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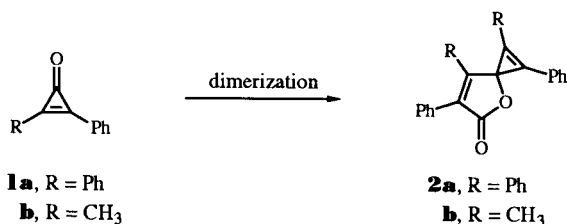
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The regiochemistry of the previously reported dimer of methylphenylcyclopropenone is corrected through analysis of the long-range  $^1\text{H}$ ,  $^{13}\text{C}$  correlated (COLOC) 2D nmr spectrum.

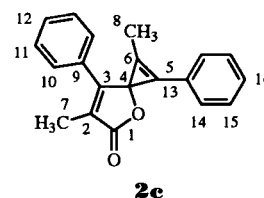
*J. Heterocyclic Chem.*, **30**, 567 (1993).

One of the earliest reported reactions of diphenylcyclopropenone (**1a**) involved a thermally induced dimerization affording spirolactone **2a** [1]. More recently, this observation has been extended to a variety of cyclopropenones, including methylphenylcyclopropenone (**1b**), for which cupric bromide has been employed as a catalyst [2]. The structure of the dimer in the latter case was assigned as **2b** on the basis of uv spectral analysis. This same structure appears in a recent report of the thermal behavior of **1b**



[3]. From a mechanistic viewpoint, dimerization requires CO-C bond-breaking *via* an ionic or radical pathway. Of the two options available in **1b**, one would expect ring opening at CO-CPh to be more favorable due to the stabilizing effect of the phenyl substituent on incipient carbanion or radical species. The regiochemistry in **2b** does not correspond to this expectation. This apparent mechanistic anomaly prompted us to re-examine the regiochemistry in **2b** with the help of modern nmr techniques.

The spectral analysis of the dimer of **1b** was carried out at 300 MHz ( $^1\text{H}$ ) and 75 MHz ( $^{13}\text{C}$ ). Only execution of  $^1\text{H}$ ,  $^{13}\text{C}$ , and COLOC [4] experiments was necessary to determine  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts and regiochemistry assignments, which are summarized in Table 1. Using the long-range heterocorrelation (COLOC) spectrum shown in Figure 1, a convenient starting point for the spectral analysis was the  $^{13}\text{C}$  carbonyl peak (C-1). This showed a long-range correlation ( $^3\text{J}$ ) with a methyl group (H-7) at  $\delta$  2.06 which must be that of the lactone ring. No such correlation would be observed for **2b**. This observation, together with the long-range correlation ( $^3\text{J}$ ) of C-4 exclusively with the remaining methyl group (H-8) at  $\delta$  2.27 (for **2b**, both methyl resonances would correlate with the oxygen bearing C-4 aliphatic carbon), defines the regiochemistry of the dimer as that shown in **2c**. A distinction between



