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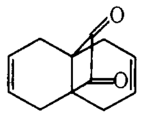
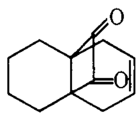
1,2-Cyclobutanediones. II. Spectral Characteristics of [4.4.2]Propella-3,8-diene-11,12-dione and Its Di- and Tetrahydro Derivatives

Sir:

The title compounds, prepared *via* acyloin condensation[1] followed by dimethyl sulfoxide–acetic anhydride oxidation,[2] exhibit rather remarkable spectral properties, particularly in the visible region (Figure 1).[3]

The diene **1**, pink in the crystalline state and in solution, possesses a complex spectrum with its longest wavelength absorption at $\lambda_{\max}$ 537.5 mμ (ϵ 71.7). This spectrum remains unchanged in ethanol, in mixtures of ethanol–cyclohexane, and in the presence of benzene, acetic acid, or triethylamine. No deviation from Beers' law is observed in any of these solutions. Compound **3**, the tetrahydro derivative of **1**, is yellow and gives yellow solutions with $\lambda_{\max}$ 461 mμ (ϵ 73). In contrast, the dihydro derivative **2** is pink in the solid state but gives orange solutions. It shows two absorption maxima at $\lambda_{\max}$ 460–464 (ϵ 38.8) and 532–535 mμ (32.0) and the spectrum appears to be almost that of a simple mixture of **1** and **3**.


1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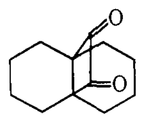

3

The infrared spectra[4] of **1**–**3** lead to a similar conclusion. Compound **1** shows two carbonyl absorptions with equal intensities at 1794 and 1759 cm^{-1}. In **3** the carbonyl spectrum is somewhat more complex, with a doublet at 1812 (strong) and 1772 cm^{-1} (very strong) and a shoulder with strong absorption at 1785 cm^{-1}. The position and shape of the very broad intense band peaking at 1772 cm^{-1} in **2** again approximate an algebraic addition of the spectra of **1** and **3**. Shifts to lower frequency in **1** relative to **3**, similar to but somewhat less than those observed in α,β-unsaturated ketones, suggest an interspatial interaction between a double bond in the six-membered ring and the dione system. The electronic spectra and molecular models of **1** and **3** make it possible to speculate upon both the origin and strength of this interaction.

Diketones **1** and **2** have the highest $\lambda_{\max}$ of all reported diketones[5-9] except for the completely conjugated perchlorodimethylene-1,2-cyclobutanedione which absorbs at 550–560 mμ (ϵ 400).[10] Cyclobutenediones absorb at somewhat higher energies, with the diphenyl[11] and benzo[12] derivatives and 3,4-bis(diphenylmethylene)cyclobutanedione[13] reported to have maxima at 410 (ϵ 163), 427 (276), and 376 mμ (7300), respectively.

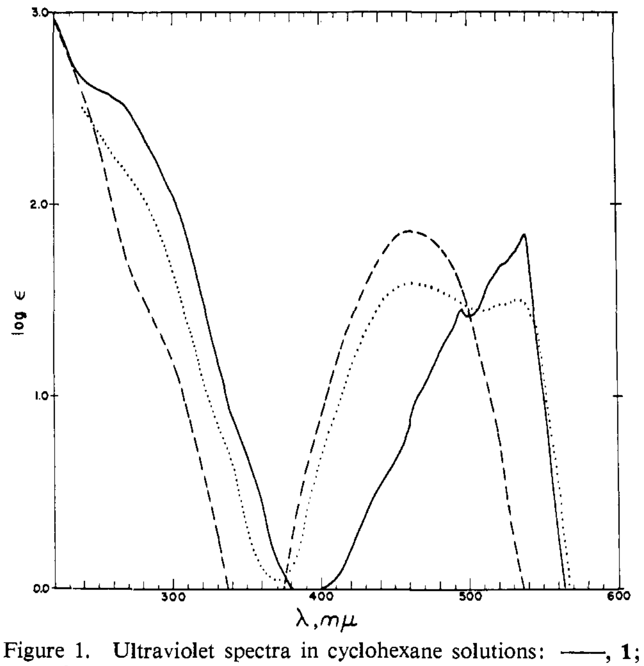
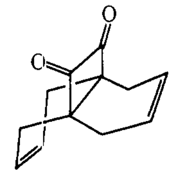
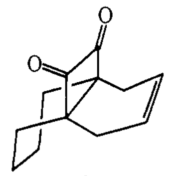
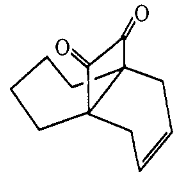


Figure 1. Ultraviolet spectra in cyclohexane solutions: ——, **1**; · · · ·, **2**; - - - -, **3**.

