMERIZATION OF METHYLCYCLOPENTANE

Expt.	Reagents used: moles per 100 moles of methylcyclopentane $AlBr_3$	HBr	*s*-C_4H_9Br	Benzene	Cyclohexane formed, mole %
1	2	1.0	0.0	0.000	0
2	2	0.9	.1	.000	51
3	2	.9	.1	.022	22
4	2	.9	.1	.072	5
5	2	.9	.1	.140	3
6	2	1.0	.0	.140	0

The concentration of benzene in methylcyclopentane was determined by ultraviolet analysis. Experiment 4 was made by the addition of benzene to a purified sample of methylcyclopentane.

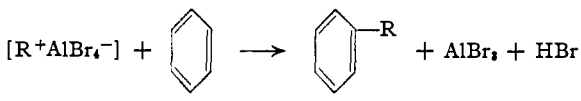
The inhibiting effect of benzene upon the isomerization, which was also observed to occur in the case of *n*-pentane,[5] is probably due to the ease with which the benzene reacts with the chain initiator. The ultraviolet absorption spectra taken of the hydrocarbons obtained from experiment 5 after removal of the catalyst by washing show that probably a mono-alkylbenzene was formed during the reaction. The absorption spectrum of the methylcyclopentane containing 0.14% of benzene and that of the reaction product was taken. The spectrum of the product showed a slight peak at 258.5 mμ where *s*-butylbenzene has a strong absorption band.

In expt. 3 the benzene caused only a partial inhibition of isomerization. This is not surprising since the molal ratio of *s*-butyl bromide to benzene used was over four, and the alkylation usually does not proceed beyond the formation of a tributylbenzene. There was therefore still some *s*-butyl bromide left to act as a chain initiator.

It was also noticed that in the experiments 3, 4, and 5 where benzene and *s*-butyl bromide were used an oily-yellow layer deposited on the walls of the reaction tube; in all the other experiments the product was homogeneous and free of color.[6] It is probable that the alkylbenzenes or cycloalkylbenzenes produced in the reaction formed a complex with the aluminum bromide and hydrogen bromide, similar to the type reported by Norris and Rubinstein.[7]

The inhibition of the isomerization of methylcyclopentane by benzene is in accordance with the proposed chain mechanism of isomerization.[1,8]

In the presence of benzene the chain may break by the reaction



R^+ may correspond to the carbonium ion obtained from the original olefin or from the product resulting from an exchange reaction between methylcyclopentane or cyclohexane formed and the *s*-butylcarbonium ion.

(4) B. J. Mair and A. F. Forziati, *J. Research Natl. Bur. Standards*, **32**, 151, 165 (1944).

(5) J. M. Mavity, H. Pines, R. C. Wackher, and J. A. Brooks, *Ind. Eng. Chem.*, **40**, 2374 (1948).

(6) In the last paper of this series[1] it was reported that the isomerization of methylcyclopentane to cyclohexane was usually accompanied by the formation of an oily layer even though the methylcyclopentane used did not contain any traces of benzene. It was observed now that when methylcyclopentane is further purified by passing it over silica gel certain impurities not detectable by spectrographic analysis and responsible for the formation of an oily layer are removed.

(7) J. F. Norris and D. Rubinstein, THIS JOURNAL, **61**, 1163 (1939).

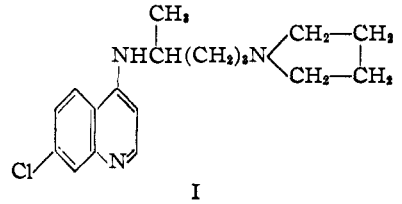
(8) H. S. Bloch, H. Pines and L. Schmerling, *ibid.*, **68**, 153 (1946).

THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS RECEIVED APRIL 5, 1948

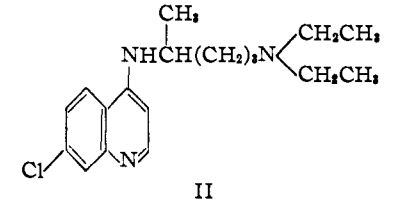
Synthesis of 7-Chloro-4-[1-methyl-(1-pyrrolidyl)-butylamino]-quinoline

BY ROBERT H. REITSEMA AND JAMES H. HUNTER

Studies on the effects resulting from an exchange of a pyrrolidyl group for a dialkylamino substituent in various chemotherapeutic agents[1] has now been extended briefly into the field of antimalarials. The synthesis of 7-chloro-4-[1-methyl-4-(1-pyrrolidyl)-butylamino]-quinoline (I), the pyrrolidyl analog of Chloroquine (II) was undertaken in consequence of the utility reported[2] for the latter in the control of malaria.



I



II

(1) (a) Wright, Kolloff and Hunter, THIS JOURNAL, **70**, 3098 (1948); (b) Reid, Wright, Kolloff and Hunter, *ibid.*, **70**, 3100 (1948); (c) Reitsema and Hunter, *ibid.*, in press.

(2) Wiselogle, "A Survey of Antimalarial Drugs," Vol. I, J. W. Edwards, Ann Arbor, 1946, pp. 388–392.

