J. Am. Chem. Soc. **1981**, *103*, 1797-1798

Pericyclic Reactions of Free Cyclopentadienone

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Received May 19, 1980. Revised Manuscript Received October 2, 1980

Abstract: Evidence showing that the existence of free cyclopentadienone is needed in reactions of 4-tosyl-2-cyclopenten-1-one is presented. The methods involve the "Three-Phase Test" to detect reactive intermediates in solution. Cyclopentadienone is generated from an insoluble polymer-bound precursor and trapped by a second solid phase by using Diels-Alder reactions. In such additions, the elusive ketone can act either as a diene or as a dienophile, according to reaction conditions.

Transient existence of cyclopentadienone (I) has been postulated in several elimination reactions. Thus, pyrolysis of 1-ketodicyclopentadiene[1] and *o*-phenylene sulfite[2] or carbonate[3] and elimination of HBr from 4-bromocyclopentenone[4] can all be interpretated as proceeding via the elusive ketone. Attempts to generate monomeric cyclopentadienone lead always to the formation of its dimer (II) or its decarbonylation products. If 1,3-dienes, i.e., cyclopentadiene, are added to the reaction mixture, they act, apparently, as a trap for cyclopentadienone,[4] giving the corresponding Diels-Alder adduct (Scheme I).

If cyclopentadienone is an intermediate for dicyclopentadienone, as postulated in Scheme I, then one molecule of monomer must serve as a diene and the other one as a dienophile. But when elimination of HBr was carried out in presence of a large excess of a variety of dienophiles, only dicyclopentadienone was obtained and no mixed adduct could be found.[4] Thus, the intermediacy of free cyclopentadienone in reactions as in Scheme I is questioned, as it does not enter into a normal Diels-Alder reaction as a diene. Recently,[5] it has been suggested that cyclopentadienones act both as dienes and as dienophiles in reactions with 6,6-dimethylfulvene. But there is not a definitive demonstration of the intermediacy of free ketone, and the resulting adducts interconvert in a Cope rearrangement process. Thus, Diels-Alder reactions are questionable.

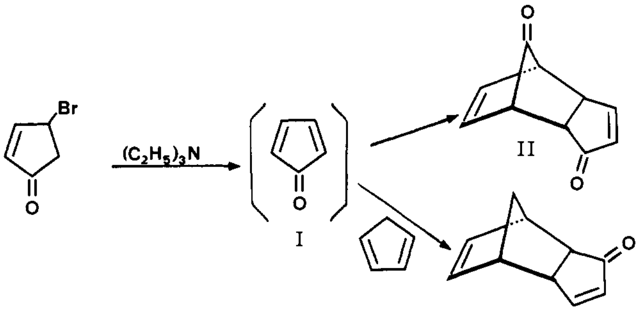
Really, incisive experimental evidence for the existence of monomeric cyclopentadienone is rare. Thus, Chapman and McIntosh[6] followed the pyrolysis reported by DeJongh[2,3] under conditions which permit spectroscopic observation. They recorded IR spectrum of a product deposited on a sodium chloride plate at -196 °C. This spectrum showed carbonyl absorption at 1709 cm^{-1} which disappeared upon warming, showing then the characteristic band of cyclopentadienone dimer. As that carbonyl frequency falls between the theoretical estimates, Chapman and McIntosh suggested that matrix isolation of free cyclopentadienone has been achieved.

In a further paper, Koenig et al.[7] used again flash pyrolysis of cyclic sulfite and orthoquinone to obtain He I photoelectron spectrum of a product believed to be free cyclopentadienone. As in the former paper, the isolated product of the pyrolysis was the cyclopentadienone dimer.

