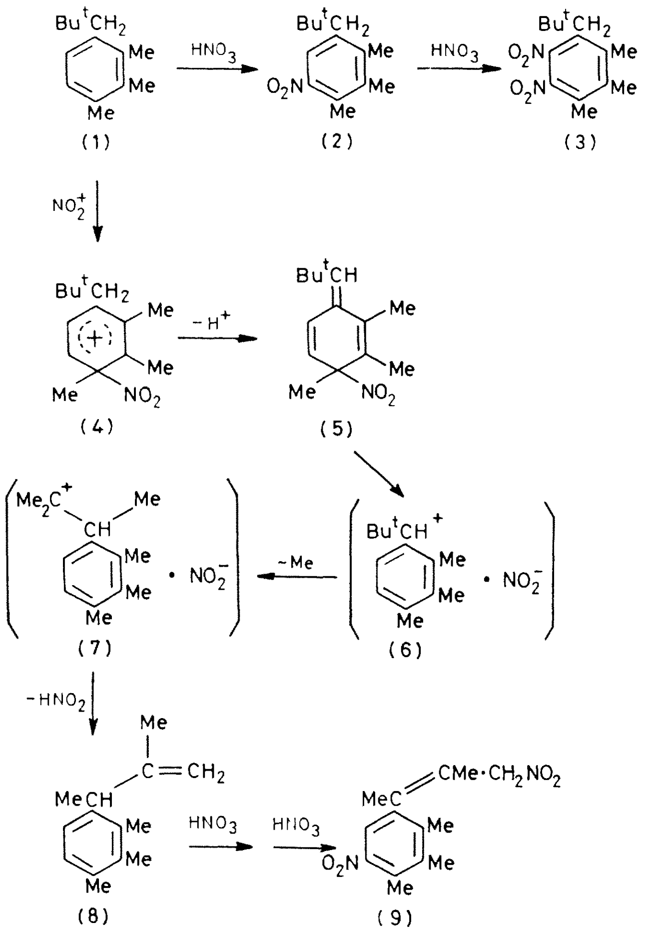
Unusual Product from the Nitration of 2,3,4-Trimethylneopentylbenzene: 3-(2,3,4-trimethyl-5-nitrophenyl)-2-methyl-1-nitrobut-2-ene. Evidence for the Heterolytic Mechanism of Side-chain Substitution of Arenes

By HITOMI SUZUKI,* KEIKO NAGAE, KAZUMASA OHNISHI, and ATSUHIRO OSUKA
(Department of Chemistry, Faculty of Science, Ehime University, Bunkyo-cho, Matsuyama 790, Japan)

Summary During nitration of 2,3,4-trimethylneopentylbenzene the neopentyl group isomerises giving the title nitro-olefin as one of the main products; the result strongly suggests the intervention of a carbonium ionic species in the side-chain substitution of arenes.

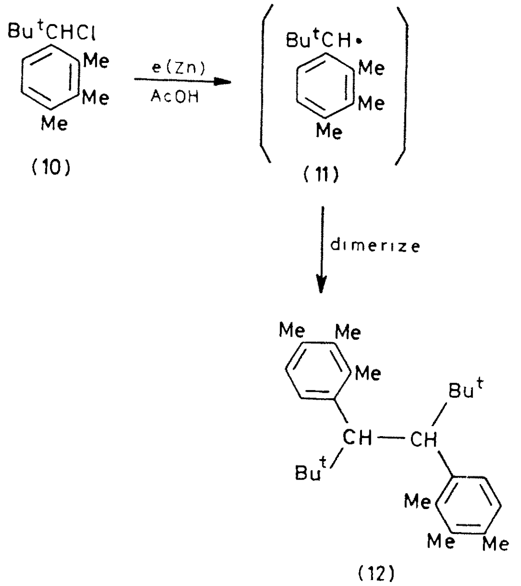
ON treatment with an electrophile at low temperatures, polyalkylated aromatic compounds often undergo substitution of a side-chain to yield benzylic compounds.[1] The mechanistic aspects of this unique reaction have received considerable attention recently,[2] and there is substantial support for the view that alkylbenzenes may undergo side-chain substitution by a heterolytic mechanism involving primary attack of an electrophile at the aromatic ring.[3] We report here the first example in which the isomerization of an alkyl group during nitration is followed by substitution in that group. These reactions provide strong support for the intervention of carbonium ionic species in the side-chain substitution of arenes.

Treatment of 2,3,4-trimethylneopentylbenzene (**1**) with nitric acid (d 1·5 g cm^{-3}) in dichloromethane at -5—0 °C followed by decomposition of the mixture with ice and extraction with ether gave a yellow syrup, which on chromatography over alumina gave the expected ring



substitution product (2) from hexane–benzene eluates and an oily substance (9) from ether eluates, the relative ratio of these products being 5 : 1 Product (9) had the molecular formula $C_{14}H_{18}N_2O_4$ (M^+, *m/e* 278·1268), *m/e* 232 ($M^+ - NO_2$), 186 ($M^+ - 2NO_2$), and 171 ($M^+ - Me - 2NO_2$) The i r spectrum (neat) demonstrated characteristic bands due to aliphatic and aromatic nitro groups (ν_{max} 1550, 1520, 1370, and 1350 cm^{-1}), while its ^1H n m r spectrum (60 MHz, $CDCl_3$) showed the presence of five different methyl groups (δ 1 61, 2 07, 2·15, 2·28, and 2 38), one nitromethyl group (δ 5·12), and one aromatic proton (δ 7·25) The ^{13}C n m r spectrum (100 MHz, $CDCl_3$) provided additional evidence for the presence of five methyl groups (δ 15 4, 16·3, 20·0, 22·1, and 29·2), one nitromethyl group (δ 77·7), and eight sp^2 carbons (δ 121·6, 122·8, 129·0, 137·7, 138·4, 140·0, 147·7, and 148 9) These spectral data are compatible with the formulation of (9) shown in the Scheme Under similar conditions, (2) was simply nitrated to the dinitro compound (3) (m p 121—123 °C) †

The formation of the nitro-olefin (9) may well be explained by a sequence (Scheme) involving an *ipso* attack of a nitronium ion at the C-4 ring carbon in (1) forming the arenium ion (4), which releases a proton from the neopentyl group to give the methylenecyclohexadiene (5) Heterolytic fission of the C–N bond in (5) forms a benzyl cation–nitrite anion pair (6), in which the cationic portion undergoes a Wagner–Meerwein type rearrangement to form the tertiary carbonium ion (7), which is then transformed into the nitro-olefin (9) *via* the terminal olefin (8)



When α-t-butyl-2,3,4-trimethylbenzyl chloride (10) was reduced with activated zinc in acetic acid, *meso*-1,2-diarylethane (12) was obtained as the sole major product In spite of the highly crowded structure of the product, the intermediary benzyl radical (11) showed no tendency to isomerize but dimerized readily, thus providing indirect support for the proposed ionic process of side-chain substitution

(*Received*, 30*th November* 1979, *Com* 1252.)

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† α-t-Butyl-2,3,4-trimethylbenzyl nitrate reacted slowly with nitrating agent under the conditions employed, thus ruling out its possible role as a precursor of the nitro-olefin (9).

[1] For a review of non-conventional processes which occur as the consequence of *ipso* attack, see S R Hartshorn *Chem Soc Rev* , 1974, **3**, 167, R B Moodie and K Schofield, *Accounts Chem Res* , 1976, **9**, 287, H Suzuki, *Synthesis*, 1977, 217, F Effenberger, *Chemie in unserer Zeit*, 1979, **13**, 87

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