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9-Methyl-9-nitro-10-nitromethylene-9,10-dihydroanthracene. The First Isolation of a Proposed Intermediate for the Side-chain Nitration of Arenes under Heterolytic Conditions#

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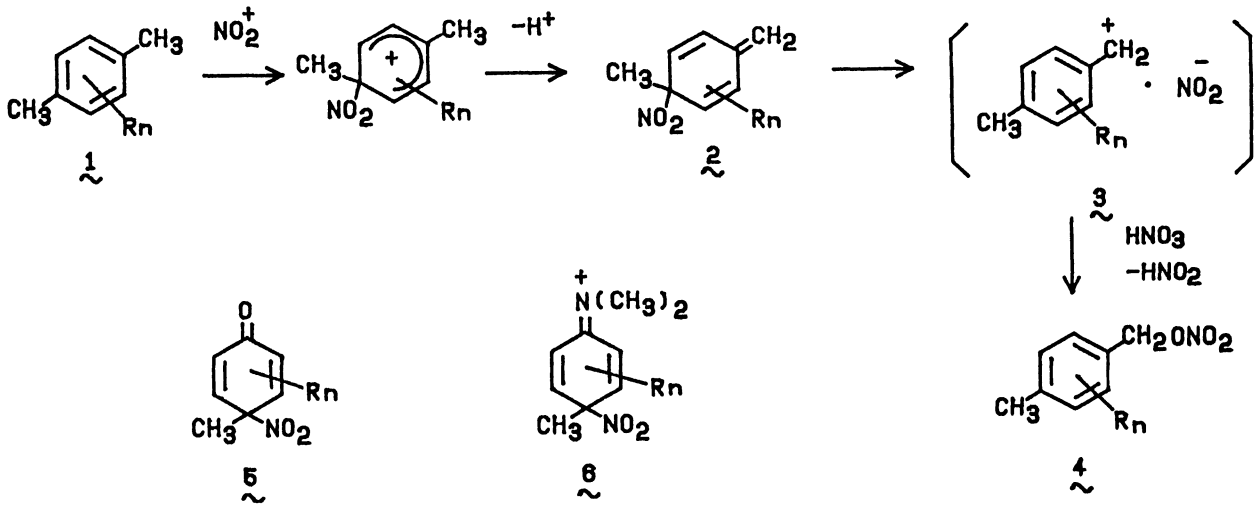
Reaction of 9-methyl-10-nitromethylanthracene with nitric acid in dichloromethane at low temperatures followed by treatment with DABCO gave 9,10-bis(nitromethyl)anthracene and the title compound. The latter is converted by further action of nitric acid to 9-methyl-10-trinitromethylanthracene, 10-methyl-9-anthrylnitrile oxide, and other oxidation products.

Action of nitric acid upon polymethylbenzenes (1) at low temperatures often leads to the formation of benzyl nitrates (4) as the main product.[1] The reaction is highly regioselective and occurs when two methyl groups are in the para relationship to each other. The process of this non-conventional side-chain reaction has been rationalized in terms of 1-methyl-4-methylene-1-nitro-2,5-cyclohexadiene intermediate (2), which would undergo the heterolytic scission of the carbon-nitrogen bond to form a benzyl cationic species/nitrite ion pair (3); recombination at benzylic carbon atom followed by oxidation

