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CIS-4a,5,8,8a-TETRAHYDRO-6,7-DI-(BROMOMETHYL)NAPHTHOQUINONE FROM 2,3-DI-(BROMOMETHYL)-1,3-BUTADIENE.

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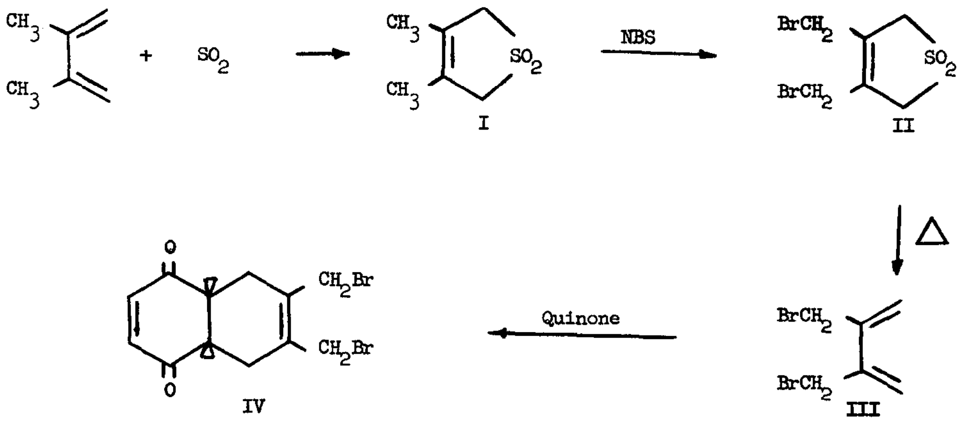
In the synthetic route of the title compound it was necessary to prepare 2,3-di-(bromomethyl)-1,3-butadiene. Recent interest in the preparation of this intermediate has prompted us to report the synthesis of this diene and some of its Diels-Alder addition products.

The 3,4-dimethyl-2,5-dihydrothiophene-1,1-dioxide (I) was prepared by heating equivalent amounts of 2,3-dimethyl-1,3-butadiene and sulfur dioxide in an autoclave for 4 hours at 85° (1). Recrystallization from methanol yielded pure I (91%), m.p. 136-137° (sublimes at 100°). This sulfone was dibrominated with N-bromosuccinimide in chloroform (2); no free radical initiator was required. A clear oil was isolated which on treatment with an equivalent volume of 95% ethanol precipitated 3,4-di-(bromomethyl)-2,5-dihydrothiophene-1,1-dioxide (II); other brominated products remained in solution. Recrystallization from ethanol yielded pure II (53%), m.p. 124-125°. Anal. Calcd. for $C_6H_6Br_2O_2S$: C, 23.89; H, 2.00; Br, 52.92. Found: C, 23.65; H, 2.01; Br, 52.49. The 60 Mc n.m.r. spectrum ($CDCl_3$) revealed two peaks of equivalent area; a singlet at 4.02 p.p.m. and a singlet at 4.07 p.p.m.

The brominated sulfone II was decomposed on heating (160-170°) to yield 2,3-di-(bromomethyl)-1,3-butadiene (III), (65%) m.p. 57-58°. The n.m.r. revealed a singlet (area 1) at 4.19 p.p.m. and a doublet (area 1) at 5.57 p.p.m. (J = 1.2 c.p.s.). IR absorption: C=C [1601 (s)]; $C{=}CH_2$[3096 (s)] and [918 (s)]; and C-Br[610 (m)]. This diene was very sensitive to light and polymerized readily. Polymerization also occurs in most solvents to yield a white fibrous material. The lower molecular weight polymer is soluble in tetrahydrofuran.

The cis-4a,5,8,8a-tetrahydro-6,7-di-(bromomethyl)naphthoquinone (IV) was prepared by allowing equivalent amounts of p-benzoquinone and the diene III to react in an acetic anhydride solution for 4 days. The product was recrystallized from benzene (69%), decomposition 154-156°. Anal. Calcd. for $C_{12}H_{12}Br_2O_2$: C, 41.41; H, 3.47; Br, 45.95. Found: C, 41.38; H, 3.45; Br, 45.98.

The n.m.r. revealed a multiplet (area 2) centered at 2.54 p.p.m., a multiplet (area 1) centered at 3.28 p.p.m., a singlet (area 2) at 3.99 p.p.m., and a singlet (area 1) at 6.71 p.p.m.



4,5-Di-(bromomethyl)-Δ^4-tetrahydrophthalic anhydride (V) was prepared by heating an equivalent mixture of maleic anhydride and 2,3-di-(bromomethyl)-1,3-butadiene in benzene under reflux for 12 hours. The product V was isolated and recrystallized from benzene (78%), m.p. 148° C. Anal. Calcd. for $C_{10}H_{10}Br_2O_3$: C, 35.53; H, 2.98. Found: C, 35.66; H, 2.95. The n.m.r. spectra revealed a singlet (area 2) at 4.03 p.p.m., a multiplet (area 1) at 3.48 p.p.m., and a doublet (area 2) at 2.68.

4,5-Di-(bromomethyl)-1,1,2,2-tetracyanocyclohex-4-ene (VI) was prepared similar to V using equivalent amounts of diene III and tetracyanoethylene. Recrystallization from benzene yielded pure VI (89%), m.p. 206°. Anal. Calcd. for $C_{12}H_{10}Br_2N_4$: C, 38.94; H, 2.72; N, 15.13. Found: C, 39.09; H, 2.53; N, 15.09. The n.m.r. spectra revealed two equivalent peaks: a singlet at 3.32 p.p.m. and a singlet at 4.02 p.p.m.

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