

Time, minutes	16	18	19
% Conversion	81.0	93.1	93.1

Ethyl maleate was treated in a similar manner with boron fluoride in carbon tetrachloride, with boron fluoride-ether complex alone and with dry hydrogen bromide added, and with hydrogen bromide in carbon tetrachloride. In every case less than 1% of the ester was isomerized. The analyses were carried out as before.⁸

Summary

It has been found that boron fluoride readily converts *cis*-stilbene to the *trans*-isomer.

(8) Price and Thorpe, *THIS JOURNAL*, **60**, 2839 (1938).

Many compounds have in common the ability to catalyze the Friedel-Crafts type of reaction, the polymerization of olefins, the condensation of olefins with aromatic compounds and the *cis-trans*-isomerization of olefins. It is suggested that the common factor in these reactions is the electron-deficient nature of the catalyst and that such catalysts may associate with the electrons of the carbon-carbon double bond to give an active intermediate common to each reaction.

URBANA, ILLINOIS

RECEIVED MARCH 31, 1939

NOTES

Note on the Leakage of Helium through Pyrex Glass at Room Temperature. III

BY G. P. BAXTER

Some years ago an experiment was begun to measure the rate of leakage of helium through Pyrex glass at room temperature.¹ A sealed globe (1044 ml.) filled with helium originally under slightly less than average atmospheric pressure in this locality, 75 cm., was occasionally compared in weight with a very similar sealed globe, containing argon under a pressure somewhat above atmospheric, 79 mm. Over a period of three and one-half years the rate of loss was about 1% per year.

Recently, after over eleven years, when a reweighing of the globe was undertaken, a small crack was discovered in the argon globe. Since the argon was originally at a pressure above atmospheric, mechanical loss of argon would diminish, not increase, the loss in weight of the helium globe. In spite of the crack the helium globe was found to have lost a total of 17.8 mg., in a little over eleven years (4128 days), or over 10% of the original helium or 109 cm.³ The over-all rate for the total period is 0.053 mm.³ per day per cm.² of Pyrex glass of average thickness 1.34 mm. This is a slightly lower rate than that calculated from the first year's experience, 0.059 mm.³ per day per cm.² but the greater part of this difference is accounted for by the diminishing helium content of the globe.²

(1) Baxter, Starkweather and Ellestad, *Science*, **68**, 516 (1928); Baxter and Starkweather, *ibid.*, **73**, 618 (1931).

(2) Original weight of helium = 0.171 g. Erroneously given in ref. 1 as 0.168 g.

In the following table are given the leakage constants (years⁻¹) assuming the rate to be proportional to the pressure, for periods from one year to over eleven years, the actual losses in weight, and the losses calculated from the average leakage constant for the first three periods.³ From the leakage constant and loss in weight for the total period it seems probable that the argon counterpoise was losing in weight owing to the crack, although in the recent weighing, which was continued over several weeks, the helium globe was still diminishing in weight by comparison.

Years	K, years ⁻¹	Actual loss in wt., mg.	Calcd. loss in wt., mg.
1	0.0102	1.73	1.78
1.5	.0106	2.71	2.66
3.5	.0106	6.23	6.15
	Av. .0105		
11.3	.0097	17.8	19.1

(3) For a discussion of the mechanism of the leakage of helium through glass, see Urry, *THIS JOURNAL*, **54**, 3887 (1932). Urry's experimental data are not inconsistent with the above.

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RECEIVED MARCH 18, 1939

Isotopes of Potassium in Phosphate Rocks and Soils

BY A. KEITH BREWER

Taylor and Urey¹ have shown recently that in the base exchange of potassium in zeolites "the heavier isotope is taken up more readily and is more difficult to replace." Since base exchange regularly occurs in nature, isotope abundance

(1) I. W. Taylor and H. C. Urey, *J. Chem. Phys.*, **6**, 429 (1938).

measurements should furnish an entirely new method of studying the mixing of potassium in soils and rocks. In order to determine the extent to which an isotope effect can be expected in nature, the base exchange method of isotope separation was applied to greensand.

The technique employed in these experiments was essentially the same as that described by Taylor and Urey, except that the 100-ft. (30-meter) column was replaced by a 4-in. (10-cm.) filtration funnel. By using a short column of greensand the "single stage" isotope effect is obtained; large effects resulting from the accumulative action taking place in a long column are not to be expected. In these tests a dilute solution of sodium chloride was allowed to trickle slowly through the greensand. From time to time a small quantity of the filtrate was collected and the isotope abundance ratio measured in the usual way.² No appreciable change was observed in the isotope ratio of the first potassium coming through in the filtrate, the ratio being $K^{39}/K^{41} = 14.20$; this is not surprising since the potassium content was high. After a moderate amount of washing in which the quantity of sodium in the solution used was three or four times the initial potassium in the greensand, abundance ratios of the order of $K^{39}/K^{41} = 14.00$ were obtained. Continued washing to the point where only minute quantities of potassium remained in the filtrate reduced the ratio to $K^{39}/K^{41} = 13.60$. Small deviations between samples were observed due to the non-uniformity of the greensand. The results showed clearly that K^{41} is more firmly held in the zeolite structure than is K^{39} ; in consequence, isotope effects of the type described by Taylor and Urey should be expected to occur in nature under conditions where base exchange processes are operative.

A wide variety of soils and phosphate rocks has been investigated for a possible isotope effect. The samples were ground and sifted to 100 mesh. No chemical treatment was needed. The results obtained are presented in Table I.

Ten typical high phosphorus rocks from various deposits were tested; the ratio was the same in each instance. The fossil bone and tooth were from the Mulberry deposit in Florida. The soils tested are described in Department Bulletin No. 1311 and Technical Bulletin No. 484, United States Department of Agriculture.

(2) A. Keith Brewer, *Ind. Eng. Chem.*, **30**, 893 (1938).

TABLE I

Soils	K ₂ O, %	Na ₂ O, %	K ³⁹ /K ⁴¹
Porto Rico red clay	14.20
Stockton clay	2.15	1.24	14.20
Susquehanna sub	0.76	0.02	14.20
W. Va. rottenstone	14.20
W. Va. diatomaceous earth	14.24
W. Va. red clay	2.00	0.50	14.20
Marshall clay 213	2.60	1.10	14.20
Cecil B	0.23	0.08	14.30
Norfolk loam	.40	.21	14.22
Las Vegas A	14.20
Chester A	2.02	.47	14.19
Chester B	1.55	.19	14.18
Frederick colloid	1.22	..	14.20
Fullerton colloid	1.28	..	14.20
Miami colloid B	2.85	1.11	14.30
Hagerstown colloid	2.84	0.45	14.23
Florida silt	14.18
Greensand	14.20
Wyomingite	14.25
Ocean water	14.20
Phosphate rocks	0.2 app.	..	14.20
Fossil tooth	Low	..	14.20
Fossil bone	Low	..	14.20
Hawaiian basalt	14.11
Bone (fresh)	13.90

In view of the results mentioned above, it is evident that a soil in which the potassium has been largely replaced by base exchange should have low isotope ratio. An example of this type of action is found in a sample of Hawaiian basalt which had been exposed to ocean water. Again it should be expected that a soil normally low in potash which is acquiring potassium from some abundant source should have a high isotope ratio. This effect is illustrated in the Cecil B soil, where the relative abundance of K^{39} is enhanced by the subsoil acquiring potash from the topsoil leachings. Bone and tooth fossil show the normal isotope ratio of 14.20, although the ratio for fresh bones averages 13.90. It is evident that the initial potassium in the bones has been entirely replaced during the long aging processes.

The fact that the potassium isotope ratio is so nearly constant, although base exchange is continuously taking place, indicates that mixing is likewise continuous. In virtue of the ease with which small deviations in the abundance ratio can be produced in the laboratory, it is surprising that the values are so uniform. While it cannot be stated with certainty, an analysis of the data indicates that actual deviations do occur which could be estimated readily with a mass spectrograph having ten-fold the sensitivity of the one in use.