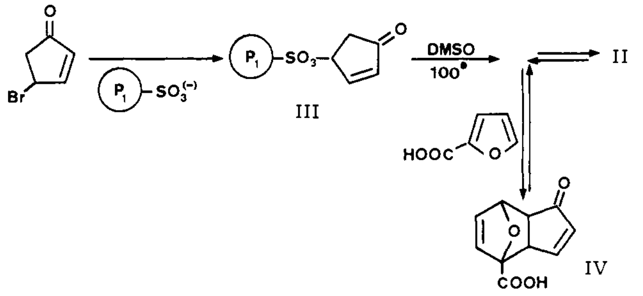
Results and Discussion

"Three-Phase Test" has been used since 1974[8] as an unambigous method to distinguish between associative and dissociative mechanisms. We used this test recently to provide evidence of pericyclic reactions in diimine.[9] Now we use the same procedure to confirm that monomeric cyclopentadienone is also the subject of pericyclic reactions and it can behave either as the diene or as the dienophile according to the conditions. Furthermore, successful trapping of this reactive species with the three-phase test would present important new evidence for the free cyclopentadienone.

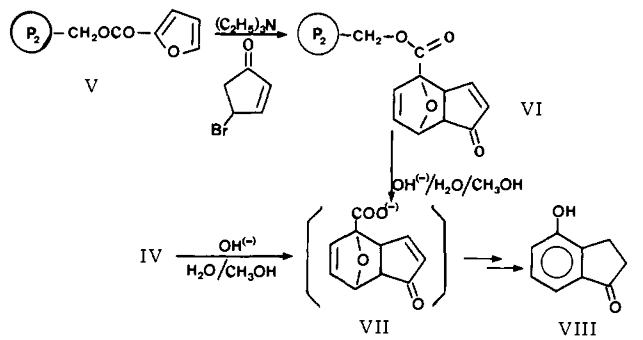
Scheme I



Scheme II



Scheme III



Cyclopentadienone as a Dienophile. A suitable precursor for cyclopentadienone was found in the polymeric tosylcyclopentenone, III (Scheme II), prepared by reaction of chlorosulfonated macroreticular resin[10] with 4-bromocyclopentenone. Reaction of III with Me_2SO gave the known adduct II and confirmed that III

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(1) Alder, K.; Flock, F. H., *Chem. Ber.* **1954**, *87*, 1916.

(2) DeJongh, D. C.; Van Fossen, R. Y.; Bourgeois, C. F. *Tetrahedron Lett.* **1967**, 271.

(3) DeJongh, D. C.; Brent, D. A. *J. Org. Chem.* **1970**, *35*, 4204.

(4) DePuy, C. H.; Isaks, M.; Eilers, K. L.; Morris, G. F. *J. Org. Chem.* **1964**, *29*, 3503.

(5) Paddon-Row, M. N.; Patney, H. K.; Warrener, R. N. *Aust. J. Chem.* **1977**, *30*, 2307.

(6) Chapman, O. L.; McIntosh, C. L. *J. Chem. Soc. O* **1971**, 770.

(7) Koenig, T.; Smith, M.; Snell, W. *J. Am. Chem. Soc.* **1977**, *99*, 6663.

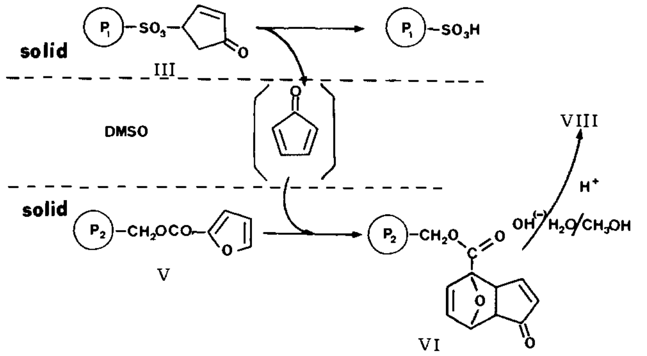
(8) Rebek, J.; Gaviña, F. *J. Am. Chem. Soc.* **1974**, *96*, 7112. *Ibid.* **1975**, *97*, 3453. *Ibid.* **1978**, *100*, 8113.

(9) Gaviña, F.; Gil, P.; Palazón, B. *Tetrahedron Lett.* **1979**, 1333.