We suggest that the shift toward longer wavelength of absorption in **1** results from the enhanced possibility for resonance stabilization of the excited state involving interaction between a double bond and the dione system. This interaction must be at a maximum when the respective π orbitals can interact end to end as in **1a** and **2a**. In conformation **2b** these orbitals are parallel but farther apart (molecular models suggest 3.0–3.5 Å), and significant interaction would seem less likely.[14] The double maxima of **2** would result then from Franck–Condon controlled excitation of **2a** (peak


1a


2a


2b

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[1] (a) J. J. Bloomfield and J. R. S. Irelan, *J. Org. Chem.*, **31**, 2017 (1966); (b) J. J. Bloomfield, *Tetrahedron Letters*, 587 (1968).

[2] (a) J. D. Albright and L. Goldman, *J. Am. Chem. Soc.*, **87**, 4214 (1965); **89**, 2416 (1967); (b) M. Van Dyke and N. D. Pritchard, *J. Org. Chem.*, **32**, 3204 (1967).

[3] The data presented in the text and the spectra recorded in Figure 1 are for cyclohexane solutions. Spectra were taken on a Bausch and Lomb Spectronic 505.

[4] Recorded on a Beckman IR-8 instrument in carbon tetrachloride solution.

[5] Previous investigators have described the spectra[6-8] and discussed the excited-state geometries[9] of a variety of cyclic and linear diketones.

[6] N. J. Leonard and P. M. Mader, *J. Am. Chem. Soc.*, **72**, 5388 (1950).

[7] K. Alder, H. K. Schafer, H. Esser, H. Krieger, and R. Reubke, *Ann.*, **593**, 23 (1955).

[8] H. Birnbaum, R. C. Cookson, and N. Lewin, *J. Chem. Soc.*, 1224 (1961).

[9] T. R. Evans and P. A. Leermakers, *J. Am. Chem. Soc.*, **89**, 4380 (1967).

[10] A. Fujino, K. Kusada, and T. Sakan, *Bull. Chem. Soc. Japan*, **39**, 160 (1966).

[11] A. T. Blomquist and E. A. LaLancette, *J. Am. Chem. Soc.*, **83**, 1387 (1961).

[12] M. P. Cava, D. R. Napier, and R. J. Pohl, *ibid.*, **85**, 2076 (1963).

[13] R. O. Uhler, H. Shecter, and G. V. D. Tiers, *ibid.*, **84**, 3397 (1962).

[14] Additional data suggesting the staggered conformation is presented in a paper which concerns the radical anions related to these diketones: J. M. Fritsch and J. J. Bloomfield, *Spectry. Letters*, in press.

at 532–535 mμ) and **2b** (peak at 460–464 mμ). Compounds with a rigid molecular structure are being prepared in order to test this point.

Since the electronic transitions occurring in **1** and **3** should not be significantly different from those in **2a** and **2b**, an equilibrium constant between the conformers can be calculated. Assuming our assignments of respective conformations and absorption maxima to be correct, form **2b** is favored over **2a** in the ground state by a ratio of 53:45. The slight destabilization of **2a** relative to **2b** in the ground state (assuming a negligible entropy differential) must then be entirely overcome by resonance stabilization amounting to at least 8.8 kcal in the excited state. Lack of a measurable solvent effect on the visible spectra suggests that the low-energy transition occurs without wide charge separation characteristic of normal charge-transfer complexes.[15]

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(15) In response to a referee's comment it is perhaps worth noting here that the monoketones related to 1 and to 3 are colorless, having no absorption maxima above 330 mμ.[16]

(16) See J. R. S. Irelan, Ph.D. Thesis, University of Oklahoma, July 1968.

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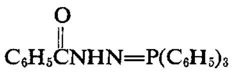
N-Acylamidotriphenylphosphinimines, Reactive Ylidic Reagents

Sir:

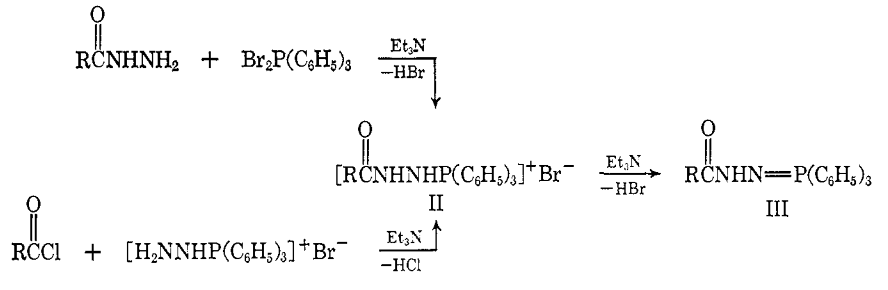
Triphenylphosphine dibromide and benzhydrazide in the presence of triethylamine are reported to give N-benzamidotriphenylphosphinimine (I) in 18% yield.[1] The chemistry of the phosphinimine was not investigated however.



