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Unexpected Entry to a Novel Carbocyclic Tricyclic System

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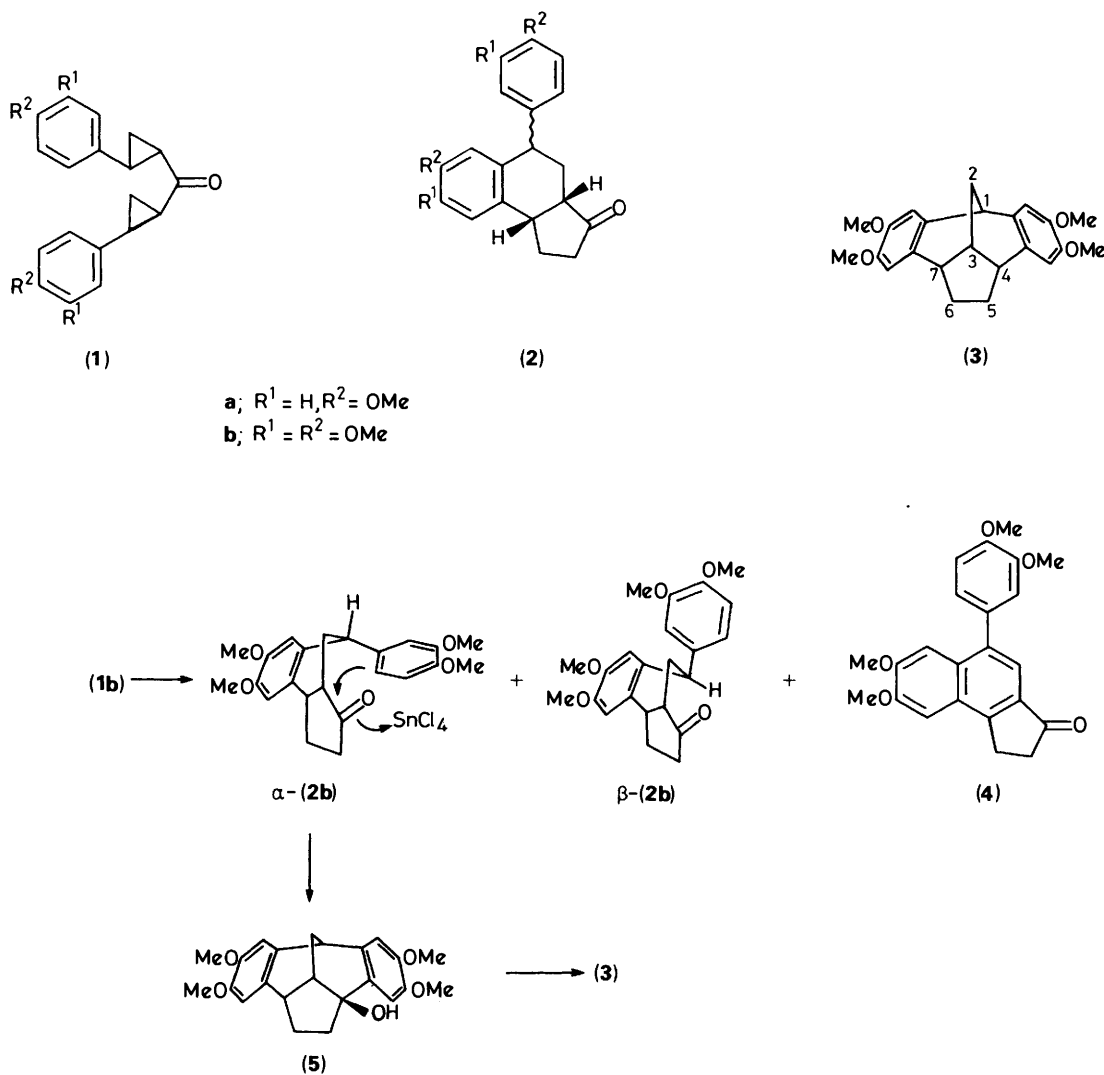
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The bis(3,4-dimethoxyphenylcyclopropyl) ketone (**1b**) undergoes rapid rearrangement in the presence of stannic chloride in nitromethane to the new highly symmetrical dibenzotricyclic systems (**3**).

