

SHORT
COMMUNICATIONS

Cyclopentane Ring Fusion to α -Iodo and α -Bromo Levoglucosenone Derivatives with 2,2-Dimethyl-1,3-dinitropropane

I. P. Tsypysheva¹, F. A. Valeev¹, L. Kh. Kalimullina²,
L. V. Spirikhin¹, and M. G. Safarov²

¹ Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences,
pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia
fax: (3472)356066; e-mail: chemorg@anrb.ru

² Bashkir State University, Ufa, Bashkortostan, Russia

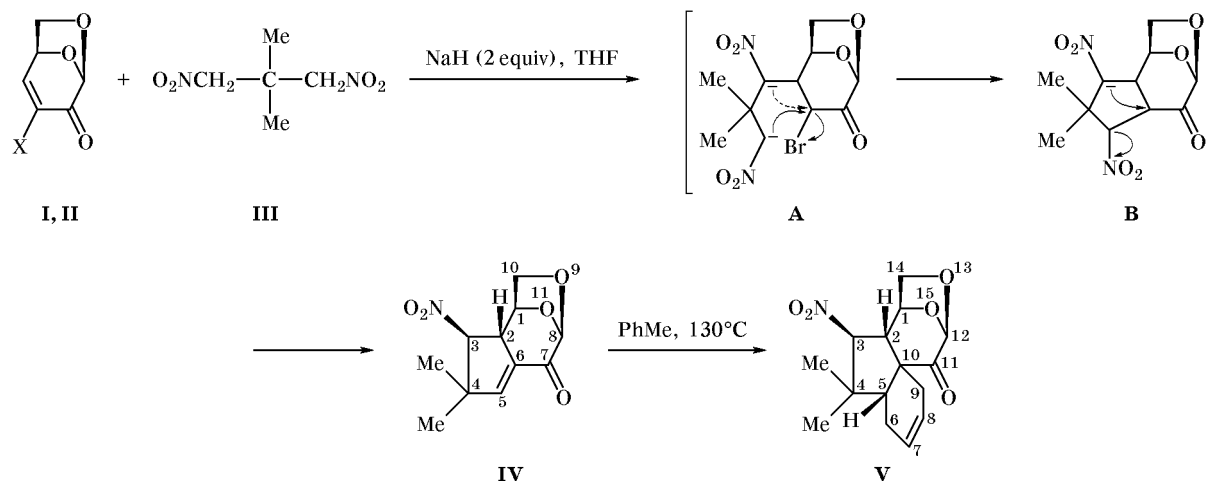
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Levoglucosenone and some its α -halo derivatives are convenient chiral synthons for cyclopropanes, cyclohexanes, norbornanes, and heterocyclic systems [1–3]. However, there are no published data on direct preparation of cyclopentane derivatives from these accessible compounds.

We now report on the stereospecific synthesis of fused cyclopentene derivative **IV** via the Michael reaction, nucleophilic substitution in α -bromo and α -iodo levoglucosenone derivatives **I** and **II** with 2,2-dimethyl-1,3-dinitropropane (**III**). The reaction involves generation of 1,3-dianion from **III**, and the product yields are 82 and 67%, respectively.

The reaction mechanism is most likely to include (as in the cyclopropanation [4]), 1,3-shift of the negative charge in the carbanion formed by conjugate 1,4-addition. Further transformation of intermediate **A** can follow two pathways (Scheme 1), but only one of these is operative. It leads to formation of less strained five-membered ring (anion **B**). Stabilization of dinitrocyclopentyl anion is achieved via intramolecular neutralization, followed by elimination of nitrite ion. The configuration of new asymmetric centers (2*R*) and (3*S*) was established on the basis of the ¹H NMR spectra. The large coupling constant $J_{2,3}$ (10.1 Hz) and the lack of coupling with 1-H indicate β -orienta-

Scheme 1.



