NEW EFFICIENT METHOD FOR THE SYNTHESIS OF HALOADAMANTANES INVOLVING RHODIUM COMPLEXES

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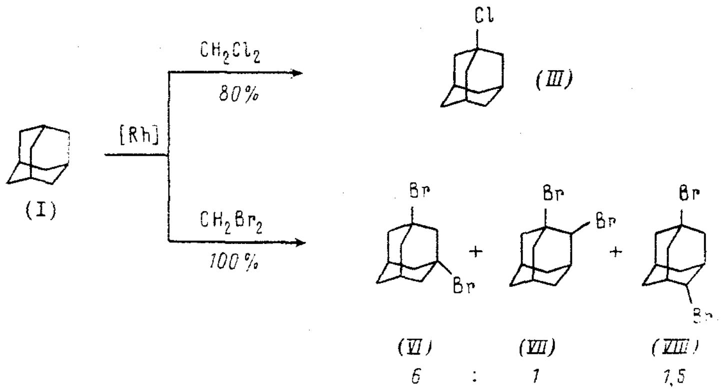
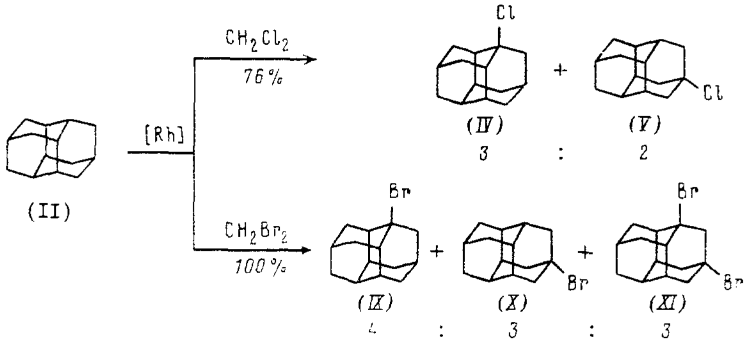
Various reagents are used in organic synthesis for introducing halogen into adamantane (I) and diamantane (II) [1]. For example, the reaction of (I) and (II) with Br_2 proved most efficient for preparation of bromo derivatives, while chlorosulfonic acid, carboxylic acid chlorides or $FeCl_3$ and $SbCl_3$ are used for the synthesis of chloroadamantanes [1].

We are the first to establish that CH_2Cl_2 or CH_2Br_2 may be used for the controlled halogenation of (I) and (II) by the action of rhodium catalysts.

Heating of 1.7 g (12.5 mmoles) (I) in the presence of 0.12 g (0.125 mmole) $Rh(PPh_3)_3Cl$ (or 0.125 mole $[Rh(CO)_2Cl]_2$) in 6 ml CH_2Cl_2 at 180°C over 30 h gave 1-chloroadamantane (III) in about 80% yield. The analogous reaction of (II) with CH_2Cl_2 leads to a 3:2 mixture of 1-(IV) and 4-chlorodiamantanes (V) in ~76% yield.

The reaction of CH_2Br_2 with (I) at 200°C over 40 h gives a 6:1:1.5 mixture of 1,3-(VI), 1,2- (VII), and 1,4-dibromoadamantanes (VIII) in ~100% yield. Diamantane (II) was converted quantitatively under the same conditions to a 4:3:3 mixture of 1-bromide (IX), 4-bromide (X), and 1,4-dibromide (XI).





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Products (III)-(XI) were characterized by comparison with authentic samples and spectral methods.

LITERATURE CITED

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UNEXPECTED HETEROCYCLIZATION OF 1,4-NAPHTHOQUINONE THIOGLUCOSIDES

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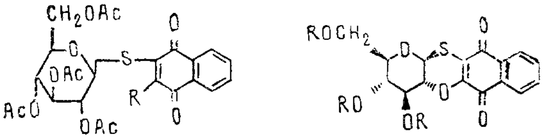
We have found that the saponification of 1,4-naphthoquinone thioglucosides (I) [1] by the action of 0.1 N sodium methylate in methanol at 20-25°C over 0.5-4 h gives quinone (II) as an orange powder with mp 337-340°C (dec.) and low solubility. The structure of (II) was established by its conversion to triacetate (III) by pyridine/acetic anhydride at 25°C over 1 h.



R = H, CH_3O, S—GLc$(Ac)_4$ (I); H (II); Ac (III).

A pure sample of (III) was isolated by preparative thin-layer chromatography according to our previous procedure [1], mp 203-204°C (methanol). ^1H NMR spectrum in $CDCl_3$ with TMS as the internal standard (δ, ppm, J, Hz): 2.08, 2.14, 2.18 (3Ac), 3.91 d.d (1H, $H^{2'}$, $J_{1',2'}$ = 8.0, $J_{2',5'}$ = 9.5), 3.95 d.d.d (1H, $H^{5'}$, $J_{5',6a'}$ = 2.3, $J_{5',6b'}$ = 4.7, $J_{4',5'}$ = 9.5), 4.20 d.d (1H, $H^{6a'}$, $J_{6a',6b'}$ = 12.0), 4.31 d.d (1H, $H^{6b'}$), 4.89 d (1H, $H^{1'}$), 5.24 d.d (1H, $H^{3'}$, $J_{3',4'}$ = 9.0), 5.48 d.d (1H, $H^{4'}$), 7.74 m (2H, H^6 and H^7), 8.08 m (2H, H^5 and H^8). Mass spectrum at 10 eV, m/z (I_{rel}, %): 476 ($M^{+\cdot}$, 100), 415 (18), 373 (40), 355 (76), 313 (75), 296 (28), 168 (15). IR spectrum in $CHCl_3$ (ν, cm^{-1}): 1750, 1670, 1660, 1596, 1572.

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1. A. M. Tolkach, S. G. Polonik, S. B. Stekhova, et al., Khim.-Farm. Zh., No. 12, 1485 (1989).

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