ratios of k_{isc} (methylated/parent), the lifetime of the aniline singlet (methylated/parent), the lifetime of the aniline triplet (methylated/parent), and k_2 (methylated/parent). The last factor is not likely responsible since the rate k_2 should be diffusion limited for **4**, **5**, and **6**.

The second important feature from Table I involves the formation of adducts and their relative amounts. The absence of adduct in the case of **6** suggests the need for the presence of N–H bonds, a situation supported by the data of Hansen[10] and the single product we observe with **5**. This is also consistent with the ratios of adduct to dimer in the last column in Table I, where the average ratio is 1.5 ± 0.2 for **4** and 0.82 ± 0.03 for **5**. This is very close to the statistical ratio of two based on the number of N–H bonds. This suggests that the radical ion pair (or charge-transfer complex) forms equally well for all of the anilines but that the product-forming (coupling) reaction depends on the number of N–H bonds. The relative amounts of aminyl vs. aminoalkyl radicals formed apparently depends on the nature of the reactive intermediates and the polarity of the reaction medium.[12-17] Our data are consistent with a substantial preference for the intermediacy of the former, a result consistent with other similar systems like styrene and amines.[12]

Further support for the formation of dimers via the triplet and for formation of adducts via a state other than the diene triplet come from data in Table II. Chrysene absorbs most of the light at 350 nm and has appropriate energy levels (E_s = 79.2 kcal/mol, E_T = 57.3 kcal/mol) to harvest all singlets and sufficiently high intersystem crossing to convert about 90% of all photons into diene triplets. (The remainder presumably are lost mostly via fluorescence and nonradiative decay.) Upon addition of chrysene CHR to solutions of **1** in **5**, the efficiency of dimer formation increases and that for adduct precipitously decreases. Certainly, adduct cannot be coming from the diene triplet. This was already suggested by energetic considerations discussed earlier. The aniline triplet and **1** predict a free-energy change of −1 kcal/mol for electron transfer, a result not very compelling in favor of this state. That prediction changes to +1 kcal/mol for **5** and does parallel the observed decrease in adduct forming efficiency. However, one might argue that aniline triplets ought to be rapidly quenched via energy transfer to the diene but that behavior is not necessarily exclusive. The increase in the quantum yields in going from 125 to 250 mM **1** in the absence of CHR (entries 1 and 3 in Table II) suggests that either of the aniline excited states could account for adduct since its formation depends on a bimolecular reaction, first order, in the concentration of **1**. Likewise, it is consistent with the singlet of **1** being the necessary intermediate because the higher concentration increases the probability of its singlet formation either by direct irradiation or by energy transfer from aniline singlets. In other words k_1 [DI] becomes competitive with or dominant over k_{isc} in eq 6. The absence of products from alkyl amines suggests that a pathway involving direct hydrogen atom abstraction from the amine to give a radical pair is not very likely.

In summary we favor the intermediacy of the singlet(s) as the necessary species for adduct formation. The accidental overlap of their excited-state energies makes the discrimination between the two unlikely from steady irradiation studies. These data are consistent with our proposed notion that four-π-electron systems give adduct formation via electron-transfer-induced coupling. The difficulties in getting this as exclusive behavior arise from the rich (and mechanistically complicated) competitive photochemistry.

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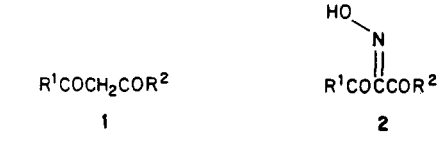
Stereochemical Assignments for 1-Phenyl-1,2,3-butanetrione 2-Oxime and Related Compounds

Summary: The 2-oximes of 3-methyl-, 3-ethyl-, and 3-isopropyl-1-phenyl-1,2,3-propanetrione formed by nitrosation of β-diketones exist preferentially in the *Z* configuration. For 3-*tert*-butyl-1-phenyl-1,2,3-propanetrione 2-oxime the (*E*)- and (*Z*)-oximes are formed in nearly equal amounts. An explanation for the steric effect of the *tert*-butyl group is suggested.

Sir: The configuration and conformation of benzil monooxime and related α-oxo oximes have been investigated extensively.[1-4] However, the stereochemistry of 1-phenyl-1,2,3-butanetrione 2-oxime and related compounds has not been similarly investigated. We wish to describe the preparation of a series of 1-phenyl-3-alkyl-1,2,3-propanetrione 2-oximes, including the first example for which both the (*E*)- and (*Z*)-oximes have been isolated. We have determined the configuration of the oximes and have observed an unexpected steric effect on the geometry of these compounds.

The oximes **2a–e** were prepared by acid-catalyzed nitrosation of the β-diketones **1** with butyl nitrite in carbon tetrachloride.[5] Nitrosation of **1a–c** resulted in the formation of only one of the two possible stereoisomeric modifications, assigned (vide infra) as the (*Z*)-oximes **2a–c**.



a, R^1 = Ph; R^2 = Me
b, R^1 = Ph; R^2 = Et
c, R^1 = Ph; R^2 = *i*-Pr
d, R^1 = Ph; R^2 = *t*-Bu
e, R^1 = *t*-Bu; R^2 = Ph

In the case of **1d**, the (*Z*)-oxime **2d** (mp 67–69 °C) and the

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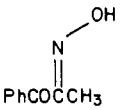
(*E*)-oxime **2e** (mp 100–102 °C) were formed in nearly equal portions. The isomers were separated by medium-pressure chromatography[6] on silica gel with hexane–acetone (19:1).