Preparation of 5-(1-pyrrolidyl)-2-aminopentane (III) from ethyl acetoacetate and β-1-pyrrolidylethyl chloride[1a] was patterned after the synthesis used for noval diamine.[3] Alkylation of III with 4,7-dichloroquinoline occurred smoothly to give the desired aminoquinoline (I).

In suppressive tests on *p. gallinaceum* in the chick, the order of activity and toxicity of I was analogous to that of Chloroquine.[4]

Experimental

5-(1-Pyrrolidyl)-3-carbethoxypentanone-2.—A solution of 400 g. (2.35 moles) of pyrrolidylethyl chloride hydrochloride in 200 ml. of water was treated with Nuchar C twice. The resulting light yellow solution was covered with 200 ml. of benzene, cooled to 5° and cold 50% potassium hydroxide was added with stirring and cooling below 12°. The upper organic layer was separated and the aqueous layer extracted twice with 100-ml. portions of benzene. Titration of a sample of the combined layers indicated 2.25 moles of base in solution or 96% of theory.

The sodium salt of 172 g. of acetoacetic ester in 1 l. of dry benzene was prepared with 26.0 g. of sodium sand. After addition of the ester was complete the mixture was boiled under reflux for one hour. One half of the above benzene solution of pyrrolidylethyl chloride was added dropwise. No reaction was apparent and the mixture was boiled under reflux for ten hours. After two hours nearly all the material was in solution.

5-Pyrrolidylpentanone-2.—To the above solution was added dilute sulfuric acid (from 160 ml. of water, 140 g. of ice, and 75 ml. of sulfuric acid). When about two-thirds of the acid had been added the solution was filtered and the layers separated. The remainder of the acid was used to dissolve the solid on the filter and to wash the benzene layer. The combined aqueous layers were washed with 100 ml. of benzene. The benzene was removed by distillation and the residual solution was boiled under reflux for seventeen hours. To the cooled solution was added 430 ml. of 30% sodium hydroxide with cooling and an organic layer of 184 g. was removed. The aqueous layer was extracted three times with 100-ml. portions of benzene. The dried organic layer was distilled to give 129 g. (74%) of material boiling at 92–98° (11–13 mm.). Redistillation of this gave a fraction which weighed 98.2 g.; b. p. 93–95° (11 mm.), $n^{20}D$ 1.4589.

Anal. Calcd. for $C_9H_{17}NO$: C, 69.63; H, 11.04; N, 9.02. Found: C, 70.10; H, 11.07; N, 8.35.

5-Pyrrolidyl-2-aminopentane.—A solution of 88.1 g. (0.568 mole) of 5-pyrrolidylpentanone-2, in a mixed solvent consisting of 100 ml. of dry ammonia and 100 ml. of dry methanol was reduced in two portions in the presence of Raney nickel catalyst. Reduction was complete after one and one-third to two hours at 100°. After filtration and removal of solvent the residue was distilled to give 86.8 g. of 5-pyrrolidyl-2-aminopentane, b. p. 92–97° (11–12 mm.), $n^{20}D$ 1.4665. This was purified through the dithiocarbamate[5] to give a product which boiled at 93–94° (11 mm.), $n^{20}D$ 1.4674.

Anal. Calcd. for $C_9H_{20}N_2$: C, 69.17; H, 12.89. Found: C, 69.45; H, 12.44.

The picrate after recrystallization from ethanol melted at 148–149°.

Anal. Calcd. for $C_{21}H_{26}N_8O_{14}$: C, 41.04; H, 4.27. Found: C, 41.06; H, 4.27.

7-Chloro-4-[1-methyl-4-(1-pyrrolidyl)-butylamino]-quinoline.—A mixture of 29.0 g. (0.147 mole) of 4,7-dichloroquinoline and 50.0 g. (0.322 mole) of 5-pyrrolidyl-2-aminopentane was heated with stirring for six hours at 160–170°. The cold mixture was taken up in 120 ml. of 50% acetic acid with cooling. After addition of 100 ml. of ether, 140 ml. of 30% sodium hydroxide was added to give a strongly basic solution. The mixture was shaken, the ether layer separated, and the aqueous layer was extracted with three 100-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate. After removal of the solvent, 20.1 g. of an oil boiling at 93° (11 mm.) was obtained leaving a residue of 45.7 g. (98%). A portion (31 g.) of this dark green fluorescent residue was taken up in 100 ml. of hot methylcyclohexane. Upon cooling 28 g. of yellow solid, m. p. 98–107°, was obtained. Three recrystallizations from methylcyclohexane gave some oily solid as a first precipitate and 13 g. of white 7-chloro-4-[1-methyl-4-(1-pyrrolidyl)-butylamino]-quinoline, m. p. 110–111°.

Anal. Calcd. for $C_{18}H_{24}N_3Cl$: C, 68.01; H, 7.61; N, 13.22. Found: C, 68.11; H, 7.52; N, 12.68.