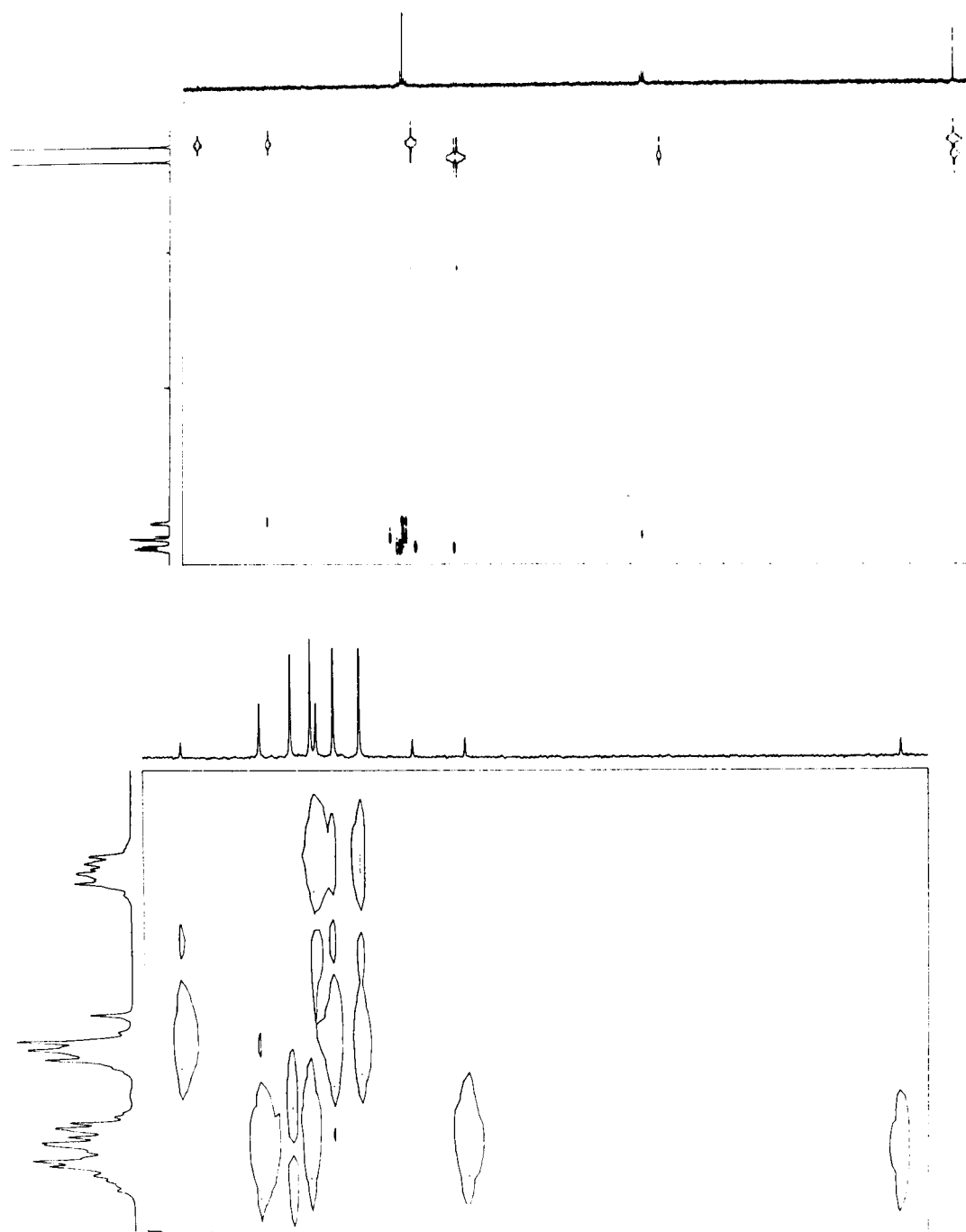
C-5 and C-6 can be made on the basis of the long-range correlation ( $^3\text{J}$ ) of C-5 with aromatic protons (H-14). Assignment of C-3 may be made in a straightforward fashion from its correlation ( $^3\text{J}$ ) with aromatic protons (H-10) in addition to H-7. Continuing this line of reasoning, the remaining designations may be extracted from Table 1.

Table 1  
 $^{13}\text{C}$  and  $^1\text{H}$  Chemical Shifts, and 2D NMR Data for **2c**

Position	$^{13}\text{C}$ Shift (ppm)	$^1\text{H}$ Shift (ppm)	COLOC [ $\delta$ ]
1	173.52 s		2.06
2	127.02 s		2.06
3	158.11 s		2.06, 7.07-7.10
4	73.42 s		2.27
5	117.68 s		2.27, 7.39-7.44
6	117.12 s		2.27
7	10.08 q	2.06 s	
8	9.87 q	2.27 s	
9	131.51 s		7.29-7.32
10	128.55 d	7.07-7.10 m	7.29-7.32
11	128.05 d	7.29-7.32 m	7.07-7.10, 7.29
12	128.89 d	7.29-7.32 m	7.07-7.10
13	126.01 s		7.39-7.44
14	129.00 d	7.39-7.44 m	
15	129.38 d	7.39-7.44 m	
16	129.98 d	7.39-7.44 m	

[a] Long-range carbon-proton correlation observed in the long-range COLOC spectrum.

In conclusion, the true regiochemistry of the dimer of **1b** is in agreement with the expected mode of ring opening of this unsymmetrical cyclopropenone.

Figure 1. COLOC Spectrum of **2c**.

## EXPERIMENTAL

One and two-dimensional nmr experiments were carried out on a Bruker AC-300 PFT-NMR spectrometer using TMS as the internal standard (50 mg of sample in 0.6 ml of deuteriochloroform). The long-range coupling delay of the COLOC experiment was optimized for 10 Hz. The melting point was determined on a Hoover-Unimelt apparatus and is uncorrected.

Dimerization of Methylphenylcyclopropenone (**1b**).

A suspension of methylphenylcyclopropenone (**1b**) (77.9 mg, 0.5 mmole) and cuprous chloride (21.7 mg, 0.2 mmole) in dioxane (4 ml) was allowed to stir overnight at room temperature. The blue solution was diluted with dichloromethane (5 ml), filtered,

extracted with water (2 x 10 ml), and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded a pale yellow solid which was triturated with pentane to yield **2c** as a colorless solid (51.5 mg, 66%), mp 166-168° (lit 169° [2]).

## REFERENCES AND NOTES

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