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SYNTHESIS OF SUBSTITUTED BUTATRIENES AND NOVEL STRUCTURES OF THEIR O_2-OXIDATION PRODUCTS

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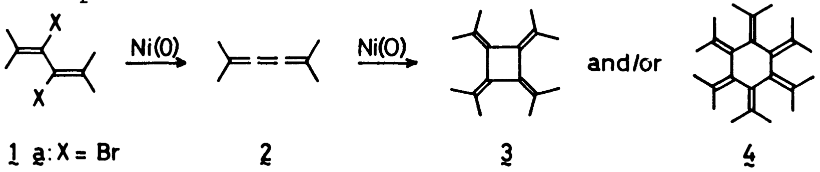
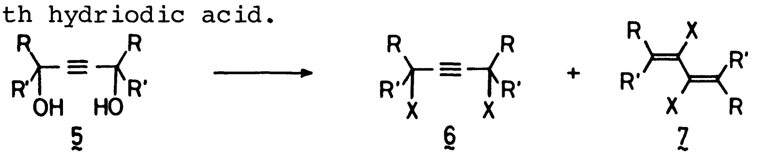
Synthesis of three 2,3-diiodo-1,3-dienes and conversion of these dienes into butatrienes are described. 2,5-Dimethylhexa-2,3,4-triene polymerizes on exposure to air to give the polymeric peroxide $(C_6H_{12}O_2)_n$ which is reassigned as the structure containing acetylene and peroxide units.

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 <u>in situ</u> 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 <u>via</u> 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.



1 **a**:X = Br
b:X = I
2
3
4

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 (**6**) or their derivatives.$^{2)}$ In this reaction hydrobromic acid and hydriodic acid are generally used. Therefore, we undertook the conversion of **5** into **7** (X=I) with hydriodic acid.



5
6
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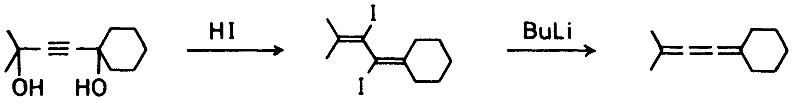
The diol (**8**)$^{3)}$ could be converted into the corresponding 2,3-diiodo-1,3-diene (**9**) on treatment with hydriodic acid under similar reaction conditions reported for **1b**$^{4)}$ (**9**,$^{5)}$ colorless cryst., 65%, mp 52.5-53.0 °C). However, treatment of **10** with hydriodic acid gave a complex mixture containing **11**.$^{6)}$ After several unsuccessful attempts, the conversion of **10** into **11** was found to be achieved with Me_3SiI. To a solution of **10** in CH_2Cl_2 was added slowly a solution of Me_3SiI

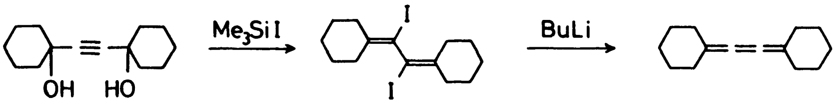
(5 equiv.) in CH_2Cl_2 at -30 °C and then the mixture was stirred at the same temperature for 1h. After usual work-up the reaction mixture was chromatographed on silica gel to give pure 11[7] (colorless cryst., 41%, mp 95.0-97.0 °C). Although treatment of 12 with hydrobromic acid gave mainly 2,5-diphenyl-1,5-dien-3-yne,[8] the conversion of 12 into 13 could be accomplished with Me_3SiI 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, PBr_3, $SOBr_2$, etc.[10] Nevertheless, the reaction product must be carefully examined in some case. For example, the reaction of 14 with PBr_3 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]

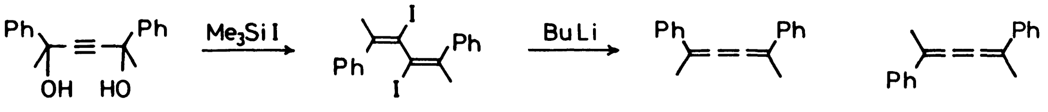
Synthesis of the butatrienes (2,[13] 17, 18, and 19[14]) can be achieved by reduction of the dihalides (1a, 1b, 9, 11, and 13) with zinc powder. However, we have studied an alternative method to prepare the air sensitive butatrienes more efficiently and also to introduce the central double bond regiospecifically.



