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SYNTHESIS OF SUBSTITUTED BUTATRIENES AND NOVEL STRUCTURES OF THEIR O2-OXIDATION PRODUCTS

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Synthesis of three 2,3-diiodo-1,3-dienes and conversion of these dienes into butatrienes are described. 2,5-Dimethylhexa-2,3,4-triene polymerizes on exposure to air to give the polymeric peroxide $(C_{6}H_{12}O_{2})_{n}$ which is reassigned as the structure containing acetylene and peroxide units.

In a previous paper we have reported the simple and efficient synthesis of octamethyl[4]radialene (3) and/or dodecamethyl[6]radialene (4) using Ni(0)-species prepared in situ from Ni(II)-species by reduction with zinc.¹⁾ Under these reaction conditions 3,4-dihalo-2,5-dimethylhexa-2,4-diene (1) could be cooligomerized to radialenes via 2,5-dimethylhexa-2,3,4-triene (2). Therefore, we investigated further the synthesis of substituted 2,3-dihalo-1,3-butadienes and butatrienes. This paper concerns the synthesis of substituted butatrienes and structures of their air-oxidation products.



It is known that the reactions of acetylenic 1,4-glycols with hydrohalogenoic acids give mainly 2,3-dihalo-1,3-dienes (7) together with small amounts of acetylenic 1,4-halides (ξ) or their derivatives.²) In this reaction hydrobromic acid and hydriodic acid are generally used. Therefore, we undertook the conversion of ξ into 7 (X=I) with hydriodic acid.

The diol $(8)^{3}$ could be converted into the corresponding 2,3-diiodo-1,3-diene (9) on treatment with hydriodic acid under similar reaction conditions reported for $1b^{4}$ $(9,^{5})$ colorless cryst., 65%, mp 52.5-53.0 °C). However, treatment of 10 with hydriodic acid gave a complex mixture containing $11.^{6}$ After several unsuccessful attempts, the conversion of 10 into 11 was found to be achieved with Me₃SiI. To a solution of 10 in CH₂Cl₂ was added slowly a solution of Me₃SiI

(5 equiv.) in CH_2Cl_2 at -30 °C and then the mixture was stirred at the same temperature for lh. After usual work-up the reaction mixture was chromatographed on silica gel to give pure 11^{7} (colorless cryst., 41%, mp 95.0-97.0 °C). Although treatment of 12 with hydrobromic acid gave mainly 2,5-diphenyl-1,5-dien-3-yne,⁸) the conversion of 12 into 13 could be accomplished with Me₃SiI in a similar manner as above (13,⁹) pale yellow liquid).

The preparation of 2,3-dihalo-1,3-dienes (7) is believed to be easy, because many acetylenic 1,4-glycols (5) give 7 on treatment with hydrohalogenoic acid, PBr₃, SOBr₂, etc.¹⁰⁾ Nevertheless, the reaction product must be carefully examined in some case. For example, the reaction of 14 with PBr₃ has been reported to give 16^{11} (mp 125-128 °C), but our experiments show that the product (mp 127.0-128.0 °C) obtained is to be assigned to the acetylenic 1,4-dibromide (15) on the basis of its spectral data.¹²)

Synthesis of the butatrienes (2, 13) 17, 18, and 19^{14}) can be achieved by reduction of the dihalides (1a, 1b, 9, 11, and 13) with zinc powder. However, we have studied an alternative method to prepare the air sensitive butatrienes more efficiently and also to introduce the central double bond regiospecifically.



