

variations in both acid and base species should be considered an evolutionary step in the development of rate-equilibrium relationships for proton transfer from carbon acids. While eq 17 does not have the sophistication of relationships that incorporate work criteria, it is applicable to analyses over the limited ΔpK_a ranges which are often the only ranges that are accessible in such studies. The A parameter must include the work terms for association of the acid and base species (and also the product species), in addition to the true intrinsic barrier at $\Delta G^\circ = 0$ within this acid-base complex. Solvation differences, which are expected to be substantial between these carbon acids and their conjugate base species, will also influence A via substantially different work terms for the assembly of the reactant and product acid-base pairs. The B parameter should be the main reflection of imbalances between those factors (resonance, solvation, etc.) that are important to the stabilization of the transition state and conjugate base product species. B values should be largest in those systems in which these imbalances are greatest; i.e., B values should be the largest in those systems in which Bernasconi's principle of nonperfect synchronization is most important.^{43,44}

In principle, the data that we present in the current work for the deprotonation of ketones may be analyzed by the technique that Grunwald⁶⁵ has recently presented for the description of transition-state structure in terms of disparate reaction events. Grunwald included an analysis of Bordwell's data²⁰ for deprotonation of phenylnitromethanes as one of his examples of the power of this method. However, in view of the caveat that has been posed⁶⁶ regarding Grunwald's analysis of this reaction, we have refrained from presenting a similar analysis that is subject to the same uncertainties.

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2-Aza-2,4-cyclopentadienone. Existence and Reactivity

F. Gaviña,* A. M. Costero, M. R. Andreu, M. Carda, and S. V. Luis

Contribution from the Departamento de Química Orgánica, Colegio Universitario de Castellón, Universidad de Valencia, Castellón de la Plana, Spain. Received June 22, 1987

Abstract: The elusive species 2-aza-2,4-cyclopentadienone has been generated from an insoluble polymeric precursor. The liberated intermediate can act either as a diene or as a dienophile in Diels-Alder reactions.

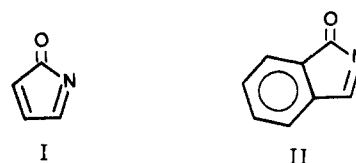
The existence of several diaza derivatives of 2,4-cyclopentadienone as reactive intermediates has been proposed by some authors. Thus, transient formation of 4,5-diphenyl-2,3-diaza-2,4-cyclopentadienone in elimination reactions has been postulated as a result of trapping experiments with 1,3-butadiene or 1,3-cyclopentadiene, giving the appropriate Diels-Alder adducts.¹ Also, generation of 5-phenyl-2,3-diaza-1,3-cyclopentadienone or 4-phenyl-5-benzyl-2,3-diaza-2,4-cyclopentadienone was proposed in some oxidation processes.^{2,3} Nevertheless, monoaza derivatives of 2,4-cyclopentadienone, I (Chart I), have received no attention until now, although related indolone II has been shown to add readily to dienes at the imine bond, to afford Diels-Alder adducts.⁴

In our attempt to determine how the presence of a nitrogen atom in the cyclopentadienone ring might affect its stability and its reactivity in Diels-Alder processes, we developed an approach to 2-aza-2,4-cyclopentadienone (I). A suitable precursor for I was found in the polymeric 5-sulfonate of 3-pyrrolin-2-one (IV) which can generate I via an elimination process.

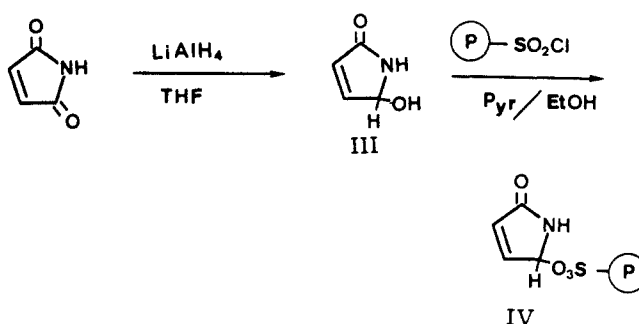
Results and Discussion

Synthesis of Precursor IV. The synthesis of polymeric compound IV was carried out as shown in Scheme I. Maleimide was reduced to III according to the procedure of Kohn and Liao for hydantoins.⁵ Reaction of III with chlorosulfonated macroreticular resin⁶ gave IV (IR: 3410, 1700, 1570, 1410, 1150 cm^{-1}). Re-