RESEARCH LABORATORIES
THE UPJOHN COMPANY
KALAMAZOO, MICHIGAN

RECEIVED OCTOBER 8, 1948

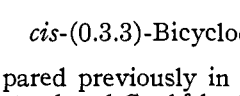
(3) Research and Manufacturing at I. G. Farbenindustrie; British Intelligence Objectives Subcommittee, Appendix 9, Processes 3–7.

(4) We wish to express our appreciation to the National Institute of Health and to William Longenecker for these pharmacological data.

(5) Jones, *Ind. Eng. Chem., Anal. Ed.*, 7, 431 (1944).

The Preparation and Properties of *cis*-(0.3.3)-Bicycloöctane

BY A. W. RYTINA,[1] ROBERT W. SCHIESSLER AND FRANK C. WHITMORE[2]

cis-(0.3.3)-Bicycloöctane  was prepared previously in very small quantity by Linstead and Cook[3] by heating the semicarbazone of *cis*-α-(0.3.3)bicycloöctanone with potassium hydroxide at 200–210°. A small-scale trial of this method by the present workers resulted in a poor (less than 40%) yield of hydrocarbon, therefore the conversion of the ketone to hydrocarbon was accomplished by the modified Wolff–Kishner reaction.[4] A 68% yield of bicycloöctane was realized, based on carefully purified material.

The hydrocarbon was purified by fractional distillation through a 25-plate helix-packed column, and the following properties determined.

°C.	Density,[a] g./ml.	Viscosity,[b] cp.
0.0	0.8863	2.839
20.0	.8695	1.859
37.8	.8543	1.350
60.0	.8353	0.9598

B. p.: 136.5° (±0.2°) at 738.3 mm.

M. p.: *ca.* −49° (much difficulty was encountered with glass formation)

$n^{20}D$: 1.4622

Mol. refraction (20°C.): found 34.85; calcd. 34.76

[a] ±0.0001; corrected for air buoyancy. [b] ±0.2%.

Experimental

Following the method of Linstead,[3] a total of 300 g. of pure *cis*-α-(0.3.3)bicycloöctanone was prepared from indene by hydrogenation to hydrindene, sulfonation, fusion with potassium hydroxide of the resultant 5-hydrin-

(1) Present address: Rohm and Haas, Philadelphia, Pa.

(2) Deceased.

(3) Linstead and Cook, *J. Chem. Soc.*, 946 (1934).

(4) Whitmore, Herr, Clarke, Rowland and Schiessler, THIS JOURNAL, 67, 2059 (1945).

denesulfonic acid, hydrogenation to 5-hydrindanol, nitric acid oxidation to 1-carboxy-2-cyclopentane-beta-propionic acid,[3] and cyclo-decarboxylation to the desired ketone over barium oxide.

To a 300-ml. Aminco hydrogenation bomb was charged 53 g. (0.43 mole) of purified *cis*-α-[0.3.3]bicycloöctanone, 43 g. (0.86 mole) of 100% hydrazine hydrate, 225 g. (4.0 moles) of potassium hydroxide and one liter of triethylene glycol.[4] The mixture was shaken at 195° for twenty-three hours in the sealed bomb. After cooling to room temperature, the reaction mixture was removed from the bomb (foaming), diluted with water, and the mixture steam-distilled. The two liters of steam distillate was acidified with 10% hydrochloric acid and extracted with 400 ml. of ethyl ether. The ether was removed from the separated, dried organic layer by distillation through a 20-plate fractionating column. To the residue was added 35 ml. of 2-octanone, and the mixture carefully fractionated through a 20-plate column to yield 32 g. of material boiling at 136–137° at 735 mm.

This product was combined with 19 g. of material prepared by the semicarbazone method[3] and distilled through a 25-plate column, yielding 49.5 g. of constant boiling, constant index *cis*-(0.3.3)bicycloöctane, b. p. 137° (735 mm.), $n^{20}D$ 1.4622. The hydrocarbon was filtered through a 2 × 20 cm. tube filled with activated silica gel (28–200 mesh), and the physical properties determined.

Acknowledgment.—The authors express their appreciation to the American Petroleum Institute for the grant which made this research possible.

THE WHITMORE LABORATORY
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PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PA. RECEIVED OCTOBER 19, 1948

The Preparation of α-Trifluoro-*p*-phenylacetophenone

BY J. H. SAUNDERS, R. J. SLOCOMBE AND EDGAR E. HARDY

Trifluoroacetic acid was converted to the acid chloride and this in turn to α-trifluoro-*p*-phenylacetophenone with an over-all yield of 53%. Recrystallization of this compound from methanol apparently gave the solvated ketone containing one molar equivalent of methanol.

