

SHORT
COMMUNICATIONS

Alkylation of *o*-Cresol with Caryophyllene on Acidic Aluminosilicate Catalysts

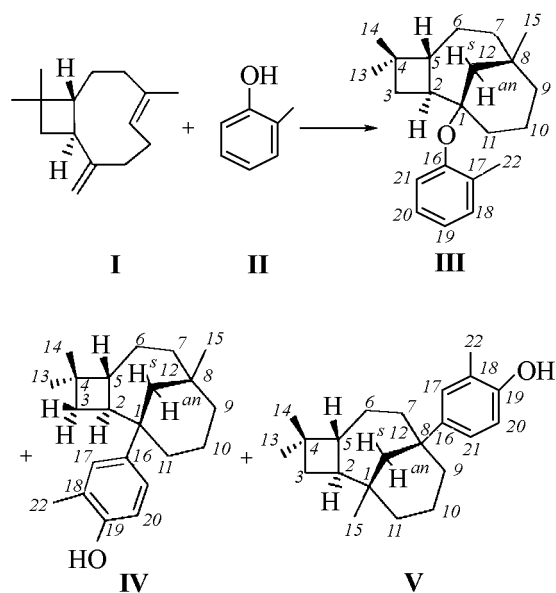
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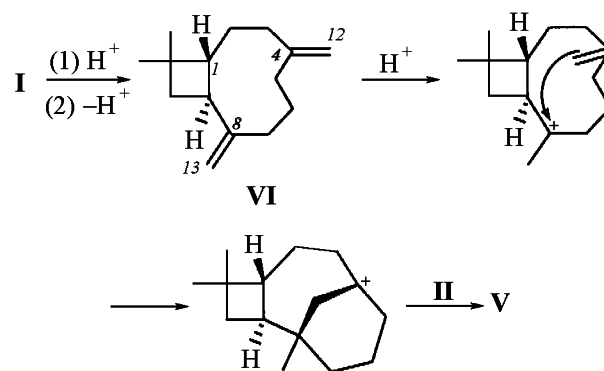
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Caryophyllene (**I**) is among the most wide-spread and accessible sesquiterpenes. Due to its structural features: a strained *trans*-substituted double bond in a nine-membered cycle and to a *trans*-annulated cyclononene and a cyclobutane fragment this substance is one of the most interesting for study polyenes with a medium-sized cycle. The rearrangements of sesquiterpene **I** and related compounds are extensively discussed. We did not find any publications (cf. [1]) on alkylation with compound **I** along Friedel–Crafts procedure. The use on an “organized medium” (clay, zeolites) as catalysts in fine organic synthesis may not only increase the yield of products and selectivity of a reaction but also strongly change the process direction to afford unusual products not available in homogeneous conditions [2].

β HB-2 type). Compounds **III–V** were obtained in 8, 16, and 6% yield respectively. On a wide-porous zeolite H-ZSM-12 and on clay K-10 in CH_2Cl_2 solution formed only compound **IV** in 23 and 37% yield respectively. We formerly by an example of a natural terpene camphene selected solvents that directed the process either to phenol or ether formation [3]. The reaction in a mixture of CH_2Cl_2 with benzene (1 : 1 by volume) on β -zeolite resulted in a single product, compound **III**, in 11% yield.



We carried out alkylation with diene **I** of *o*-cresol (**II**) (25°C, 20 h, solvent CH_2Cl_2 , catalyst zeolite of



In formation of an unusual alkylation product **V** presumably first arises a bismethylene derivative of caryophyllene **VI** [1] where cyclization starts by protonation of the 8(13) double bond and not the 4(12) one; consequently the nucleophile attack is directed to position 4 and not 8 of the alicyclic skeleton.

^1H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-400 at 400.13 and 100.61 MHz respectively from solutions in $\text{CCl}_4\text{-CDCl}_3$ mixtures (1 : 1 by volume), internal reference chloroform signal (δ_{H} 7.24, δ_{C} 76.90 ppm). The structure of newly synthesized compounds was established with the use of double resonance $^1\text{H}\text{-}^1\text{H}$ NMR spectra for analysis of geminal, vicinal and long-range coupling

constants, and also with application of ^{13}C NMR spectra. In the latter the signals were assigned with the help of spectra with selective and off-resonance proton irradiation, and in some cases with the use of differential spectra modulated with long-range coupling $^{13}\text{C}-^1\text{H}$ (LRJMD, experimental conditions optimized for the long-range coupling constants of J_{CH} 10 Hz). For all the new compounds were also recorded the two-dimensional spectra of $^{13}\text{C}-^1\text{H}$ heteronuclear correlation (COSY) using the value of direct coupling constant $^1J_{\text{C-H}}$ 134 Hz).