Chart I



Scheme I



actions of IV with several eliminating agents, such as DMSO or $\text{LiNH}_2/\text{HMPT}$, always led to sulfonic resin and complex mixtures in solution. This behavior corresponds to that observed for nonnitrogenated 2,4-cyclopentadienones, which can only be isolated as dimers or as their decarbonylation products.^{6,7}

2-Aza-2,4-cyclopentadienone as a Diene. The existence and reactivity of I were established by using the three-phase test.⁸ A dienophilic reagent, the polymeric monoester of acetylenedi-

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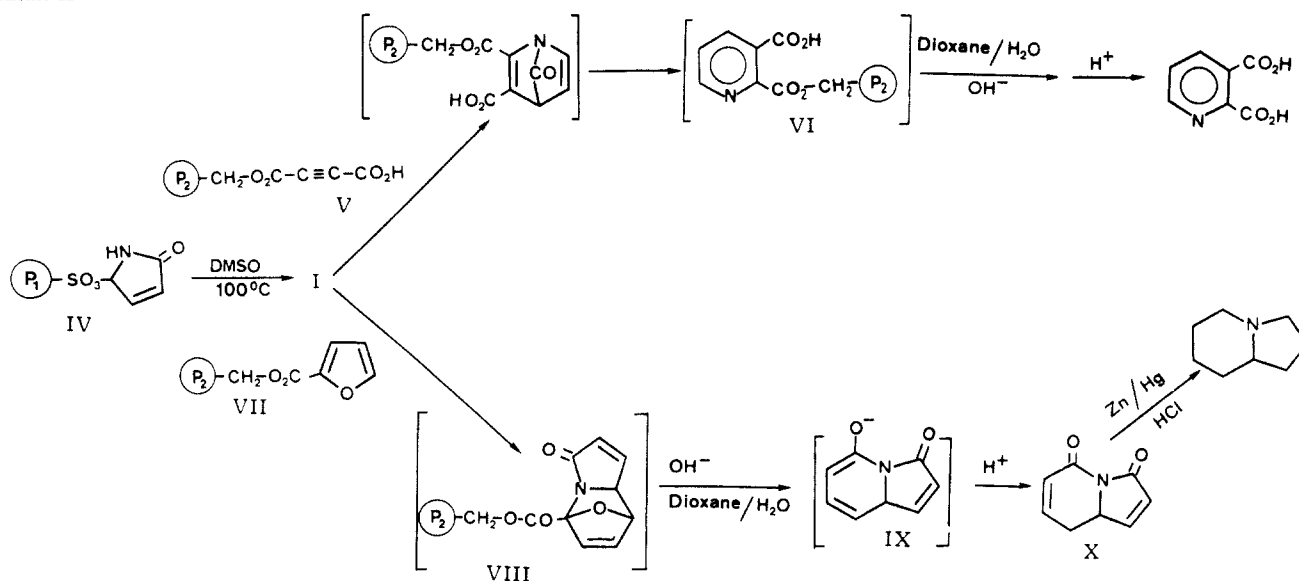
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Scheme II



carboxylic acid^{7a} (V), was first used as a trapping agent for this test. A suspension of IV and V in Me₂SO was heated at 100 °C (Scheme II). The resins were separated in the usual way, and the adduct resin, VI, was saponified to give, after acidification, a mixture of acetylenedicarboxylic and pyridine-2,3-dicarboxylic acids, from which the latter could be isolated by preparative TLC. The formation of pyridine-2,3-dicarboxylic acid can be explained by the reaction of free 2-aza-2,4-cyclopentadienone with V, followed by carbonyl extrusion and aromatization. A similar process has been observed with 2,4-cyclopentadienone.⁷

2-Aza-2,4-cyclopentadienone as a Dienophile. As the results were consistent with the existence of I, the next step was to demonstrate that free 2-aza-2,4-cyclopentadienone was likewise able to act as a dienophile in a Diels–Alder reaction. As a dienic trapping agent, the polymeric ester of 2-furoic acid^{7a} (VII) was used. Reaction of IV with VII in Me₂SO at 100 °C (Scheme II) yielded the polymeric adduct VIII, from which imidic diketone X was obtained by basic hydrolysis (probably via enolate IX⁹) followed by acidification and preparative TLC. A Clemmensen reduction of X gave δ -coniceine, identical with an authentic sample.

Conclusions

For the first time we have demonstrated the free existence in solution of the heterocyclic compound 2-aza-2,4-cyclopentadienone.