Trifluoroacetyl Chloride.—A 1-liter 3-necked flask was equipped with a dropping funnel, stopper, and an 8-in. helix-packed column. A partial take-off still-head and a Hopkins type, Dry Ice-cooled condenser were attached to the column. The head and condenser gas outlet were then connected to a Dry Ice trap. Two hundred sixty grams (1.25 moles) of phosphorus pentachloride was placed in the flask and 96 g. (0.84 mole) of trifluoroacetic acid was added in 5-cc. portions. To ensure complete reaction the system was maintained under total reflux while the first 5 cc. of acid was added and for an additional ten minutes. Then all of the acid chloride produced from this portion of acid was distilled into the cold receiver before adding the next 5 cc. of acid. Proceeding in this manner about six hours were required for the entire reaction. When all of the acid had been added and had reacted the flask and its contents were warmed to 50° to drive out the last traces of acid chloride. The yield of the clear, straw-colored liquid, which contained some hydrogen chloride, was 119 g.

α-Trifluoro-*p*-phenylacetophenone.—The method of Simons and Ramler[1] was followed. From 205 g. (1.33 moles) of biphenyl, 178.5 g. (1.33 moles) of aluminum chloride, and the acid chloride from 96 g. (0.84 mole) of trifluoroacetic acid there was obtained 114 g. (55.6%) of recovered biphenyl and 112 g. (53.4% based on trifluoroacetic acid, 75.6% based on biphenyl consumed) of α-trifluoro-*p*-phenylacetophenone, b. p. 130–133° (3 mm.). After recrystallization from 60–70° petroleum solvent the compound melted at 51.2–51.4°.

Anal.[2] Calcd. for $C_{14}H_9OF_3$: C, 67.20; H, 3.62. Found: C, 67.48; H, 3.84.

When this product was recrystallized from methanol or methanol and water a new compound, m. p. 102.5–103.5°, was obtained. When this compound was heated above its melting point a condensable gas, presumably methanol, was evolved, and the residue again melted at 51.0–51.4°. Analysis indicated the presence of one mole of methanol per mole of ketone. The difficulty with which a solid of constant melting point was obtained indicated that this compound may have been unstable in methanol solution or that other states of solvation may have existed.

Anal. Calcd. for $C_{15}H_{13}O_2F_3$: C, 63.83; H, 4.64. Found: C, 64.03; H, 4.37.

The α-trifluoro-*p*-phenylacetophenone was insoluble in 10% sodium hydroxide solution but was rapidly hydrolyzed by warm alkali. The observed products were a gas, doubtless fluoroform,[1] and biphenyl-4-carboxylic acid, m. p. 226–228°. Gull and Turner reported m. p. 228° for this acid.[3]

(1) Simons and Ramler, THIS JOURNAL, **65**, 389 (1943).

(2) Microanalyses were made by the Clark Microanalytical Laboratory, Urbana, Illinois.

(3) Gull and Turner, *J. Chem. Soc.*, 491 (1929).

RESEARCH LABORATORY
PHOSPHATE DIVISION
MONSANTO CHEMICAL COMPANY
ANNISTON, ALABAMA RECEIVED SEPTEMBER 24, 1948

Chlorination of *t*-Butylbenzene to 1-Chloro-2-methyl-2-phenylpropane

BY WILLIAM E. TRUCE, E. T. MCBEE AND C. C. ALFIERI

The side chain of *t*-butylbenzene has been considered too inert to undergo reaction directly with the halogens. It was claimed that chlorination of *t*-butylbenzene in the presence of sunlight caused ring substitution only.[1] However, we chlorinated *t*-butylbenzene to 1-chloro-2-methyl-2-phenylpropane in 48% conversion. (This compound had been obtained previously by the peroxide-induced chlorination of *t*-butylbenzene with sulfuryl chloride.[2])

Proof of structure consisted of oxidizing the product to benzoic acid in small yield with alkaline potassium permanganate,[3] and carbonation of the corresponding Grignard reagent to the known 3-methyl-3-phenylbutyric acid[4] in 49% over-all conversion. The poor yield of benzoic acid in the above oxidation is to be anticipated for *t*-alkylbenzenes.[5] The preparation of the Grignard reagent was difficult to initiate. When the reaction started, it proceeded slowly but smoothly and an

(1) Salibil, *Chem. Ztg.*, **35**, 97 (1911); *Chem. Zentr.*, **83**, 1581 (1912).

(2) Kharasch and Brown, THIS JOURNAL, **61**, 2142 (1939).

(3) Shriner and Fuson, "Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 163.

(4) Saboor, *J. Chem. Soc.*, 922 (1945); Hoffman, THIS JOURNAL, **51**, 2545 (1929).

(5) Legge, *ibid.*, **69**, 2079 (1947).

82% conversion of halide to Grignard reagent was achieved as determined by titration.[6]

Experimental

Three moles (402 g.) of *t*-butylbenzene was placed in a long reaction tube which was strongly illuminated. Chlorine, which was first bubbled through a sulfuric acid absorption tube, was slowly bubbled through the hydrocarbon over a period of three hours until a total of three moles had passed. Subsequent rectification yielded 90 g. (0.67 mole) of *t*-butylbenzene, 240 g. (1.42 moles) of 1-chloro-2-methyl-2-phenylpropane, 45 g. of polychlorinated material and 70 g. of still residue. The physical constants of 1-chloro-2-methyl-2-phenylpropane are b. p. 111–112° (18 mm.), $n^{20}D$ 1.5245, and d^{20}_4 1.047.