The writer is especially indebted to Mr. Donald L. Reed for making the isotope extractions with greensand.

BUREAU OF CHEMISTRY AND SOILS
WASHINGTON, D. C. RECEIVED MARCH 31, 1939

Hydrogen Bonding by Negatively Substituted CH Groups. VI. Acetylenic Compounds¹

BY M. J. COPLEY AND C. E. HOLLEY, JR.

In a series of articles²⁻⁵ the solubilities of several gaseous halogenated methanes (of the types CH_3X , CH_2X_2 , CHX_3 and CX_4) in a number of donor solvents were reported. The extremely high solubilities (or large negative deviations from Raoult's law) observed for the haloforms were accounted for on the basis that complexes are formed through the bonding of the hydrogen of the haloform to an exposed pair of electrons on an oxygen or nitrogen atom present in the solvent. New evidence for the existence of complexes of this type was observed recently by Buswell, Rodebush and Roy⁶ while studying the infrared absorption spectra of solutions in carbon tetrachloride of chloroform with an ether, a ketone, or an amine.

Since the presence of the highly electronegative halogen atoms on the carbon atom of a haloform activates the hydrogen and makes it available for coordination, it is logical to suspect that other strongly negative groups attached to a CH radical will lead to the same behavior on the part of the hydrogen. Among the compounds in which such CH groups occur are the acetylenes (1-alkynes), the derivatives of formic acid, the triarylmethanes, molecules containing an active methylene group, etc.

In Table I the mole fraction solubilities of acetylene at a partial pressure of one atmosphere are compared with the theoretical mole fractions calculated from Raoult's law. The observed mole

fractions are calculated from data in the "International Critical Tables," Vol. III, p. 269, and in an article by James.⁷ There exists a close parallelism between the observed order of solubilities and the order^{3,4} observed for chloroform or monofluorodichloromethane in similar types of solvents. Solubilities are greatly in excess of those predicted by Raoult's law in the ethers, esters, and ketones; solubilities are much less than the theoretical in solvents containing an active hydrogen (ethyl alcohol and acetic acid) where the solvent molecules are already associated by means of the more stable O-H-O bonds; no enhancement of solubility is obtained in aromatic compounds when the donor atom is attached to the benzene

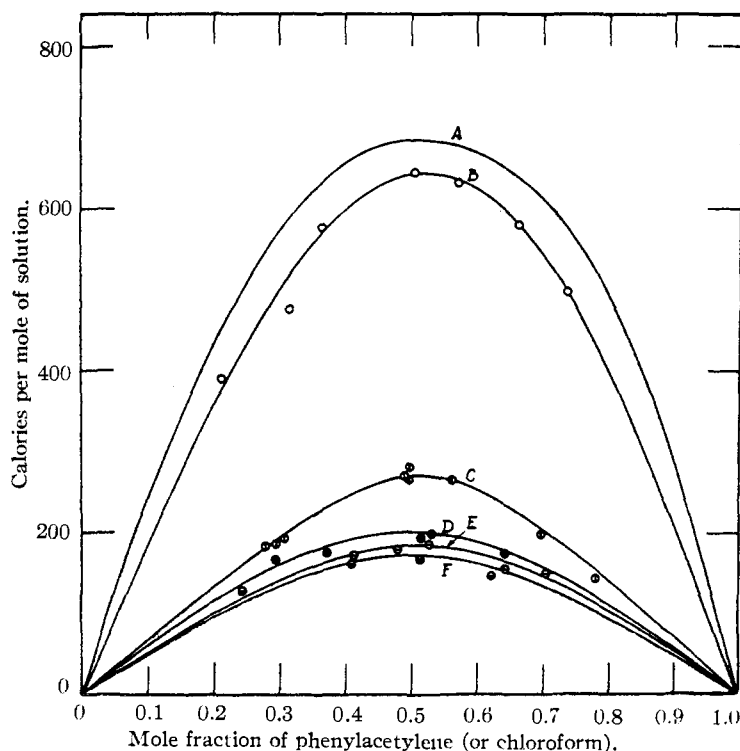


Fig. 1.—The heat evolved per mole of solution at 3° versus the mole fraction of phenylacetylene (or chloroform): A, chloroform and diethyl ether; B-F, phenylacetylene and, respectively, N,N-dimethylacetamide, diethyl ether, acetone, cyclohexylamine, methyl acetate.

ring; and normal or less than normal solubilities are found in compounds which do not contain a donor atom. The appreciably lower solubilities in formates than in acetates possibly are due to activity of the hydrogen of the acid residue of formates which leads to some intermolecular association. The solubilities⁴ of monofluorodichloromethane are also appreciably lower in the N-disub-

(1) Original manuscript received July 11, 1938.
(2) G. F. Zellhoefer, *Ind. Eng. Chem.*, **29**, 584 (1937).
(3) Zellhoefer, Copley and Marvel, *THIS JOURNAL*, **60**, 1337 (1938).
(4) Copley, Zellhoefer and Marvel, *ibid.*, **60**, 2666 (1938).
(5) Copley, Zellhoefer and Marvel, *ibid.*, **60**, 2714 (1938).
(6) Buswell, Rodebush and Roy, *ibid.*, **60**, 2528 (1938). See also Gordy, *ibid.*, **60**, 605 (1938).

(7) James, *Ind. Eng. Chem.*, **5**, 118 (1913).

TABLE I
SOLUBILITIES OF ACETYLENE AT A PARTIAL PRESSURE OF 1
ATMOSPHERE IN ORGANIC SOLVENTS

Compound	Temp., °C	Mole fraction	
		Obsd.	Calcd.
Acetal, $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$	-10	0.200	0.04
Methylal, $\text{CH}_2(\text{OCH}_3)_2$	-10	.192	.04
Acetaldehyde, CH_3CHO	-10	.177	.04
Ethyl acetate, $\text{CH}_3\text{COOC}_2\text{H}_5$	-10	.168	.04
Ethyl formate, HCOOC_2H_5	-10	.144	.04
Methyl acetate, $\text{CH}_3\text{COOCH}_3$	-10	.163	.04
Methyl formate, HCOOCH_3	-10	.142	.04
Isoamyl acetate, $\text{CH}_3\text{COOC}_5\text{H}_{11}$	-10	.166	.04
Isoamyl formate, $\text{HCOOC}_5\text{H}_{11}$	-10	.095	.04
Acetic acid, CH_3COOH	18	.0150	.0245
Ethyl alcohol, $\text{C}_2\text{H}_5\text{OH}$	18	.0151	.0245
Benzene, C_6H_6	4	.0252	.0342
Aniline, $\text{C}_6\text{H}_5\text{NH}_2$	4.2	.0223	.034
Dimethylaniline, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$	0.3	.037	.0382
Nitrobenzene, $\text{C}_6\text{H}_5\text{NO}_2$	3.8	.0223	.0345
Cyclohexane, C_6H_{12}	3	.0175	.0352
Acetone, CH_3COCH_3	0.0	.092	.038
Acetone, CH_3COCH_3	15	.074	.026
Acetone, CH_3COCH_3	15	.490	.312 ^a
Acetone, CH_3COCH_3	25	.0402	.0206

^a Pressure of acetylene 12 atmospheres.

stituted formamides than in N-disubstituted acetamides.

A further test of this idea is being made by means of vapor pressure-composition studies and by measuring the heats of mixing of a monosubstituted acetylene (phenylacetylene) with a number of donor solvents.

Figure 1 shows the heat evolved at 3° per mole of solution as a function of the mole fraction of phenylacetylene when it is mixed with, respectively, N,N-dimethylacetamide, diethyl ether, acetone, cyclohexylamine, and methyl acetate. The calorimeter and method of making the heat measurements were described previously by Zellhoefer and Copley.⁸ The maxima of the curves in Fig. 1 occur very close to a mole fraction of 0.5 and indicate that in each case an equimolar complex is formed. Curve A is a plot of the heat of mixing data for chloroform and diethyl ether obtained by McLeod and Wilson.⁹ Comparison of curves A and C shows that the hydrogen of chloroform is a better acceptor than the hydrogen of phenylacetylene, although the latter is more acidic, and thus emphasizes the influence of different groups on the carbon to which the active hydrogen is attached. Gordy¹⁰ has observed that when CH_3OD is mixed with ethers, esters, or ke-

tones, the largest shift in the OD fundamental band is shown with ethers. The somewhat larger amount of heat obtained here with dimethyl ether than with methyl acetate or acetone also indicates that with phenylacetylene an ether oxygen is a better electron donor than an ester or ketone oxygen.

