Russian Journal of Organic Chemistry, Vol. 38, No. 2, 2002, pp. 295–296. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 2, 2002, pp. 316–317.
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SHORT COMMUNICATIONS

Preparation of α-Adamantyl-substituted Aliphatic Ketones

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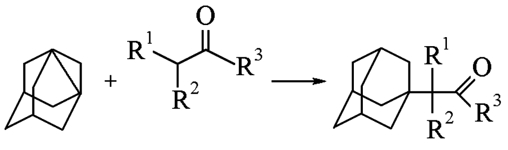
Received January 9, 2001

The known synthetic methods for ketones with adamantyl fragment [1–4] are not fit for preparation of branched products. They are also multistage, provide the target products in low yield, require application of Grignard reagents or strong acids [1, 2].

With the goal to develop a convenient preparation method for α-adamantyl-substituted ketones we carried out condensation of 1,3-dehydroadamantane (**I**) with aliphatic ketones at the α-carbon.



I **IIa–e**

II, $R^1 = R^2 = H$, $R^3 = Me$ (**a**); $R^1 = R^2 = H$, $R^3 = t\text{-Bu}$ (**b**); $R^1 = H$, $R^2 = R^3 = Me$ (**c**); $R^1 = H$, $R^2 = Me$, $R^3 = Et$ (**d**); $R^1 = R^2 = Me$, $R^3 = i\text{-Pr}$ (**e**).

The reaction was performed in the medium of 4–6-fold excess of the initial ketone at 60–120°C within 6–12 h.

This reaction is possible obviously because of unique properties of hydrocarbon **I** for his structure ensures its high reactivity with respect to a wide range of OH-, NH-, SH, and CH-acids. The reaction of compound **I** with aliphatic ketones that are relatively weak CH-acids (®*K* ~20) is important for preparative chemistry, and we are the first who has established this fact. We found that the yield of the target ketones is affected by reaction temperature, duration, and by the structure of the original ketone. The reaction of methyl ethyl ketone with 1,3-dehydroadamantane (**I**) gave rise (79°C, 12 h) mainly to 3-(1-adamantyl)-2-butanone, resulting from addition at the methylene and not methyl group.

The optimal condition for condensation of compound **I** with ketones is to perform the reaction in the medium of the original ketone at the molar ratio 1,3-dehydroadamantane to ketone equal to 1 : 4–6. The yield of condensation products varies within 65–75%.

Compounds **IIa–e** were purified by vacuum distillation. Crystalline substances **IIc–e** were additionally recrystallized from 2-propanol. The structure of compounds obtained **IIa–e** was proved by IR, ^{1}H NMR, and mass spectroscopy. Their purity was confirmed by GC-MS method.

1-(1-Adamantyl)acetone (IIa). The ketone properties are consistent with the published data [4].

1-(1-Adamantyl)-3,3-dimethyl-2-butanone (IIb). Yield 70%. bp 181–183°C (8 mm Hg). IR spectrum, cm^{-1}: 2840–2900 (CH, Ad), 1712 (C–O), 1456 (CH). ^{1}H NMR spectrum, δ, ppm: 0.88 m [9H, $C(CH_3)_3$], 1.62, 1.90, 2.08 three s (15H, Ad), 2.22 m [2H, $CH_2C(O)$]. Found, %: C 82.03; H 11.21. *M* 234. $C_{16}H_{26}O$. Calculated, %: C 81.99; H 11.18. *M* 234.38.

3-(1-Adamantyl)-2-butanone (IIc). Yield 72%. mp 41°C, bp 155°C (10 mm Hg). IR spectrum, cm^{-1}: 2840–2900 (CH, Ad), 1704 (C–O), 1416–1455 (CH). ^{1}H NMR spectrum, δ, ppm: 0.94 m (3H, CH_3), 1.46, 1.63, 1.98 three s (15H, Ad), 2.1 m (3H, CH_3), 2.32 m (1H, CH). Found, %: C 81.54; H 10.81. *M* 206. $C_{14}H_{22}O$. Calculated, %: C 81.50; H 10.75. *M* 206.32.

2-(1-Adamantyl)-3-pentanone (IId). Yield 69%. bp 129°C (4 mm Hg), mp 25°C. IR spectrum, cm^{-1}: 2840–2900 (CH, Ad), 1712 (C–O), 1456 (CH). Found, %: C 81.79; H 11.02. *M* 220. $C_{15}H_{24}O$. Calculated, %: C 81.76; H 10.98. *M* 220.18.

4-(1-Adamantyl)-2,4-dimethyl-3-pentanone (IIe). Yield 75%. bp 127°C (1 mm Hg), mp 25°C. IR

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spectrum, cm^{-1}: 2840–2900 (CH, Ad), 1712 (C–O), 1456 (CH). ^{1}H NMR spectrum, δ, ppm: 0.94–1.10 m (12H, $4CH_3$), 1.42, 1.55, 1.95 3 s (15H, Ad), 2.48 m (1H, CH). Found, %: C 82.36; H 11.52. *M* 248. $C_{17}H_{28}O$. Calculated, %: C 82.20; H 11.36. *M* 248.40.

REFERENCES

1. Lunn, W.H. and Szinai, S.S., UK Patent, 1207954, 1970. *Ref. Zh. Khim.*, 1971, 23N305P.
2. Szinai, S.S. and Lunn, W.H., French Patent 7474M, 1970. *Ref. Zh. Khim.*, 1971, 8N219P.
3. Moiseev, I.K., Klimochkin, Yu.N., Zimichev, A.V., and Stulin, N.V., *VII nauchno-prakticheskoi konferentsii stran SNG “Perspektivy razvitiya khimii i prakticheskogo primeneniya karkasnykh soedinenii”* (7th Scientific Conf. of FSU on Prospects of Development Chemistry and Applications of Cage-like Compounds), Volgograd, 1995, pp. 22–23.
4. Klimochkin, Yu.N. and Moiseev, I.K., *USSR Inventor*’s Certificate, 1512963, 1989. *SSSR Byull. Izobr.*, 1989, no. 37, p. 106.