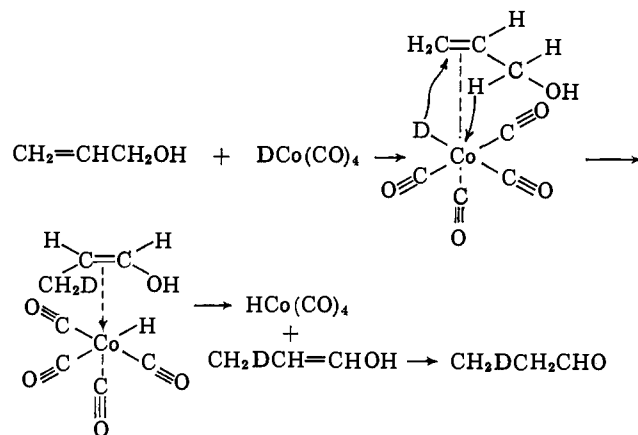


TABLE I
 THE REACTION OF ALKYL ALCOHOLS WITH COBALT HYDROCARBYL (1 ATM. CO, 25°)

Alcohol		HCo(CO) ₄ , mmoles	Gas absorbed, mmoles	Products		
Structure	mmoles			Compound	mmoles	Yield, %
CH ₂ =CHCH ₂ OH	9.0	4.65	0.7	CH ₃ CH ₂ CHO	1.9	21 ^a
				CH ₂ =CH(CH ₂) ₂ CH=CH ₂	Trace	
				Hydroxyaldehyde ^b	0.7 ^c	30 ^{c,d}
CH ₃ CH=CHCH ₂ OH	16.5	3.3	-1.1 ^e	CH ₃ CH ₂ CH ₂ CHO	0.5	3.0 ^a
CH ₂ =CHCHOHCH ₃	30	6.2	2.0	CH ₃ CH ₂ COCH ₃	1.1	3.7 ^a
				Hydroxyaldehyde ^b	2.9 ^f	94 ^d
CH ₂ =CHCOH(CH ₃) ₂	23	4.6	1.6	Hydroxyaldehyde ^b	1.1 ^f	48 ^d

^a Based on starting alcohol. ^b Not identified. ^c Estimated from gas absorption. ^d Based on starting HCo(CO)₄ and the following stoichiometry: 2HCo(CO)₄ + alcohol + CO → products. ^e This gas was evolved. Approximately 3 mmoles of starting material was unaccounted for which may have gone to products or complexes with accompanying CO evolution. ^f By Fritz analysis.³

exclusively CH₂DCH₂CHO. This fact and the data of Table I may be rationalized on the basis of the 1,3-hydrogen shift previously proposed² for the olefin isomerization, which when applied to the allyl alcohols may be written



The failure to secure any isomerization with CH₂=CHCOH(CH₃)₂ (Table I) may be ascribed to the absence of an allylic hydrogen.

Although the products (hydroxyaldehydes, hemiacetal, dihydrofuran or its polymers) which would result from hydroformylation were not isolated or identified, hydroformylation requires CO absorption and the formation of Co₂(CO)₈, both of which were observed.

When CH₂=CHCH₂OD was treated with HCo(CO)₄ and the propanol isolated and examined, the n.m.r. spectrum definitely indicated the absence of CH₃CHDCHO which might have been expected on the basis of the above mechanism. However, rapid exchange of the enolic form, either with HCo(CO)₄ or possibly with the α-methylene of the deuterated allyl alcohol may have occurred. The n.m.r. spectrum did not completely exclude the possibility of trace amounts of CH₂DCH₂CHO nor was a deuterium balance attempted.