As would be expected from previous solubility measurements⁴ on monofluorodichloromethane in ethers and N-disubstituted amides, considerably more heat is evolved on mixing phenylacetylene with N,N-dimethylacetamide than with diethyl ether. The nitrogen atom of N-disubstituted amides appears to be the best electron donor atom for forming hydrogen bonds.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED MARCH 23, 1939

The Preparation and Melting Point of 1-Iodoanthraquinone

BY ALBERT E. GOLDSTEIN

In the course of an investigation involving halogenated anthraquinones,¹ it became necessary to prepare 1-iodoanthraquinone. Investigation of the literature revealed but one procedure for the purpose—the method of Laubé.² The recorded yield of crude product appears as 27 g. (90%). It was found that, if the reported procedure were carefully followed, the crude yield invariably amounted to 7–8 g. If the procedure of Laubé is modified in the light of an observation made by Scholl and Mansfeld,³ then the results obtained are in agreement with those of Laubé.

The melting point of 1-iodoanthraquinone is given by Laubé as 177°. Brass and Eichler⁴ give the melting point as 176°. Nowhere is any mention made of the color of the compound. The repeated preparation of 1-iodoanthraquinone by the author and by others in these Laboratories invariably has yielded a crude compound melting at 195–197°. Two recrystallizations of the crude material yielded a compound melting at 204–205° instead of 177° as given by Laubé. Nitrobenzene has been found to be a more satisfactory solvent for the recrystallization than glacial acetic acid. The color of the product varies from brownish-yellow to dark brown.

(1) A. E. Goldstein with J. H. Gardner, *THIS JOURNAL*, **56**, 2130 (1934).

(2) Laubé, *Ber.*, **40**, 3566 (1907).

(3) Scholl and Mansfeld, *ibid.*, **43**, 1739 (1910).

(4) Brass and Eichler, *ibid.*, **67B**, 785 (1934).

(8) Zellhoefer and Copley, *THIS JOURNAL*, **60**, 1343 (1938).

(9) McLeod and Wilson, *Trans. Faraday Soc.*, **31**, 596 (1935).

(10) Gordy, *J. Chem. Phys.*, **7**, 93 (1939).

References to the preparation and melting point of 1-iodoanthraquinone found in the chemical literature are all based on the results reported by Laubé and consequently require revision.

Experimental

1-Iodoanthraquinone.—Twenty grams of 1-aminoanthraquinone, Eastman (Technical), was dissolved in 80 g. of concentrated sulfuric acid. To this solution 6 g. of sodium nitrite was added a little at a time at room temperature. The mixture was stirred mechanically during the addition of the sodium nitrite and for an additional two-hour period. This solution was then poured slowly into 1 liter of ice water with continual stirring. The mixture was stirred mechanically for one hour. The solution was next filtered and to the filtrate 10 g. of potassium iodide was added. This mixture was allowed to stand at room temperature for three hours and then heated for one hour on a steam-bath. After adding 10 cc. of a saturated sodium bisulfite solution, the mixture was filtered, and the residue was washed with distilled water and dried at 100°. The crude 1-iodoanthraquinone was light chocolate-brown; yield 7.5 g. (25%); m. p. 195.5–197.5°.

The residue from the first filtration mentioned above was put into 1 liter of water and stirred mechanically at room temperature for thirty minutes. The mixture was filtered and the filtrate treated with 10 g. of potassium iodide. By continuing the procedure as described above, an additional yield of crude product was obtained, light brown in color, weighing 19.5 g. (65%), m. p. 195.5–197.5°.

Two recrystallizations of the combined crude product from nitrobenzene produced a yellowish-brown crystalline compound, m. p. 204–205°.

Anal. Calcd. for $C_{14}H_7O_2I$: I, 37.99. Found: I, 38.02.

(5) All melting points are corrected.

DEPARTMENT OF CHEMISTRY
WASHINGTON UNIVERSITY
ST. LOUIS, MISSOURI

RECEIVED MARCH 24, 1939

Note on the Molecular Structure of 1,2,4,5-Tetrabromocyclohexane (m. p. 185°)

BY E. HALMÖY AND O. HASSEL

In some papers from the Oslo Institute of Physical Chemistry dealing with the structure of cyclohexane and its derivatives¹ investigations carried out on the 1,2,4,5-tetrabromocyclohexane of melting point 185° have been referred to. Although these investigations have not yet been brought as far as we could have wished in the case of the X-ray crystallographic part, we should not like to delay publication much longer, and

(1) A list of previous papers is found in a paper published by J. G. Gudmundsen and O. Hassel, *Z. physik. Chem.* **B40**, 326 (1938); see also O. Hassel and A. M. Sommerfeldt, *ibid.*, **B40**, 391 (1938).

are therefore publishing our results now, in a preliminary form.

The substance was obtained from the 1,4-dibromo compound of melting point 111° on eliminating two moles of hydrogen bromide and adding two moles of bromine to the 1,4-cyclohexadiene thus obtained. The crystals were rather well developed, having a size suitable for examination by the simple single crystal methods. They were found to be orthorhombic with axial ratios 1.010₃:1:0.997₇, and the following faces were observed: {110}, {101}, {011}, and in some cases also {001}. The optical axes were nearly perpendicular to (110) and (1 $\bar{1}$ 0).

The X-Ray Examination.—Approximate determinations of axial lengths (using the layer line method) gave the values $a = 7.92$ Å., $b = 7.85$ Å., and $c = 7.88$ Å. More accurate values were obtained from Bragg photographs on (001), (110), and (011) combined with the goniometrically determined axial ratios given above. We found $a = 7.98$ Å., $b = 7.90$ Å., $c = 7.89$ Å.

From our X-ray data (chiefly using Weissenberg photographs) we found that no other systematic extinctions can be observed than those of ($h00$) and ($0k0$), h or k being odd. The only space group of the orthorhombic system characterized by the absence of these reflections and showing no other regular extinctions is the Schönflies group $D_2^3-P2_12_12$. This space group contains only twofold and fourfold positions, the former being characterized by the point symmetry C_2 (twofold axis of symmetry) and one degree of freedom, the latter by three degrees of freedom. The density of the crystals being 2.66, the number of molecules in the unit cell must be 2 (calculated 2.01) and the single molecule must have a twofold axis of symmetry. The coordinates of the bromine atoms are of the form xyz , etc., four and four being crystallographically equivalent. It is not possible to evaluate the parameters of the bromine atoms with any accuracy, neglecting the influence of the carbon atoms, but a rough estimate of their positions can be made and this was found useful when trying to interpret the structure with the help of classical conceptions of the configuration of the cyclohexane ring using newer data concerning the interatomic distances. Assuming the carbon-carbon distance to be 1.54 Å. and the carbon-bromine distance to be 1.93 Å., the distribution of the bromine atoms was found to be in fairly

good agreement with positions which may be derived from the highly symmetrical rigid staggered form of the cyclohexane ring. In the model in question the C-Br linkages of two neighboring C-atoms (say 1 and 2) are parallel to the threefold axis of the cyclohexane ring, but point in opposite directions. The angles between the C-Br linkages of the two remaining carbon atoms attached to bromine (4 and 5) and the axis of the carbon ring are both equal to the tetrahedral angle. That is, two of the C-Br bonds (for C_1 and C_2) project above and below the ring, and the other two (for C_4 and C_5) lie nearly in the median plane of the ring. The twofold axis shown by the molecule as a whole (parallel to the c -axis of the crystal) lies in the plane of the four carbon atoms 1, 2, 4, and 5, running parallel to the lines joining 1 and 5 (2 and 4) and through the middle point of the rectangle 1, 2, 4, 5.

