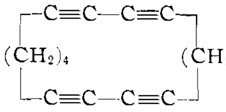
was essentially the only product formed. However when the reaction was carried out in aqueous ethanol at 55°, air being bubbled through the mixture, three substances were formed. The first (*ca.* 40% yield) was the dimer Ib, which on hydrogenation gave hexadecane. The second (*ca.* 20% yield) was the tetramer, dotriaconta-1,7,9,15,17,-23,25,31-octayne (Ic) (m.p. 92–93°, $\lambda_{\max.}$ 226, 240 and 254 mμ, log ϵ 1190, 1140 and 720, respectively, $\nu_{\max.}$ 3310 and 2235 cm.$^{-1}$, found: C, 92.11; H, 7.93), the structure of which was confirmed by hydrogenation to dotriacontane. The third (*ca.* 10% yield) was the cyclic dimer II [m.p. 158–160° (dec.), $\lambda_{\max.}$ 227, 239 and 254 mμ, log ϵ, 580, 600 and 360, respectively, $\nu_{\max.}$ 2235 cm.$^{-1}$ (–C≡C–) but not at *ca.* 3330 cm.$^{-1}$ (no ≡C–H), found: C, 92.48; H, 7.62]. The structure was confirmed by the infrared spectrum, the absence of a precipitate with alcoholic silver nitrate and by full hydrogenation to cyclohexadecane, identified by direct comparison with an authentic sample.

$H[—C\equiv C—(CH_2)_4—C\equiv C—]_nH$

Ia, $n = 1$
b, $n = 2$
c, $n = 4$



(II)

The cyclic dimer II must have been formed directly from two molecules of the monomer by coupling at both ends, rather than via the dimer Ib which cyclizes internally, for separate oxidative coupling of the dimer Ib yielded only the tetramer Ic and none of the cyclic dimer II.

The cyclic tetra-acetylene II, the first carbocyclic compound incorporating more than two acetylenic linkages,[2] contains two parallel straight α-diacetylene chains bound together on both sides by a tetramethylene bridge. As in the compounds studied by Cram, *et al.*, in which two parallel groups ( or -C≡C-) are joined by two tetramethylene bridges,[2,3] the chromophoric systems in II are too far apart for appreciable interaction to occur, as judged by the normal ultraviolet spectrum.

The scope of the new cyclization reaction and the properties and transformations of II are now being investigated. We are indebted to Prof. V. Prelog for a sample of cyclohexadecane.

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(2) D. J. Cram and N. L. Allinger (THIS JOURNAL, **78**, 2518 (1956)) have recently described the preparation of cyclododeca-1,7-diyne via an acyloin type cyclization. Moreover G. Eglinton and A. R. Galbraith have privately communicated to us that they have prepared cyclic polyacetylenes by the coupling of terminal diacetylenes.

(3) D. J. Cram, *et al.*, *ibid.*, **76**, 6132 (1954); **77**, 4090 (1955).

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ACTION OF GAMMA RAYS ON FERROUS ION SOLUTIONS IN HEAVY WATER

Sir:

The action of cobalt 60 gamma radiation on solutions of ferrous ammonium sulfate in light and heavy water mixtures has been investigated. Irradiations were carried out in six cylindrical sample holders rotating about their own axes and around two central 2-Curie Co^{60} sources. Ferric ion concentrations were determined colorimetrically using the ferric thiocyanate complex. We found extinction curves to be dependent on the concentration of heavy water and have determined these curves experimentally for all water compositions used. The solutions irradiated were 0.8 *N* in H_2SO_4 and 1 mM. in ferrous ammonium sulfate and contained oxygen. Radiation doses varied from 1 to 20 × 10^{20} ev./liter. Results of our experiments are shown in Table I:

TABLE I

FERRIC ION YIELDS FOR H_2O–D_2O MIXTURES

Atom % D in solvent hydrogen	$G_{Fe^{+++}}$
0	15.5 (assumed)
55	16.1 ± 0.2
85	17.0 ± 0.5
98	18.6 ± 0.8

It is reported by Hart[1] that the primary yield for molecular hydrogen is higher in light than in heavy water. Probably this means that the radical DO_2 is formed with a higher yield than HO_2 and this difference may play an important role in the differences we have observed. He also indicates that the difference between the yield of free radicals in heavy water and in light water is more than equivalent to the first difference. If this excess is real it is reasonable to ascribe it to a higher recombination rate of hydroxyl radicals with free atoms of light hydrogen than of deuterium. For both these reasons it is of interest to consider our *G*-values as a function of the ratio of light hydrogen to deuterium in the free hydrogen radicals in the solution. If we calculate the light hydrogen to deuterium ratio in the free atoms from the figures given by Topley and Eyring,[2] we find that our *G*-values depend on the isotope ratio in the free atoms in a way which is not far from linear. It should be kept in mind, however, that representations of similar simplicity of the value of *G* can be obtained as a function of other quantities such as the mole fraction of DOD molecules in the liquid. These considerations seem to make it important to compare by direct measurement the G-values of molecular H_2, HD and D_2 in solutions of ferrous sulfate in various concentrations of light and heavy water.

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(1) E. J. Hart, W. R. McDonell, and S. Gordon Proceedings of the Geneva Conference on Peaceful Uses of Atomic Energy (United Nations, New York, 1956) Volume 7, p. 593 (1955).

(2) B. Topley and H. Eyring, *J. Chem. Phys.*, **2**, 217 (1934).