

It is clear that the "polar state" rule gives incorrect results in whole or in part when applied to dienones IV-VIII. We therefore doubt that the rule has theoretical significance; it would be useful only in those cases where structural features exclude path b (Chart II). Moreover, these results also cast doubt on suggestions that the excited state produced on photolysis of cross-conjugated cyclohexadienones is adequately represented by dipolar structures such as II. Ionic intermediates are most consistently regarded as arising from further transformations of the excited state.

We are now investigating the scope and mechanistic details of the photochemical fragmentation reactions of a variety of substituted cyclohexadienones.

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Diene Complexes from the Reaction of Activated Vinylcyclopropanes with Iron Pentacarbonyl

Sir:

In this communication we show that vinylcyclopropanes bearing *para*-substituted phenyl groups (Ia-Ic)^{1,2} can enter into reaction with iron pentacarbonyl to yield π -complexes of the structure of 2-aryl-1,3-*trans*-penta-dieneiron tricarbonyl (IIa-IIc). A mixture of equimolar quantities of iron pentacarbonyl and α -cyclo-

of IIa in 61% yield. Similar reactions of Ib and Ic with iron pentacarbonyl furnished the respective products IIb (57% yield) and IIc (55% yield). The properties and analysis of products are summarized in Table I.

The structural assignments follow from: (i) analysis, (ii) solubility in nonpolar solvents (petroleum ether), (iii) infrared spectrum, and (iv) n.m.r. spectrum³ (Table II). An examination of the n.m.r. spectrum of IIa reveals that the transformation Ia \rightarrow IIa is accompanied by a disappearance of the cyclopropane protons (H-1 and H-2 in Ia), leaving behind the anisyl group protons, at 3.78 and 7.20 p.p.m., essentially unchanged. Instead new signals appeared as a doublet at 1.49 p.p.m. (three protons) assigned to methyl group hydrogens linked to a diene metal complex (H-5),⁴ a double quartet at 1.07 p.p.m. (single hydrogen) assigned to a terminal dienic proton *endo* to the metal (H-1),^{5,6} and a broad doublet at 5.55 p.p.m. (single hydrogen) assigned to a central dienic proton (H-2).⁶ The two vinylic hydrogens of the substrate (H-3 in Ia) are differentially shifted toward higher field on Ia \rightarrow IIa conversion so that the proton *exo* to the metal (H-4 in IIa) now appears at 2.19 p.p.m., whereas the *endo*-oriented proton (H-3) appears at the highest field of the spectrum, at 0.35 p.p.m.⁶

A *trans* relationship between the vinylic hydrogens at the 3,4- double bond in IIa is inferred both from the chemical shift of H-1⁷ and from the coupling constant, $J_{H-1,H-2} = 9$ c.p.s.⁸ Final proof of structure follows

Table I

Product	M.p., °C.	$\bar{\nu}$ (CO), ^a cm. ⁻¹	Formula	Calcd., %			Found, %		
				C	H	Fe	C	H	Fe
IIa	70-71.7	1975, ^b 2051 ^c	C ₁₃ H ₁₄ O ₄ Fe	57.3	4.4	17.8	57.3	4.4	17.6
IIb	Oil ^d	1996, ^b 2079 ^{c,e}	C ₁₄ H ₁₂ O ₃ Fe	59.1	4.2	...	59.6	4.4	...
IIc	28.0	1998, ^b 2079 ^c	C ₁₄ H ₁₁ O ₃ ClFe	52.7	3.4	...	51.7	3.3	...

^a In KBr. ^b Broad. ^c Sharp. ^d Distilled at 10⁻⁵ mm. at room temperature. ^e In sandwich cell.