We have tried to get a close agreement with our observed intensities assuming the carbon atoms to occupy the positions of this model and allowing for small changes in the positions of the bromine atoms. A certain difficulty arose as we were somewhat in doubt as to the true intensity of some reflections from (100) and (010), especially the sixth and eighth orders. The values of the bromine parameters to which we have been led are the following ones: $x_1 = -0.018$, $y_1 = 0.282$, $z_1 = -0.106$; $x_2 = 0.218$, $y_2 = 0.018$, $z_2 = 0.442$.

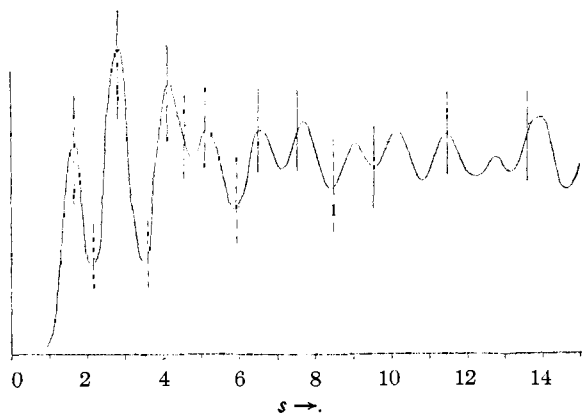


Fig. 1.

The Dipole Moment.—The measurements were carried out some years ago in benzene solution and at room temperature, the method being that described in a series of papers from our institute. The molar polarization P_{A+O} , the sum

of atomic and orientation polarization, is given in Table I for the molar concentrations m employed:

m	0.07536	0.05946	0.04165	0.02525
P_{A+O}	96.5	95.0	98.9	101.4

Extrapolation to infinite dilution gives the value $P_{A+O} = 104.6$, and, neglecting the atomic polarization, $\mu = 2.2_2 D$.

Electron Diffraction Diagrams of the Vapor.—Some electron diffraction diagrams of the evaporated substance were taken, using electrons of about 35 kv. velocity. The s values of the observed maxima and minima are listed in Table II, s meaning $4\pi \sin \vartheta/\lambda$. We have drawn theoretical curves for all possible models of the 1,2,4,5-tetrabromocyclohexane molecule based on the rigid symmetrical form of the carbon ring, assuming all valency angles to be $109^\circ 28'$, and using the values 1.54 and 1.93 Å. for the C-C and C-Br distances. A comparison with the electron diffraction plates showed clearly that the model used above and fitting the X-ray data is the only one of these models which accounts for the observed maxima and minima, the agreement being

TABLE II
S-VALUES OF OBSERVED MAXIMA AND MINIMA ON ELECTRON DIFFRACTION PLATES

Maxima	Minima
1.66	
	2.18
2.28	
	3.65
4.12	
	4.54
5.10	
	5.95
6.49	
7.53	
	8.52
9.56*	
11.51	
13.62	

* Some plates indicate here not a single, rather broad maximum, but rather two maxima, but we have nevertheless recorded the mean value $s = 9.56$ in Fig. 1.

surprisingly good. The curve in question is shown in Fig. 1, the observed maxima being indicated by vertical lines, and the minima by dotted lines.

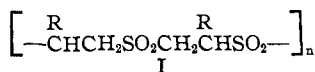
MOLDE, NORWAY
PASADENA, CALIF.

RECEIVED MARCH 29, 1939

Structural Identity of Polysulfones Prepared by Peroxide Catalysis and Under the Influence of Ultraviolet Light¹

BY C. S. MARVEL AND WM. H. SHARKEY

Olefins of the type $RCH=CH_2$ combine with sulfur dioxide in the presence of peroxides to give polysulfones with the structure shown in formula I.² The unusual orientation of the units sug-



gested to us that the peroxides present might be exerting an effect similar to that which has been discovered by Kharasch and his students³ in connection with the addition of hydrogen bromide to olefins. It has been reported⁴ that ultraviolet light promotes the addition of sulfur dioxide to olefins. While previous work in this Laboratory has indicated that it will not induce polymer formation in all cases,⁵ we have now found that it does bring about the combination of 1-pentene with sulfur dioxide. This has made it possible for us to compare the structure of 1-pentenepolysulfone prepared with peroxide catalysts with that of the polymer prepared by photochemical activation in the absence of peroxides. The two products apparently are identical and beyond question have the same structural units.

1-Pentene was shaken with concentrated aqueous hydrochloric acid until it gave no test for peroxides with ferrous sulfate and ammonium thiocyanate.⁶ The olefin was then distilled and again found to give no test for peroxides. A 5-cc. sample of this peroxide-free olefin and 5 cc. of liquid sulfur dioxide were placed in a Pyrex tube and nitrogen was passed through the tube for about twenty minutes to remove all of the air. The tube was then sealed and placed under an ultraviolet lamp. Evidence of polymer formation was noticed after twenty-four hours. After one week the tube was opened and the polymer was isolated. The yield was 5 to 5.2 g. The polymeric product had the same physical properties and solubilities as reported for the 1-pentenepolysulfone prepared by peroxide catalysts.²

(1) This is the ninth communication on The Reaction between Sulfur Dioxide and Olefins. For the eighth see THIS JOURNAL, **60**, 2622 (1938).

(2) Glavis, Ryden and Marvel, *ibid.*, **59**, 707 (1937).

(3) For leading references see Kharasch, Norton and Mayo, *J. Org. Chem.*, **3**, 48 (1938).

(4) Mathews and Elder, British Patent 11,835 (1914); *C. A.*, **9**, 2971 (1915).

(5) Frederick, Cogan and Marvel, THIS JOURNAL, **56**, 1815 (1934).

(6) Kharasch and Mayo, *ibid.*, **55**, 2468 (1933).

Treatment of 3 g. of this polymer with 150 cc. of liquid ammonia as described previously² followed by recrystallization of the resulting product from alcohol gave 0.9 g. (30%) of 2,6-di-*n*-propyl-1,4-dithian-*bis*-(dioxide), m. p. 257°. This product was identical with the synthetic product and that formed by the action of liquid ammonia on 1-pentenepolysulfone prepared in the presence of peroxides.²

CHEMICAL LABORATORY
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RECEIVED MARCH 3, 1939

The Oxidation of Phenyllithium

BY H. A. PACEVITZ AND HENRY GILMAN

The formation of significant quantities of coupling or R·R compounds by oxidation of RLi compounds of the dibenzofuran series¹ suggested an examination of the oxidation products of phenyllithium. Ether-free phenyllithium was used because we wished to exclude the marked secondary reactions known to take place when ether solutions of arylmagnesium halides are oxidized.²

We found that biphenyl and phenol are formed in essentially equal quantities. In addition, a small quantity of *p*-phenylphenol was isolated from each of the oxidation reactions. It is possible that the *p*-phenylphenol may owe its formation to the oxidation of some *p*-phenylphenyllithium formed by metalation of biphenyl, for biphenyl is known to metalate in a para position.³

It was also observed that when phenyllithium was allowed to take fire in the air, a pronounced odor of biphenyl accompanied the combustion. Incidentally, the solid phenyllithium, phenylsodium, and phenylpotassium, like the phenylmagnesium halides, show chemiluminescence when oxidized.⁴

Müller and Töpel⁵ have just reported on the oxidation of some organolithium compounds. Working in ether solutions, these authors found more biphenyl, but less phenol than we did under our conditions. Their phenylmethylcarbinol arose as a consequence of the usual secondary reaction with ether,² and they found no other products. With most of the other aryllithium compounds

(1) Gilman, Cheney and Willis, THIS JOURNAL, **61**, 951 (1939).

(2) Wuyts, *Compt. rend.*, **148**, 930 (1909); Porter and Steele, THIS JOURNAL, **42**, 2650 (1920); Gilman and Wood, *ibid.*, **48**, 806 (1926).

