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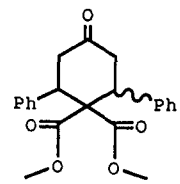
The Correct Stereochemistry Of Dimethyl 2,6-Diphenyl-4-Oxo-Cyclohexane-1,1-Dicarboxylate

Alex T. Rowland,*[a] Mark D. Winemiller,[b] Michal Sabat[b]
[a]Department of Chemistry, Gettysburg College, Gettysburg, PA 17325
[b]Department of Chemistry, University of Virginia, Charlottesville, VA 22901

Abstract: Conflicting literature reports dealing with the stereochemistry of the cyclohexanone formed from the Michael reaction of dibenzalacetone with dimethyl malonate have been resolved by X-ray structure analysis. The compound is the trans isomer with a twist conformation.

This report concerns the stereochemistry of the cyclohexanone formed from the Michael reaction of dimethyl malonate with dibenzalacetone. An early study of this combination was reported by Kohler,[1] who expanded upon work by Borsche[2] to correctly identify the product as a dimethyl 2,6-diphenyl-4-oxocyclohexane-1,1-dicarboxylate (1) with undetermined stereochemistry.



(1)

In 1973 Otto[3] revisited Kohler's work and concluded that the product was the meso isomer in which the phenyl groups occupy equatorial positions. One of us (ATR) investigated this oxo diester in 1982[4] and naively assumed that the product was the meso, as stated by Otto, in spite of ^{13}C NMR data which clearly indicated that the ester carbonyl carbons are homotopic, as are the ester methyl carbons. At the same time in 1982, Theobald[5] clarified the situation by suggesting that this Michael product was the dl pair which adopts a twist conformation with the phenyl groups in quasi-equatorial positions. The stereochemistry of the oxo diester seemed to be settled by Theobald's work.

Papers by Reddy in 1992, however, again confounded the stereochemistry issue. Two separate signals for the carbonyl carbons of the ester groups were reported[6] in the δ 165 region of the ^{13}C NMR spectrum and separate methyl singlets were observed at ca. δ 3.4 in the ^{1}H NMR spectrum. Another paper[7] repeated the diastereotopic ester group theory and incorrectly assigned the methyl absorption at δ 51.86 (^{13}C NMR) to C-2 (C-6). The assumption of cis stereochemistry was carried forward in a subsequent study of the synthesis of spiropyrimidines.[8]

In order to settle the issue we have recorded the ^{1}H NMR spectrum at 500 MHz and the ^{13}C NMR spectrum at 125 MHz of 1.[9] The results were virtually identical to those reported earlier[4] and confirmed the homotopic relationship of the ester groups in a trans/twist arrangement. The carbonyl carbon signal at δ 169.7 exhibited a singlet even at -40 °C.

The stereochemistry was determined unambiguously by X-ray crystallography[10] which clearly shows the oxo diester to be the trans isomer with a twist conformation (Figure 1).

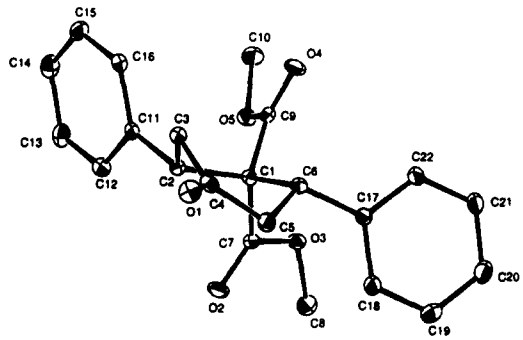


Figure 1. ORTEP Representation of the X-ray Model of 1 Without Hydrogens.

The cis (or meso) isomer of 1 remains unknown. We continue to examine related Michael reactions in order to determine the correct stereochemistry of 2,6-diaryl-4-oxo-cyclohexanes which bear identical or dissimilar groups at C-1.[1,4,11,12,13,14]

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9. NMR spectra were obtained in $CDCl_3$ solutions with a GE Omega 500 spectrometer operating at 500.1 MHz for ^1H and 125.7 MHz for ^{13}C. The oxo diester was prepared according to the procedure described by Reddy:[6] mp 136-137°. ^{13}C NMR δ 42.2, 43.7, 51.7, 63.6, 127.3, 127.9, 128.3, 139.4, 169.7, 209.5.
10. X-ray crystallographic analysis of 1: colorless block, $C_{22}H_{22}O_5$, FW = 366.41, monoclinic; a = 12.698(5), b = 7.644(3), c = 19.410(7) Å, β = 105.74(2)°, V = 1813(2) Å^3, Z = 4, space group $P2_1/n$ (No. 14, alternate setting). Measurements were carried out on a Rigaku AFC6S diffractometer using MoKα radiation (λ = 0.71069 Å) at -120 °C to 2θ max of 46°; number of reflections measured, 2894; numberof unique reflections, 2752 (R_{int} = 0.033); number of reflections I>3σ(I), 1805; number of variables, 245; residuals R, R_W, 0.056, 0.075; goodness of fit, 2.20. A list of refined coordinates and e.s.d.'s has been deposited by the Editor at the Cambridge Crystallographic Center.
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