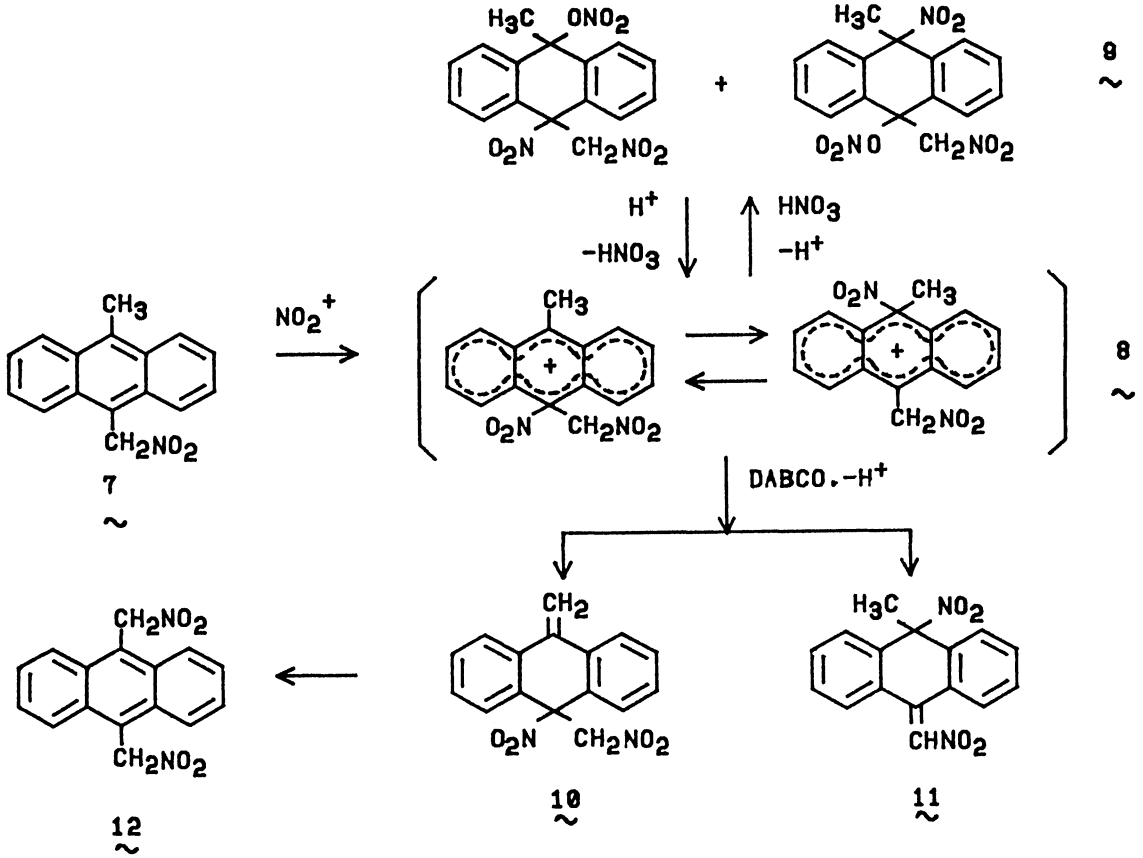


Scheme 1.

#This paper is dedicated to the late Professor Ryozo Goto, Kyoto University.

affords benzyl nitrate 4.[2] A similar intermediate has been assumed to be involved in other side-chain substitutions of arenes under heterolytic conditions.[3] Until now, however, no such trienes have ever been observed as a discrete species, although the structural analogs (5 and 6) were easily obtained from the nitration of substituted phenols and anilines.[4,5] In the present paper, we wish to report the first isolation of such a compound and its transformation into side-chain modification products.

Nitration of 9,10-dimethylanthracene with nitric acid in dichloromethane at low temperatures gave 9-methyl-10-nitromethylanthracene (7) as the main product.[6] When this compound was allowed to react with 2 equiv. of nitric acid in a dilute solution of dichloromethane for 2 h at -10 - -5 °C and then treated with DABCO (1,5-diazabicyclo[3.4.0]non-5-ene), it gave after usual work-up a syrupy product, from which 9,10-bis(nitromethyl)anthracene (12) separated out as pale yellow needles in 17% yield, mp 238-240 °C. The mother liquor was dissolved into a mixture of hexane/dichloromethane and allowed to evaporate at room temperature to afford another product as a yellow crystalline solid with the composition of $C_{16}H_{12}N_2O_4$ (67% yield), which melted at 130-135 °C with decomposition and showed infrared bands (KBr) at 1640, 1540, 1520, 1350, 835, 780 cm^{-1}; ^1H NMR peaks ($CDCl_3$) at 2.35(s, 3H), 7.40(s, 1H), 7.57(m, 8H); ^{13}C NMR peaks ($CDCl_3$) at 25.53(q), 91.13(s), 124.7(d), 125.36(d), 125.97(d), 128.53(d), 129.57(s), 130.67(d), 130.89(d), 132.98(s), 134.06(d), 135.17(s), 135.67(s), 138.25(s).

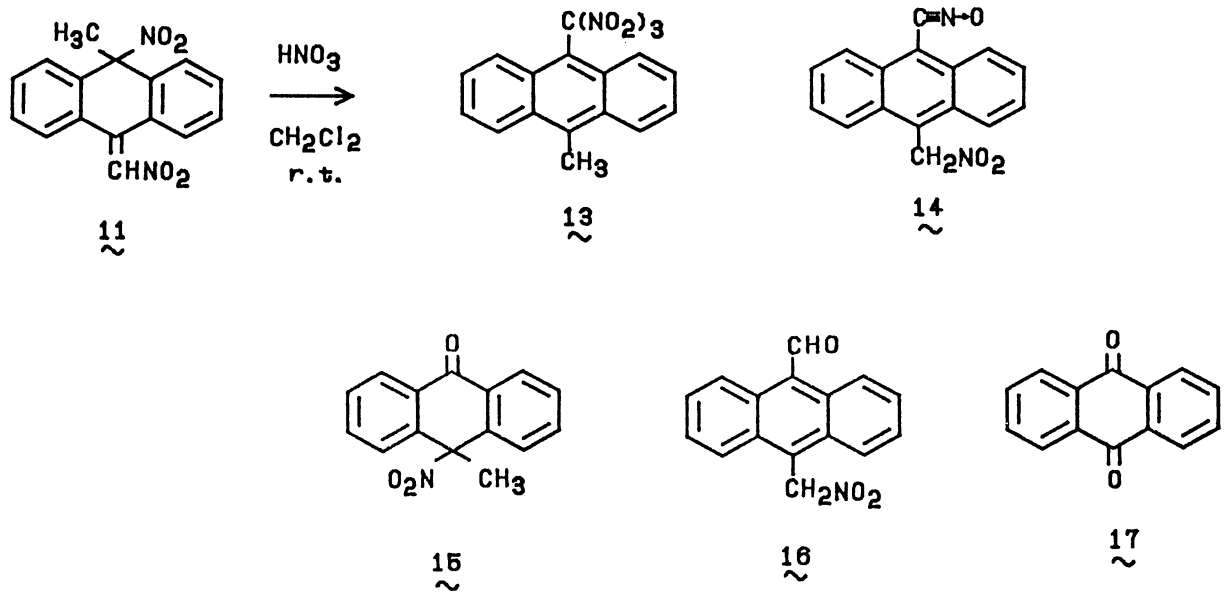


Scheme 2.