The numeration of atoms on the schemes corresponds to that on the NMR spectra.

Elemental composition of the compounds obtained was established from high-resolution mass spectra measured on Finnigan 8200 instrument, GC-MS spectra were recorded on HP G 1800A device.

4,4,8-Trimethyl-1-*o*-tolylxytricyclo[6.3.1.0^{2,5}]-dodecane (III). ^1H NMR spectrum (δ , ppm, J , Hz): 1.02 s (C^{15}H_3), 1.10 s (C^{14}H_3), 1.12 s (C^{13}H_3), 1.13 m (H^9), 1.29 m and 1.67 m (2H^7), 1.43 d ($\text{H}^{12\text{an}}$, $J_{12\text{an},12\text{s}}$ 13), 1.37–1.53 m ($\text{H}^{6,9,11}$), 1.62 m (H^6), 1.75 m and 1.84 m (2H^{10}), 1.81 d.d (H^3 , $J_{3,3'}$ 10, $J_{3,2}$ 8), 1.85 d.d ($\text{H}^{3'}$, J 10, $J_{3',2}$ 10), 2.04–2.15 m ($\text{H}^{5,11',12\text{s}}$), 2.28 s (C^{22}H_3), 2.46 d.d.d (H^2 , $J_{2,5}$ 12, J 10, 8), 6.80 d.d (H^{21} , $J_{21,20}$ 8, $J_{21,19}$ 1.2), 6.84 t.d (H^{19} , J 8, 1.2), 7.02 t.d (H^{20} , J 8, $J_{20,18}$ 1.5), 7.12 br.d (H^{18} , J 8). ^{13}C NMR spectrum (δ_{C} , ppm): 17.48 q (C^{22}), 20.90 t (C^{10}), 21.08 q (C^{13}), 22.91 t (C^6), 30.52 q (C^{14}), 33.66 q (C^{15}), 34.53 s (C^4), 34.77 s (C^8), 35.38 t (C^{11}), 36.66 t (C^9), 38.06 t (C^7), 38.14 t (C^3), 42.38 d (C^2), 45.77 d (C^5), 47.76 t (C^{12}), 80.40 s (C^1), 119.78 d (C^{21}), 120.87 d (C^{19}), 125.47 d (C^{20}), 129.94 s (C^{17}), 130.58 d (C^{18}), 154.12 s (C^{16}). Mass spectrum, m/z (I , %): 312 (M^+ , 34), 205 (100), 161 (14), 149 (76), 135 (53), 123 (66), 121 (45), 109 (69), 95 (80), 81 (78), 69 (55), 67 (34), 55 (40), 41 (41). Found: M 312.24473 $\text{C}_{22}\text{H}_{32}\text{O}$. Calculated: M 312.24530.

2-Methyl-4-(4,4,8-trimethyltricyclo[6.3.1.0^{2,5}]-dodec-1-yl)phenol (IV). ^1H NMR spectrum (δ , ppm, J , Hz): 0.56 d.d (H^3 , $J_{3,3'}$ 10, $J_{3,2}$ 10), 0.85 s (C^{14}H_3), 0.99 s (C^{15}H_3), 1.00 s (C^{13}H_3), 1.14 d.d.d ($\text{H}^{9\text{a}}$, $J_{9\text{a},9\text{e}}$ 13, $J_{9\text{a},10\text{a}}$ 13, $J_{9\text{a},10\text{e}}$ 4.5), 1.15 d ($\text{H}^{12\text{an}}$, $J_{12\text{an},12\text{s}}$ 13), 1.23 d.d.d (H^7 , $J_{7,7'}$ 14, $J_{7,6}$ 7, $J_{7,6'}$ 4), 1.32 d.d.d ($\text{H}^{11\text{a}}$, $J_{11\text{a},11\text{e}}$ 13, $J_{11\text{a},10\text{a}}$ 13, $J_{11\text{a},10\text{e}}$ 5), 1.39 d.d ($\text{H}^{3'}$, J 10, $J_{3',2}$ 8), 1.45 m (H^6), 1.54 br.d ($\text{H}^{9\text{e}}$, J 13), 1.57 m (H^6), 1.66 m (H^5), 1.67 m ($\text{H}^{10\text{e}}$), 1.73 d.d.d ($\text{H}^{7'}$, J 14, $J_{7',6'}$ 9, $J_{7',6}$ 4),