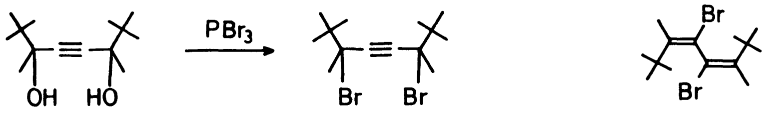
8 9 17



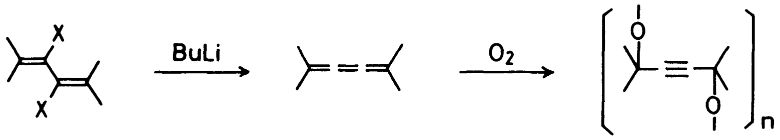
10 11 18



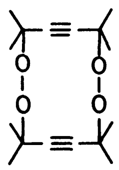
12 13 19 19'



14 15 16



1a,b 2 20



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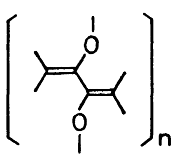

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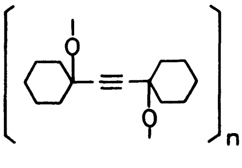

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A typical procedure is as follows. To a solution of **1b** (10 mmol) in ether (100 ml) was added a solution of BuLi (1.05 equiv.) in hexane at -70 °C and the reaction mixture was stirred at -70 °C for 1h. Pentane (50 ml) was added and then the mixture was allowed to warm to -20 °C. Water (3 ml) was added and the mixture was finally warmed to room temperature. Anhydrous $MgSO_4$ was added to remove water and filtered off. Removal of the solvents gave pure **2** in an almost quantitative yield [^{1}H-NMR in CCl_4 shows only a signal peak at δ 1.85 (s)]. Similar treatment of **9** 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 ^{1}H- and ^{13}C-NMR data with those of (Z)-2,5-diphenylhexa-2,3,4-triene obtained by Vermeer et al.[17] Reduction of **13** with zinc (CH_3CN, reflux, 4h) resulted in the formation of a 1:1 mixture of the (Z)- and (E)-butatrienes (**19** and **19'**[18]), which were also formed by heating a solution of **19** at 80 °C for 4h.

When a solution of **2** in CCl_4 (0.03-0.5 mol dm^{-3}) was allowed to stand at room temperature for several days, a new signal at δ 1.47 (s) was observed in the ^{1}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 $(C_8H_{12}O_2)_n$: C, 68.54; H, 8.63%. ^{13}C-NMR (CCl_4) δ 85.6 (-C$\equiv$C-), 74.6 ($\equiv$C-$\overset{|}{\underset{|}{C}}$-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_4 showed no absorption at 4000-3050 cm^{-1} corresponding to the hydroxyperoxide (-O-O-H) and the Raman spectrum (KBr-disk) showed the absorptions at 2230 s (-C$\equiv$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}H- and ^{13}C-NMR spectra [**23**, ^{1}H-NMR (CCl_4) δ 1.98-1.34 (m); ^{13}C-NMR (CCl_4) δ 86.5 (-C$\equiv$C-), 77.9 ($\equiv$C-$\overset{|}{\underset{|}{C}}$-O), 35.8, 25.8, 22.8 (-$CH_2$-)]. Skattebϕl[13b] and Köbrich[13e] obtained independently the insoluble polymeric peroxide on exposure of **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 (**22**). Although our polymeric peroxide is more soluble (smoothly in CCl_4, benzene, CH_2Cl_2, $CHCl_3$, etc.) than that obtained by Skattebϕl and Köblich, the ^{1}H-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 **2** and **18** are to be assigned as the novel cyclic peroxide polymers (**20** and **23**) containing acetylene and peroxide units.

We thank Prof. P. Vermeer, State University, Utrecht, The Netherlands, for providing the ^{1}H- and ^{13}C-NMR data of (Z)-2,5-diphenylhexa-2,3,4-triene (**19**).

References

1) M. Iyoda, S. Tanaka, M. Nose, and M. Oda, *J. Chem. Soc., Chem. Commun.*, 1983, 1058.

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.

3) The diol (**8**) was prepared by the reaction of cyclohexanone with the Grignard derivatives of 3-methyl-1-butyn-3-ol in 80% yield.

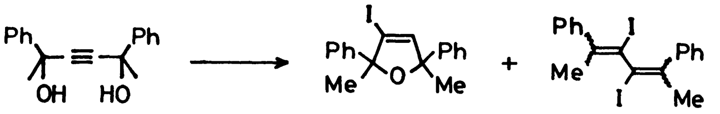
4) Y. S. Zalkind, B. Rubin, and A. Kruglov, *J. Russ. Phys.-Chem. Soc.*, 58, 1044 (1926); *Chem. Abstr.*, 22, 1137 (1928).

5) **9**, Mass (m/e) 402 (M$^+$); ^{1}H-NMR (CDCl$_3$) δ 2.5-2.2 (m, 4H), 1.94 (s, 3H), 1.73 (s, 3H), 1.7-1.4 (m, 6H); ^{13}C-NMR (CDCl$_3$) δ 146.5, 139.7, 100.0, 98.7 (sp^2), 39.9, 31.5, 29.8, 27.2, 26.5, 26.1, 20.4 (sp^3).