Previously we have described the Lewis acid catalysed rearrangement of arylcyclopropyl ketones to α -tetralones¹ and developed it into a methodology for the synthesis of picropophyllone² and epipodophyllotoxin.³ A related approach has been successfully applied to the synthesis of steganone by Magnus and co-workers.⁴ Subsequently, we undertook an

investigation of bis(cyclopropyl)ketones. We noted that bis(*p*-methoxyphenylcyclopropyl) ketone (**1a**) also undergoes rapid rearrangement under the same conditions [SnCl_4 , (0.06 M, 1.5 equiv.), MeNO_2 , room temp., 20 min]. An epimeric mixture of benzindenones, (**2**), is formed.⁵

We now find that when the aryl groups in (**1**) are further



activated as in (**1b**) the reaction follows a new path.* The first example of the new dibenzo tricyclic system (**3**)^{†,‡} is formed. The structure of this highly symmetrical, relatively strain-free compound has been unambiguously determined by spectroscopic methods.* Although the detailed reaction pathway of the conversion of (**1b**) to (**3**) remains to be determined, it appears that a combination of the activating effect of the second aryl methoxyl group in (**1b**), coupled with the requisite *endo* stereochemistry of α -(**2b**), is crucial to the success of this

conversion. Consistent with this hypothesis, was the isolation of β -(**2b**) from the reaction of (**1b**). None of α -(**2b**) was detected. We consider that (**5**) slowly forms a carbocation which by an intermolecular hydride abstraction undergoes conversion to (**3**). Consistently, the dehydro product (**4**) was also formed in the reaction.

Although (**3**) is formed in low yield, this one-step synthesis from readily accessible⁵ (**1b**)* opens for study this interesting new ring system. The analogous product* is formed in similar yield when the substrate (**1**) ($R^1-R^2 = -OCH_2O-$) is employed.⁷

* The conditions employed were: SnCl₄ (0.1M, 1.5 equiv.), MeNO₂, room temp., 5 min. The substrates (**1a**) and (**1b**) thus appear to have similar reactivities.

† All new compounds had satisfactory microanalysis and unequivocal spectra.

‡ C₂₃H₂₆O₄, M⁺, 366; 14% yield; m.p. 151–152 °C; δ_{H} (400 MHz, CDCl₃ with additional comprehensive decoupling experiments at 250 MHz) 6.7 (s, 2 × ArH), 6.64 (s, 2 × ArH), 3.87 (6 H, s, 2 × OMe), 3.81 (6 H, s, 2 × OMe) 3.71 (dt, $J_{1,2}$ 3.2 and $J_{1,3}$ 1.6 Hz, 1-H), 3.34 (2 H, m, 4-H and 7-H), 2.75 (1 H, dtt $J_{1,3}$ 1.6, $J_{2,3}$ 3.2, and $J_{3,4}$ 8.0 Hz, 3-H), 2.11 (2 H, m, $J_{5\beta,5\alpha}$ 7.2, $J_{5\beta,6\alpha}$ 4.8, $J_{4,5\beta}$ 8.0 Hz, 5 β -H and 6 β -H), 2.07 (2 H, t, $J_{3,4}$ 8.0, $J_{4,5}$ 8.0 Hz, 4-H and 7-H), 1.51 (2 H, m, $J_{5\alpha,5\beta}$ 7.2, $J_{5\alpha,6\beta}$ 4.8, $J_{4,5\alpha}$ 8.0 Hz, 5 α -H and 6 α -H); δ_{C} (62.5 Mz, assignments confirmed by a series of INEPT⁶ spectra) 148.84 (s, C-5'), 147.81 (s, C(4')), 134.43 (s, C-1'), 132.22 (s, C-2'), 111.56 (d, C-3'), 110.65 (d, C-6'), 56.01 (q, Me), 40.35 (d, C-1), 42.23 (d, C-4, C-7), 36.58 (d, C-3), 35.15 (t, C-6 and C-5) and 28.98 (t, C-2).

References

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- 7 Full details will be published elsewhere.

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