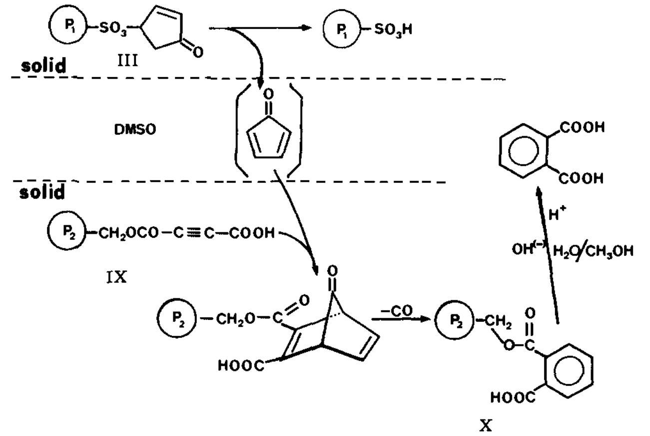
(10) Roush, W.; Feitler, D.; Rebek, J. *Tetrahedron Lett.* **1974**, 1391.

0002-7863/81/1503-1797$01.25/0

Scheme IV



Scheme V



behaves as 4-bromocyclopentenone with an elimination agent. If furoic acid is added to the reaction mixture, then the major product is the racemic 4-carboxy-4,7-epoxy-3a,4,7,7a-tetrahydroinden-1-one (IV).

Dienic polymeric trapping agent, V (Scheme III), was prepared from the chloromethylated Merrifield resin by treatment with furoic acid and triethylamine. A suspension of V in diethyl ether containing Et_3N was treated with an excess of 4-bromocyclopentenone to give polymeric adduct VI, from which 4-hydroxyindanone (VIII) was obtained by basic hydrolysis followed by acidification. Relation between adducts IV and VI and 4-hydroxyindanone (probably by the intermediacy of carboxylate VII) was established by basic hydrolysis of IV.

For the three-phase test, a suspension of III and V in Me_2SO was heated at 110 °C. The resins were separated in the usual way,[8] and the adduct resin was saponified to give a mixture of furoic acid and 4-hydroxyindanone, from which 4-hydroxyindanone could be isolated by preparative TLC (Scheme IV).

Cyclopentadienone as a Diene. The next step was to demonstrate that free cyclopentadienone (whose existence from resin III was unambiguously proved) was likewise able to act as a diene in a Diels–Alder reaction. A polymeric monoester of acetylenedicarboxylic acid, IX (Scheme V), was selected as a suitable dienophile. IX was easily prepared from the acid and the chloromethylated Merrifield resin. When polymers III and IX were suspended in Me_2SO at 120 °C, cyclopentadienone transfer between the two polymers was detected, generating X, probably via carbonyl extrusion and aromatization. Saponification of X and acidification gave phthalic acid.

Conclusions

The present trapping results support the conclusion that elimination reactions of compounds like 4-tosyl-2-cyclopenten-1-one generates free cyclopentadienone. Appearance of cyclopentadienone moiety into the trapping polymers after three-phase tests strongly requires the free existence of such a ketone, as has been suggested by spectroscopic methods. Further, the ability of cyclopentadienone to react either as a diene or as a dienophile in Diels–Alder reactions has been demonstrated.

Experimental Section

General methods for manipuling the polymers and multiphase systems have been described.[8]

Polymeric Tosylcyclopentenone (III). A suspension of chlorosulfonated macroreticular resin[10] (2.5 g, 9 mequiv) in 60 mL of dioxane was treated with 6.23 g of $AgNO_3$ in 15 mL of water at 80 °C for 13 h to give the polymeric sulfonic silver salt. A 1-g sample of this salt was refluxed with 2.028 g of 4-bromocyclopentenone[4] in 40 mL of dioxane for 67 h. After being washed with 5% aqueous KCN (to eliminate AgBr), water, dioxane, and ethanol, the resin showed IR absorptions at 1690, 1600, 1420, 1230 cm^{-1}.

