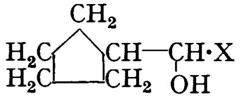
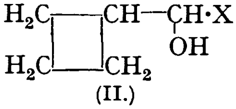
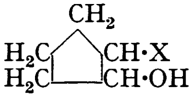
97.—*The Reformatsky Reaction with Compounds of the Ethylene Oxide Type.*

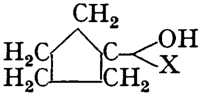
By G. R. Clemo and J. Ormston.

In a previous paper (J., **1932**, 1778), we investigated the course of the Reformatsky reaction on *cyclo*hexene oxide, using ethyl bromoacetate, and stated that possibly the oxide first isomerised to give *cyclo*pentane aldehyde, which then reacted to give ethyl β-hydroxy-β-*cyclo*pentylpropionate (I).


(I.)


(II.)


(III.)


(IV.)

($X = CH_2{\cdot}CO_2Et$.)

This has now been found to be the case. *cyclo*Pentane aldehyde was prepared according to the method of Bedos (*Compt. rend.*, 1929, **189**, 255), who, however, gives no experimental details. The Reformatsky reaction with the aldehyde gave (I) as an oil which readily formed a hydrazide, m. p. 154°, identical with that obtained from *cyclo*hexene oxide.

It was clearly of interest to repeat the work, *cyclo*pentene oxide being used. If this reaction were analogous to the previous one, the product would be the *cyclo*butane derivative (II), but it seemed more probable, however, that the reaction would either give (III) or that the *cyclo*pentene oxide would first isomerise in the course of the reaction to *cyclo*pentanone and then give ultimately ethyl *cyclo*pentan-1-ol-1-acetate (IV). The latter alternative has been found to be correct, since when either *cyclo*pentene oxide or *cyclo*pentanone is treated with zinc and bromoacetic ester the resulting ester (IV) gives in both cases the same crystalline hydrazide, m. p. 143°.

cyclo*Pentane Aldehyde*.—12 G. of *cyclo*hexene oxide were added to magnesium bromide etherate prepared from Mg (3 g.), Br (20 g.), and Et_2O (200 c.c.) according to the method of Menschutkin (*Z. anorg. Chem.*, 1906, **49**, 34). It was necessary to cool the reaction flask. The whole was then kept over-night, the Et_2O removed, and to the cooled residue H_2O was cautiously added. The dark-coloured upper layer was extracted with Et_2O and to the ethereal solution sat. $NaHSO_3$ aq. was added. After 12 hr., the bisulphite compound was collected, added to K_2CO_3 aq. and, after 2 hr., steam-distilled. The *cyclo*pentane aldehyde (2·5 g., b. p. 135°) was obtained from the distillate in the usual way and gave a cryst. semicarbazone, m. p. 123° (Found : C, 54·3; H, 8·3. Calc. for $C_7H_{13}ON_3$: C, 54·2; H, 8·4%).

Ethyl β-*Hydroxy*-β-cyclo*pentylpropionate* (I).—*cyclo*Pentane aldehyde (2 g.), ethyl bromoacetate (4·5 g.), and Zn wool (2 g.) in dry C_6H_6 (15 c.c.) were heated on the water-bath for 3 hr. The usual method of working up (cf. J., 1932, 1782) gave the *ester* (I) (3·25 g.), b. p. 117°/14 mm. (Found : C, 64·5; H, 9·2. $C_{10}H_{18}O_3$ requires C, 64·5; H, 9·7%). The ester, mixed with hydrazine hydrate (90—95%), gave a *hydrazide*, needles from H_2O, m. p. 154° alone or mixed with the hydrazide of the product of the Reformatsky reaction on *cyclo*hexene oxide (Found : C, 56·2; H, 9·15; N, 16·25. $C_8H_{16}O_2N_2$ requires C, 55·8; H, 9·3; N, 16·3%).

The Action of Zinc and Ethyl Bromoacetate on cyclo*Pentene Oxide*.—The oxide (2 g.), made in the same way as *cyclo*hexene oxide (" Organic Syntheses," Vol. **5**, p. 35), bromoacetic ester (4·5 g.), and Zn wool (2 g.) in C_6H_6 (15 c.c.) were heated for 3 hr. on the water-bath. The usual method of working up yielded a sweet-smelling ester (1 g.), b. p. 108°/18 mm. (Found : C, 63·25; H, 9·1. Calc. for $C_9H_{16}O_3$: C, 62·8; H, 9·3%), which gave a *hydrazide*, shining platelets from EtOAc, m. p. 143° (Found : C, 52·8; H, 8·8. $C_7H_{14}O_2N_2$ requires C, 53·2; H, 8·9%).

Ethyl cyclo*Pentan*-1-*ol*-1-*acetate* (IV).—The reaction was carried out as just described, except that *cyclo*pentanone (2 g.) was used instead of *cyclo*pentene oxide. The usual method of working up gave ethyl *cyclo*pentan-1-ol-1-acetate, b. p. 108°/18 mm., which with hydrazine hydrate gave a hydrazide, m. p. 143°, identical with that obtained above.

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[*Received, March* 1*st*, 1933.]