nine residues,[16] exhibits a potential of only +0.18 V[15] which does not differ significantly from the aquocopper value.[17])

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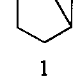
The Photochemical Synthesis of a Tricyclo[2.2.0.0^{2,5}]hexane[1]

Sir:

A considerable amount of research on small ring compounds has been devoted to the study of tricyclohexane ring systems. A number of papers have been published in recent years on the synthesis and properties of compounds possessing the highly strained tricyclo[3.1.0.0^{2,6}]-, tricyclo[2.2.0.0^{2,6}], and tricyclo[3.1.0.0^{2,4}]hexane structures **1**, **2**, and **3**.[3-18] In this communication we wish to report the first successful synthesis of a compound, which possesses the hitherto unknown tricyclo[2.2.0.0^{2,5}]hexane ring (**4a**), namely, 1,2-diphenyltricyclo[2.2.0.0^{2,5}]hexan-2-ol (**4b**). Our synthesis consists of five steps from 2-phenylbicyclo[1.1.1]pentan-2-ol (**5**),[19] and affords the tricyclohexanol (**4b**) in 20% overall yield.



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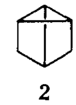

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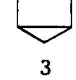

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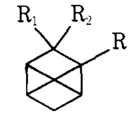
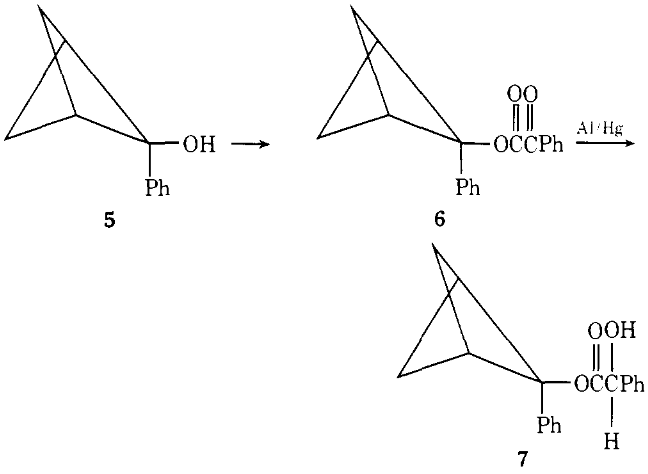


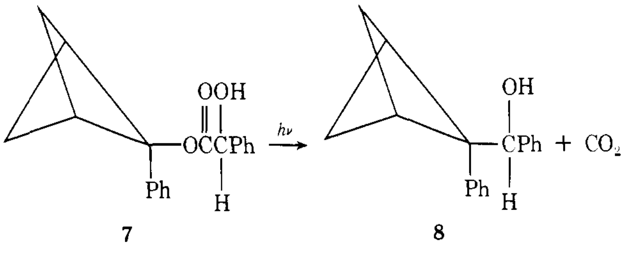
4a, R$_1$ = R$_2$ = H
4b, R$_1$ = Ph; R$_2$ = OH

2-Phenylbicyclo[1.1.1]pentane 2-benzoylformate (**6**) was prepared by stirring an equimolar mixture of 2-phenylbicyclo[1.1.1]pentan-2-ol (**5**), benzoyl formic acid chloride,[20] and pyridine at 10 °C for 1 h in benzene. The benzoylformate ester **6** was recrystallized from petroleum ether and was isolated as a white crystalline solid mp 63–64 °C (ir (CCl$_4$) 3.34, 3.45, 5.77, 5.91, 6.25 μ; NMR (CCl$_4$) methylene δ 2.61 (doublet of doublets J = 2.7, 10.3 Hz (1 H)), 1.58 (doublet of doublets J = 3.0, 10.3 Hz (1 H)), 1.89 (doublet J = 2.7 Hz (1 H)), 1.72 (doublet J = 3.0 Hz (1 H)), bridgehead δ 3.37 (singlet (2H)), aromatic δ 7.30 (multiplet (8 H)), 7.86 (multiplet (2 H)).

