

TABLE I
 PROPERTIES OF COMPOUNDS R—O—C₂H₄—C≡CH

R—	B. p., °C.	Mm.	<i>n</i> _D	Temp., °C.	<i>d</i> ₄	Calcd. <i>M</i> _R D	Found	Hg deriv., m. p., °C.
CH— ^a	87.5	748	1.4117	22	0.8505	24.9	24.6	113.9
C ₂ H ₅ —	104.0	747	1.4148	22	.8273	29.6	29.7	98.6–99.0
C ₄ H ₉ —	147–148	747	1.4191	27	.8185	38.8	39.1	42.2–42.5
HC≡C—C ₂ H ₄ —								
CH ₂ —	164–165	750	1.4519	26	.8980	36.8	36.6	^a
BrCH ₂ —CH ₂ —	99–100	35	1.4788	25	1.3271	37.3	37.8	85.0–86.0
C ₂ H ₅ —O—C ₂ H ₄	84.5–85.5	34	1.4381	24	0.9267	40.23	40.25	^a

^a The mercury derivatives of these two compounds could not be crystallized and decomposed above 100°.

 TABLE II
 ANALYTICAL DATA

Compound	Calculated	Found
C ₂ H ₅ OC ₂ H ₄ C≡CH	C, 73.5; H, 10.2	73.3; 10.1
C ₄ H ₉ OC ₂ H ₄ C≡CH	C, 76.1; H, 11.2	75.8; 10.1
C ₂ H ₅ OC ₂ H ₄ OC ₂ H ₄ C≡CH	C, 67.5; H, 9.9	67.2; 9.3
HC≡CC ₂ H ₄ OC ₂ H ₄ C≡CH	C, 78.7; H, 8.2	78.4; 8.0
BrC ₂ H ₄ OC ₂ H ₄ C≡CH	Br, 45.1	45.3
BrC ₂ H ₄ OC ₂ H ₄ Br	Br, 68.9	68.7
BrC ₂ H ₄ OC ₂ H ₄ OC ₂ H ₅	Br, 40.6	40.6
(CH ₃ OC ₂ H ₄ C≡C) ₂ Hg	Hg, 54.4	54.0
(C ₂ H ₅ OC ₂ H ₄ C≡C) ₂ Hg	Hg, 50.8	50.5
(C ₄ H ₉ OC ₂ H ₄ C≡C) ₂ Hg	Hg, 44.6	44.6
(BrC ₂ H ₄ OC ₂ H ₄ C≡C) ₂ Hg	Hg, 36.3	41.1 ^a

^a This derivative was apparently contaminated with a more highly mercurated compound.

sodium carbonate solution and finally was dried over sodium sulfate and fractionated. The properties of the acetylenes prepared in this manner are given in Table I. In the reaction of sodium acetylide with dibromodiethyl ether, some 2'-bromo-1-ethoxy-3-butyne was also obtained.

The mercury derivatives mentioned in Table I were prepared by the method of Johnson and McEwen⁶ and were recrystallized from benzene.

Summary

1. Some new acetylenic ethers have been described.

2. The physical constants of 2,2'-dibromo-diethyl ether and ethyl 2-bromoethyl glycol ether are reported.

(6) Johnson and McEwen, *THIS JOURNAL*, **48**, 471 (1926).

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NOTES

Concerning the Alleged Absorption of Gaseous Nitrogen by Benzene Solutions of Rubber and Guttapercha Hydrocarbons

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Experiments described by De Jong² have been interpreted as indicating that dilute benzene solutions of rubber or guttapercha hydrocarbon from sheet balata, when exposed to sunlight for a few days in either quartz or ordinary glass vessels, absorb gaseous nitrogen in appreciable amounts.³ If such a photochemical combination of rubber

(1) Now employed at the Whittier, Calif., station of the Bureau of Entomology and Plant Quarantine.

(2) De Jong, *Rec. trav. chim.*, **51**, 153 (1931).

(3) In one case a tube containing 54 cc. of a 1.05% solution of rubber in benzene under an atmosphere of nitrogen was found to draw in 11 cc. of water when opened under the surface of this liquid after six days of irradiation. This was considered to indicate an absorption of 12.8 mg. of nitrogen which according to his calculations represented 2.5% of the weight of the rubber.

and nitrogen actually occurs, one might reasonably expect other unsaturated hydrocarbons containing isoprene units such as carotene and xanthophyll to behave similarly. These substances which always are found closely associated with chlorophyll in green plants possess physiological functions which, as yet, remain quite obscure. It therefore seemed of very great importance from both a theoretical and a practical standpoint to attempt to confirm these results of De Jong.

