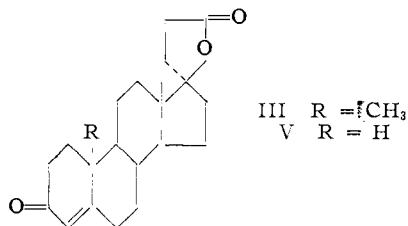


with metallic lithium<sup>4</sup> thereby causing reduction of both the triple bond and the aromatic A ring. Hydrolysis with mineral acid followed by chromatography yielded 3-(3-oxo-17 $\beta$ -hydroxy-19-nor-4-androsten-17 $\alpha$ -yl)propionic acid  $\gamma$ -lactone (V), m.p. 126.5–127° (137–138°),  $[\alpha]_D^{25} +22.7^\circ$  (CHCl<sub>3</sub>); *Anal.* Calcd. for C<sub>21</sub>H<sub>28</sub>O<sub>3</sub>: C, 76.79; H, 8.59. Found: C, 76.49; H, 8.34.



Bioassay<sup>5</sup>—reversal of the effect of desoxycorticosterone (DOC) on the urinary Na-K ratio of adrenalectomized rats was used as a measure of potency. If progesterone, recently described as capable of reversing the effect of DOC,<sup>6</sup> is assigned an activity of 1, then III and V were found to have an activity of approximately 8 and 27, respectively. In similar tests III and V also reversed the electrolyte effects of aldosterone.

(4) A. L. Wilds and N. A. Nelson, *THIS JOURNAL*, **75**, 5360 (1953).

(5) The details of bioassay will be reported elsewhere.

(6) R. L. Landau, D. M. Bergenstal, K. Lugibihl, and M. E. Kaschl, *J. Clin. Endocrinol. and Metabolism*, **15**, 1194 (1955).

DIVISIONS OF CHEMICAL AND BIOLOGICAL RESEARCH  
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RECEIVED JULY 24, 1957

#### CYCLIZATION IN GAMMA RAY IRRADIATED HIGH DENSITY POLYETHYLENE

Sir:

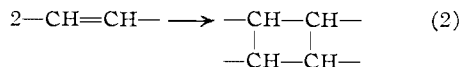
Material balance in the irradiation of polyethylene has never been convincingly attained, especially at liquid nitrogen temperatures where  $G(H_2)$  and  $G(-CH=CH-)$  are essentially equal to their values at room temperature while cross link formation is sharply reduced.<sup>1</sup>

As adapted to the high density polyethylene, Marlex-50, and considering no chain scission, the material balance equation can be written

$$[H_2] + [Vi^0 - Vi] = \frac{1}{2}[R] + [VI] + [C.L.] + [E.L.] + [S.L.] + [R.L.] \quad (1)$$

where brackets signify moles per gram of substances produced during the irradiation except for  $Vi^0 - Vi$  which represents moles/g. of vinyl groups destroyed. R, VI, C.L., E.L., S.L. and R.L. signify free radicals, vinylene groups, cross, end,<sup>2</sup> square and ring links, respectively.

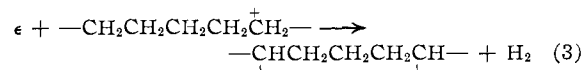
By "square" links we mean double cross links formed by a reaction such as



(1) A. Charlesby and W. H. T. Davison, *Chem. and Ind.*, 232 (1957).

(2) A. Charlesby has proposed the term "end link," *Proc. Roy. Soc.*, **A231**, 521 (1955).

Such a square link is assumed in Eq. (1) to constitute one cross link as well as one square link. By "ring" links we mean intramolecular bonds formed by reactions such as



( $\epsilon$  represents the electron). Equation (3) is similar to a reaction proposed earlier.<sup>3</sup> Other ring forming reactions could be proposed.

Cross links and vinylene groups formed by irradiation have been recognized since 1950,<sup>3</sup> but ring or square links have never before been observed in the irradiation of any substance as far as we know. It is the purpose of this note to present evidence for cyclization during irradiation.

1,2-Disubstituted cyclopentane and cyclohexane derivatives absorb<sup>4</sup> in the infrared approximately at wave lengths of 10.2  $\mu$  with extinction coefficients varying between 6 and 28 l. cm<sup>-1</sup>. mole<sup>-1</sup>. In Marlex-50 the initial absorption at 10.0 and 10.98  $\mu$  due to the vinyl group rapidly falls with irradiation at room temperature and *in vacuo* (initial  $G(-vinyl)$  equal to 7.7), revealing the growth of another absorption at 10.1  $\mu$  which is approximately the wave length at which *trans* 1,2-disubstituted cyclopentanes and hexanes absorb. We have attributed the growth of this peak to the formation of ring links of this size (other ring or square links which might absorb at this wave length are not excluded). A similar growth in the peak at 10.1  $\mu$  was found also in the case of a Ziegler-type polyethylene.

An order of magnitude estimate of  $G$  (*trans* ring links) is 1.0 which is of sufficient magnitude to show the necessity of considering cyclization in attempting to achieve a material balance.

In the case of a low density polyethylene, the vinylene peak at 10.3  $\mu$  is broader than in the case of Marlex-50 and possibly obscures the peak due to the ring systems. The 10.3  $\mu$  peak is unsymmetrical, however, which suggests that ring links are produced in low as well as high density polyethylenes.

This research was supported by a grant from the U.S. Atomic Energy Commission.

(3) M. Dole, Report of Symposium IV, "Chemistry and Physics of Radiation Dosimetry," Army Chemical Center, Md., September, 1950.

(4) "Catalog of Infrared Spectral Data" of the American Petroleum Institute Research Project, Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

(5) Fulbright Fellow, 1956.

(6) On leave from A.E.R.E., Harwell, England.

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RECEIVED JUNE 17, 1957

#### ENZYMATIC OXYGEN FIXATION INTO ACETATE CONCOMITANT WITH THE ENZYMATIC DECARBOXYLATION OF L-LACTATE

Sir:

The enzymatic incorporation of molecular oxygen into various organic substrates recently has been