Upon treatment with aluminum amalgam in wet ether, ester **6** was reduced quantitatively to the mandelate ester **7**. Ester **7** is a white solid mp 127–128° (ir (CCl$_4$) 2.82, 3.32, 5.78 μ; NMR (CCl$_4$) methylene δ 1.94 (doublet of doublets J = 3.0, 10.5 Hz (1 H)), 1.48 (doublet of doublets J = 2.5, 10.5 Hz (1 H)), 1.61 (overlapping doublets (2 H)), bridgehead δ 3.25 (singlet (2 H)), benzyl δ 4.87 (singlet (1 H)), aromatic δ 7.20 (multiplet (10 H))).



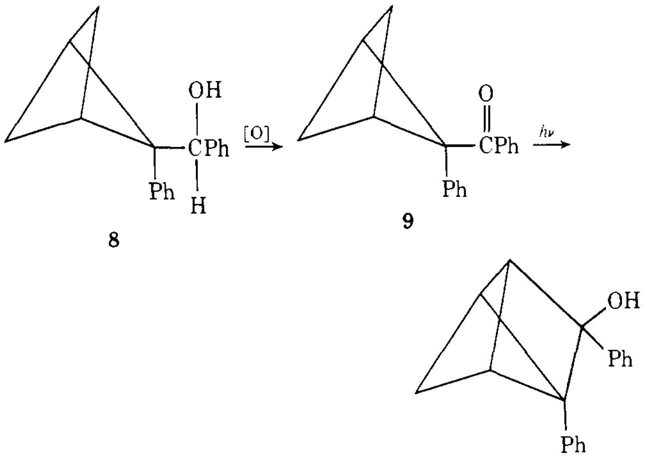
Irradiation of a 0.004 M solution of **7** in *tert*-butyl alcohol at 2537 Å for 5 h led to decarboxylation[21] and afforded the bicyclopentylphenylcarbinol **8** (20%). The carbinol **8** was purified by silica gel chromatography and was isolated as a colorless oil (ir (CCl$_4$) 2.80, 3.40, 6.28 μ; NMR (CCl$_4$) methylene δ 3.27 (doublet of doublets J = 3.5, 10.5 Hz (1 H)), 1.87 (doublet of doublets J = 2.2, 10.5 Hz (1 H)), 2.17 (doublet J = 3.5 Hz (1 H)), 1.31 (doublet J = 2.2 Hz (1 H)), bridgehead δ 3.05 (doublet J = 18.0 Hz (1 H)), 3.38 (doublet J = 18.0 Hz (1 H)), benzyl δ 5.57 (singlet (1 H)), aromatic δ 6.90 (multiplet (9 H)), 6.07 (doublet J = 7 Hz (1 H)); m/e 232, 143 (base peak), 128, 107, 79, 77.



Oxidation of the carbinol **8** in acetone with 0.7 M Jones reagent[23] afforded 2-phenyl-2-benzoylbicyclo[1.1.1]pentane

(**9**) in quantitative yield. Ketone **9** is a white solid mp 101–102° (ir (CCl_4) 3.40, 5.98, 6.26 μ; NMR (CCl_4) methylene δ 2.00 (doublet of doublets $J = 2.5$, 10.0 Hz (1 H)), 1.86 (doublet $J = 2.5$ Hz (1 H)), 1.71 (doublet $J = 2.2$ (1 H)), 2.06 (doublet of doublets $J = 2.2$, 10.0 Hz (1 H)), bridgehead δ 3.31 (singlet (2 H)), aromatic δ 7.26 (multiplet (8 H)), 7.88 (multiplet (2 H)); *m/e* 248 M^+, 233, 143, 128, 105 (base peak), 77.

Irradiation of ketone **9** at 310 nm (0.01 M in *tert*-butyl alcohol) resulted in 100% conversion to 1,2-diphenyltricyclo[2.2.0.0^{2,5}]hexan-2-ol (**4b**). The photocyclization[24] was complete after 10 min of irradiation.