Table II

N.M.R. Spectrum of Free Ligand and Metal Complex							
Free Ligand Ia				Metal Complex IIa			
Chemical Shift (p.p.m.)	Relative intensity	Splitting	Coupling constants	Chemical Shift (p.p.m.)	Relative intensity	Splitting	Coupling constants
H ₁₁₁	0.69	4	multiplet centered 0.89 o.p.m.	1.07	1	double quartet	$J_{H_{111},H_{121}} = 9$ c.p.s.
H ₁₂₁	1.56	1	multiplet	5.55	1	broad doublet	
H ₁₃₁	4.92	1	singlet	0.35	1	doublet	$J_{H_{111},H_{121}} = 2.5$ c.p.s.
H ₁₄₁	5.25	1	singlet				
H ₁₅₁	7.29	4	AB quartet centered 7.29 o.p.m.	2.19	1	double doublet	
H ₁₆₁	2.05	3	singlet	1.49	3	doublet	
H ₁₇₁				7.20	4	AB quartet centered 7.70 o.p.m.	
H ₁₈₁				3.78	3	singlet	

propyl-*p*-methoxystyrene (Ia)² in *n*-butyl ether was refluxed for 10 hr. in an atmosphere of pure nitrogen. The reaction mixture was filtered, the solvent was removed *in vacuo*, and the residue was chromatographed over alumina, using petroleum ether (b.p. 40-60°) as eluent. The first fraction eluted provided yellow plates

- (1) S. Sarel and E. Breuer, *J. Am. Chem. Soc.*, **81**, 6522 (1959).
 (2) S. Sarel and E. Breuer, *Israel J. Chem.*, **1**, 451 (1963).

from an unambiguous synthesis of IIa and IIb involving predisposed geometry of the 3,4- double bond, following the path III^{9a,b} \rightarrow IV \rightarrow V¹⁰ \rightarrow VI \rightarrow II,¹¹ as outlined in Chart I.

The free ligands VI (not isolated), resulting from the thermal dehydration-decarboxylation of V, are highly unstable.¹² They presumably react with iron pentacarbonyl as soon as they are formed.

The alternative syntheses of IIa-IIb provide not only

- (3) The n.m.r. spectrum in CDCl₃ was obtained on a Varian A-60 spectrometer.

- (4) Compare R. B. King, T. A. Manuel, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961).

- (5) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

- (6) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 12 (1964).

- (7) Compare J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963).

- (8) Compare E. Weiss, *et al.*, *Helv. Chim. Acta*, **46**, 288 (1963); see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

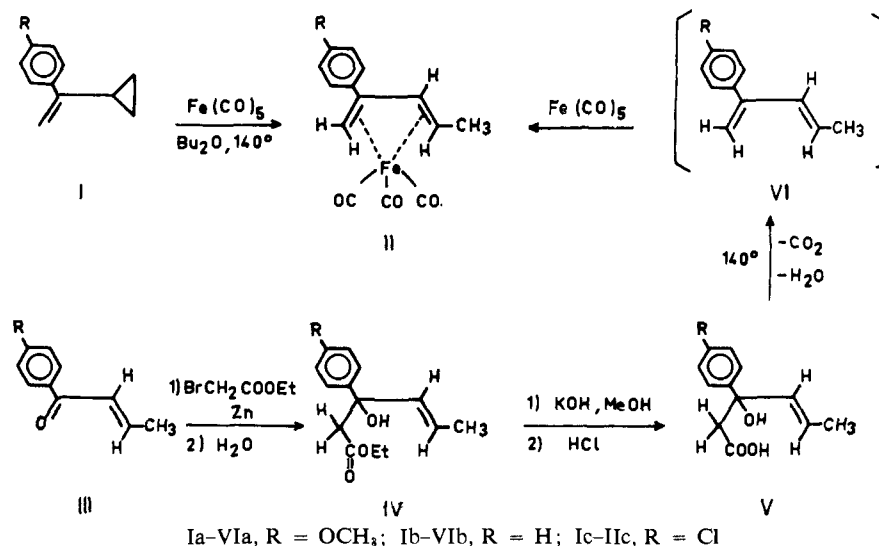
- (9) (a) S. Dev, *J. Indian Chem. Soc.*, **33**, 703 (1956); (b) T. M. Patrick, Jr., *J. Org. Chem.*, **17**, 1269 (1952).

- (10) R. Kuhn and M. Hoffer, *Chem. Ber.*, **66**, 1263 (1933).

- (11) The physical properties and infrared and n.m.r. spectra of metal complexes obtained by this route proved to be identical with IIa and IIb.