The spectral data and elemental analysis are in line with the structure, 9-methyl-9-nitro-10-nitromethylene-9,10-dihydroanthracene (11). A probable route to 11 and 12 is depicted in Scheme 2.

Compound 7 undergoes electrophilic attack of nitronium ion at meso position to form two arenium ions (8), which are in equilibrium with addition products (9) in the presence of excess nitric acid. Action of DABCO on 8/9 results in removal of proton from activated methyl and methylene groups to yield the nitromethylenecyclohexadienes (10 and 11). Triene 10, in which exo-methylene group is free from electron-withdrawing group would undergo a facile rearrangement into arylnitromethane 12. However, cleavage of the carbon-nitrogen bond at tertiary carbon of 11 would be less favored as such dissociation inevitably results in the formation of benzyl cation in which nitro group is attached to the benzylic position. Thus compound 11 is isolable as a comparatively stable crystalline solid.

When triene 11 was treated with 0.5 equiv. of nitric acid in a dilute dichloromethane solution at room temperature for 3 h and the resulting product mixture was carefully chromatograghed on a silica gel column using a mixture of hexane and dichloromethane as eluent, 9-methyl-10-trinitromethylanthracene (13) and 10-nitromethyl-9-anthrylnitrile oxide (14)[7] were obtained as the main products. Side products identified included 10-methyl-10-nitroanthrone (15),[8] 9-formyl-10-nitromethylanthracene (16), and anthraquinone (17). Structures of compounds 13-16 were assigned on the basis of spectral data and elemental analyses.[9] Both trinitro compound 13 and nitrile oxide 14 are stable toward further attack of nitric acid and can be stored without appreciable change for days. The mechanism of this interesting transformation is now under investigation.



11 13 14

15 16 17

Scheme 3.

We are also successful in isolating a triene compound of similar structure during the nitration of 9-cyanomethyl-10-methylanthracene.[10] However, all attempts to obtain 1-methyl-4-methylene-1-nitro-2,5-hexadienes with no fused aromatic rings were futile.

References

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9) **12**; mp 238-240 °C. IR(KBr); 1540, 1440, 1360, 1300, 1190, 825, 760 cm^{-1}. ^1H NMR ($CDCl_3$); δ = 6.60(s, 4H), 7.5-8.6(m, 8H). Calcd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.45%. Found: C, 64.82; H, 4.22; N, 9.33%.
13; mp 155-155.5 °C. IR(KBr); 1675, 1540, 1330, 1300, 1280, 830, 780, 770, 695 cm^{-1}. ^1H NMR ($CDCl_3$); δ = 2.44(s, 3H), 7.30-7.79(m, 7H), 8.00-8.48(m, 1H). ^{13}C NMR ($CDCl_3$); δ = 23.44(q), 125.77, 126.11, 127.09, 128.11, 129.77, 130.06, 130.25, 131.72, 134.44, 135.47. MS(70eV) m/e (rel intensity) 295(M^+-NO_2, 3), 249($M^+-(NO_2)_2$, 12). Calcd for $C_{16}H_{11}N_3O_6$: C, 56.31; H, 3.25; N, 12.31%. Found: C, 56.00; H, 3.01; N, 12.25%.
14; mp >300 °C. IR(KBr); 2300, 1545, 1405, 1320, 1250, 1060, 770, 760 cm^{-1}. ^1H NMR ($CDCl_3$); δ = 6.87(s, 2H), 7.51-8.10(m, 4H), 8.18-8.71(m, 4H). MS(70eV) m/e (rel intensity) 278(M^+, 9), 232(M^+-NO_2, 100), 216(26), 203(19). Calcd for $C_{16}H_{10}N_2O_3$: C, 69.06; H, 3.62; N, 10.07%. Found: C, 68.70; H, 3.79; N, 10.07%.
16; mp 188-190.5 °C. IR(KBr); 1675, 1550, 1450, 1380, 1365, 770 cm^{-1}. ^1H NMR ($CDCl_3$); δ = 6.63 (s, 2H), 7.0-9.0(m, 8H), 11.56(s, 1H). ^{13}C NMR ($CDCl_3$); δ = 72.27, 123.87, 124.65, 126.84, 128.01, 128.45, 194.09. MS(70eV) m/e (rel intensity) 265(M^+, 32), 219(M^+-NO_2, 43).
10) To be published.

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