The allyl alcohol was injected into a 50-ml. flask containing an octane solution of HCo(CO)₄ under CO. The solution was stirred rapidly at room temperature until all the HCo(CO)₄ disappeared,⁴ usually about 10 min. Triphenylphosphine was added to remove the cobalt complexes from solution and the supernatant solution was removed and analyzed by vapor phase chromatography (v.p.c.). DCo(CO)₄ was prepared by exchange of HCo(CO)₄ in octane solution with pure D₂O.⁵ After treatment of the allyl alcohol with DCo(CO)₄, the propanol was removed by vacuum distillation and purified by v.p.c. The n.m.r. spectrum was obtained with a CCl₄ solution, using the Varian A-60 instrument. The methylene produced a complex

(3) J. S. Fritz, S. S. Yamamura and E. C. Bradford, *Anal. Chem.*, **31**, 260 (1959).

(4) R. W. Goetz and M. Orchin, *J. Org. Chem.*, **27**, 3698 (1962).

(5) G. L. Karapinka, Ph.D. Dissertation, University of Cincinnati, 1962.

triplet centered at 138 c.p.s. from the Si(CH₃)₄ band. The n.m.r. spectrum of the propanal from treatment of CH₂=CHCH₂OD with HCo(CO)₄ showed a triplet centered at 578 c.p.s. due to the carbonyl hydrogen.

Acknowledgment.—We wish to thank the National Science Foundation and The Standard Oil Company (Ohio) for financial support, and Professor F. Kaplan for help with the n.m.r. spectra.

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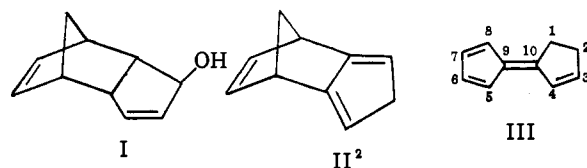
RICHARD W. GOETZ
MILTON ORCHIN

RECEIVED FEBRUARY 18, 1963

DIHYDROFULVALENE

Sir:

Small amounts of a deep red hydrocarbon, not further characterized, have been reported to accompany dehydroisodicyclopentadiene (II) when the latter is prepared by gas-phase dehydration of 1-dicyclopentadienol (I) over alumina at 260°.¹ We have found that a deep red hydrocarbon (III), presumably the same substance, may be obtained in about 30% yield and a good state of purity by steam-distilling a mixture of I and dilute aqueous acid, and have shown III to be 1,2-dihydrofulvalene.



When a solution of I³ in a minimum of carbon tetrachloride is added dropwise to boiling 0.2% aqueous tartaric acid, and the distillate, after rectification through a 36-cm. vacuum-jacketed Vigreux column, is passed continuously through carbon tetrachloride, III accumulates in the organic phase. The use of a less acidic aqueous solution leads to significant distillation of starting alcohol while a more acidic solution causes excessive formation of a tan, insoluble polymer. The fulvene is very oxygen-sensitive,⁴ and the entire operation must be conducted in an atmosphere of prepurified nitrogen. The solution of III was dried over anhydrous magnesium sulfate, and polar impurities were removed by passing it through a short (ca. 5 cm.) column of silica gel. Removal of the solvent at 10–15 mm. pressure and room temperature left a deep red oil, the infrared spectrum of which showed no detectable impurities. The hydrocarbon could be evaporatively distilled, with some loss, under high vacuum at room

(1) K. Alder, F. H. Flock and P. Janssen, *Ber.*, **89**, 2689 (1956).

(2) The conclusions of Alder, Flock and Janssen regarding the location of the double bonds in II and in isodicyclopentadiene are sustained by an n.m.r. study of the latter by T. J. Katz and M. Rosenberger, *J. Am. Chem. Soc.*, **84**, 865 (1962).

(3) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(4) J. H. Day, *Chem. Rev.*, **53**, 167 (1953), and references cited therein.

temperature. Material so purified melted at about -2° . It has been stored under nitrogen at -195° for several months without apparent change, but a sample stored at -40° contained some insoluble material when opened.

