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, %	$\frac{\text{G. ats. A}}{\text{G. ats. K}}$	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.

DEPARTMENT OF CHEMISTRY AND
CHEMICAL ENGINEERING
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON
R. L. FARRAR, JR.
GEORGE H. CADY

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).