Evidence that **2a–d** shared the same oxime geometry was apparent in their ^{1}H NMR spectra. In particular, the signals for the ortho protons on the phenyl groups of each of the compounds appeared as a two-proton multiplet centered at δ 7.78 (signal width at half-height, 12 Hz) for samples run in deuteriochloroform. However, the signal for the corresponding phenyl protons in **2e** occurred at δ 8.00. Acetylation of **2a–e** with acetyl chloride in ether–pyridine gave the oxime acetates. For **2e** conversion to the acetate resulted in a marked downfield shift of the ortho proton signal to δ 8.20. Baas and Cerfontain have reported a similar 0.2 ppm downfield shift on acetylation for the ortho proton signal of (*E*)-1-phenyl-1,2-propanedione 2-oxime (**3**).[3] In contrast, acetylation of **2a–d** resulted in



3

only a small shift of 0.04 ppm for the ortho proton signal to about δ 7.82. Baas and Cerfontain likewise report that the ortho proton signal for (*Z*)-1-phenyl-1,2-propanedione 2-oxime is insensitive to acetylation.

The NMR spectral observations suggested that **2a–d** possessed the *Z* configuration, while **2e** was a unique example of the isomeric (*E*)-oxime series. However, if that was the case, the origin of the steric effect of the *tert*-butyl group on isomer distribution was not obvious. An X-ray crystallographic analysis of **2a** was carried out, which not only confirmed the assignment of the *Z* configuration for **2a–d** but provided insight into the steric effect as well.

The X-ray analysis revealed that most of the atoms of **2a**, excepting only two of the hydrogen atoms of the methyl group, resided in two clearly defined and nearly orthogonal planes. One plane, the principal plane, included the oxime, the C3 carbonyl group, and C4. The atoms of the phenyl group (R^1 in **2a**) along with the C1 carbonyl group, defined a second plane nearly perpendicular to the principal plane (Ph–C1–C2–N dihedral angle, 88.2°). This arrangement minimizes steric crowding for the bulky phenyl group while reducing unfavorable dipolar repulsions between the benzoyl group and the oxime or C3 carbonyl group. The difference in the C1–C2 bond length (1.512 (2) Å) and the C2–C3 bond length (1.487 (3) Å) is consistent with conjugation involving the oxime and the C3 carbonyl group. The oxime hydroxyl group is not involved in intramolecular hydrogen bonding but is intermolecularly hydrogen bonded in the solid.

Within the principal plane the C3 carbonyl group and the oxime are directed in an *s*-trans relationship with respect to the C2–C3 bond. The *s*-trans conformation has been shown to be preferred for α-oxo oximes in which the oxime hydroxyl group is oriented anti to the carbonyl group, as in (*E*)-benzil monooxime.[2,3,7]

Baldwin and Norris report that for 2,3-dihydro-1,4-benzoquinone monooximes, stereoelectronic effects favor an anti relationship between the oxime hydroxyl group and the carbon–carbon double bond.[8] The system they describe is essentially a vinylogous α-oxo oxime, and the oxime geometry in **2a** might be expected to exhibit a similar stereoelectronic preference for the anti orientation of the hydroxyl group with respect to the C3 carbonyl group with which the oxime is conjugated.

Assuming that the geometry of the compounds **2a–e** in solution bears a reasonable resemblance to that of **2a** in the solid, the steric effect of the *tert*-butyl group is readily explained. In **2a–c** the bulky phenyl group assumes the orientation orthogonal to the oxime plane, permitting the hydroxyl group to occupy a sterically unhindered and stereoelectronically favorable anti relationship with the C3 carbonyl group. The isomer distribution between **2d** and **2e** reflects competition between the bulky *tert*-butyl group and the phenyl group for the less crowded orthogonal plane, with the hydroxyl group orientated anti to the other carbonyl group, which is coplanar with the oxime. Thus, when the phenyl group is in the orthogonal plane, the oxime has the *Z* configuration, **2d**, but if the *tert*-butyl group is in the orthogonal plane, the *E* configuration, **2e**, is preferred.

The effect of acetylation on the chemical shift of the ortho proton signal in the NMR spectrum of **2e** may be explained as the result of decreased electron donation by the oxime oxygen to the benzoyl group with which it is conjugated when the hydroxyl group is converted to the acetate ester. Since the benzoyl groups in **2a–d** are not conjugated with the oxime, acetylation has only a small effect on their NMR signals. Presumably the related effect observed by Baas and Cerfontain reflects a similar change in electron distribution in the α-oxo oxime **3** rather than a simple anisotropic deshielding effect.

Supplementary Material Available: An ORTEP diagram of **2a** and tables of coordinates, thermal parameters, and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

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