- (12) The reaction of IIIa with triphenylphosphinemethylene (Wittig reaction) leads to the formation of polymeric forms of VIa.

Chart I



conclusive evidence for the structural assignment, but also suggest the possible use of β -hydroxy γ,δ -unsaturated acids as convenient precursors for the formation of diene-iron tricarbonyl complexes in cases where the diene is highly unstable. Examination of the infrared data permits the conclusion that carbonyl bond orders in IIa-IIc vary according to the polar characteristics of substituents at the *para* position in the phenyl group and that the electrons in the whole complex system are considerably delocalized, in harmony with theory.¹³

the n.m.r. spectra, and to Professor M. Cais for helpful discussions.

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A New Synthetic Approach to the Penicillins

Sir:

For several years we have been engaged in the investigation of new synthetic routes to the penicillins with the ultimate objective of developing efficient syntheses of known antibiotics in this series and various types of structural analogs.¹ In this communication we describe an approach which has been applied successfully to the formation of simple model structures and which appears to offer considerable promise as a general method of penicillin synthesis.

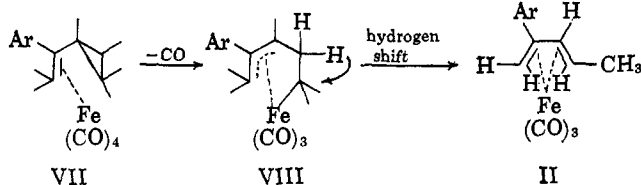
Acylation of *dl*-5,5-dimethyl-4-carbomethoxythiazolidine (I)² by the benzenesulfonylhydrazone of benzoylformic acid (II)³ was carried out using *N,N'*-dicyclohexylcarbodiimide as reagent to give the ester amide III. Reaction of III with 1 equiv. of sodium hydride in dry 1,2-dimethoxyethane at 60–65° for 15 min. produced the corresponding α -dialdo amide (IV) and sodium benzenesulfinate. The diazo compound IV, obtained as a solid foam, manifested infrared absorption (in CCl₄) at 4.82 and 4.83 μ (shoulder) due to the diazo function and at 5.82 and 6.18 μ due to ester and amide carbonyl groups, respectively, and ultraviolet absorption maxima (in ethanol) at 265 m μ (ϵ 11,100), 335 (1500), and 425 (55). Irradiation of the α -dialdo amide IV at 10° in methylene chloride solution using a 100-w.

(1) For a recent review of the penicillins including the pioneering synthetic studies of J. C. Sheehan, see F. P. Doyle and J. H. C. Nayler, *Advan. Drug. Res.*, 1, 1 (1964).

(2) H. T. Clark, J. R. Johnson, and R. Robinson, Ed., "Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, p. 958.

(3) Prepared from benzoylformic acid and benzenesulfonylhydrazine in acetic acid. The structures assigned to this and other key intermediates described herein are fully supported by spectroscopic and analytical data.

Chart II



This study shows that vinylcyclopropanes, when properly activated, afford a novel source of four π -electrons suitable for complexing with iron pentacarbonyl. A schematic description for the mechanism of the reaction is given in Chart II. It postulates an initial complexing¹⁴ at the vinyl group, VII, followed by cyclopropane ring opening, to yield a four-electron donor complex intermediate, VIII, in which the organic moiety is bound to the metal by both a π -allyl and a σ -component. The formation of the final compound, II, involves a hydrogen shift toward the terminal carbon atom, σ -bonded to the metal, to obtain the more stable *trans*-dienic π -complex (VIII \rightarrow II). Complete discussion of the mechanism will be given in the full paper.

Acknowledgment. We wish to thank Dr. Yuval Shvo of the Department of Organic Chemistry, Weizmann Institute of Science, Rehovoth, for determining

(13) See D. A. Brown and H. Sloan, *J. Chem. Soc.*, 3849 (1962).

(14) In exclusion of iron pentacarbonyl, the free ligand shows no tendency to undergo isomerization into VI, since quantitative recovery of I could be obtained upon its subjection to comparable reaction conditions.