Anal. Calcd. for $C_{10}H_{13}Cl$: Cl, 21.02. Found: Cl, 21.0, 21.0.

We gratefully acknowledge the financial support of this work by the Procter and Gamble Company.

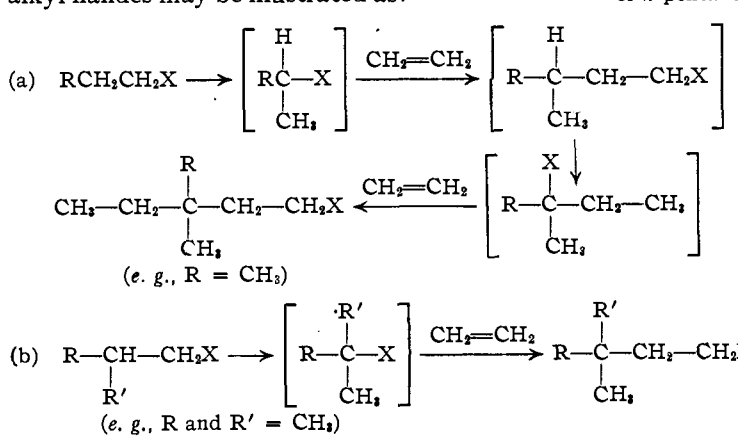
(6) Gilman, *et al.*, THIS JOURNAL, **45**, 150 (1923).

DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY
AND PURDUE RESEARCH FOUNDATION
LAFAYETTE, INDIANA RECEIVED AUGUST 5, 1948

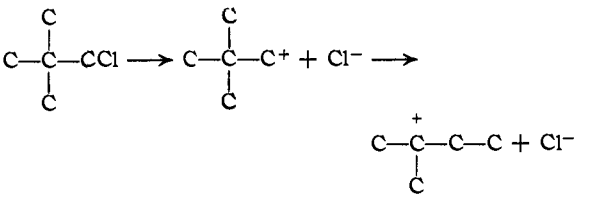
Condensation of Saturated Halides with Unsaturated Compounds. VII. Condensation of Neopentyl Chloride with Ethylene[1]

BY LOUIS SCHMERLING AND E. E. MEISINGER

The metal halide catalyzed condensation of ethylene with alkyl halides (particularly chlorides and bromides) containing at least three carbon atoms offers a means of preparing 1-halo-3,3-dialkylalkanes.[2] The reaction of typical primary alkyl halides may be illustrated as:



An example of the reaction of ethylene with a third type of primary alkyl halide, namely, a 1-halo-2,2-dialkylalkane, will now be described. The condensation of neopentyl chloride with ethylene proceeded smoothly at −14 to −20° in the presence of aluminum chloride. There was obtained a 38% yield of chloroheptane which was identified as 1-chloro-3,3-dimethylpentane which is also the product of the condensation of ethylene with *t*-pentyl chloride. Isomerization of the neopentyl group to *t*-pentyl apparently occurred



The dissociation of the neopentyl chloride into the unstable positive neopentyl ion and the negative chloride ion is probably brought about by formation of a complex with the catalyst, $(CH_3)_3CCH_2^+AlCl_4^-$.

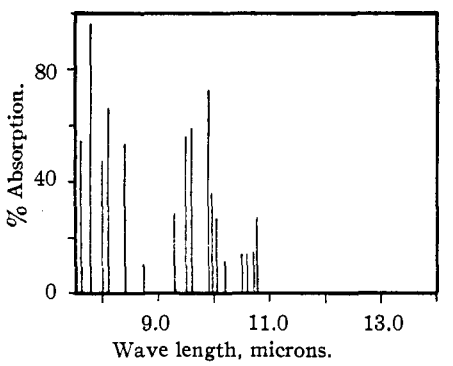


Fig. 1.—Infrared absorption spectrum of 1-chloro-3,3-dimethylpentane.

Experimental

Condensation of Neopentyl Chloride with Ethylene.—A mixture of 40 g. (0.37 mole) of neopentyl chloride,[3] 50 g. of *n*-pentane diluent and 5 g. of aluminum chloride was placed in a three-necked flask immersed in a Dry Ice–acetone-bath. Ethylene was bubbled into the stirred mixture while the temperature was permitted to rise from −70 to −15° at which point absorption began (determined by difference of gas rates in inlet and outlet bubblers). The temperature was maintained at −14 to −20° for the duration of the addition of ethylene (three quarters of an hour) during which time the catalyst gradually coagulated. The liquid product was decanted from the 12 g. of yellow sludge and powder, washed with water, dried and distilled. There was obtained 19 g. (0.14 mole) of product b. p. 50–51° at 20 mm. pressure (150–151° at 760 mm.); $n^{20}D$ 1.4300. There was also obtained 22 g. of unidentified higher-boiling material which apparently consisted largely of chlorononane and chlorohendecane.

