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THE REACTION OF AZIBENZIL WITH SULFUR DIOXIDE:
STRUCTURAL REVISION AND ITS PROOF BY ^{13}C NMR SPECTROSCOPY

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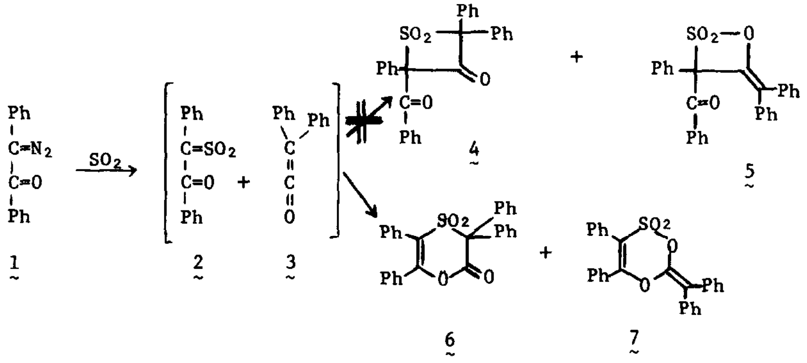
It has been reported[1] that the reaction of azibenzil (**1**) and sulfur dioxide leads amongst other materials to two new products which were assigned structures **4** and **5**. These were formulated as arising from [2+2] cycloaddition of phenylbenzoylsulfene (**2**) and diphenylketene (**3**), intermediates both readily derivable from **1** by precedented routes. Upon examination of the evidence it appeared to us that the spectroscopic features described for these compounds would be more satisfactorily explained by structures **6** and **7**, which could arise from [4+2] cycloaddition of the same intermediates.



In particular these revised structures would account for the complete absence in the infrared spectra of either of these products of any significant absorption between 1630 and 1750 cm^{-1}, as is clearly required for the benzoyl carbonyl group in both 4 and 5. No previous examples of a cycloaddition of a sulfene and a ketene had been reported, and the only earlier account of a α-ketosulfene describes the formation of a six-membered ring dimer from benzoylsulfene,[2] a reaction which provides a measure of precedent for our proposed structures (6 and 7).

An interest in both the chemistry of sulfenes[3] and in the application of ^{13}C n.m.r. spectroscopy to structural problems,[4] prompted us to apply this method to the determination of the structures of the azibenzil-SO_2 products. Accordingly we have repeated the reactions as described by Nagai, et al.[1] and have obtained products which are evidently the same materials, although a few differences in their infrared spectra were noted;[5] the compound melting at 238-240° we refer to as the "high-melting compound" and that of m.p. 178-179° as the "low-melting compound".

The major difference between the structures generated by [2+2] and [4+2] addition is the presence of ketonic carbonyl functions in the former and their absence in the latter. It is well known that the ^{13}C absorptions of carbonyl carbons appear at appreciably lower fields than those of other sp^2-hybridized carbons such as olefinic and aryl nuclei.[6] It is also known that the carbonyl carbon in an ester function is significantly shielded relative to ketonic carbonyls. Consequently the ^{13}C spectra of these cycloadducts should provide a clearcut distinction between the two structural types: 4 and 5 vs. 6 and 7. The ^{13}C spectrum[7] of the "low-melting" isomer contains, in addition to the major pattern for the phenyl groups in the range 124-133 ppm, four signals at δ_C 121.8, 137.6, 147.5 and 157.8. Careful scrutiny of the lower field region (down to 235 ppm) revealed no additional absorption; similarly no signals apart from those arising from solvent molecules were detected in the region 30-121 ppm. The absence of solute signals in these regions clearly rules out structure 5 as a possible formulation since the benzoyl carbonyl would be expected to absorb in the low field portion and the quaternary ring carbon in the high field region; although it is difficult to predict the precise shieldings that would be expected for these nuclei in structure 5, there is no precedent for either to absorb close to the positions of the observed signals.[8] On the other hand, structure 7 has two carbons bearing oxygen which are expected to be appreciably deshielded relative to the aryl carbons and presumably give rise to the signals at 157.8 and 147.5 ppm; the 137.6 and 121.8 ppm signals seem reasonable for the remaining olefinic carbons.

The ^{13}C spectrum of the high-melting compound also contains four one-carbon signals in addition to the aryl absorption (125-133 ppm); these appear at δ_C 79.1, 123.2, 152.7 and 163.0. Again, these values are not compatible with structure **4** for which one expects two lower field peaks (the ketonic carbonyls) and two high field signals. Structure **6**, however, contains *one* saturated quaternary carbon (79.1 ppm), the lactonic carbonyl (163.0 ppm) and two signals similar to those found for **7** (123.2 and 152.7 ppm). It may be noted that the unsubstituted six-membered ring lactone cyclopentanolide exhibits carbonyl absorption at 167.5 ppm.[9] Consequently the ^{13}C data are completely consistent with structures **6** and **7** and quite incompatible with the previously proposed structures **4** and **5**.

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3. *Cf*. J.F. King, B.L. Huston, A. Hawson, J. Komery, D.M. Deaken, and D.R.K. Harding, *Canad. J. Chem.* **49**, 936 (1971), and earlier papers cited.
4. This paper is Part XV in the series ^{13}C NMR Studies; Part XIV, G.W. Buchanan and J.B. Stothers, *Canad. J. Chem.* **47**, 3605 (1969).
5. The high-melting compound was obtained from both the thermal and photochemical reactions of **1** and SO_2, in about 20% and 9% yields, respectively. Elemental analysis showed C, 74.64; H, 4.15; S, 7.10%; $C_{28}H_{20}O_4S$ requires C, 74.33; H, 4.46; S, 7.07%. The infrared showed bands at 1785(s), 1629(m), 1329(s), 1157 and 1139 cm^{-1}(s), in rough agreement with the infrared bands reported by Nagai, *et al.*[1]: 1785, 1605, 1350, and 1140 cm^{-1}. In addition, we also note the following additional bands at 1495(m), 1448(m), 1299(m), 965(w), 907(w), and 695 cm^{-1}(m). We obtained the low-melting compound only from the photochemical reaction. The infrared spectrum showed

bands at 1600(m), 1575(w), 1365(s), 1180(s) and 1130 cm^{-1}(m); reported[1]: 1605, 1585, 1350 and 1130 cm^{-1}. We also observed bands at 1492(w), 1448(w), 1290(m), 1240 and 1210(s), 1060(w), 1005(w), 905(w), and 695 cm^{-1}(m).

6. J.B. Stothers and P.C. Lauterbur, Canad. J. Chem. **42**, 1563 (1964). While the vast majority of published ^{13}C shielding data have been reported relative to CS_2 or C_6H_6, recently a trend toward the use of tetramethylsilane (TMS) as the primary reference material has developed. Consequently, the data in the above reference may be converted to the TMS scale (δ_C) using the value, $\delta_C^{CS_2}$ 192.8.

7. The ^{13}C spectra were obtained at 25.2 MHz on a Varian XL-100 spectrometer system under conditions of complete proton decoupling. In each case sufficient acetone-$\underline{d}_6$ was added to the solution to give a signal suitable for a deuterium lock. Chloroform and methylene chloride were employed as solvents for the low and high-melting materials, respectively. In each case time-averaged spectra were recorded for 500 or 1000 Hz sweep-widths over the range 30-235 ppm from TMS. Peak positions were measured relative to the acetone carbonyl signals and converted to the TMS scale using the value 205.1 ppm.[8]

8. J.B. Stothers, in "Carbon-13 NMR Spectroscopy", Academic Press (in press).

9. K. Overton and J.B. Stothers, unpublished observations.