(3) Gilman and Bebb, *ibid.*, **61**, 109 (1939).

(4) Ether solutions of phenyllithium were reported earlier to show chemiluminescence on oxidation [Gilman, Zoellner and Selby, *ibid.*, **54**, 1957 (1932)].

(5) Müller and Töpel, *Ber.*, **72**, 273 (1939).

examined by them, the yield of coupling product was less than that observed with phenyllithium, and in the case of *o*-tolylithium the yield of bi-*o*-tolyl was 5% and the yield of *o*-cresol, 54%.

Experimental Part

The suspension of 4.5 g. of phenyllithium in 100 cc. of benzene, prepared in a nitrogen atmosphere, was oxidized by dry air, free of carbon dioxide, at 10–15°. A negative color test⁶ was obtained in about ten hours. The phenol was characterized as 2,4,6-tribromophenol, and the *p*-phenylphenol as the acetate.

In three experiments the yields of phenol were 25.9, 23.1, and 22%; of biphenyl, 25, 23.7 and 22.6%; and of *p*-phenylphenol, 0.05, 0.06 and 0.05 g., respectively. The extent of the Wurtz-Fittig reaction with the bromobenzene is quite slight, for only 0.12 g. of biphenyl was isolated from the benzene washings of a 0.1 mole run.

(6) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

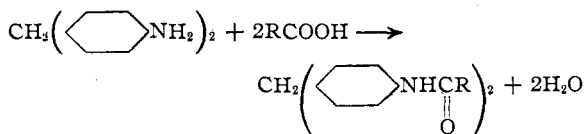
CONTRIBUTION FROM THE
CHEMICAL LABORATORY OF
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RECEIVED MARCH 29, 1939

4,4'-Diaminodiphenylmethane as a Reagent for the Identification of Monobasic Saturated Aliphatic Acids

BY A. W. RALSTON AND M. R. McCORKLE

4,4'-Diaminodiphenylmethane has been found to give diamides of aliphatic acids by heating the theoretical proportions of the diamine with the respective acids.



Because of the ease of preparation and purification and their high melting points, these compounds serve as excellent derivatives for the identification of aliphatic acids. With the lower members there was considerable depression of mixed melting points but this became increasingly smaller as the series was ascended.

In order to establish the structure of the diamides prepared by this method, the diamides of acetic, propionic and lauric acids were prepared from the diamine and either the anhydrides or the acid chlorides. These gave no depression of mixed melting points with the corresponding com-

pounds prepared from the acids. *p,p'*-Methylenediacetanilide has been prepared previously from acetic anhydride and 4,4'-diaminodiphenylmethane.

Experimental

A mixture of 1 g. (0.005 mole) of 4,4'-diaminodiphenylmethane¹ and slightly more than 0.01 mole of the respective acid were mixed in a large Pyrex test-tube and heated at the boiling temperature until water ceased to be evolved. With the lower members of the series a reflux condenser was used and the period of heating was approximately one hour. The time necessary to complete the reaction decreased with the higher members of the series and in the case of stearic acid five minutes is sufficient. The products were crystallized to a constant melting point from a mixture of benzene and methanol except with some of

TABLE I
CONSTANTS OF DIAMIDES OF 4,4'-DIAMINODIPHENYLMETHANE

Acid	M. p., °C. (corr.)	Mixed m. p. with next highest homolog	N Analyses, %	
			Calcd.	Found
Acetic ^{a,b}	227–228	205–210		
Propionic	212–213	188–193	9.03	9.33
Butyric	197–198	185–188	8.28	8.58
Valeric	188–189	179–181	7.65	7.92
Caproic	185–186	179–181	7.10	7.46
Heptylic	183–184	176–178	6.64	6.86
Caprylic	182–183	176–179	6.22	6.53
Pelargonic	176–177	175–177	5.83	6.11
Capric	178–179	173–175	5.54	5.93
Undecylic	175–176	172–174	5.25	5.45
Lauric ^c	174–175	171–173	4.99	5.38
Tridecylic	172–173	170–172	4.78	5.12
Myristic	170–171	167–169	4.53	4.73
Pentadecylic	167–168	166–168	4.34	4.36
Palmitic	167–168	164–166	4.15	4.39
Margaric	164–165	163–165	3.99	4.40
Stearic	164–165		3.83	4.12

^a In order to purify this sample it was necessary to dissolve it in ethanol and add alkali until basic to phenolphthalein. Upon dilution with water and crystallization from benzene and methanol the product, m. p. 227–228°, was obtained. ^b Stoedel and Hause, *Ber.*, **23**, 2577 (1890); Rivier and Farine, *Helv. Chim. Acta*, **12**, 865 (1929); Parkes and Morley, *J. Chem. Soc.*, 315 (1936); Butler and Adams, *THIS JOURNAL*, **47**, 2617 (1925), reported m. p. 236–237°. ^c The authors are indebted to Mr. W. M. Selby for the samples of lauric, myristic and stearic acids. The remainder of the acids were obtained from the Eastman Kodak Company.

(1) The 4,4'-diaminodiphenylmethane used was prepared by crystallization from petroleum ether of Eastman Kodak Co. (practical), 4,4'-diaminodiphenylmethane, m. p. 90–91.5°. The melting point was 92–93°.

the higher derivatives where the methanol was replaced by *n*-butanol.

RESEARCH LABORATORY OF
ARMOUR AND COMPANY
CHICAGO, ILLINOIS

RECEIVED MARCH 25, 1939

The Colloid Chemistry of Leaf and Flower Pigments and the Precursors of the Anthocyanins

BY ROBERT ROBINSON AND GERTRUDE M. ROBINSON

In an interesting memoir¹ under the above title, W. D. Bancroft and J. E. Rutzler, Jr., have attributed views to us which we do not hold, the divergence being largely one of emphasis and due to generalization from the particular. These authors contrast the idea of Willstätter that anthocyanins result in nature from the reduction of flavonols with our supposed hypothesis that they normally originate from the oxidation of leuco-anthocyanins.

We are aware that Willstätter (and Everest also) showed that flavonols could be reduced in the laboratory to anthocyanidins, but are not certain that he founded any general theory of biogenesis on these observations. It may be that we have overlooked a statement of this kind. For our own part it has been made abundantly clear that we do not regard the ordinary anthocyanins as derived from leuco-anthocyanins. Here it should be interpolated that by leuco-anthocyanin (idin) we do not mean the colorless pseudo-bases or the readily oxidizable hydrocyanidin of Kuhn, but a special widely distributed class of natural products which are somewhat hard to convert into anthocyanidins, and are recognized by this transformation *in vitro* under certain conditions. Not one of the true leuco-anthocyanins (idins) has been isolated but cyanomaclurin and peltogynol are similar substances. Until they have been purified and characterized by analysis it is idle to speculate on their state of oxidation. A suggestion of a possible structure for a leuco-anthocyanidin having the same state of oxidation as cyanidin has been advanced.² Some leuco-anthocyanins undoubtedly are in a lower state of oxidation and it is to these alone that we consider the biogenetic oxidation hypothesis applies.

It is true that we have stated that oxidation *in vitro* is a more likely process than reduction

but this was an argument against the flavonol theory and it was not coupled with adherence to any general oxidation theory, though we can understand how a misconception of our attitude could arise.

As the concentration of leuco-anthocyanins cannot be determined independently, and in view of the possibility of disproportionation, it is hard to devise a sound experimental test for the oxygen requirement in any particular case. In some examples we can see that an oxidizing agent is necessary; the negative results cannot be interpreted unambiguously.

The following citation³ explains our view of the part played by leuco-anthocyanins:

"Inevitably the transformation of these substances (leuco-anthocyanins) into coloring matters of flavylum type must occur in nature occasionally, but it does not follow that this route represents the standard mechanism. Two dihydro-anthocyanidins, namely, cyanomaclurin and peltogynol, have been isolated and characterized; these are stabilized by the possession of a glucose-like oxide ring, and the related anthocyanidins are not found in the form of naturally occurring anthocyanins. The true leuco-anthocyanidins usually afford cyanidin on hydrolysis and autoxidation.