In the present study the experimental procedure of the original investigation was followed as closely as the description of the work allowed. Several variable factors, such as temperature, barometric pressure, vapor pressure of the benzene solutions and the heating effect of sealing the tubes, were controlled. In one experiment Pyrex tubes of 150-cc. capacity were filled with

100 cc. of nitrogen gas and 50 cc. of benzene solutions containing about 0.5% of either pale crepe rubber or balata. After sealing, these tubes and a benzene control were exposed to direct sunlight during the summer for various lengths of time up to five weeks. At the end of the tests the changes in volume of the nitrogen in the tubes containing the rubber solutions differed from that of the benzene control by a maximum of 0.5 cc. which was found to be about the limit of experimental error.

Another series of experiments was carried out in an apparatus which consisted of several volumetric reaction chambers in the form of glass tubes fitted with stopcocks and attached to a mercury leveling bulb. The tubes were charged with about 100 cc. of nitrogen and one, reserved for a control, with 50 cc. of pure benzene and the others with 50 cc. each of 1.1% benzene solutions of one of the following types of rubber: pale crepe (from a shipment just received), fine Para from South America, smoked sheet or balata. Even though the tubes were exposed to direct sunlight for three months during the summer the slight changes in volume of the gas were in every case less than 1 cc. and, in each of the rubber solutions, were actual *increases*.

It may be concluded that under the conditions described and with the specimens of rubber, nitrogen and benzene used, nitrogen gas is not absorbed to any appreciable extent.

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The Formation of Atacamite by the Incorporation of Copper Powder in Magnesium Oxychloride Compositions

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When magnesium oxychloride compositions that contain copper harden in the presence of air,

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the formation of a new phase is indicated by the development of a blue-green color as well as by an increase in strength and a reduction in solubility.

The new blue-green phase was found by X-ray examinations to be identical with atacamite and also cupric oxychloride prepared by dissolving freshly precipitated cupric carbonate in a solution of cupric chloride. This is in harmony with the observations of other investigators² who have shown that copper is corroded by certain chloride

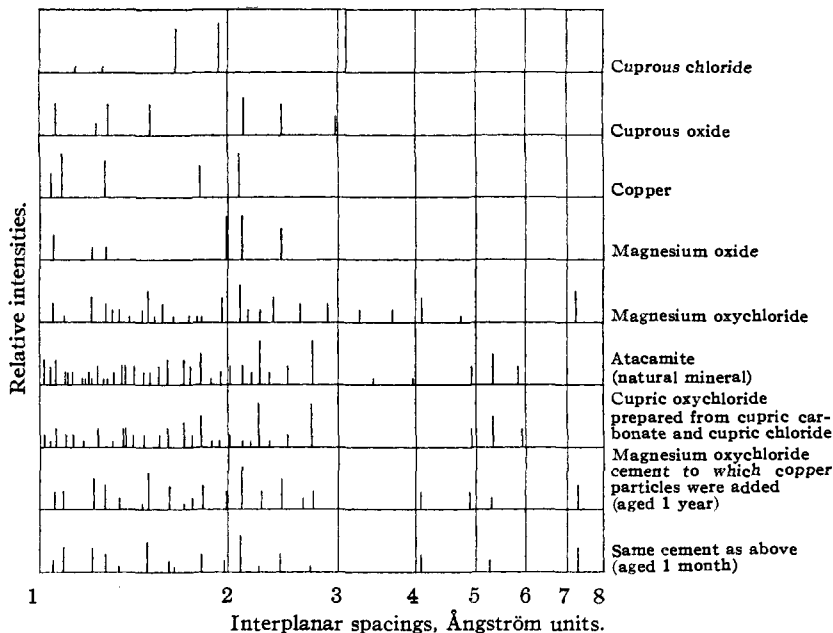


Fig. 1.—Diffraction data.

solutions in the presence of air to form a basic chloride resembling atacamite.

X-Ray diffraction analyses were made by the Debye-Scherrer method on a sample of the oxychloride cement after aging first for one month and then for one year. The radiation from an X-ray tube provided with a copper target was used, after filtering through nickel, in a camera of 57.3-mm. effective diameter. The specimens used were rods of 0.7-mm. diameter formed from the powdered samples with collodion as a binder. The interplanar spacings obtained from the photograms are shown in the accompanying figure, which includes data obtained in a similar way for cupric oxychloride, atacamite, magnesium oxychloride, copper, cupric chloride, cuprous chloride and magnesium oxide. The relative intensities of the corresponding diffraction lines were estimated visually.

Both unaged and aged oxychloride cements contain, as a major constituent, a material corresponding to magnesium oxychloride, as the similarity of the diffraction data indicates. Diffraction lines corresponding to the stronger

(2) Benough and May, *J. Inst. Metals*, **32**, 131 (1924); Vernon and Whitby, *ibid.*, **34**, 389 (1930); Mellor, "Inorganic and Theoretical Chemistry," Vol. III, pp. 15, 69, 77, 150, 161; Rooksby and Churnside, *J. Soc. Chem. Ind., Trans.*, **53**, 33 (1934).