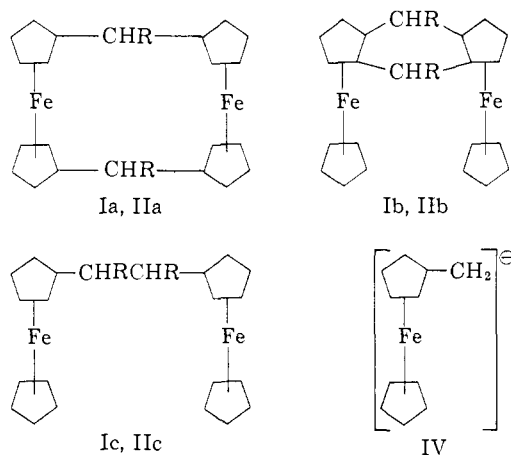


ment to structure Ib (1,2-bis-ferrocenylmethane), on the basis of the presence of bands at 1110 and 1004 cm^{-1} (9 and 10 μ bands)⁵ in the infrared spectrum of I, indicative of at least one unsubstituted cyclopentadienyl ring. Both of these formulations (Ia and Ib) are incorrect; the structure of the condensation product (I) is 1,2-diferrocenylethane (Ic).



Ia, Ib, Ic, R = H; Iaa, Iib, Iic, R = C₆H₅

Compound I, prepared by the sulfuric acid method,¹ melts 190–192° (lit.^{1,2} m.p. 191°). Microanalyses agree better with its formulation as Ic than as Ia or Ib [Anal. Calcd. for C₂₂H₂₂Fe₂ (Ic): C, 66.37; H, 5.57; Fe 28.06. Calcd. for C₂₂H₂₀Fe₂ (Ia or Ib): C, 66.70; H, 5.09; Fe, 28.20. Found: C, 66.67; H, 5.77; Fe, 27.92; C-CH₃, 0.00].⁶ Its infrared spectrum resembles closely that of ethylferrocene.^{5,7} A mixture melting point of I with an authentic sample of 1,2-diferrocenylethane (Ic) [Anal. Found: C, 66.38; H, 5.59; Fe, 28.24], m.p. 193–195°, showed no depression and the infrared spectra (CS₂) of the compound (I \equiv Ic) from the two routes were superimposable. The latter compound was prepared by hydrogenation of ferrocenylacetylferrocene (desoxyferrocene) [Anal. Found: C, 63.95; H, 4.92; Fe, 27.20], m.p. 159–161°, the product of Friedel-Crafts' acylation of ferrocene with the acid chloride of ferrocenylacetic acid.⁸

The structure of the similar condensation product (II) from ferrocene and benzaldehyde (first assigned structure IIa,^{1,2,3} later IIb⁴) is, presumably, analogous, *i.e.*, 1,2-diferrocenyl-1,2-diphenylethane (IIc) [Anal. Calcd. for C₃₄H₃₀Fe₂: C, 74.21; H, 5.50; Fe, 20.30. Calcd. for C₃₄H₂₈Fe₂: C, 74.48; H, 5.15; Fe, 20.38. Found: C, 74.37; H, 5.77; Fe, 20.10] since the infrared spectrum of this compound (II) is similar to that of I. Experiments now in progress are designed to establish unequivocally the structure of II.

Reflection on possible mechanisms for the for-

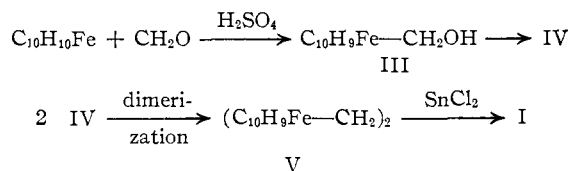
(5) M. Rosenblum, Ph.D. Thesis, Harvard University, August, 1953; M. Rosenblum and R. B. Woodward, *THIS JOURNAL*, **80**, 5443 (1958).

(6) Microanalyses for hydrogen reported by the earlier authors^{1,2} are also higher than those expected for Ia or Ib.

(7) The present sample of ethylferrocene was prepared by D. J. Casey.

(8) K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, *THIS JOURNAL*, **79**, 3420 (1957).

mation of I and II suggests the reaction path shown, in which the key intermediate is the novel cation IV. In accord with this pathway,⁹ α -hydroxymethylferrocene (III)¹⁰ has been converted to I under conditions identical to those employed for the conversion of ferrocene and formaldehyde to I, and the blue-green, water-soluble di-cation (V) of I has been isolated as its dipicrate.