I, X = Br; **II**, X = I.

tion of the 2-H proton with the torsion angles $H^2C^2C^3H^3$ and $H^2C^2C^1H^1$ approaching 180 and 90°, respectively. This result is consistent with the known *exo*-selectivity in the addition of nucleophiles to levoglucosenone. The structure of compound **IV** was additionally proved by the Diels–Alder reaction with 1,3-butadiene, which afforded adduct **V** (**IV**-to-1,3-butadiene molar ratio 1:3, toluene, 130°C, 4 h, sealed ampule).

(1S,2R,3S,8R)-4,4-Dimethyl-3-nitro-9,11-dioxatricyclo[6.2.1.0^{2,6}]undec-5-en-7-one (IV). mp 139–140°C, $[\alpha]_D^{20} = -220.7^\circ$ ($c = 1.0$, $CHCl_3$). 1H NMR spectrum, δ , ppm: 1.1 s (3H, CH_3), 1.5 s (3H, CH_3), 3.7 d.d (1H, 2-H, $J = 10.1, 2.8$ Hz), 3.84 d.d (1H, *exo*-10-H, $J = 7.3, 4.4$ Hz), 3.98 d (1H, *endo*-10-H, $J = 7.3$ Hz), 4.72 d (1H, 1-H, $J = 4.4$ Hz), 4.78 d (1H, 3-H, $J = 10.1$ Hz), 5.18 s (1H, 8-H), 6.48 d (1H, 5-H, $J = 2.8$ Hz). ^{13}C NMR spectrum, δ_C , ppm: 19.39 (CH_3), 26.38 (CH_3), 47.42 (C^2), 48.48 (C^4), 70.86 (C^{10}), 73.52 (C^1), 96.59 (C^3), 99.44 (C^8), 130.6 (C^6), 147.8 (C^5), 188.32 (C^7). Mass spectrum (EI), m/z (I_{rel} , %): 239 [M]⁺ (21). Found, %: C 55.16; H 5.56; N 6.02. $C_{11}H_{13}NO_5$. Calculated, %: C 55.23; H 5.48; N 5.86.

(1S,2R,3S,5R,10R,12R)-4,4-Dimethyl-3-nitro-13,15-dioxatetracyclo[7.5.1.0.0^{2,10}]pentadec-7-en-11-one (V). mp 108–110°C, $[\alpha]_D^{20} = -138.1^\circ$ ($c = 1.0$, $CHCl_3$). 1H NMR spectrum, δ , ppm: 0.78 s (3H, CH_3), 1.28 s (3H, CH_3), 2.04 m (2H, CH_2), 2.30 m (2H, CH_2), 2.60 d.d.d (1H, 5-H, $J = 17.7, 2.5, 2.5$ Hz), 3.02 d (1H, 2-H, $J = 10.9$ Hz), 4.0 d.d (1H, *exo*-14-H, $J = 7.6, 5.0$ Hz), 4.0 d (1H, *endo*-14-H,

$J = 7.6$ Hz), 4.61 d (1H, 1-H, $J = 5.0$ Hz), 4.68 d (1H, 3-H, $J = 10.9$ Hz), 5.18 s (1H, 12-H), 5.70 m (1H, =CH), 5.90 m (1H, =CH). ^{13}C NMR spectrum, δ_C , ppm: 17.61 (CH_3), 21.72 (C^6), 27.05 (CH_3), 29.69 (C^{10}), 35.81 (C^9), 45.49 (C^4), 47.22 (C^5), 53.40 (C^2), 68.16 (C^{14}), 73.82 (C^1), 95.14 (C^3), 100.92 (C^{12}), 123.04 (C^8), 126.88 (C^7), 202.42 (C^{11}). Found, %: C 61.59; H 6.24; N 5.03. $C_{15}H_{19}NO_5$. Calculated, %: C 61.42; H 6.53; N 4.78.

The 1H and ^{13}C NMR spectra of compounds **IV** and **V** were recorded on a Bruker AM-300 instrument at 300.13 (1H) and 75.47 MHz (^{13}C) using $CDCl_3$ as solvent. The mass spectrum was obtained on an MKh-1320 mass spectrometer (electron impact, 70 eV). The optical rotations were measured on a Perkin–Elmer 141 polarimeter.

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