ISSN 1070-4280, Russian Journal of Organic Chemistry, 2020, Vol. 56, No. 6, pp. 1041–1045. © Pleiades Publishing, Ltd., 2020.
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Chemical Transformations of Tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane (1,3-Dehydroadamantane): IX.[1] Noncatalytic Reactions with Alkylarenes

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Received December 28, 2019; revised March 23, 2020; accepted March 23, 2020

Abstract—The reaction of 1,3-dehydroadamantane with alkylbenzenes was studied for the first time. It involved the C–H bond of the alkyl substituent in the α-position with respect to the aromatic ring. The proposed radical mechanism of the reaction was confirmed by the isolation of 1,1′-biadamantane and 1,2-diphenylethane derivatives. Difficultly accessible (adamantan-1-ylmethyl)arenes were synthesized in 53–78% yields.

Keywords: 1,3-dehydroadamantane, alkylarenes, alkylation

DOI: 10.1134/S1070428020060123

Aromatic compounds in which an adamantan-1-yl radical is linked to a benzene ring through a methylene bridge are currently synthesized by alkylation of aromatic compounds with halomethyl- or hydroxymethyladamantanes. However, preparation of the latter involves some difficulties related to a large number of steps [2] or the necessity of reacting 1-azidohomoadamantane with alkylarenes in the presence of aluminum chloride [3].

According to published data on the chemical properties of 1,3-dehydroadamantane (**1**, tetracyclo[3.3.1.1^{3,7}.0^{1,3}]decane) and its reactions with aromatic compounds, such functional groups in the aromatic ring as amino [4], hydroxy [5], or highly C–H acidic groups activated by benzoyl group [6, 7] participated in these reactions. Except for reactions with polycyclic aromatics [8], we have found no information on reactions of **1** with non-functionalized fatty aromatic compounds. Therefore, study of the behavior of propellane **1** in reactions with alkylbenzenes with the goal of obtaining new difficultly accessible aromatic adamantane derivatives seemed to be important and promising.

Herein, we propose a new approach to the formation of $ArCH_2$–$C_{1\text{-}Ad}$ bond, according to which dehydroadamantane **1** reacts with fatty aromatic hydrocarbons at the alkyl C–H bond of the latter. This approach makes it possible to significantly shorten and simplify the synthetic scheme and also to solve the regioselectivity problem intrinsic to electrophilic substitution in an aromatic ring.

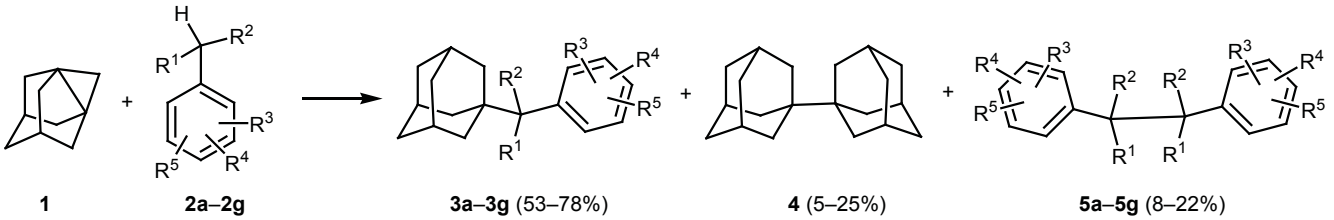
Originally, participation of the methyl group of toluene in the reaction with **1** was observed when toluene was used as a solvent. In addition to the target compound, we isolated a small amount of an unexpected product which was identified as 1-benzyladamantane. This result prompted us to perform a systematic study of the reactions of **1** with alkylbenzenes.

We used as substrates mono-, di-, tri-, and tetraalkylbenzenes **2a**–**2g**, namely methylbenzene (**2a**, toluene), isopropylbenzene (**2b**, cumene), isomeric xylenes (**2c**–**2e**), 1,3,5-trimethylbenzene (**2f**, mesitylene), and 1,2,4,5-tetramethylbenzene (**2g**, durene). The reactions were carried out using 4 equiv of alkylbenzene **2a**–**2g** at 110–130°C (1–1.5 h) in a nitrogen atmosphere without a catalyst (Scheme 1). When the reaction was complete, excess alkylbenzene was removed, and the products were analyzed by GC/MS. Their structure was also confirmed by ^{1}H NMR spectra and elemental analyses.

The major products were identified as (adamantan-1-ylmethyl)(alkyl)benzenes **3a**–**3g** (yield 53–78%), which confirmed our assumption that side alkyl groups of alkylbenzenes are involved in reactions with propel-

[1] For communication VIII, see [1].

Scheme 1.