2,4-Cyclopentadienone and 2-aza-2,4-cyclopentadienone show similar behavior in pericyclic reactions, both of them being able to act either as a diene or as a dienophile in Diels–Alder processes. The carbon–nitrogen double bond in the azacyclopentadienone seems to be more active as a dienophile than the carbon–carbon double bond, as only adducts at the 2,3-position have been detected from this species. If any other adduct was formed it had to be in much lower quantity (less than 1/25th of the 2,3-adduct).

The study of other azaannulenes and their behavior as dienes and/or dienophiles is under way, so that we should be able to discuss the Diels–Alder reactions of I in that context.

Experimental Section

Preparation of the Polymeric Sulfonate of 3-Pyrrolin-2-one (IV). Maleimide (26.0 g) was treated with LiAlH₄ (9.1 g) in 500 mL of THF for 2 days at room temperature. Then, an excess of water was added and the solution was filtered and evaporated, giving III, as an oil. IR: 3400–3200, 2950, 2860, 1710, 1640, 1400, 1210, 1100 cm⁻¹. ¹H NMR ((CD₃)₂CO): δ 5.55 (s, br, 1 H), 6.5–6.7 (m, 2 H), 7.1 (d, 1 H), 7.66

(s, 1 H). Anal. (C₄H₅NO₂) C, H, N.

Polymeric tosyl chloride (5.0 g, 3.5 mequiv/g) was stirred with III (12.5 g) and pyridine (60 mL) in 600 mL of ethanol for 3 days at room temperature. After the reaction, the resin was filtered and washed sequentially with aqueous 10% HCl, dioxane, acetone, and ether. IV was obtained. IR: 3410, 2920, 1700, 1590, 1570, 1410, 1380, 1150, 700 cm⁻¹. Analysis indicated 2.4 mequiv/g (3.36% N).

Reaction of I as a Diene. A 1.0-g sample of IV and 1.0 g of the polymeric monoester of acetylenedicarboxylic acid (V) were suspended in 800 mL of dimethyl sulfoxide. The mixture was heated under stirring for 48 h at 100 °C. After the reaction, washing and then separation of the resins gave VI (2.09% N, 1.49 mequiv/g). IR: 3100, 3020, 3000, 1700, 1680, 1600, 1530, 1445, 1300, 1205, 1160, 1010 cm⁻¹. Hydrolysis of VI with 0.4 M NaOH (dioxane–water, 1:1) under reflux for 2 days, followed by acidification and separation by preparative TLC (ether–hexane), gave 0.22 g of pyridine-2,3-dicarboxylic acid, identical (IR, NMR, TLC) with an authentic sample (Merck).

Preparation of VI Separately. Chloromethylated resin (0.5 g, 0.53 mequiv) was suspended in 30 mL of xylene containing 0.82 g of pyridine-2,3-dicarboxylic acid and 5 mL of Et₃N, and the resultant mixture was heated and stirred at 110–120 °C for 70 h. After being washed with xylene, dioxane, and ether, the resin was acidified (HCl in aqueous dioxane) and washed again with water, acetone, and ether to give a polymer with the same IR as VI.

Reaction of I as a Dienophile. A suspension of IV (2.5 g) and VII (2.5 g) in 200 mL of Me₂SO was stirred at 100 °C for 48 h. Washing and then separation of the resins gave VIII (1.75% N, 1.25 mequiv/g). Hydrolysis of VIII, as described before, gave a mixture of compounds, from which furoic acid (168 mg) and X (75 mg) could be isolated as principal products by chromatography (acetone–ethanol, 1:1). X appeared as a yellow oil. IR: 3400, 3090, 3020, 2910, 1640, 1630, 1450 cm⁻¹. ¹H NMR (CDCl₃): δ 2.0 (dd, 2 H), 3.9 (m, 1 H), 6.29 (dd, 1 H), 6.40 (m, 1 H), 6.55 (d, 1 H), 6.70 (d, 1 H). MS: *m/z* 149, 132, 121, 81, 68, 40. Anal. (C₈H₇NO₂) C, H, N.

Reduction of X was carried out via the Clemmensen reduction conditions used by several authors in similar cases.¹⁰ X (65 mg) was heated under reflux with amalgamated zinc wool and hydrochloric acid for 5 h. The mixture was neutralized with NaOH until pH 8 and then extracted with ether. The ethereal solution gave, by evaporation, 44 mg (81% yield) of the known compound octahydroindolizine (δ -coniceine), identical (IR, NMR, TLC) with an authentic sample.¹¹

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