Acknowledgment.—The authors wish to express their appreciation to the Me Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, for financial assistance.

(9) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957).

(10) The electronic nature of the coupling intermediate (IV) is unspecified as to singlet or triplet state. Another attractive mechanistic possibility involves coupling of the neutral radical derived from IV in a chain sequence of intermolecular oxidation-reduction reactions.

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RECEIVED MARCH 31, 1959

NOVEL HETEROCYCLO PENTADIENES

Sir:

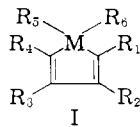
Five-membered heterocyclic rings containing two conjugated double bonds in an alternating sequence with the hetero atom, as in thiophene, have been known for some time. However, preparation of such rings involving hetero atoms other than O, N, S, Se or Te in such ring systems have not been reported. We wish to report the synthesis of such five-membered heterocycles containing other hetero elements such as P, Ge, Sn, As or Sb. The method of preparation appears to be generally applicable with many elements having a positive valence of two or greater.

The procedure we have followed in preparing organometal (or organometalloid) heterocycles involves the condensation of an active metal (or metalloid) dihalide with a 1,4-dilithiobutadiene derivative. The dilithium derivative, 1,4-dilithio-1,2,3,4-tetraphenylbutadiene, is prepared as reported by Smith and Hoehn¹ by the dimerization of diphenylacetylene with lithium in ether. An ether solution of dihalide of the hetero atom having a molar concentration approximately equal to that of dilithium reagent solution is prepared. Using normal precautions to avoid exposure to air, carbon dioxide or moisture, the dilithium solution may be added dropwise to the dihalide solution under an atmosphere of dry nitrogen. The reaction is extremely rapid as indicated by the immediate disappearance of the dark red color characteristic of the organolithium reactant.

The reaction of dilithiumtetraphenylbutadiene (LTPBD) with SCl₂ formed tetraphenylthiophene. This previously has been prepared by other

(1) L. I. Smith and H. H. Hoehn, *THIS JOURNAL*, **63**, 1184 (1941).

methods.² However, it served as a basis for study of a series of compounds having the conjugated diene structure plus one hetero atom. The basic structure is



The compounds reported here all contain phenyl R₁, R₂, R₃, R₄. The nature of R₅ and R₆ substituents may vary with the possibility of one or both being absent, *e.g.*, with As, R₅ = C₆H₅ and R₆ is not present. Also, R₅ and R₆ may represent a second ring as in a spiro compound. Preparation of spiro compounds imposes several limitations on the general reaction, *i.e.*, the need for (1) a hetero atom with a valence of four or greater and (2) use of 1 mole of a tetrahalide of the hetero atom plus 2 moles of LTPBD.

Referring to structure I, compounds have been prepared with M = S, P, Sn, As, Sb and Ge (also spiro compounds with M = Sn and Ge). These are all high melting (>160°) crystalline solids. Molecular weight determinations and elemental analysis verified the ring structure. A typical member of the series is pentaphenylphosphole (M = P, R₅ = C₆H₅) m.p. 261–262°; mol. wt. calcd. 464, found 463 (mass spec.); calcd: C, 88.1; H, 5.4; P, 6.65; found: C, 88.2; H, 5.5; P, 6.55.

Work is in progress to prepare heterocycles of this type with R groups I–IV other than phenyl. Other synthetic routes to these compounds and the preparation of other type compounds having this basic unit are being investigated. Concurrent with the synthetic studies, we are attempting to determine the chemical nature of these new ring systems with regard to the possible aromaticity of the five-membered ring, ability to form π electron complexes with metals and the normal diene reactions.

(2) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, New York, N. Y., 1952, pp. 473 f.

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COMPARISON OF COVALENTLY BONDED ELECTRO-NEGATIVE ATOMS AS PROTON ACCEPTOR GROUPS IN HYDROGEN BONDING

Sir:

Generalization,^{1,2} widely held and widely quoted, concerning the requirements for hydrogen bonding, has emphasized the necessity of having as the