The infrared spectrum (CCl_4) of III: 3.27μ (m), 3.41 (s), 6.13 (s), 6.41 (w), 6.88 (s), 6.95 (m), 7.30 (s), 7.40 (m), 8.05 (w), 9.12 (m), 9.27 (m), 10.12 (m), 10.58 (w), 10.89 (m), 11.11 (w), 11.47 (s), is consistent with its formulation as a fulvene,⁵ first inferred from the red color. Its n.m.r. spectrum (neat) possesses a single sharp line at 3.73τ assigned to the four protons of the cyclopentadiene ring, a pair of poorly resolved complex multiplets at 7.2 and 7.55τ assigned to the methylene groups, and a quartet of triplets centered at 3.5τ and assigned to the protons of C-3 and C-4.

For the ultraviolet spectrum of III— $\lambda_{\text{max}}^{\text{isooctane}} m\mu$ (ϵ) 290 (sh.), 303 (sh.), 313 (22,000), 322 (sh.), 337 (sh.), 383 (260), $\epsilon_{200m\mu}$ 3000; $\lambda_{\text{max}}^{\text{dimethylsulfoxide}}$ 316 (28,000)⁶—no appropriate model could be located, but it is noteworthy that it differs from the spectrum— $\lambda_{\text{max}}^{\text{pentane}}$ 240 (4900), 335 (12,000)—of the hydrocarbon prepared by Doering and Matzner by oxidative coupling of sodium cyclopentadienide and assigned by them the 1,5-dihydrofulvalene structure on the basis of spectra and formation of a 1:2 adduct with tetracyanoethylene.⁷ Šorm has reported the isolation of a dihydroazulene with an orange color and a spectrum— λ_{max} 220 (14,000), 291 (3670), 432 (49)—suggesting that an additional double bond is in conjugation with a fulvene chromophore⁸; his substance is now best formulated as a 1-vinyl rather than a 6-vinyl fulvene (*i.e.*, as a 5,6-dihydroazulene rather than a 4,5-).

III forms a mono-adduct with N-phenylmaleimide⁹ (IV), m.p. 143–145.5 dec., $\lambda_{\text{max}}^{\text{EtOH}}$ 242 (26,200), 287 (sh., 1000), (Calcd. for $\text{C}_{20}\text{H}_{17}\text{NO}_2$: C, 79.18; H, 5.65; N, 4.62; O, 10.55. Found: C, 79.09; H, 5.72; N, 4.64) which slowly dissociates in solution¹⁰ (as evidenced by gradual appearance of a red-orange color) and which absorbs 3.0 molecules of hydrogen on reduction in absolute ethanol over reduced platinum oxide at atmospheric pressure.

Further evidence for the structure of III is adduced from its ready oxidation to fulvalene, identified by its characteristic ultraviolet spectrum.^{7,11} When a dilute (*ca.* $10^{-5} M$) solution of III in methanol is passed through a 4×10 -mm. column of freshly-prepared anhydrous silver oxide,¹² the relatively featureless spectrum of III is replaced by the strikingly sharp maxima of fulvalene: λ_{max} 313 (37,500), 299 (30,000), 289 (15,200), 278 (7,000) 265 (3,500), the last two being rather indistinct. The extinction coefficients are based on an $\epsilon_{316 m\mu}$ of 28,000 for III, and are somewhat lower than the values of Doering and Matzner.⁷ Probably, dissolved molecular oxygen is responsible for the oxidation of III, with the silver oxide functioning only as a base, since attempts to reproduce the oxidation in degassed dimethyl sulfoxide were unsuccessful.

(5) J. Thiec and J. Wiemann, *Bull. soc. chim. France*, 207 (1958).

(6) The different extinction coefficients may reflect differing degrees of purity in the two samples.

(7) W. von E. Doering in "Theoretical Organic Chemistry—The Kekulé Symposium," Butterworths, London, 1959, p. 45; E. A. Matzner, "Fulvalene," dissertation, Yale University, 1958.

