

as a colorless oil which solidifies in white needles. The compound is purified by crystallization in pentane at -10°C . (M.P. ($\text{R}=\text{CH}_3$) : $39.5 - 40^{\circ}\text{C}$; ($\text{R}=\text{C}_2\text{H}_5$) : $47-49^{\circ}\text{C}$; ($\text{R}=\text{n},\text{C}_4\text{H}_9$) : $57-59^{\circ}\text{C}$). The yield is of 70 % calculated on the diazoester. Maleate and fumarate (the usual by-products of the reactions of diazoesters) are completely absent even in the raw material as shown by G.L.C. In fact only a single compound could be detected beside the diimide in excess and the missing 30 % may be accounted for by the presence of polymeric residue in the distillation flask.

In the absence of catalyst, the nitrogen evolution is observed only at 150°C and runs to completion within 180 minutes (yield : 15 %).

Identification of product (III, $\text{R}=\text{CH}_3$) : The elemental analysis corresponds to the formula ($\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_2$). (Calculated : C, 60.6; H, 9.15; N, 14.14 % ; found : C, 60.6; H, 9.5; N, 14.4 %). The mass spectrum shows a main peak at $M/e = 198$ (calculated : 198) and fragments at $M/e = 183$ ($\text{M}^+ - \text{CH}_3$), 155 ($\text{M}^+ - \text{C}_3\text{H}_7$), 139 ($\text{M}^+ - \text{CH}_3\text{-CO}_2$), 72 ($\text{CH-CO}_2\text{-CH}_3$). The i.r. spectrum shows the absence of the typical cumulene absorption at 2148 cm^{-1} and the presence of two new bands at 1725 ($\text{C}=\text{O}$ ester) and 1665 ($\text{C}=\text{N}$ - imine) cm^{-1} . This last absorption band allows the rejection of formula IV.

The ^1H n.m.r. spectrum (100 MHz, TMS as reference) shows singlets at δ (ppm) = 5.33 ($\underline{\text{H}}$ aziridine), 3.71 ($\underline{\text{CH}}_3\text{-O}$), two heptuplets ($\underline{\text{CH}}$ isopropyl) at 4.14 ($^3\text{J} = 6.7$) ($\text{C} = \text{N} - \underline{\text{CH}}$) and 3.64 ($^3\text{J} = 6.3$) ($\text{N} - \underline{\text{CH}}$) and two doublets (corresponding $\underline{\text{CH}}_3$ isopropyl) at 1.16 ($^3\text{J} = 6.7$) and 1.03 ($^3\text{J} = 6.3$ Hz).

The ^{13}C n.m.r. spectrum (total decoupling, TMS as reference) shows signals at 150.9 ppm ($\underline{\text{C}}=\text{O}$), 147 ($\underline{\text{C}}=\text{N}$), 58.6 ($\underline{\text{CH}}_3\text{-O}$), 84.6 ($\underline{\text{CH}}$ aziridine) as well as the typical peaks of both isopropyl groups (46.7 and 45.2 for the two different $\underline{\text{CH}}$ isopropyl moieties and 25 and 20.7 for the corresponding $\underline{\text{CH}}_3$ groups).

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DIASTEREOTOPIC gem-DIMETHOXY GROUPS WITH A RING-PUCKERED MEISENHEIMER-TYPE σ -ADDUCT

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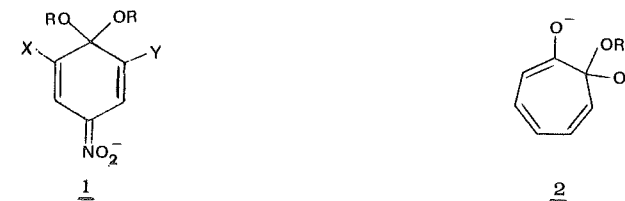
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Equivalence of the gem-dialkoxy groups of σ -adducts is a firm notion in chemistry since the time of Meisenheimer.¹ However, this situation, when it is recognized that it simply relies on the planarity (or mean planarity) of the ring for all systems reported so far, such as with cyclohexadiene (1)² or cycloheptatriene (2)³ systems, is open to question.

We report, therefore, the first σ -adduct where ring puckering induces nonequivalence of the gem-dialkoxy groups. Thus, during our efforts towards the total synthesis of zoanthoxanthins,⁴ the idea was to induce ring puckering in a type-2 adduct by inhibiting negative charge dispersal on the seven-membered ring³ through benzene annelation.

The idea, though unprofitable with 2-methoxy-4,5-benzotropone, where



reluctancy towards o-quinoid forms resulted in resistance to potassium methoxide addition, worked well with 2-methoxy-3-nitro-4,5-benzotropone.⁵ In fact, on the mixing of a ca. 2.5 M solution of 2-methoxy-3-nitro-4,5-benzotropone (3) in dried DMSO with the five-fold excess of a concentrated methanolic solution of potassium methoxide, orange crystals of 4, m.p. 189° from DMSO, precipitated. The structure of 4, which is the first σ -adduct isolated from tropenoids,⁶ is supported by elemental analysis, by the observation that on acidification of a DMSO solution of 4, 3 is immediately reformed in quantitative yield, and, finally, by the ^1H nmr