The product boiling at 50–51° at 20 mm. was shown to be 1-chloro-3,3-dimethylpentane by converting it to β-*t*-pentylpropionanilide by the method of Schwartz and Johnson[4]: m. p. 95–96°. This anilide did not depress the melting point of the analogous derivative of 1-chloro-3,3-dimethylpentane prepared by the condensation of *t*-pentyl chloride with ethylene.[2]

(1) Preceding paper in this series, THIS JOURNAL, **71**, 107 (1949).

(2) L. Schmerling, *ibid.*, **67**, 1152 (1945).

(3) Obtained by the chlorination of neopentane according to the method of F. C. Whitmore and G. H. Fleming, *ibid.*, **55**, 4161 (1933). We wish to thank Dr. Vladimir Haensel for the sample of neopentane which was prepared by the demethylation of neohexane: V. Haensel and V. N. Ipatieff, *Ind. Eng. Chem.*, **39**, 853 (1947).

(4) A. M. Schwartz and J. R. Johnson, THIS JOURNAL, **53**, 1063 (1931); see also H. W. Underwood, Jr., and J. C. Gale, *ibid.*, **56**, 2117 (1934).

Comparison of the infrared spectrum[5] (Fig. 1) of the product boiling at 50–51° at 20 mm. with that of the 1-chloro-3,3-dimethylpentane prepared from *t*-pentyl chloride and ethylene showed that samples contained at least 95% material in common.

(5) We are indebted to Dr. W. S. Gallaway, Physics Division, Universal Oil Products Company, for the infrared absorption analysis. For a description of the procedure used, see THIS JOURNAL, **69**, 1124 (1947).

RESEARCH AND DEVELOPMENT LABORATORIES
UNIVERSAL OIL PRODUCTS COMPANY
RIVERSIDE, ILLINOIS RECEIVED JULY 22, 1948

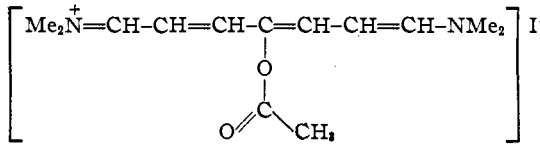
Two Simple Amidinium Vinylogs[1]

BY WILLIAM T. SIMPSON[2]

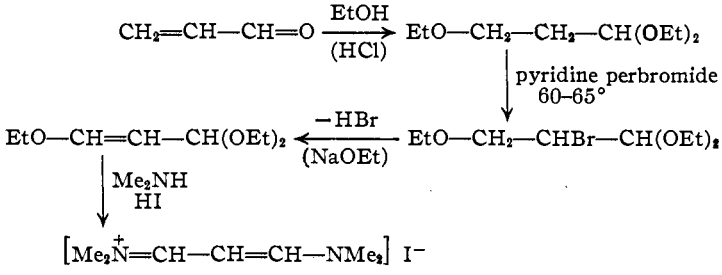
The vinylene homologous series

$$[Me_2\overset{+}{N}{=}CH{-}(CH{=}CH)_n{-}NMe_2]\ X^-$$

is interesting because of its simplicity[3] and yet its close relationship to several large families of dyestuffs. The second member ($n = 2$) was obtained by König and Regner.[4] Now the first member, ($n = 1$), N-methyl-(2-dimethylaminovinyl)-formimine methiodide, and a substance which is very closely related to the third member ($n = 3$) have been synthesized. The latter compound is N-methyl-(6-dimethylamino-3-acetoxy-1,3,5-hexatrienyl)-formimine methiodide



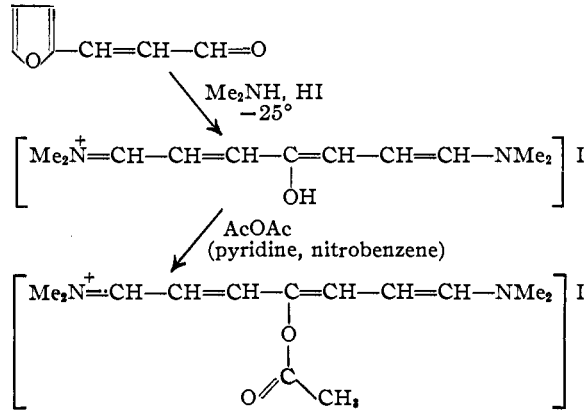
The former substance was prepared according to the scheme



The latter was synthesized by a splitting of the furan ring,[5] followed immediately by acetylation.

Experimental

β-Ethoxypropionaldehyde Diethylacetal.—This material was prepared substantially as described by Pingert.[6] Since the yield of acrolein acetal is not important, the following changes in the procedure were made. The starting material, 80 g. (95 cc., 1.36 mole) of acrolein



(95% with stabilizer) was combined with 325 cc. (5.56 mole) of absolute ethanol (commercial). Approximately 0.7 g. of hydrochloric acid was used as a catalyst. The alcohol was removed under reduced pressure at 40–50°. The yield was 125.1 g. (52%); b. p. 95–97° (39 mm.). The material was used without further purification in the next step.

