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CAN Mediated Fragmentation of 1-Phenylcycloalkenes: Synthesis of Monoacetals of 1,n-Dicarbonyl Compounds.

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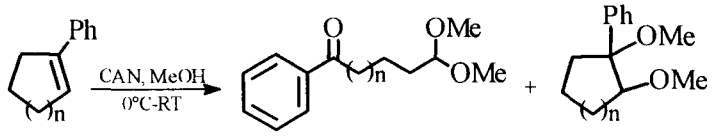
Abstract

Phenylcycloalkenes undergo facile oxidative fragmentation in presence of CAN in methanol giving ketoacetals of 1,n-dicarbonyl compounds.

Key words: Phenylcycloalkenes; Oxidative fragmentation; CAN; Ketoacetals.

In view of the facile cerium (IV) ammonium nitrate (CAN) mediated addition of dimethylmalonate to styrene [1-2], it was of interest to explore the addition of malononitrile to 1-arylcycloalkenes. Expecting a similar reaction, a solution of 1-phenyl-1-cyclohexene and malononitrile in methanol was treated with CAN. In the event, no addition of malononitrile to phenylcyclohexene occurred and instead the latter underwent oxidative fragmentation resulting in the ketoacetal **2b** that was characterised by comparing its spectral data with those reported in the literature [3].

In view of the remarkable ease of the oxidative fragmentation and its potential use as a method for the formation of 1,n-dicarbonyl compounds that are important intermediates in organic synthesis [3], we studied the reactions of CAN with other 1-phenylcycloalkenes (Scheme 1).



1a, n = 1	**2a** (48%)	**3a** (20%)
1b, n = 2	**2b** (68%)	**3b** (18%)
1c, n = 3	**2c** (56%)	**3c** (32%)
1d, n = 4	**2d** (45%)	**3d** (37%)

Scheme 1

Although the mechanistic details of the reaction are unclear, the following rationalisation may be invoked to account the formation of the product. Reaction of methanol with the phenylcycloalkene cation radical can lead to a benzylic radical. The latter can trap molecular oxygen leading to a hydroperoxide. Alternatively the benzylic radical can give rise to a nitrate by ligand transfer. It is conceivable that the hydroperoxide as well as the nitrate can undergo

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fragmentation and ultimately lead to the ketoacetal. Interestingly along with the fragmentation product considerable amount of byproducts (**3a-d**) were also obtained, the latter presumably resulting from the oxidation of the benzylic radical to the cation followed by methanol quenching.

In conclusion, we have encountered a novel Ce (IV) mediated oxidative fragmentation of phenylcycloalkenes[2] resulting in an efficient and direct synthesis of monoacetals of 1,n-dicarbonyl compounds. It is worthy of note that the existing methods for the synthesis of such compounds rely largely on ozonolysis of alkenes, and oxidation with reagents such as OsO_4, $KMnO_4$ etc. [4-5], which appear to be less convenient than the method reported here.

Typical Experimental Procedure:

A solution of CAN (1.260g, 2.3 mmol) in methanol (15 mL) was added dropwise to a solution of **1b** (0.158g, 1mmol) in methanol (10 mL) and stirred at ice temperature for 30 min. The reaction mixture was diluted with water (60 mL) and extracted with CH_2Cl_2 (4x30 mL). The combined organic extracts were washed with water, brine and dried over Na_2SO_4 and the solvent was evaporated. The residue on chromatography on silica gel (100-200 mesh) using ethylacetate in hexanes as eluent afforded **3b** (18 %) and on further elution **2b** (68%).

Spectral data for **2b** and **3b.** 5-Benzoylpentanal dimethylacetal **(2b)**[3]; IR (CCl_4) ν_{max}: 3062, 2938, 1681, 1593, 1128 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 1.427-1.773 (m, 6H); 2.935-2.984 (t, 2H); 3.299 (s, 6H); 4.359 (t, 1H); 7.432-7.945 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.148, 137.013, 132.902, 128.547, 128.004, 104.425, 52.753, 38.421, 32.407, 24.341, 24.067. 1-Phenyl-1,2-dimethoxycyclohexane **(3b)**; ^1H NMR ($CDCl_3$, 300MHz) δ 1.255-2.122 (m, 8H), 2.976 (s, 3H) 3.017-3.066 (m, 1H), 3.154(s, 3H), 7.264-7.463 (m, 5H). EIMS Calcd. for $C_{14}H_{20}O_2$: 220. Found 219 (M^+-1) (2.14), 189(100), 156(53.88), 147(94.25), 130(59.63), 115(54.81), 105(28.07), 84(82.49). Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.33 H, 9.15. Found, C, 76.12; H, 8.97.

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References:

[1 Nair V, Mathew J, Nair LG. Syn. Commun. 1997;27:3053-3064.

[2] Nair V, Mathew J, Prabhakaran J. Chem. Soc. Rev.1997;127-132.

[3] Ojibin YN, Ilavoisky AI, Nikishin GI. Russ. Chem. Bull.1996; 45:1939-1941 and references cited therein.

[4] Haines AH. Methods for the Oxidation of Organic Compounds, Academic Press; Toronto, 1985:117.

[5 Lee DG. Oxidising agents in Organic Chemistry, ed. Trahanovsky WS. Academic Press; NewYork, 1982: vol.5, Part D, 147.

[6] Schmizu I, Fujita M, Nakajima T, Sato T. Synlett 1997:887-888.

2.During the course of our work fragmentation of cyclic olefins to ketonitriles by photooxidative cleavage was reported[6].