(1) These references may serve as illustrations: M. Davies, *Ann. Repts. on Prog. Chem.* (Chem. Soc. London), **43**, 5 (1946); L. Hunter, *ibid.*, p. 141; L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., Second Edition, 1948, pp. 286 f.; C. A. Coulson, "Valence," Oxford University Press, London, 1952, pp. 298 f.; T. Moeller, "Inorganic Chemistry," John Wiley and Sons, New York, N. Y., 1952, pp. 188–189; G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1955, pp. 49 f.; E. Cartmell and G. W. A. Fowles, "Valency and Molecular Structure," Butterworths Scientific Publications, London, 1956, p. 138; G. M. Badger, *Revs. Pure Appl. Chem. (Australia)*, **7**,

proton acceptor group an element of small atomic radius and strong electronegativity (*i.e.*, N, O, F). Although these conclusions may be valid when very strong hydrogen bonding to anions is involved (*e.g.*, HF₂⁻), their extension to covalently bonded negative atoms is not possible. On the contrary, we wish to present spectroscopic evidence which demonstrates that the relative electron donor abilities of the alkyl halides decreases in the order I > Br > Cl > F. Furthermore, the hydrogen bonds formed by compounds of these elements with suitable proton donors are weak relative to those of the other electronegative elements.

The order given above has long been known to hold for the intramolecular hydrogen bonding exhibited by the *o*-halophenols.³ The criteria for strength, or more precisely the enthalpy, of the hydrogen bond is taken to be related to $\Delta\nu$, the spectral shift in cm.⁻¹ from the "free" to the "bonded" peaks.⁴ However, the interpretation of the *o*-halophenol data is ambiguous because, in the rigidly held aromatic systems, the small covalent radii of the lower atomic weight halogen atoms may

TABLE I⁵

$\Delta\nu$ VALUES OF β -SUBSTITUTED ETHANOLS

Substituent	F	Cl	Br	I	EtO	EtS	Et ₂ N
$\Delta\nu$, cm. ⁻¹	12	32	38	46	30	92	166

TABLE II⁵

FREQUENCY SHIFTS DUE TO INTERMOLECULAR HYDROGEN BONDING (cm.⁻¹)

Compound	$\Delta\nu$ CH ₃ OH ^b	$\Delta\nu$ Phenol ^b
<i>n</i> -Butyl fluoride	19	40
Cyclohexyl fluoride	..	53
<i>n</i> -Butyl chloride	37	59
Cyclohexyl chloride	..	66
<i>n</i> -Butyl bromide	41	69
Cyclohexyl bromide	..	82
<i>n</i> -Butyl iodide	47	77
Isopropyl iodide	..	85
Di- <i>n</i> -butyl ether	155	281
Di- <i>n</i> -butyl sulfide	155	258
Tri- <i>n</i> -butylamine ^a	396	..
Tri- <i>n</i> -butylphosphine ^a	267	..
Tri-ethylarsine ^a	310	..

^a Solution in C₂Cl₄. ^b Positions of the free peaks: 3610 cm.⁻¹ for phenol; 3643 cm.⁻¹ for methanol in both CCl₄ and C₂Cl₄.

55 (1957); J. A. A. Ketelaar, "Chemical Constitution," Elsevier, Publ. Co., New York, N. Y., Second Edition, 1958, p. 408.

(2) For recent reviews on hydrogen bonding not referred to above: L. Kellner, *Repts. Progr. in Phys.*, **15**, 1 (1952); L. Hunter in W. Klyne, Ed., "Progress in Stereochemistry," Vol. I, Academic Press, Inc., New York, N. Y., 1954, pp. 223 f.; C. A. Coulson, *Research*, **10**, 149 (1957); C. G. Cannon, *Spectrochimica Acta*, **10**, 341 (1958).

(3) O. R. Wulf, U. Liddel and S. B. Hendricks, *THIS JOURNAL*, **58**, 2287 (1936); O. R. Wulf and E. J. Jones, *J. Chem. Phys.*, **8**, 745 (1940); G. Rossmly, W. Lüttke and R. Mecke, *ibid.*, **21**, 1606 (1953); and especially A. W. Baker and A. T. Shulgin, *THIS JOURNAL*, **80**, 5358 (1958); A. W. Baker, *ibid.*, **80**, 3598 (1958).

(4) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937); R. M. Badger, *ibid.*, **8**, 288 (1940); R. C. Lord and R. E. Merrifield, *ibid.*, **21**, 166 (1953); K. Nakamoto, M. Margoshes and R. E. Rundle, *THIS JOURNAL*, **77**, 6480 (1955); G. C. Pimentel and C. H. Sederholm, *J. Chem. Phys.*, **24**, 639 (1956).

(5) Perkin-Elmer Model 21 and Model 112 Spectrophotometers, LiF prisms, CCl₄ solutions except where noted. Intramolecular concentrations were about 0.005 M. Intermolecular concentrations were about 1 M for the proton acceptor and 0.01 M for the donor.