Reaction of III with Me_2SO. A 800-mg sample of the resin III was suspended in 100 mL of Me_2SO and heated with stirring at 100 °C for 30 h. The resulting suspension was filtered, and the filtrate was concentrated. Chromatography gave 66 mg of adduct II identical with that prepared in solution in melting point and spectroscopic features.[11] We were unable to obtain the same results with Et_3N. Nevertheless, we found that Et_3N was able to give II from nonpolymeric 4-tosyl-2-cyclopenten-1-one.

4-Carboxy-4,7-epoxy-3a,4,7,7a-tetrahydroinden-1-one (IV). A suspension of 800 mg of III in 100 mL of Me_2SO containing 4.36 g of furoic acid was heated with stirring at 100 °C for 60 h. The mixture was filtered, and the filtrate was diluted with 100 mL of water and extracted with three 100-mL portions of hexane. Chromatography of the hexane solution gave unreacted furoic acid and 95 mg of IV: IR 3200, 1725, 1710, 1080 cm^{-1}; ^1H NMR ($(CD_3)_2CO$) δ 7.45 (d, 1 H), 6.7–6.3 (broad, 3 H), 4.51 (m, 1 H), 3.75 (d, 1 H), 3.52 (d, 1 H); $R_f = 0.80$ ($(CH_3)_2CO$).

Anal. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.16. Found: C, 62.21; H, 4.22.

Basic hydrolysis (NaOH in aqueous MeOH) of IV followed by acidification gave 4-hydroxyindanone (VIII) identical with an authentic sample.

Preparation of Polymeric Trapping Agent V and Its Reaction with 4-Bromocyclopentenone in Solution. Chloromethylated Merrified resin (1.2 g, 1.272 mequiv) was suspended in xylene containing 0.428 g of furoic acid and 1.5 mL of Et_3N and heated at 164 °C with stirring for 72 h. Washing with dioxane, acetone, and ether gave the polymer-bound furoate V (1.29 g). A sample showed IR absorptions at 1740 and 1110 cm^{-1}. Titration indicated 1.05 mequiv of ester/g.

A solution of 0.213 g of 4-bromocyclopentenone in 15 mL of diethyl ether was added dropwise (2 h) to a stirred suspension of 0.5 g of V and 0.225 g of Et_3N in ether at room temperature. After another 120 h of stirring at room temperature, the resin was filtered and washed with water, dioxane, and ether. The IR of adduct VI showed changes in the carbonyl region (1735, 1715 cm^{-1}). Basic hydrolysis (KOH in aqueous MeOH) of VI followed by acidification gave VIII again.

Preparation of Polymeric Monoester of Acetylenedicarboxylic Acid (IX). Chloromethylated resin (1 g, 1.06 mequiv) was suspended in dioxane/water (1:1, 20 mL), containing 1.6 g of acetylenedicarboxylic acid and 10 mL of Et_3N and heated at 100 °C with stirring for 120 h. After being washed with dioxane, acetone, and ether, the resin was acidified (HCl in aqueous dioxane) and washed again with water, acetone, and ether, giving IX: IR 1735, 1720, 1450, 1260, 1100 cm^{-1}. Titration indicated 0.90 mequiv of CO_2H/g.

Three-Phase Tests. A. Cyclopentadienone Transfer to V. A suspension of III (2 g) and V (3 g) was stirred in Me_2SO at 110 °C for 64 h. Washing and then separation of the resins gave VI. Hydrolysis of VI as described before gave a mixture of furoic acid and VIII, from which VIII (20 mg) could be isolated by preparative TLC (acetone/ethanol, 1:1).

B. Cyclopentadienone Transfer to IX. A suspension of III (2 g) and IX (2 g) in 300 mL of Me_2SO was heated at 120 °C for 87 h. The resins were separated and washed with ethanol and ether. IR revealed the presence of X (1730, 1700, 1180 cm^{-1}). Basic hydrolysis of X followed by acidification gave phthalic acid (230 mg).

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(11) DePuy, C. H.; Ponder, B. W. *J. Am. Chem. Soc.* **1959**, *81*, 4629.