

SHORT
COMMUNICATIONS

Uncommonly Easy Nitrodealkylation in Nitration of *para*-Substituted Benzylcyclopropanes

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The nitrodealkylation, electrophilic substitution of an alkyl group at the aromatic ring with a nitro group, frequently accompanies the nitration of *para*- or *ortho*-dialkylbenzenes.

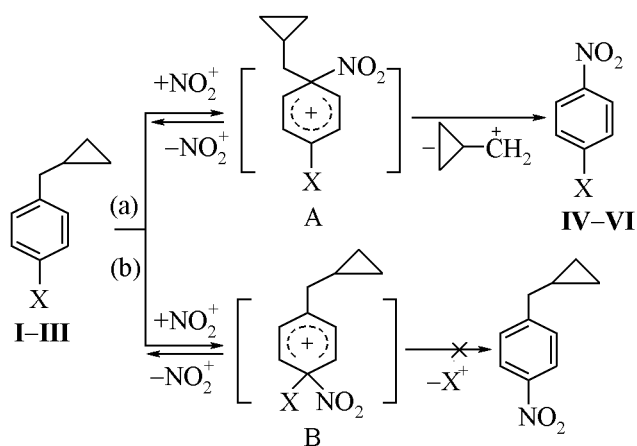
This process is usually a side reaction, and conversion of dialkylbenzenes into the corresponding *para*- or *ortho*-alkylnitrobenzenes does not exceed 10–17%. Most often the nitrodealkylation occurs at nitration of dialkylbenzenes containing isopropyl [1–3] or *tert*-butyl [3, 4] groups. As to replacement with the nitro group of methyl or ethyl, it was observed only once in nitration of *para*-methyl- and *para*-ethylphenylcyclopropanes [3]. We found that a cyclopropylmethyl substituent in the *para*-substituted benzylcyclopropanes was readily replaced with nitro group at nitrating these substrates with nitric acid in the acetic anhydride at -50°C .

is directed only to the position occupied by the cyclopropylmethyl substituent (*ipso*- σ -complex A, see the scheme). The known high stability of the methylcyclopropyl-cation concurrently eliminated from the *ipso*-position obviously is just the driving force of the process taking predominantly the path (a).

It is not improbable that *ipso*- σ -complexes of the B type also may arise in the course of the reaction. However, firstly, their formation is considerably hampered by sterical [2, 4] and electronic [5] reasons, and secondly, the elimination from these *ipso*- σ -complexes of X substituents presumably cannot successfully compete with the leaving ability of nitronium cation.

To 50 ml of freshly distilled Ac_2O at -50°C was added dropwise 13 ml of HNO_3 (d 1.5 g cm^{-3}) and at the same temperature was added 17.4 g (0.1 mol) of hydrocarbon (I). The reaction mixture was stirred for 1 h at -50°C , then poured into 0.5 liter of water, the reaction products were extracted into ether, the extract was washed with water, 2 N solution of sodium carbonate, again with water, and dried on MgSO_4 . On evaporation of the solvent the residue was subjected to column chromatography on Al_2O_3 , II grade of activity, eluent ethyl ether–petroleum ether, 1:3. We obtained 14.5 g (88%) of *p*-nitroisopropylbenzene (IV), bp $128^{\circ}\text{C}/12$ mm Hg, n_{D}^{20} 1.5380 [6].

Similarly from 18.8 g of *p*-*tert*-butylbenzylcyclopropane (II) we obtained 16.4 g (92%) of *p*-*tert*-butylnitrobenzene (V), bp 142 – $143^{\circ}\text{C}/17$ mm Hg, n_{D}^{20} 1.5340 [7], and from 16.6 g of *p*-chlorobenzylcyclopropane (III) we obtained 12.3 g (78%) of *p*-nitrochlorobenzene (VI), mp 84 – 85°C [8].



X = *i*-Pr (I, IV), *t*-Bu (II, V), Cl (III, VI).

The high yield of nitrodealkylation products shows that the *ipso*-attack of the electrophile during nitration

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