2, **3**, **5**, $R^1 = R^2 = R^3 = R^4 = R^5 = H$ (**a**); $R^1 = R^2$ =Me, $R^3 = R^4 = R^5 = H$ (**b**); $R^1 = R^2 = R^3 = R^4 = H$, R^5 = 2-Me (**c**), 3-Me (**d**), R^5 = 4-Me (**e**); $R^1 = R^2 = R^3 = H$, R^4 = 3-Me, R^5 = 5-Me (**f**); $R^1 = R^2$ =H, R^3 = 2-Me, R^4 = 4-Me, R^5 = 5-Me (**g**).

lane **1**. 1,1′-Biadamantane (**4**, ~5–25%) [9, 10] and the corresponding alkylbenzene dimers, 1,2-diarylethanes **5a**–**5g** (~8–22%) [11–14] were also formed as by-products which can be isolated by fractional distillation of the reaction mixture (Table 1).

The major products were isolated and purified by fractional distillation under reduced pressure, sublimation, or recrystallization. The impurity of 1,1′-biadamantane (**4**) was removed by recrystallization from propan-2-ol (from crystalline products) or by its precipitation with hexane, followed by distillation of the mother liquor (from liquid products).

In the mass spectra of **3a**–**3g**, the molecular ion peaks had a low intensity, and the base peak for all compounds of this series was that of the adamantyl ion with *m*/*z* 135. It should be noted that the formation of Ad^+ ion (*m*/*z* 135, I_{rel} 100%) is the main proof of the formation of compounds **3a**–**3g**; no such peak is observed (or its intensity is low) in the mass spectra of compounds in which the adamantyl radical is linked directly to benzene ring; in these cases, the most abundant is the molecular ion [8].

The ^{1}H NMR spectra of **3a**–**3g** showed signals of the adamantane fragment in the region δ 1.53–2.12 ppm, signals of aromatic protons at δ 6.62–7.31 ppm, and signals from alkyl groups and methylene bridge.

Our results indicated that polyalkylbenzenes are converted to (adamantan-1-ylmethyl)-substituted derivatives with higher yields than mono- and dialkylbenzenes. Thus, the yield of **3a** in the reaction of **1** with toluene (**2a**) was 53%, *o*-, *m*-, and *p*-xylenes **2c**–**2e** reacted with dehydroadamantane **1** to give 60–70% of **3c**–**3e**, and the yield of tetrasubstituted benzene **3g** was 78%. In no case products of alkylation of the aromatic ring were detected.

The addition of propellane **1** at the side-chain C^{α}–H bond of alkylbenzenes led us to presume radical mechanism of the reaction [15]. Analysis of the product composition suggests that the reaction includes three main stages:

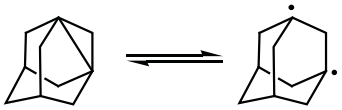
(1) Thermally induced homolytic dissociation of the propellane bond in molecule **1** gives adamantane-1,3-diyl diradical (Scheme 2). The formation of adamantane-1,3-diyl diradical was observed in the reaction of **1** with atmospheric oxygen and vinyl monomers [16, 17]. Its structure was studied by ESR spectroscopy [18]; it was found that cleavage of the propellane bond generates two singly occupied *p* orbitals which do not interact with each other, i.e., adamantane-1,3-diyl diradical is formed.

(2) Adamantane-1,3-diyl diradical abstracts a hydrogen atom from the α-position of the side alkyl group

Table 1. Reactions of 1,3-dehydroadamantane **1** with alkylbenzenes

Compound no.	Alkylbenzene	Yield, %		
		3a–**3g**	**4** [9, 10]	**5a**–**5g**
2a	Toluene	53	25	22 [11, 12]
2b	Cumene	61	21	18 [13]
2c	*o*-Xylene	58	5–6	8–9 [14]
2d	*m*-Xylene	68	5–6	8–9 [14]
2e	*p*-Xylene	65	5–6	8–9 [14]
2f	Mesitylene	62	3	
2g	1,2,4,5-Tetramethylbenzene	78	3	

Scheme 2.



of alkylbenzene with the formation of adamantan-1-yl radical and stable arylalkyl radical (Scheme 3).

(3) Recombination of these radicals yields both major and minor products (Scheme 4).

The proposed mechanism explains the addition of propellane **1** to alkylarenes just at the side-chain α-carbon atom with account taken of possible stabilization of intermediate radical species. Benzyl radical is stable due to delocalization of the unpaired electron over the aromatic π-electron system. Since the stability of radical species increases in going from primary radicals to secondary and tertiary, enhanced reactivity of cumene in comparison to toluene should be expected in the reaction with compound **1**. In fact, the yield of 1-benzyladamantane (**3a**) was 55% in 1.5 h against 63% yield of 2-(adamantan-1-yl)-2-phenylpropane (**3b**) in 1 h (according to the GLC data).