Chemistry Letters, 1 9 8 4

A typical procedure is as follows. To a solution of 1b (10 mmol) in ether (100 ml) was added a solution of BuLi (1.05 equiv.) in hexane at -70 °C and the reaction mixture was stirred at -70 °C for lh. Pentane (50 ml) was added and then the mixture was allowed to warm to -20 °C. Water (3 ml) was added and the mixture was finally warmed to room temperature. Anhydrous MgSO4 was added to remove water and filtered off. Removal of the solvents gave pure $\frac{2}{2}$ in an almost quantitative yield [¹H-NMR in CCl₄ shows only a signal peak at δ 1.85 (s)]. Similar treatment of 2 and 11 with BuLi afforded 17 and 18, respectively, in almost quantitative yields (17,15) colorless liquid, bp 32 °C/ 0.1 Torr; 18,16) colorless cryst., mp 81.5-82.0 °C). Conversion of 13 into 19 was likewise carried out with BuLi. In this case only one isomer of the butatriene (19, yellow cryst., 48%, mp 125.0-127.0 °C) was obtained and the structure was assigned to the (Z)-isomer by comparing its ¹H- and ¹³C-NMR data with those of (Z)-2,5-diphenylhexa-2,3,4-triene obtained by Vermeer et al.¹⁷⁾ Reduction of $13_{\sqrt{2}}$ with zinc (CH₃CN, reflux, 4h) resulted in the formation of a 1:1 mixture of the (Z) - and (E)-butatrienes (19 and 19¹⁸⁾), which were also formed by heating a solution of 19 at 80 °C for 4h.

When a solution of 2 in CCl₄ (0.03-0.5 moldm⁻³) was allowed to stand at room temperature for several days, a new signal at δ 1.47 (s) was observed in the $^1\text{H-}$ NMR spectrum. Removal of the solvent gave a colorless crystalline compound [mp 106.5-108.0 °C, 47% based on 1b, Found: C, 68.35; H, 8.60%. Calcd for (C₈H₁₂O₂)_n: C, 68.54; H, 8.63%. ¹³C-NMR (CCl₄) δ 85.6 (-C=C-), 74.6 (=C-C-O), 27.1 (Me)]. The FD-Mass spectrum of the product obtained from the dilute solution of 2 showed molecular ion peak at m/e 280 together with the intense peak at m/e 281, which may suggest the formation of the cyclic peroxide (21), but the measurement by vapor pressure osmometer (benzene as solvent) indicates the average molecular weight of 3490. The IR spectrum of the product in CCl_A showed no absorption at 4000-3050 cm⁻¹ corresponding to the hydroxyperoxide (-O-O-H) and the Raman spectrum (KBrdisk) showed the absorptions at 2230 s (-C≡C-) and 868 vs (-O-O-). Therefore, the crystalline compound obtained from 2 has proved to be the cyclic peroxide polymer (20, n \simeq 25) presumably containing the dimer (21), which could not be separated by chromatography owing to decomposition on silica gel or alumina. The butatriene (18) bearing cyclohexane rings as terminal groups also gave the cyclic peroxide polymer (23) on exposure to air. The structure of 23 was found to be analogous to that of 20 by comparison of $^1\text{H-}$ and $^{13}\text{C-NMR}$ spectra [23, $^1\text{H-NMR}$ (CCl_4) δ 1.98-1.34 (m); ${}^{13}C-NMR$ (CCl₄) δ 86.5 (-C=C-), 77.9 (=C-C-O), 35.8, 25.8, 22.8 (-CH₂-)]. Skatteb ϕ l^{13b)} and Köbrich^{13e)} obtained independently the insoluble polymeric peroxide on exposure of $\frac{2}{2}$ to air both in solution and in the crystalline state, and assigned the structure of the peroxide to the 1,3-butadiene-like peroxide $\binom{22}{20}$. Although our polymeric peroxide is more soluble (smoothly in CCl₄, benzene, CH₂Cl₂, CHCl₂, etc.) than that obtained by Skatteb¢l and Köblich, the ¹H-NMR, IR, and Raman spectra of both peroxides are identical (the difference in the solubility may be due to the configuration of the polymer). Consequently, we conclude that the structures of the polymeric peroxides obtained from $\frac{2}{2}$ and $\frac{18}{20}$ are to be assigned as the novel cyclic peroxide polymers (20 and 23) containing acetylene and peroxide units.