2.00–2.09 m ($\text{H}^{10\text{a},11\text{e}}$), 2.14 d.d.d ($\text{H}^{12\text{s}}$, J 13, $J_{12\text{s},9\text{e}}$ 2.5, $J_{12\text{s},11\text{e}}$ 2.5), 2.27 s (C^{22}H_3), 2.43 d.d.d (H^2 , $J_{2,5}$ 12, J 10, 8), 5.10 br.s (OH), 6.65 d (H^{20} , J 8), 6.91 d.d (H^{21} , J 8, 2), 6.96 d (H^{17} , J 2). ^{13}C NMR spectrum (δ_{C} , ppm): 16.21 q (C^{22}), 20.02 t (C^{10}), 20.99 q (C^{13}), 22.80 t (C^6), 30.52 q (C^{14}), 34.06 s (C^4), 34.09 s (C^8), 34.68 q (C^{15}), 37.79 t (C^7), 37.88 t (C^{11}), 38.10 t (C^9), 39.05 t (C^3), 39.70 s (C^1), 40.56 d (C^2), 45.02 t (C^{12}), 46.12 d (C^5), 114.09 d (C^{20}), 122.43 s (C^{18}), 124.52 d (C^{21}), 128.68 d (C^{17}), 141.64 s (C^{16}), 151.09 s (C^{19}). Mass spectrum, m/z (I , %): 312 (M^+ , 29), 202 (16), 201 (100), 148 (7), 121 (21), 95 (6), 81 (7), 55 (6), 41 (9). Found: M 312.24504 $\text{C}_{22}\text{H}_{32}\text{O}$. Calculated: M 312.24530.

2-Methyl-4-(1,4,4-trimethyltricyclo[6.3.1.0^{2,5}]-dodec-8-yl)phenol (V). ^1H NMR spectrum (δ , ppm, J , Hz): 0.87 s (C^{15}H_3), 1.04 s (C^{14}H_3), 1.047 s (C^{13}H_3), 1.053 d ($\text{H}^{12\text{an}}$, $J_{12\text{an},12\text{s}}$ 13), 1.12 m and 1.46 m (2H^{11}), 1.38 d.d (H^3 , $J_{3,3'}$ 10, $J_{3,2}$ 10), 1.38 m and 1.55 m (2H^6), 1.42 m and 1.98 m (2H^9), 1.46 m and 1.94 m (2H^7), 1.54 d.d ($\text{H}^{3'}$, J 10, $J_{3',2}$ 8), 1.68 m and 2.07 m (2H^{10}), 1.87 m (H^5), 2.04 d.m ($\text{H}^{12\text{s}}$, J 13), 2.26 s (C^{22}H_3), 2.37 d.d.d (H^2 , $J_{2,5}$ 12, J 10, 8), 4.90 br.s (OH), 6.62 d (H^{20} , J 8), 7.05 d.d (H^{21} , J 8, 2), 7.10 d (H^{17} , J 2). ^{13}C NMR spectrum (δ_{C} , ppm): 16.19 q (C^{22}), 19.75 t (C^{10}), 21.06 q (C^{13}), 21.84 t (C^6), 27.69 q (C^{15}), 30.88 q (C^{14}), 32.41 s (C^4), 34.87 s (C^8), 35.95 t (C^3), 37.28 t (C^9), 37.47 d (C^2), 37.58 t (C^{11}), 37.67 t (C^7), 40.12 s (C^8), 44.92 d (C^5), 46.67 t (C^{12}), 114.27 d (C^{20}), 122.68 s (C^{18}), 123.50 d (C^{21}), 127.72 d (C^{17}), 146.10 s (C^{16}), 151.16 s (C^{19}). Mass spectrum, m/z (I , %): 312 (M^+ , 24), 202 (17), 201 (100), 148 (8), 121 (18), 108 (20), 46 (21), 45 (36), 31 (71). Found: M 312.24497 $\text{C}_{22}\text{H}_{32}\text{O}$. Calculated: M 312.24530.

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