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7,10,14-TRI-*t*-BUTYL-3-METHOXY-1,8-BISDEHYDRO[14]ANNULENE. A NOVEL AROMATIZATION REACTION OF A CARBOXY DERIVATIVE OF 14-MEMBERED CYCLIC TETRAENDIYNE GLYCOL

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As reported in a previous paper (1), we have prepared 14-membered cyclic tetraendiyne glycol (II) as a precursor of 7,10,14-tri-*t*-butyl-3-carboxy-1,8-bisdehydro[14]annulene (V), *i.e.*, treatment of II at -40°C with stannous chloride dihydrate in ether saturated with hydrogen chloride yielded the carboxyannulene (V) in a reasonable yield. Development of red color was observed when a solution of II in ether saturated with hydrogen chloride was kept for a while at -40°C. This fact indicates that II undergoes transformation into conjugated system by the action of hydrogen chloride.

In this communication, we wish to report the formation of tri-*t*-butylmethoxybisdehydro[14]annulene (IV) under non-reductive condition.

Ketone (I, 207 mg, 0.457 mmol) (1) in tetrahydrofuran (50 ml) was added over a period of 7 hr. to a suspension of finely powdered potassium hydroxide (2.0 g) in liquid ammonia (500 ml) (2). After the mixture had been stirred for 11 hr., ammonium chloride (4.0 g) was added to the reaction mixture, and the ammonia was allowed to evaporate. The residue was extracted with ether, and the extract was worked up in the usual way to give crude II, which could not be crystallized. Ether saturated with hydrogen chloride (10 ml) was added at room temperature to a stirred solution of crude II in ether (20 ml). After being stirred for 10 min., the reaction mixture was mixed with water (50 ml), and extracted with ether. The crude product obtained by working up the extract in the usual manner was chromatographed on silica gel (Merck, Kiesel Gel 60, 20 g). Elution with benzene-hexane (3:7) afforded red prisms [80 mg, 46% based on I; mp 164-166°C (dec.) (from ether-hexane)]. Analytical and spectral data indicate that the red prisms are 7,10,14-tri-*t*-butyl-3-methoxy-1,8-bisdehydro[14]annulene (IV) [Anal. Found: C, 86.18; H, 9.69%. Calcd. for $C_{27}H_{36}O$: C, 86.11; H, 9.64%, Mol. Wt., 376; Mass (m/e): 376 (M^+), 361 (M-15); IR(KBr-disk): 2970, 2900, 2860, 2105, 2030, 966 cm^{-1} ; UV(THF): λ_{max} (ε) 243.5 (7760), 249 (9290), 255 (10600), 261 (8780), 304sh (28800), 330 (148000), 438sh (11000), 460 (18800), 528 (416), 549 (480), 593.5 (2430) nm; NMR($CDCl_3$): τ 0.71d (1H, J=14), 0.77d (1H, J=14),

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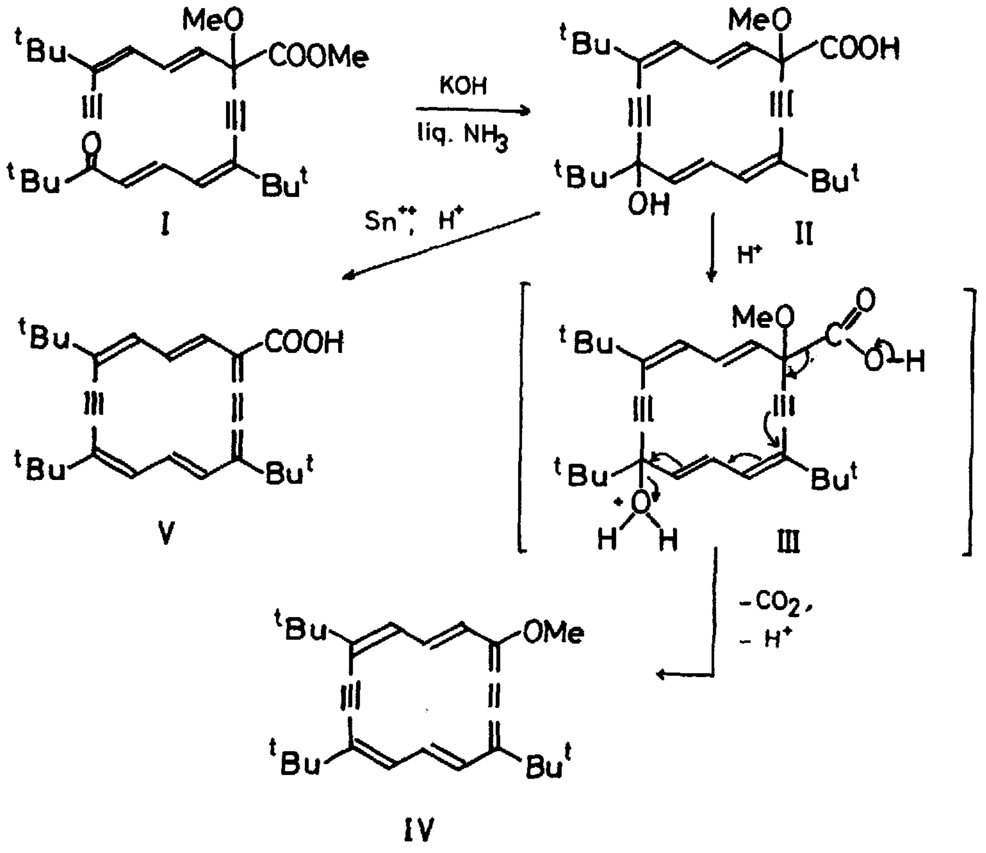

0.85d (1H, J=14), 1.05d (1H, J=14) (outer protons); 5.47s (3H, OCH_3); 8.12s (18H, *t*-Bu); 8.15s (9H, *t*-Bu); 14.28t (2H, J=14, inner protons)]. The NMR spectrum indicates that the methoxyannulene (IV) is strongly diatropic.

Formation of tri-*t*-butylmethoxybisdehydro[14]annulene (IV) from II by the action of hydrogen chloride can be explained reasonably assuming intermediacy of protonated species (III), *i.e.*, separation of a water molecule from III followed by electron displacement accompanied by decarboxylation should result in the formation in the methoxyannulene (IV).

Decarboxylative aromatization of carboxy derivative of cyclic glycol seems to offer a new route to the synthesis of hydroxy or alkoxy substituted dehydroannulenes, and the studies along this line are now in progress.

References

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