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133

References

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- 2) F. Théron, M. Verny, and R. Vessière, "The Chemistry of the Carbon-Carbon Triple Bond, Part 1," ed by S. Patai, John Wiley (1978), Chap. 10 and references cited therein.
- The diol (8) was prepared by the reaction of cyclohexanone with the Grignard derivatives of 3-methyl-l-butyn-3-ol in 80% yield.
- 4) Y. S. Zalkind, B. Rubin, and A. Kruglov, J. Russ. Phys.-Chem. Soc., <u>58</u>, 1044 (1926); Chem. Abstr., <u>22</u>, 1137 (1928).
- 5) 2, Mass (m/e) 402 (M⁺); ¹H-NMR (CDCl₃) δ 2.5-2.2 (m, 4H), 1.94 (s, 3H), 1.73 (s, 3H), 1.7-1.4 (m, 6H); ¹³C-NMR (CDCl₃) δ 146.5, 139.7, 100.0, 98.7 (sp²), 39.9, 31.5, 29.8, 27.2, 26.5, 26.1, 20.4 (sp³).
- 6) Dehydration occurs easily by treatment of 10 with acids, see R. A. Raphael, "Acetylenic Compounds in Organic Synthesis", Butterworth Scientific Publications (1955).
- 7) 11, Mass (m/e) 442 (M⁺); ¹H-NMR (CDCl₃) δ 2.33-2.25 (m, 8H), 1.53 (m, 12H); ¹³C-NMR(CDCl₃) δ 146.5, 97.6 (sp^2), 40.1, 31.8, 27.3, 26.7, 26.3 (sp^3).
- 8) Zalkind et al. reported¹⁹⁾ that the reaction of 12 with hydriodic acid gave the dihydrofuran derivative (24) and 2,5-diphenyl-3,4-diiodo-2,4-diene (13, mp 145-146 °C. However, the structure should be reinvestigated, because reduction of the compound (13) with zinc did not yield a mixture of the butatrienes (19 and 19'). On the other hand, Jasiobedzki reported²⁰⁾ the formation of 25 by the reaction of 12 with HI in ethanol.



- 9) 13, Mass (m/e) 486 (M⁺); ¹H-NMR (CDCl₃) & 7.25-7.08 (m, 6H), 6.96-6.76 (m, 4H), 2.02 (s, 6H); ¹³C-NMR (CDCl₃) & 140.3, 127.3, 127.0, 126.8 (aromatic sp²), 143.5, 108.9 (sp²), 31.1 (Me). The geometry of 13 was determined by the symmetrical ¹H-NMR and high field shift of *o*-protons of benzene rings.
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- 12) 15, Mass (m/e) 350, 352, 354 (M⁺); ¹H-NMR (CDCl₃) δ 1.99 (s, 6H, Me), 1.21 (s, 18H, *t*-Bu); ¹³C-NMR (CDCl₃) δ 89.4 (-C=C-), 66.8 (=C-C-Br), 40.7 (-CMe₃), 29.8 (Me), 26.5 (Me of *t*-Bu groups).
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- 14) H. Westmijze, T. Meijer, and P. Vermeer, Tetrahedron Lett., 1975, 2923.
- 15) 17, Mass (m/e) 148 (M⁺); ¹H-NMR (CCl₄) δ 2.3-2.1 (m, 4H, -CH₂-), 1.83 (s, 6H, Me), 1.7-1.5 (m, 6H, -CH₂-); ¹³C-NMR (CCl₄) δ 154.9, 151.5 (*sp*), 114.7, 106.3 (*sp*²), 34.6, 27.7, 26.1 (-CH₂-), 23.8 (Me).
- 16) 18, Mass (m/e) 188 (M⁺); ¹H-NMR (CCl₄) δ 2.20 (br. s, 8H, allylic CH₂), 1.59 (br. s, 12H, nonallylic CH₂); ¹³C-NMR (CCl₄) δ 152.0 (sp), 114.8 (sp²), 34.6, 27.5, 26.1 (-CH₂-).
- 17) 19, Mass (m/e) 232 (M⁺); ¹H-NMR (CDCl₃) δ 7.6-7.1 (m, aromatic), 2.40 (s, Me); ¹³C-NMR (CDCl₃) δ 152.1 (sp), 139.0, 128.4, 127.3, 126.1 (aromatic sp²), 113.7 (sp²), 20.6 (Me).
- 18) 19', ¹H-NMR (CDCl₃) δ 7.6 \sim 7.1 (m, aromatic), 2.35 (s, Me); ¹³C-NMR (CDCl₃) δ 152.1 (sp), 139.4, 128.4, 127.3, 116.5 (aromatic sp²), 114.0 (sp²), 20.5 (Me).
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