"It is too early to attribute a predominant role to the leuco-anthocyanidins, but it is already safe to assume that their modification represents an auxiliary pigmentation process. It is possibly operative in autumnal reddening and in the coloration following injuries or decortication of leaves."

Analogously we do not wish to exclude even flavonol reduction in *special* cases; we think there is ample evidence that it is not the *usual* mechanism of phyto-synthesis.

We have consistently maintained that the anthoxanthins, and anthocyanins are formed in the plant from a common progenitor by forking of the roads. Furthermore, we discern a C₆ unit and a C₆-C₃ unit and assuming an origin from carbohydrate have pointed out that cyanidin represents the normal state of oxidation. This hypothesis was first advanced in 1921⁴; it has been developed in various lectures and publications.⁵ The

(3) Robinson and Robinson, *Nature*, **137**, 172 (1936).

(4) British Association Report, 89th Meeting, Edinburgh, p. 417.

(5) Ref. 3 and Report of the IXth International Congress of Pure and Applied Chemistry, Madrid, Vol. V, 1934, p. 25. *Proc. Univ. Durham Philosophical Society*, **8**, (i), 17 (1927-1928).

(1) Bancroft and Rutzler, *THIS JOURNAL*, **60**, 2738 (1938).

(2) Robinson and Robinson, *Biochem. J.*, **27**, 207 (1933).

chromogens are doubtless colorless but must not on this account be confused with the leucoanthocyanins.

Finally we remark that attention was pointedly drawn to the importance of colloid association of anthocyanins in the Presidential Address to Section B of the British Association (Leicester, 1933).⁶ We showed *inter alia* that cyanin is blue in the acid cornflower cell-sap because it is adsorbed on colloidal particles which stabilize the anions at a *pH* of 4.9.

Co-pigmentation is, however, a different phenomenon and is observable in dilute, strongly acid solutions. In the heterogeneous systems of a flower petal the two factors probably merge and in addition surface phenomena become important in relation to flower color. In this connection it is interesting to note that all the colors of hydrangeas (blue, violet, red) can be exactly reproduced by pouring acid solutions of synthetic delphinidin 3-monoglucoside⁷ (now recognized as the hydrangea anthocyanin) on filter paper. The best results are obtained with optimum concentrations of organic acids and in the presence of tannin. Dilute (red) solutions give blue on the paper, more concentrated solutions, red, and the hydrangea violet is intermediate. Blue margins are noted in all cases unless the acid concentration is too high. Hence we reject the view that the blue color is due to ferric salts, physical conditions being obviously paramount. The function of iron salts, etc., added to the soil is probably to initiate physiological disturbances whereby the anthocyanin concentration is diminished. Further relevant facts are reported in the following note.

(6) Cf. Report of the British Association for the Advancement of Science, 1933, and *Nature*, **132**, 625 (1933).

(7) Reynolds and Robinson, *J. Chem. Soc.*, 1039 (1934).

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RECEIVED DECEMBER 5, 1938

Notes on Variable Colors of Flower Petals

BY GERTRUDE M. ROBINSON

These notes refer to variations not due to change in the basic anthocyanins.

It has already been noted that a factor for flower color is the concentration of the anthocyanin and the ratio of this to the concentration of co-pigments of the tannin and flavonol classes. A good example is the ordinary lilac in which the co-pigment remains substantially constant. The

pale mauve colored flowers contain much less anthocyanin than the red flowers.¹ In the latter case the co-pigment is unable to modify the color of all the anthocyanin present. A second factor is colloid association, probably with polysaccharides (see the preceding note) and in this case too the development of much anthocyanin may produce a new shade. A third factor is virtual change of *pH* due to surface phenomena (diffusion of mobile ions), and fourth and fifth may be dyeing of the fibers and crystallization of the pigment, respectively. Modifications due to traces of elements such as iron are also possible but have not yet been recognized with certainty in any one case. A common phenomenon is that of a red bud which becomes mauve, purple, violet or blue when the flower opens or a little later; changes due to fading and loss of vigor are not under consideration. This sequence has only been observed in flowers characterized by *relatively high pH* (about 6.0). The following are representative observations and some notes on exceptional cases are appended. *pH* was determined after trituration of the material (3 g.) with distilled water (14 cc.).

Ageratum.—Young red buds (*pH* 6.0) develop into violet flowers (*pH* 5.8). The anthocyanin is an acylated cyanidin diglucoside. The concentration of anthocyanin is higher in the buds than in the flowers but the ratio of flavone to anthocyanin is higher in the flowers than in the buds.

Anchusa (Dropmore var.).—Red buds (*pH* 6.35) become blue flowers (*pH* 6.2). The flavone remains constant but the ratio of anthocyanin in buds to flowers is 34.4:22.5. In this case colloid association in the flowers, as in the cornflower, is indicated.

Centaurea.—The concentration of anthocyanin in purple flowers of the annual cornflower is higher than in the blue flowers.

Cheiranthus mutabilis.—The color changes are due to the gradual formation of anthocyanin superposed on the yellow ground of the petals; subsequently the anthocyanin is destroyed. This anthocyanin is an acylated glucoside of an acylated cyanidin. The reddish bracts contain unacylated cyanidin diglucoside.

Delphinium (vars. Dr. B. Crane, Lorenzo di Medici, Blue Bird).—Blue petals or parts of petals (*pH* about 5.6) contain less anthocyanin and relatively less flavone than violet petals (*pH* about 5.7) of the same plant. Here again colloid association is indicated.

Hydrangea.—Red and blue flowers contain the same anthocyanin, namely, delphinidin 3-monoglucoside. There is a little more flavone in the red than in the blue flowers. The ratio of anthocyanin concentrations, red to blue, is usually from 6:1 to 7:1 and using a specially deep-colored blue variety it was still 4:1. The *pH* of hydrangeas is

(1) Robinson and Robinson, *Nature*, **130**, 21 (1932).

variable, the red flowers being slightly more acid than the blue; varieties which do not blue have unusually low pH . If the petals of a blue variety are allowed to develop in a weak light more anthocyanin is produced and a red color partly masks the blue.

Ipomea Learii.—Young red buds (pH 6.4) become blue flowers (pH 6.2–6.3) and the pigment concentration diminishes slightly. This process does not occur in cut flowers kept in hard tap water, but always when distilled water is used. Here again the change of color is associated with a flower of unusually high pH . The range in the majority of flower petals is from 4.0 to 5.0.

Malcomia maritima.—The buds and young flowers are red and change to dullish violet. The pH in both cases is about 6.4. The anthocyanin concentrations, red to violet, are about in the ratio 3:2. Flavone is present in approximately the same concentration in both cases. It is very interesting that the variety "Crimson King," which does not blue, has pH 5.17. All varieties of the virginian stock are colored by cyanidin diglucoside.

Meconopsis Baileyi.—The purple flowers contain more anthocyanin than the blue.

Rosa.—The "Veilchen" rambler rose has red buds (pH 6.3) changing to dullish violet flowers (pH 6.3). The anthocyanin ratio, red to violet, is 29.6:22.9. In a dry season the flowers become violet almost as soon as they open but in a wet season the change occurs just before fading. In the latter case the anthocyanin concentration is higher than in the former.

The rose, Madame Ed. Herriot, has salmon-pink young flowers changing to bluish-pink. The pH in both cases is 5.9. The anthocyanin ratio of young to older flower petals is 44:26. Flavones are present but show little change.

The rambler "Excelsior," like "Veilchen," is colored by cyanin but the pH is 5.6 and the color change does not occur.

Chlorogenic Acid.—The method of Gorter² has been employed and it appears that this plant constituent may have some significance in relation to flower color. Blue hydrangea flowers do not contain any chlorogenic acid but the red flowers have a substantial amount.

Blue flowers of *Ipomea Laurii* are free from the acid but fading, accompanied by reddening, causes the development of this substance. Red buds and purple flowers of *Centaurea* contain chlorogenic acid but there is none in blue cornflowers.