The formation of 1,1′-biadamantane (**4**), as well as alkylbenzene dimers **5**, is also well explainable in the framework of the radical mechanism. These compounds are chain termination products resulting from recombination of adamantan-1-yl and substituted benzyl radicals, respectively.

In summary, we have developed a short synthetic route to adamantan-1-ylmethyl-substituted alkylbenzenes via reaction of 1,3-dehydroadamantane at the side CH bond of alkylbenzene, which involves cleavage of the central propellane bond.

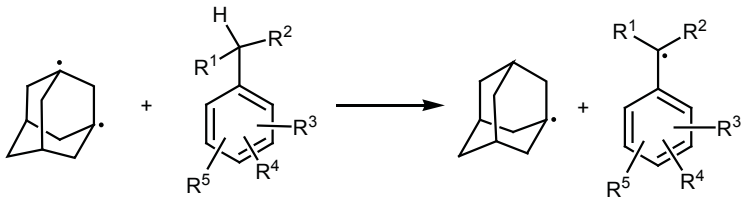
EXPERIMENTAL

Initial alkylbenzenes were preliminarily dried and distilled. Mesitylene and 1,2,4,5-tetramethylbenzene were purchased from Aldrich (CAS nos. 108-67-8 and CAS 95-93-2, respectively).

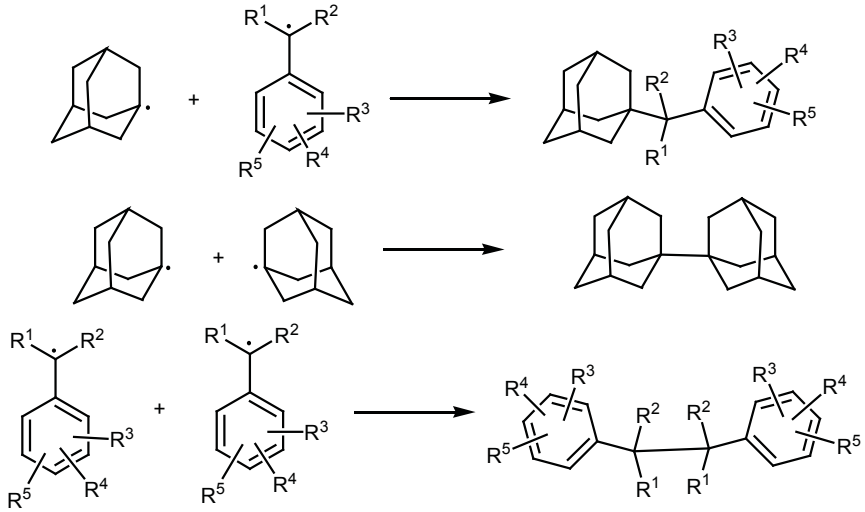
The ^{1}H NMR spectra were recorded on a Varian Mercury 300 spectrometer (USA) at 300 MHz from solutions in CCl_4 using HMDS as internal standard. The mass spectra (electron impact, 70 eV) were obtained with an Agilent GC 7820A/MSD 5975 Series instrument (USA).

1-Benzyladamantane (3a). A solution of 4 g (0.03 mol) of 1,3-dehydroadamantane (**1**) in 20 mL of diethyl ether was added at room temperature in a dry nitrogen atmosphere to 11.0 g (0.12 mol) of toluene.

Scheme 3.



Scheme 4.



Diethyl ether was distilled off, and the mixture was heated for 1 h at 110°C. It was then cooled to 20°C, 20 mL of *n*-hexane was added, and the white precipitate of 1,1′-biadamantane (**4**) was filtered off. *n*-Hexane and excess toluene were distilled off from the filtrate, and the product was isolated from the residue by fractional distillation under reduced pressure. Yield 3.5 g (0.0154 mol, 53%), bp 164°C (3 mm Hg), mp 42–43°C [19, 20]. Mass spectrum, *m*/*z* (I_{rel}, %): 226 (7) $[M]^+$, 135 (100) $[Ad]^+$, 107 (8) $[C_8H_{11}]^+$, 91 (18) $[C_7H_7]^+$, 79 (15) $[C_6H_7]^+$, 41 (8) $[C_3H_5]^+$. Found, %: C 90.25; H 9.71. $C_{17}H_{22}$. Calculated: %: C 90.20; H 9.80. *M* 226.2.

2-(Adamantan-1-yl)-2-phenylpropane (3b) was synthesized in a similar way from 14.4 g (0.12 mol) of cumene (**2b**) and 4 g (0.03 mol) of **1**. Yield 4.6 g (0.0183 mol, 61%), mp 61°C, bp 150–152° (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.10 s (6H, CH_3), 1.61–2.21 m (15H, Ad), 7.15–7.81 m (5H, Ph). Mass spectrum, *m*/*z* (I_{rel}, %): 254 (30) $[M]^+$, 135 (100) $[Ad]^+$, 119 (80) $[C_6H_5C(CH_3)_2]^+$, 107 (36) $[C_8H_{11}]^+$, 93 (52) $[C_7H_9]^+$, 91 (20) $[C_7H_7]^+$, 79 (52) $[C_6H_7]^+$, 77 (43) $[C_6H_5]^+$. Found, %: C 89.62; H 10.37. $C_{19}H_{26}$. Calculated, %: C 89.70; H 10.30. *M* 254.2.