8

9

4b

The tricyclic alcohol **4b** was isolated as a pale yellow oil and was purified by preparative gas chromatography. Its structure is consistent with its spectral characteristics: ir (CCl_4) 2.81, 3.40 μ; NMR (CCl_4) methylene δ 2.23 (doublet $J = 5.0$ Hz (1 H)), 2.19 (doublet $J = 5.0$ Hz (1 H)), bridgehead δ 2.79 (doublet $J = 17.0$ Hz (1 H)), 3.65 (doublet $J = 17.0$ Hz (1 H)), 3.86 (singlet (1 H)), aromatic δ 7.20 (multiplet (10 H)), *m/e* 248 M^+, 233, 230, 143, 128, 105 (base peak), 77.

The tricyclohexanol **4b** is found to be thermally stable below 100 °C. When heated under vacuum to 160°, however, it undergoes rapid decomposition to a mixture of products the major of which has been identified as ketone **9**.

We are presently investigating the physical and chemical properties of the tricyclo[2.2.0.0^{2,5}]hexanol (**4b**). The general synthetic utility of mandelate ester photodecarboxylation is also being explored in our laboratory.

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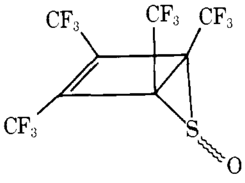
An Extraordinarily Facile Sulfoxide Automerization

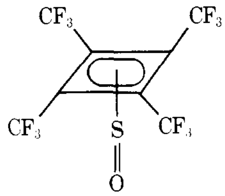
Sir:

Perfluorotetramethyl(Dewar thiophene) (**2**)[1] is rapidly transformed by peroxytrifluoroacetic acid into a very sensitive and unusual compound (**1**). Careful sublimation of the crude product at room temperature (aspirator) gives colorless blocks, mp 31–32°, with these spectral characteristics:[2] ir (CH_2Cl_2) 1664 (w), 1410 (w), 1364 (m), 1188 (br, s) cm^{-1}; ^{19}F NMR (CH_2Cl_2) δ 18.17;[2] ms 372 (parent).

Although the new compound clearly has the composition of the anticipated sulfoxide **1a,** its ^{19}F NMR spectrum down to temperatures as low as −95° (where it remains a narrow singlet) is more easily accommodated by the highly symmetrical structure **1b.** Certainly that structure is unconventional, requiring as it does that sulfur play a role previously reserved for metals,[3] but the opportunities for S–C bonding in such a C_{4v} sulfur monoxide–cyclobutadiene complex are not bad.[4]



1a



1b

The infrared and Raman spectra of **1a,** of course, should each reveal only a single C=C stretching band, at the same frequency. While the C_{4v} structure **1b** should give rise to a single ring stretching fundamental (of E symmetry) in the infrared spectrum at >1500 cm^{-1}, two may be expected in this region of the Raman spectrum (B_1, E). Since the E band should be weak,[5] the major Raman feature should appear at a different frequency from the infrared absorption. In fact, a single band was found in the 1500–1800 cm^{-1} region of the Raman spectrum,[6] identical in position and similar in shape to the infrared band.[7] Hence **1a** must be the correct structure, and the anomalous ^{19}F spectrum must reflect the existence of a degenerate rearrangement facile enough to render all 12 fluorines magnetically equivalent even at −95°. This surmise has now been confirmed by NMR measurements at still lower temperatures. Below −100° in Freon 21 the signal broadens rapidly and evolves into two resonances of equal area separated by 2.82 ppm at the slow exchange limit ($T_c = -124 \pm 3°$ [8]). The free energy of activation for exchange at −124° is thus 6.8 ± 0.3 kcal/mol.

The high reactivity of **1a** is manifest in its rapid destruction at room temperature by such reagents as methanol, dimethyl sulfoxide, and furan. Reaction with the last yields a 1:1 adduct