Arnebia cornuta.—This plant, known as Mahomet's Fingers, produces yellow flowers and shortly after opening (incipiently also in the bud) dark purplish-brown areas appear on each petal; the colored spots later disappear. The anthocyanin is malvidin diglucoside. The colored areas are opposite the anthers and in the bud follow their shape. If tissue paper is interposed at an early stage between anther and petal, the spot does not develop. Also, if the petal is tied away the same result is achieved in a large majority of cases. The petals on which this operation is performed grow, but do not reach full normal size. It would appear that the anther contains a stimulant (? volatile) to anthocyanin formation although this view is necessarily tentative because the normal physiology of the plant may have been modified by the mechanical operation.

(2) Gorter, *Rec. trav. chim.*, **31**, 281 (1912).

In one case the anthers were successfully excised and a good flower developed. It was always pure yellow.

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The Identity of Pyrethrosin with Chrysanthin and Non-identity with Geigerin

BY MILTON S. SCHECHTER AND H. L. HALLER

A crystalline compound isolated from pyrethrum flowers (*Chrysanthemum cinerariaefolium*) has been described recently by Rose and Haller.¹ The compound was named "chrysanthin" because its physical properties appeared to be identical with those of a compound obtained by Chou and Chu² from benzene extracts of pyrethrum flowers, and named by them "chrysanthine."³ The compound described by Rose and Haller melted at 201° when crystallized from ethyl acetate and at 177–178° when crystallized from ethanol. Its optical rotation in chloroform was $[\alpha]^{20}_D -30.5^\circ$. Analyses and molecular weight determinations showed it to have the molecular formula $C_{17}H_{22}O_5$.

Chou and Chu stated that the compound isolated by them had a melting point of 200° and a rotation of $[\alpha]^{20}_D -30^\circ$ in chloroform. The empirical formula, $C_{10}H_{13}O_3$, assigned by them was based on combustion analyses only, no molecular weight determinations having been made.

Thoms⁴ in 1891, during a study on the insecticidal principle of pyrethrum flowers, isolated an insecticidally inert product which he termed "pyrethrosin," and which he regarded as being identical with one obtained by Marino-Zuco⁵ in a similar study. Thoms found that pyrethrosin had a melting point of 189° and suggested the provisional formula $C_{34}H_{44}O_{10}$ on the basis of four combustions but no molecular weight determination. This formula is exactly twice that proposed for chrysanthin by Rose and Haller.

In the course of a chemical study of *Geigeria aspera*, a plant that causes "vermeersickte" or vomiting disease of sheep, Rimington and Roets⁶ isolated a bitter principle which they called

(1) Rose and Haller, *J. Org. Chem.*, **2**, 484 (1937).

(2) Chou and Chu, *Chinese J. Physiol.*, **8**, 187 (1934).

(3) The final e was dropped by Rose and Haller in accordance with present standards of nomenclature.

(4) Thoms, *Ber. deut. pharm. Ges.*, **1**, 241 (1891).

(5) Marino-Zuco, *Atti accad. Lincei*, I Sem., 571 (1890); abstr. in *Ber.*, **24**, 201 (1891).

(6) Rimington and Roets, *Onderstepoort J. Vet. Sci. Animal Ind.*, **7**, 485 (1936).

TABLE I
 SOME PROPERTIES AND REACTIONS OF CHRYSANTHIN, PYRETHROSIN AND GEIGERIN

Property or reaction	Chrysanthin ¹	Pyrethrosin ⁴	Geigerin ⁸
Melting point, °C.	{ 201 from EtOAc 177-178 from EtOH	188-189 from EtOH	α-Form 78 and 189 β-Form 68 and 169
Taste	Bitter	Bitter	Bitter
Crystalline form	Orthorhombic octahedra	Rhombic octahedra	Rhombic
Optical rotation {	(α) ²⁰ D in CHCl ₃ (-30.5) c = 5.16	...	(-42.58) c = 0.335
(α) ²⁰ D in abs. EtOH	(-38.1) c = 0.315	...	(-60.23) c = 0.349
Carbon, % (av.)	66.73	66.49	68.20
Hydrogen, % (av.)	7.25	7.27	7.75
Molecular weight (av.)	311	Not detd.	303 on monohydrate
Formula	C ₁₇ H ₂₂ O ₅	C ₃₄ H ₄₄ O ₁₀	C ₁₅ H ₂₀ O ₄
Color tests	Warm 25% HCl	Violet soln., amorphous yellow ppt. on dilution	Cherry-red soln.
	Warm 20% HCl	Pink-violet soln., yellow amorphous ppt. on diln.	Cherry-red soln., unchanged geigerin on diln.
	Concd. H ₂ SO ₄	Yellow-brown solution	Yellow-brown solution
Tetranitromethane	No color	...	No color
Bromine in CHCl ₃	No decol., excess reacts	...	No decol.
Cold aq. KMnO ₄	Reduction	Rapid redn. warm	None; reduc. warm
Fehling's solution	Sl. redn. prolonged boiling	...	Sl. redn. prolonged boiling
2,4-Dinitrophenylhydrazone	None	...	Formed
Lactone group	Present	...	Present

geigerin. It has the empirical formula C₁₅H₂₀O₄ and exists in two isomeric forms, an alpha form which shows a double melting point, the final one being 189°, and a beta form which also exhibits two melting points, melting finally at 169°. Both forms have the same composition and the same optical rotation, [α]²⁰D -42.71°, in chloroform or ethyl acetate.

Largely on the basis of a comparison of melting point of the alpha form of geigerin with that of pyrethrosin, both 189°, and a color test of each with hydrochloric acid, Rimington and Roets have concluded that geigerin and pyrethrosin are identical, a conclusion with which we are not in accord.

Some of the properties and reactions of each compound are recorded in Table I.

All three substances are bitter in taste.

The melting point reported by Thoms for pyrethrosin is 189°; that for chrysanthin, as already indicated, is 178 or 201°. However, it has been shown that the melting point behavior of chrysanthin varies with the solvent from which it is crystallized and also with the rate of heating.

The carbon and hydrogen combustion values for pyrethrosin and chrysanthin are almost identical, both sets of values being satisfactory for the empirical formula C₁₇H₂₂O₅. Both carbon and hydrogen combustion values of geigerin are higher than those of pyrethrosin and with consideration of molecular weight data indicate an empirical formula of C₁₅H₂₀O₄.

Neither chrysanthin nor geigerin decolorizes bromine in chloroform solution; however, chrysanthin reacts with a concentrated solution of bromine in chloroform with the liberation of hydrogen bromide and the separation of an oil.

Chrysanthin reacts readily with 2 moles of alkali with the formation of acetic acid and an acid, C₁₅H₂₆O₇, which is very soluble in water, only slightly soluble in ether, and difficult to crystallize. Geigerin reacts with 1 mole of alkali with the formation of an acid, C₁₅H₂₂O₅, which is not very soluble in water, dissolves readily in ether, and is crystalline.

The color test given by chrysanthin with hydrochloric acid is the same as that recorded for pyrethrosin; the color test given by geigerin with this reagent is similar but not the same.

The presence of a carbonyl group can be demonstrated in geigerin by the formation of a 2,4-dinitrophenylhydrazone, but it has not been possible to prepare such a derivative from chrysanthin.

All the foregoing evidence, together with the fact that chrysanthin or pyrethrosin has been obtained by several investigators from only one species of plant, *Chrysanthemum cinerariaefolium*, seems to establish their identity.

It is clear from the recorded data that chrysanthin and geigerin are not identical, and therefore it follows that geigerin and pyrethrosin are not the same.

It is suggested that the name "pyrethrosin" be retained for this crystalline product obtained from *Chrysanthemum cinerariaefolium* and that all others be discarded.

BUREAU OF ENTOMOLOGY AND
PLANT QUARANTINE
U. S. DEPT. OF AGRICULTURE
WASHINGTON, D. C.