1-(Adamantan-1-ylmethyl)-2-methylbenzene (3c) was synthesized in a similar way from 12.8 g (0.12 mol) of *o*-xylene (**2c**) and 4 g (0.03 mol) of **1**. Yield 4.2 g (0.0174 mol, 58%), n_D^{20} = 1.5612, bp 148–149°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.53–1.92 m (15H, Ad), 2.39 s (3H, CH_3), 2.40 s (2H, CH_2), 7.05–7.24 m (4H, C_6H_4). Found, %: C 90.90; H 10.08. $C_{18}H_{24}$. Calculated, %: C 89.94; H 10.06. *M* 240.2.

1-(Adamantan-1-ylmethyl)-3-methylbenzene (3d) was synthesized in a similar way from 12.8 g (0.12 mol) of *m*-xylene (**2d**) and 4 g (0.03 mol) of **1**. Yield 4.9 g (0.0204 mol, 68%), n_D^{20} = 1.5529, bp 145–147°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.63–2.12 m (15H, Ad), 2.47–2.55 m (5H, CH_2, CH_3), 7.07–7.31 m (4H, C_6H_4). Mass spectrum, *m*/*z* (I_{rel}, %): 240 (28) $[M]^+$, 135 (100) $[Ad]^+$, 107 (48) $[C_8H_{11}]^+$, 105 (54) $[MeC_6H_4CH_2]$, 93 (74) $[C_7H_9]$, 91 (50) $[C_7H_7]^+$, 79 (77) $[C_6H_7]^+$, 77 (54) $[C_6H_5]^+$, 67 (64) $[C_5H_7]^+$, 41 (77) $[C_3H_5]^+$. Found, %: C 89.86; H 10.13. $C_{18}H_{24}$. Calculated: %: C 89.94; H 10.06. *M* 240.2.

1-(Adamantan-1-ylmethyl)-4-methylbenzene (3e) was synthesized in a similar way from 12.8 g (0.12 mol) of *m*-xylene (**2d**) and 4 g (0.03 mol) of **1**. Yield 4.7 g (0.0196 mol, 65%), mp 39–40.5°C, bp 143–145°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.55–2.02 m (15H, Ad), 2.35–2.43 m (5H, CH_2, CH_3), 7.01–7.22 m (4H, C_6H_4). Mass spectrum, *m*/*z* (I_{rel}, %): 240 (58) $[M]^+$, 136 (47) 135 (100) $[Ad]^+$, 107 (31) $[C_8H_{11}]^+$, 105 (57) $[C_8H_9]$, 93 (62) $[C_7H_9]^+$, 91 (38) $[C_7H_7]^+$, 79 (69) $[C_6H_7]^+$, 77 (61) $[C_6H_5]^+$, 67 (31) $[C_5H_6]^+$, 41 (33) $[C_3H_5]^+$. Found, %: C 89.99; H 10.01. $C_{18}H_{24}$. Calculated, %: C 89.94; H 10.06. *M* 240.2.

1-(Adamantan-1-ylmethyl)-3,5-dimethylbenzene (3f) was synthesized in a similar way from 14.3 g (0.12 mol) of mesitylene (**2f**) and 4.0 g (0.03 mol) of **1**. Yield 4.7 g (0.0186 mol, 62%), mp 71–73°C, bp 165–166°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.45–1.82 m (15H, Ad), 2.18–2.27 m (8H, CH_3, CH_2), 6.10–6.23 m (3H, C_6H_3). Found, %: C 89.78; H 10.22. $C_{19}H_{26}$. Calculated, %: C 89.70; H 10.30. *M* 254.2.

1-(Adamantan-1-ylmethyl)-2,4,5-trimethylbenzene (3g) was synthesized in a similar way from 16.10 g (0.12 mol) of 1,2,4,5-tetramethylbenzene (**2g**) and 4.0 g (0.03 mol) of **1**. Yield 6.2 g (0.023 mol, 77%), mp 69–71°C, bp 171–173°C (1 mm Hg). ^{1}H NMR spectrum, δ, ppm: 1.51–1.91 m (15H, Ad), 2.16 d (9H, CH_3), 2.31 s (2H, CH_2), 6.62 d (2H, C_6H_2). Found, %: C 89.54; H 10.46. $C_{20}H_{28}$. Calculated, %: C 89.49; H 10.51. *M* 268.2.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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