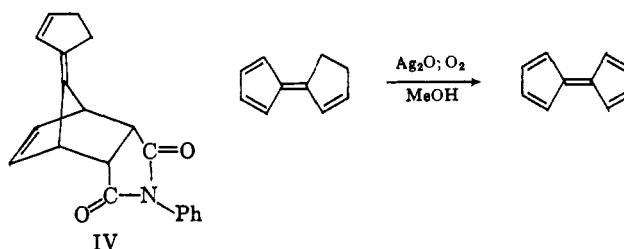
(8) F. Šorm, F. Vonašek and V. Herout, *Collection Czech. Chem. Commun.*, **14**, 91 (1949); Z. Čekan, V. Herout and F. Šorm, *Chem. Ind. (London)*, 604 (1954).

(9) M. P. Cava, A. A. Deana, K. Muth and M. J. Mitchell, *Org. Syn.*, **41**, 93 (1961).

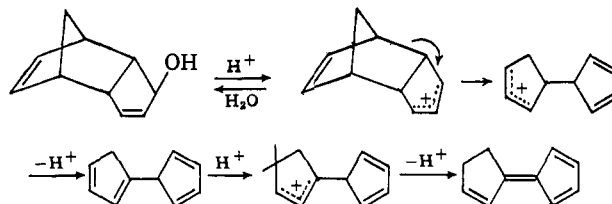
(10) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **66**, 645 (1944), and references cited therein.

(11) W. B. DeMore, H. O. Pritchard and N. Davidson, *ibid.*, **81**, 5874 (1959).

(12) R. Willstatter and A. Pfannenstiel, *Ber.*, **37**, 4744 (1904).



A reasonable mechanism for the formation of III is presented below.



Formation of the initial allylic carbonium ion presumably is reversible, since Woodward and Katz have effected acid-catalyzed epimerization of a dicyclopentadien-1-ol under conditions in which no fragmentation is observed.³ The second step is merely the reverse of the solvolytic ring closure reaction recently reviewed by Bartlett.¹³

Acknowledgment.—The author is indebted to Professor R. B. Woodward and Dr. Tadamiichi Fukunaga for valuable discussions, and to the National Science Foundation for a fellowship.

(13) P. D. Bartlett, *Ann.*, **663**, 45 (1962).

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RECEIVED APRIL 1, 1963

THE STRUCTURE OF ARGEMONINE. A NEW NATURALLY-OCCURRING ALKALOID RING SYSTEM

Sir:

The alkaloid argemonine is present in *Argemone munita* Dur. & Hilg. subsp. *rotundata* (Rybd.) G. B. Ownb. along with norargemonine and bisnorargemonine, which are related to argemonine as mono- and bis-O-demethyl derivatives.^{1a-c} As a result of a number of degradative experiments, it was suggested^{1d,e} that argemonine was 2,3,9,10-tetramethoxyaporphine, although a 10,11 or 8,9 placement of the two methoxyl groups in ring D was not eliminated. (Such structures were disputed on the basis of optical and spectral data.^{1f})

It did not seem to us that the ultraviolet spectra of the above alkaloids (λ_{max} 287 $m\mu$) were consistent with an aporphine structure and, indeed, we found that the spectrum of bisnorargemonine shows a large enhancement of absorption and bathochromic shift in the presence of base. This indicates that the observed absorption is due to the phenol or methylated phenol chromophore and not a biphenyl system such as is present in the aporphine alkaloids.²

(1) (a) T. O. Soine and O. Gisvold, *J. Pharm. Sci.*, **33**, 185 (1944); (b) T. O. Soine and J. W. Schermerhorn, *ibid.*, **40**, 19 (1951); (c) T. O. Soine and L. B. Kier, *ibid.*, **49**, 187 (1960); (d) L. B. Kier and T. O. Soine, *ibid.*, **50**, 321 (1961); (e) T. O. Soine and L. B. Kier, *ibid.*, **51**, 1198 (1962); (f) M. Shamma, *Experientia*, **18**, 64 (1962).

(2) The 2,3,9,10- and 2,3,10,11-tetramethoxyaporphine structures suggested by Soine and Kier are in any case not valid since both are known compounds (ref. 3) whose physical characteristics do not match those of argemonine.

(3) R. K. Callow, J. M. Gulland and R. D. Haworth, *J. Chem. Soc.*, **192**, 658 (1929).