RECEIVED MARCH 11, 1939

Tetraphenyllead and Diphenyllead Dihalides

BY W. C. SETZER, R. W. LEEPER AND HENRY GILMAN

The Pfeiffer¹ procedure for the preparation of R_4Pb compounds by interaction of the Grignard reagent and lead chloride is admirably suited for laboratory purposes. However, the yields of tetraphenyllead by this method are about 50% in moderate sized runs.²

Incidental to a study on the mechanism of formation of some organometallic compounds, it has been found possible to increase the yield of tetraphenyllead to 83%. An occasional by-product is triphenyllead bromide, isolated in yields up to 6%. This compound does not owe its formation to a secondary reaction between tetraphenyllead and magnesium bromide or the binary system ($Mg + MgBr_2$), inasmuch as tetraphenyllead is unaffected by these substances under the conditions of the Pfeiffer reaction. A recent³ study showed that R_3Pb compounds react with magnesium iodide to give R_3PbI compounds. A corresponding reaction of triphenyllead and magnesium bromide suggests itself for the formation of triphenyllead bromide. Actually, we have found that triphenyllead and magnesium bromide give triphenyllead bromide. Triphenyllead is undoubtedly an intermediate in the preparation of tetraphenyllead; and when the time of reaction (in the directions which follow) is decreased, the tetraphenyllead is contaminated with some triphenyllead.

To a vigorously stirred solution of phenylmagnesium bromide (prepared from 1.5 moles of bromobenzene) in 500 cc. of ether, is added 500 cc. of dry toluene and 181 g. (0.65 mole) of dry, finely ground lead chloride. The lead chloride is added in three portions at five-minute intervals. The mixture is stirred with gentle refluxing for five hours, and thins out appreciably after the initial fifteen to thirty minutes of heating.

(1) Pfeiffer and Truskier, *Ber.*, **37**, 1125 (1904).

(2) Gilman and Robinson, *THIS JOURNAL*, **49**, 2315 (1927).

(3) Gilman and Bailie, *ibid.*, **61**, 731 (1939).

Hydrolysis is effected by pouring upon crushed ice mixed with ammonium chloride or hydrochloric acid. Vigorous stirring should be maintained during hydrolysis.

The toluene-ether layer is decanted and the water layer filtered. Distillation of the organic solvent layer leaves a residue consisting of a few grams of tetraphenyllead and triphenyllead bromide together with about 10 g. of biphenyl which probably came largely incidental to the formation of the Grignard reagent. The filtered solid from the aqueous layer is air dried, and extracted with 400 cc. of chloroform in a Soxhlet extractor to give an 82-83% yield of crystalline, pure tetraphenyllead (m. p. 225-226°). In the directions just noted, which do not necessarily give maximum yields, no inert atmosphere was used and the Grignard reagent was not filtered free of magnesium.

Diphenyllead dibromide and diphenyllead diiodide are prepared conveniently and in excellent yields in essential accordance with the procedure of Polis.⁴ To 50 cc. of *boiling* concentrated nitric acid is added slowly 10 g. (0.019 mole) of tetraphenyllead. The mixture is cooled, filtered through glass wool, and washed with a little water. The diphenyllead dinitrate is dissolved in boiling water acidulated with a little nitric acid, and to the hot solution is added a solution of sodium bromide (4.1 g., 0.04 mole). The diphenyllead dibromide precipitates immediately, and the yield is 96%. In a corresponding manner, diphenyllead diiodide is obtained in a 98% yield when sodium iodide is used. Diphenyllead dichloride is most conveniently prepared, in a 98% yield, from tetraphenyllead and hydrogen chloride.⁵ It can be prepared in a 93% yield by the addition of concd. hydrochloric acid to an aqueous solution of diphenyllead dinitrate.

Diphenyllead difluoride is obtainable in a 92% yield by the addition of an aqueous solution of potassium fluoride to an alcoholic solution of diphenyllead diiodide. Diphenyllead difluoride is insoluble in the usual organic solvents and does not melt up to 300°.

Anal. Calcd. for $C_{12}H_{10}PbF_2$: Pb, 51.88.
Found: Pb, 52.07, 51.65.

Diphenyllead difluoride and phenylmagnesium bromide give tetraphenyllead.

(4) Polis, *Ber.*, **20**, 720 (1887).

(5) Gilman and Robinson, *THIS JOURNAL*, **51**, 3112 (1929).

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The Reduction of α -Bromocyclohexanone with Aluminum Isopropoxide

BY S. WINSTEIN

The reduction of some α -bromo ketones by aluminum isopropoxide was the subject of a recent communication to the Editor by Stevens,¹ who obtained from α -bromopropiophenone a 35% yield of bromohydrin and about an equal yield of product not containing bromine. Presumably hydrogen bromide was split out. Tertiary α -bromo ketones and cyclic secondary α -bromo ketones were reported to yield not bromohydrins but products almost entirely free of bromine. What type of product he obtained was not indicated. In the course of other work the author has had occasion to reduce with aluminum isopropoxide the cyclic secondary α -bromo ketone, α -bromocyclohexanone. Since Stevens is continuing his investigation of the reaction of α -bromo ketones with aluminum isopropoxide, the results obtained with this cyclic ketone should be reported.

The reaction product from the reduction of α -bromocyclohexanone was found to be a mixture

(1) Stevens, *THIS JOURNAL*, **60**, 3089 (1938).

of bromohydrin and cyclohexanol, in yields of 30 and 33%, respectively, with no unsaturated compound being isolated. It is possible that the cyclohexanol arises from dismutation of bromocyclohexanone to cyclohexanone and dibromocyclohexanone with subsequent reduction of the cyclohexanone to cyclohexanol.

Experimental

75.8 g. (0.428 mole) of α -bromocyclohexanone, b. p. 69–71° (1.5 mm.), prepared by the method of Kötzt,² dissolved in 200 ml. of anhydrous isopropanol (Shell) was added to aluminum isopropoxide solution prepared from 7.5 g. of aluminum and 75 ml. of anhydrous isopropanol, according to the directions of Young, Hartung and Crossley.³ The mixture was refluxed for three and one-half hours. Then it was concentrated to a thick residue by distillation first of acetone, then of solvent through a 20-cm. column of glass helices for two hours at atmospheric pressure and finally with the aid of an aspirator. One hundred ml. of water and 130 ml. of 6 *N* sulfuric acid were added to the residue and all lumps were broken up. A little ether was added and the oil phase was separated, washed with bicarbonate solution and dried over sodium sulfate. Distillation and then refractionation at reduced pressure through a 40-cm. Weston⁴ column yielded 22.6 g. (30%) of 2-bromocyclohexanol, b. p. (10 mm.) 85.5–86.5°, n_D^{25} 1.5164, and 14.3 g. (33%) of cyclohexanol, b. p. (10 mm.) 61.0–61.2°, n_D^{25} 1.4649, m. p. of 3,5-dinitrobenzoate and mixed m. p. with authentic specimen, 112°.

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(2) Kötzt, *Ann.*, **358**, 195 (1907).

(3) Young, Hartung and Crossley, *THIS JOURNAL*, **58**, 100 (1936).

(4) Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).

COMMUNICATIONS TO THE EDITOR

COLOR REACTIONS IN VITAMIN K CONCENTRATES

Sir:

During studies of the inactivation of vitamin K by its reaction with bases, we have detected and separated an alcohol-soluble reddish pigment. Recently, Dam, *et al.* [*Helv. Chim. Acta*, **22**, 310 (1939)] described a color reaction of vitamin K concentrates with sodium ethylate in which a transient purple color changing to a reddish-brown color developed. We have determined that our pigment is the end stage of this color reaction and that the quantity of pigment formed

is closely correlated with antihemorrhagic activity. The transient, deep purple color is considerably masked when carotenoid pigments are present; however, it is possible to employ the final, less intense but relatively stable, reddish-brown color as a quantitative measure of the vitamin.

The color reaction is carried out easily by dissolving a few milligrams of concentrate in 1 or 2 cc. of methanol and then adding 1 cc. of sodium methylate (2 to 3 g. of sodium dissolved in 50 cc. of methanol). When warmed for a few minutes, the mixture slowly develops a distinct purple