Bromination of β-Ethoxypropionaldehyde Diethylacetal.[7]—The acetal (67 g., 76 cc., 0.38 mole) and 30 g. (30.5 cc., 0.38 mole) of dry pyridine were combined. Then 61 g. (19.5 cc., 0.38 mole) of bromine was added at a rate of several drops a second. A mechanical stirrer operated continuously until the reaction was complete. After the bromine had been added the temperature was adjusted to 60–65°. The reaction was complete in two to four hours, as indicated by the disappearance of the red color of the pyridine perbromide. The reaction vessel was then washed with dry ether and the precipitate triturated with dry ether. Combined ether extracts were dried over anhydrous potassium carbonate and stored in an ice chest. Removal of the ether left 81 g. (83%) of the crude product. It was found that distillation of the crude material produced decomposition to the extent that a better yield in the next step was obtained if purification at this stage had been eliminated.

Dehydrobromination was carried out as described by Reitzenstein and Bonitsch.[8]

N-Methyl-(2-dimethylamino-vinyl)-formimine Methiodide.—Dimethylammonium iodide (6.0 g., 0.034 mole), 6.0 g. (0.034 mole) β-ethoxyacrolein diethylacetal, 4.8 g. (0.036 mole) 33% dimethylamine in methanol, and 10 cc. absolute methanol were sealed in a bomb tube. The tube was heated at 100° for five hours in the dark. The reaction mixture was washed with 200 cc. of ether; the precipitate which formed filtered and purified by several recrystallizations from acetic anhydride followed by ether throwdown. The material was dissolved in acetic anhydride at 100° and maintained at this temperature for five or ten minutes during each recrystallization. (This heating during recrystallization converted unchanged dimethylammonium iodide into ether soluble materials.) The yield after three recrystallizations was 3.8 g. (44%). An analytical sample was obtained after several additional recrystallizations from *n*-butyl alcohol. The pure material is crystalline, white with a faint suggestion of a metallic luster: m. p.[9] 188–188.5°.

Anal.[10] Calcd. for $C_7H_{15}N_2I$: C, 33.08; H, 5.95. Found: C, 33.18; H, 5.95.

(1) Taken from the writer's Ph.D. thesis.

(2) Present address: Department of Chemistry and Chemical Engineering, University of Washington, Seattle, Washington.

(3) Simpson, *J. Chem. Phys.*, **16**, 1124 (1948).

(4) König and Regner, *Ber.*, **63**, 2823 (1930).

(5) König, *ibid.*, **67**, 1274 (1934).

(6) Pingert, *Org. Syn.*, **25**, 1 (1945).

(7) This procedure was taken from the work of McElvain and Walters, THIS JOURNAL, **64**, 1963 (1942).

(8) Reitzenstein and Bonitsch, *J. prakt. Chem.*, **86**, 1 (1912).

(9) All melting points are corrected.

(10) The analyses were performed under the direction of Mr. Charles Koch.

N-Methyl-(6-dimethylamino-3-acetoxy-1,3,5-hexatrienyl)-formimine Methiodide.—Furylacrolein (1.0 g., 0.0082 mole) (Eastman Kodak Co., once recrystallized from ligroin), dissolved in 10 cc. of commercial isopropyl alcohol, was cooled to approximately −25°. A solution containing 1.4 g. (0.0079 mole) dimethylammonium iodide, 1.0 g. (0.0075 mole) of a 33% methanol solution of dimethylamine, and 5 cc. of isopropyl alcohol at room temperature was added to the furylacrolein suspension immediately upon its removal from the cooling bath. The addition, with shaking, required thirty seconds. The mixture was cooled immediately to −25° and kept at this temperature except for brief removal periods for stirring (at five-minute intervals). After thirty minutes the reaction mixture was removed from the cooling bath, 10 cc. of dry ether at 0° added, the solution stirred and filtered. The reaction flask and residue were washed with another cold 10-cc. ether portion. The residue was dried three minutes at the pump, and then transferred to a solution containing nitrobenzene (commercial) 100 cc., dry pyridine 10 cc., and acetic anhydride 10 cc. The solution was swirled until all of the crude material dissolved. The reaction required an hour at room temperature. The product was then thrown out with ether to give 1.2 g. (44%) of crude dye. Several recrystallizations from n-butyl alcohol gave an analytical sample with m. p. 191° (dec.). The crystals are a deep purple and possess a metallic luster.

Anal. Calcd. for $C_{13}H_{21}N_2O_2I$: C, 42.86; H, 5.81. Found: C, 42.89; H, 5.79.

of halogen compound and benzenesulfonhydrazide in the presence of one mole of hydrogen chloride (added as concentrated hydrochloric acid) increased the yields to 80–90%; the rate of condensation was also appreciably increased by this modification. The hydrochlorides were purified by crystallization from dilute or glacial acetic acid; excepting the pyrimidine derivative, the products were almost insoluble in water or dilute acids. Dilute bases produced the expected decomposition.[2]

1-Benzenesulfonyl-2-(7-chloroquinolyl-4)-hydrazine hydrochloride was also prepared, in 35% yield, by the action of benzenesulfonyl chloride on 7-chloro-4-hydrazinoquinoline in dry pyridine in the usual manner, followed by treatment of the product with dry hydrogen chloride in alcohol. The latter compound was prepared in 88.6% yield from 4,7-dichloroquinoline essentially by the general procedure of Koenigs and Loesch.[3] The compound formed white needles from alcohol, m. p. 231–232° (cor.) (dec.).