$\mathrm{C_6H_5}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NHN{=}P(C_6H_5)_3}$

I

It has been found that N-acylamidotriphenylphosphinimines (III) can be prepared conveniently and essentially quantitatively from N-acylamidotriphenylphosphiniminium bromides (II, eq 1b) by reaction with bases. N-Acylamidotriphenylphosphiniminium bromides (II) are generated efficiently *in situ* or are isolable in high yields from either (1) acyl hydrazides, triphenylphosphine dibromide, and triethylamine (eq 1a) or (2) hydrazinotriphenylphosphinium bromide (as derived from triphenylphosphine dibromide and hydrazine),[2] acyl chlorides, and triethylamine (eq 1c). We now describe the advantageous properties and chemistry of typical N-acylamidotriphenylphosphinimines (III) and in particular the extraordinary intramolecular reactivity of their O-acylated intermediates, α-acyloxytriphenylphosphazines (see example IX below), as ylidic reagents to yield 1,3,4-oxadiazoles.



$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NHNH_2} + \mathrm{Br_2P(C_6H_5)_3} \xrightarrow[-\mathrm{HBr}]{\mathrm{Et_3N}} \qquad (1a)$$

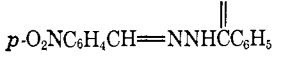
$$[\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NHNHP(C_6H_5)_3}]^+\mathrm{Br}^- \ (\mathrm{II}) \xrightarrow[-\mathrm{HBr}]{\mathrm{Et_3N}} \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{NHN{=}P(C_6H_5)_3} \ (\mathrm{III}) \qquad (1b)$$

$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{Cl} + [\mathrm{H_2NNHP(C_6H_5)_3}]^+\mathrm{Br}^- \xrightarrow[-\mathrm{HCl}]{\mathrm{Et_3N}} \qquad (1c)$$

N-Benzamidotriphenylphosphinimine (I, white crystals, mp 202–203° from ethyl acetate, lit.[1] mp 177–180°)[3] is obtained immediately upon adding aqueous sodium hydroxide or excess triethylamine to N-benzamidotriphenylphosphiniminium bromide[3] (IV, white crystals, mp 180° from isopropyl alcohol; strong infrared absorption at 3.6, 5.9, 6.9, 9.0, and 13.7 μ) in chloroform. The structure of I as an ylidic hydrazide is indicated by its strong absorption at 5.8 (–CONH–) and 7.5 μ (–P=N–) and its near-transparency in the 3.0-μ (hydroxyl) region. The behavior of I as a phosphorus–nitrogen ylidic reagent is demonstrated by its exothermic reactions with *p*-nitrobenzaldehyde and with *m*-nitrobenzaldehyde in benzene to give, along with triphenylphosphine oxide, *p*-nitrobenzaldehyde benzoylhydrazone (V, >82% yield; mp, lit.[4] mp, and mmp 243°) and *m*-nitrobenzaldehyde benzoylhydrazone (79% yield, mp and lit.[4] mp 197°), respectively. It is also noteworthy that IV, upon heating, undergoes dehydrobromination, bimolecular condensation, and dehydrogenation to 3,6-diphenyl-1,2,4,5-tetrazine (VI, red crystals, mp 199–200°, lit.[5a] mp 195°, identical infrared absorption with that of authentic material[5a]) and triphenylphosphine oxide.[5b]

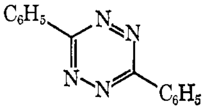
N-Acylamidotriphenylphosphinimines are acids and they exhibit enolic behavior. I gives a deep blue color with ferric chloride and is converted to its isolable lithium salt (VII, yellow, mp 205°) by butyllithium in hexane. Acidification of VII with hydrogen bromide results in generation of N-benzamidotriphenylphosphiniminium bromide (IV). Occasionally the enol, α-hydroxybenzylidenetriphenylphosphazine (VIII, infrared absorption at 3.1 and 7.4 μ (P=N); very weak C=O absorption at 5.8 μ) can be precipitated from chloroform; on heating or on storage it isomerizes essentially quantitatively to I.

What is presently of principal interest is that the lithium salt VII of I reacts rapidly with benzoyl chloride at 20–25° to give 2,5-diphenyl-1,3,4-oxadiazole (XI,



$p\text{-}\mathrm{O_2NC_6H_4CH{=}NNH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{C_6H_5}$

V



VI

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(1) L. Horner and H. Oediger, *Ann.*, **627**, 142 (1959).

(2) (a) H. Zimmer and G. Singh, *J. Org. Chem.*, **29**, 1579 (1964); (b) H. Appel and R. Schöllhorn, *Angew. Chem.*, **76**, 991 (1964); (c) C. C. Walker and H. Shechter, *Tetrahedron Letters*, 1447 (1965).

(3) All new compounds obtained in the present work gave satisfactory analyses.

(4) P. Grammaticakis, *Bull. Soc. Chim. France*, 690 (1950).

(5) (a) E. Muller and L. Herrdegen, *J. Prakt. Chem.*, **102**, 136 (1921). (b) For a related reaction see C. E. Griffin and G. Witschard, *J. Org. Chem.*, **27**, 3334 (1962).