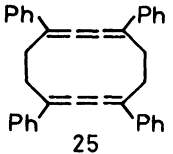
6) Dehydration occurs easily by treatment of **10** with acids, see R. A. Raphael, "Acetylenic Compounds in Organic Synthesis", Butterworth Scientific Publications (1955).

7) **11**, Mass (m/e) 442 (M$^+$); ^{1}H-NMR (CDCl$_3$) δ 2.33-2.25 (m, 8H), 1.53 (m, 12H); ^{13}C-NMR(CDCl$_3$) δ 146.5, 97.6 (sp^2), 40.1, 31.8, 27.3, 26.7, 26.3 (sp^3).

8) Zalkind et al. reported[19] 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 reported[20] the formation of **25** by the reaction of **12** with HI in ethanol.



12 **24** **13**



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9) **13**, Mass (m/e) 486 (M$^+$); ^{1}H-NMR (CDCl$_3$) δ 7.25-7.08 (m, 6H), 6.96-6.76 (m, 4H), 2.02 (s, 6H); ^{13}C-NMR (CDCl$_3$) δ 140.3, 127.3, 127.0, 126.8 (aromatic sp^2), 143.5, 108.9 (sp^2), 31.1 (Me). The geometry of **13** was determined by the symmetrical ^{1}H-NMR and high field shift of *o*-protons of benzene rings.

10) *Cf.*, W. Jasiobedzki, A. Zimniak, and T. Glinka, *Rocz. Chem.*, 49, 111 (1975) and references cited therein.

11) W. Jasiobedzki, *Rocz. Chem.*, 36, 455 (1962); *Chem. Abstr.*, 58, 5490a (1963).

12) **15**, Mass (m/e) 350, 352, 354 (M$^+$); ^{1}H-NMR (CDCl$_3$) δ 1.99 (s, 6H, Me), 1.21 (s, 18H, *t*-Bu); ^{13}C-NMR (CDCl$_3$) δ 89.4 (-C≡C-), 66.8 ($\equiv C-\overset{|}{\underset{|}{C}}-Br$), 40.7 (-CMe$_3$), 29.8 (Me), 26.5 (Me of *t*-Bu groups).

13) a) L. Skattebφl, *Tetrahedron Lett.*, 1965, 2175; b) L. Skattebφl, *Tetrahedron*, 21, 1357 (1965); c) F. T. Bond and D. E. Bradway, *J. Am. Chem. Soc.*, 87, 4977 (1965); G. Maier, *Tetrahedron Lett.*, 1965, 3603; e) G. Köbrich, H. Heinemann, and W. Zündorf, *Tetrahedron*, 23, 565 (1967).

14) H. Westmijze, T. Meijer, and P. Vermeer, *Tetrahedron Lett.*, 1975, 2923.

15) **17**, Mass (m/e) 148 (M$^+$); ^{1}H-NMR (CCl$_4$) δ 2.3-2.1 (m, 4H, -CH$_2$-), 1.83 (s, 6H, Me), 1.7-1.5 (m, 6H, -CH$_2$-); ^{13}C-NMR (CCl$_4$) δ 154.9, 151.5 (sp), 114.7, 106.3 (sp^2), 34.6, 27.7, 26.1 (-CH$_2$-), 23.8 (Me).

16) **18**, Mass (m/e) 188 (M$^+$); ^{1}H-NMR (CCl$_4$) δ 2.20 (br. s, 8H, allylic CH$_2$), 1.59 (br. s, 12H, non-allylic CH$_2$); ^{13}C-NMR (CCl$_4$) δ 152.0 (sp), 114.8 (sp^2), 34.6, 27.5, 26.1 (-CH$_2$-).

17) **19**, Mass (m/e) 232 (M$^+$); ^{1}H-NMR (CDCl$_3$) δ 7.6-7.1 (m, aromatic), 2.40 (s, Me); ^{13}C-NMR (CDCl$_3$) δ 152.1 (sp), 139.0, 128.4, 127.3, 126.1 (aromatic sp^2), 113.7 (sp^2), 20.6 (Me).

18) **19'**, ^{1}H-NMR (CDCl$_3$) δ 7.6 ∿ 7.1 (m, aromatic), 2.35 (s, Me); ^{13}C-NMR (CDCl$_3$) δ 152.1 (sp), 139.4, 128.4, 127.3, 116.5 (aromatic sp^2), 114.0 (sp^2), 20.5 (Me).

19) Y. S. Zalkind and S. V. Nedzvetzkii, *J. Russ. Phys.-Chem. Soc.*, 62, 1011 (1930).

20) W. Jasiobedzki, *Rocz. Chem.*, 41, 1265 (1967).

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