Anal. Calcd. for $C_9H_8ClN_3$: N, 21.70. Found: N, 21.68.

Surrey and Cutler[4] reported m. p. 220–221°.

1-Benzenesulfonyl-2-(5-nitropyridyl-2)-hydrazine was prepared from 2-hydrazino-5-nitropyridine[5] and benzenesulfonyl chloride in dry pyridine. This compound could not be prepared by the direct condensation of 2-chloro-5-nitropyridine with benzenesulfonhydrazide in either the presence or absence of hydrochloric acid.

The substituted hydrazines are listed in the accompanying table.

TABLE I

N¹-BENZENESULFONYL-N²-SUBSTITUTED HYDRAZINE HYDROCHLORIDES

N²-Substituent	M. p., °C.	Formula	Analyses, % Sulfur Calcd.	Sulfur Found	Chlorine Calcd.	Chlorine Found
Quinolyl-2-	207–209[a]	$C_{15}H_{14}ClN_3O_2S$	9.55	9.60	10.56	10.58
4-Methylquinolyl-2-[b]	171–172	$C_{16}H_{16}ClN_3O_3S$	8.72	8.69	9.64	9.65
5-Chloroquinolyl-4-	219.5–220.0[a]	$C_{15}H_{13}Cl_2N_3O_2S$	8.66	8.35	9.58[e]	9.56
7-Chloroquinolyl-4-	203–204[a]	$C_{15}H_{13}Cl_2N_3O_2S$	8.66	8.36	9.58[e]	9.66
7-Chloro-3-methylquinolyl-4-[c]	196–197[a]	$C_{16}H_{15}Cl_2N_3O_4S$	7.22	7.27	15.96	15.98
7-Phenoxyquinolyl-4-	209–210[a]	$C_{21}H_{18}ClN_3O_3S$	7.49	7.51	8.29	8.20
2-Aminopyrimidyl-4-	237–239[a]	$C_{10}H_{12}ClN_5O_2S$	10.63	10.52	11.75	11.61
5-Nitropyridyl-2-[d]	196–197[a]	$C_{11}H_{10}N_4O_4S$	10.89	11.00	...	...

[a] With decomposition. [b] As the monohydrate. [c] With one mole of acetic acid of crystallization. [d] Free base. [e] Ionic halogen only.

I should like to thank Dr. L. G. S. Brooker for showing me an unpublished modification of reference 8, and Professors W. G. Dauben and G. E. K. Branch for much helpful advice.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

RECEIVED AUGUST 9, 1948

NEW COMPOUNDS

Some Heterocyclic-Substituted Hydrazines

The condensation of a 2- or 4-chloroquinoline or of 2-amino-4-chloropyrimidine with benzenesulfonhydrazide was carried out in two ways. Refluxing a mixture of one mole of the halogen compound and two moles of benzenesulfonhydrazide in alcohol for two to six hours gave 40–50% yields of condensation product as the hydrochloride. In confirmation of the observations of Banks[1] it was found that the condensation of molal proportions

(1) Banks, THIS JOURNAL, **66**, 1127 (1944).

(2) 1-Benzenesulfonyl-2-(7-chloroquinolyl-4)-hydrazine hydrochloride gave a 43.2% yield of 7-chloroquinoline, m. p. 31–32°, when steam distilled from excess sodium carbonate solution. 1-Benzenesulfonyl-2-(5-nitropyridyl-2)-hydrazine similarly gave a 32% yield of 3-nitropyridine, m. p. 39.5–40.5°. *Cf.* McFadyen and Stevens, *J. Chem. Soc.*, 584 (1936).

(3) Koenigs and Loesch, *J. prakt. Chem.*, **143**, 59 (1935); *cf.* Perkin and Robinson, *J. Chem. Soc.*, **103**, 1978 (1913).

(4) Surrey and Cutler, THIS JOURNAL, **68**, 2570 (1946).

(5) Rath, U. S. Patent 1,733,695.

STERLING–WINTHROP RESEARCH INSTITUTE
RENSSELAER, NEW YORK R. O. CLINTON

RECEIVED NOVEMBER 16, 1948

Preparation of Organic Silicon Chlorides[1]

The general method of synthesis was to add the appropriate Grignard reagent dropwise into an excess of silicon

(1) This work was performed in 1945 as part of the research program of the Research and Development Branch, Military Planning Division, of the Office of the Quartermaster General. The opinions and conclusions contained in this report are those of the authors. They are not to be construed as necessarily reflecting the views or endorsement of the Department of the Army. Article not copyrighted. This work was performed with the assistance of Charles A. Miller, Joseph Rynasiewicz, Nelda Gulbransen, Esther Nielson and Eleanor Swenson.