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UNUSUAL CYCLIZATION OF 1,2-DIBENZOYLCYCLOHEXA-1,4-DIENE DURING CATALYTIC HYDROGENATION

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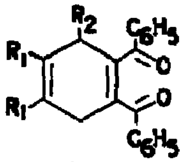
Abstract: Catalytic hydrogenation of 1,2-dibenzoylcyclohexa-1,4-dienes gave the corresponding dihydro- and tetrahydroisobenzofuran derivatives possibly via a 1,4-addition followed by water-elimination.

Because of our interest in 1,2-dibenzoylcyclohex-1-ene derivatives, we attempted to prepare them by catalytic hydrogenation of more easily prepared 1,2-dibenzoylcyclohexa-1,4-diene. Previously Dupont and Germain[1]had carried out catalytic hydrogenation of 2,3-dibenzoylbicyclo[2.2.1]hepta-2,5-diene, where hydrogenation occured across $\Delta^{5,6}$-bond.

When we subjected 1,2-dibenzoyl-4,5-dimethylcyclohexa-1,4-diene (1a) to hydrogenation in presence of Pd-C (10%) as catalyst (30-40 mg/mmol) in ethanol, at room-temperature and atmospheric pressure for 15 hr, an unusual reaction sequence was observed. Usual work-up of the reaction mixture gave highly fluorescent green needles of 1,3-diphenyl-5,6-dimethyl-4,7-dihydroisobenzofuran (2), mp 223-224° C (55%) from benzene soluble portion. The ethanol soluble portion gave 1,3-diphenyl-5,6-dimethyl-4,5,6,7-tetrahydroisobenzofuran (3a) mp 138° C (5%).



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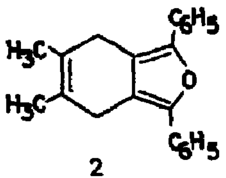

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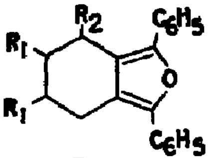

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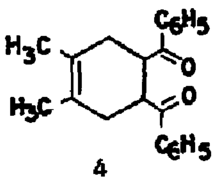


4

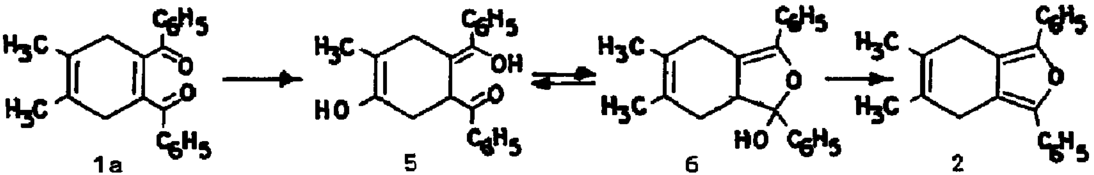
a) $R_1 = CH_3$; $R_2 = H$ a) $R_1 = CH_3$; $R_2 = H$
b) $R_1 = H$; $R_2 = CH_3$ b) $R_1 = H$; $R_2 = CH_3$

The product 2 was identified by preparing an authentic sample[2] and comparing the spectral data. [IR (KBr) ν max: 1612, 1600, 1495, 760, 685 cm^{-1}; NMR ($CDCl_3$) δ : 1.8 (6H,d,-CH_3), 3.3 (4H,s,-CH_2-), 7.07 (10H,m,aromatic)p.p.m].

The structure of 3a was established from its spectral data. IR(KBr) ν max : 1612, 1600, 1495, 765, 690 cm^{-1}. NMR ($CDCl_3$) δ :1.01 (6H,d,-CH_3), 1.19 (2H,m,$-CH\lessgtr$), 2.73 (4H,m-CH_2-), 7.06 (10H,m,aromatic) p.p.m; UV (EtOH) λ max : 330 nm (log ϵ 2.56), 240 nm (log ϵ 2.25); m/e 302 (M^+).

Earlier several workers have attempted hydrogenation of 1,2-dibenzoylalkenes[1,3,4], but such cyclization has not been observed before. That this cyclization occurs only during hydrogenation, was proved by stirring 1a under identical condition in nitrogen atmosphere, where 1a was recovered unchanged. A same reaction-course in DMF indicated insensitivity of the reaction towards protic nature of the medium. Absence of 2 or 3 during the hydrogenation of 4 eliminated 4 as an intermediate in this process. The present observations led us to propose a 1,4-addition of hydrogen across the dibenzoylalkene moiety, giving a tautomeric mixture which then with easy elimination of water form 2 (Scheme 1).

Scheme 1



1a 5 6 2

Tautomerism like 5 ⇌ 6 have been observed in formoins by Goto and Miyagi[5].

In such cases 1,4-hydrogen addition appeared to be a more preferred route than the reduction of $\Delta^{4,5}$-bond. When 1b was subjected to hydrogenation under similar condition, 1,3-diphenyl-4-methyl-4,5,6,7-tetrahydroisobenzofuran (3b), mp 78° C was obtained. Its structural assignment was also confirmed from the spectral data. IR (KBr) ν max: 1608, 1590, 1490, 760, 685 cm^{-1}; NMR (CCl_4) δ :1.2 (3H,d,J=7 cps,-CH_3), 1.83 (4H,m,-CH_2-), 2.75 (2H,m,-CH_2-), 3.31 (1H,m,$-CH\lessgtr$), 7.4 (10H,m,aromatic)p.p.m; UV (EtOH) λ max: 330 nm (log ϵ 2.54), 240 nm (log ϵ 2.23), m/e 288 (M^+).

The generality and applicability of such transformation for making condensed isobenzofurans is now under investigation.

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