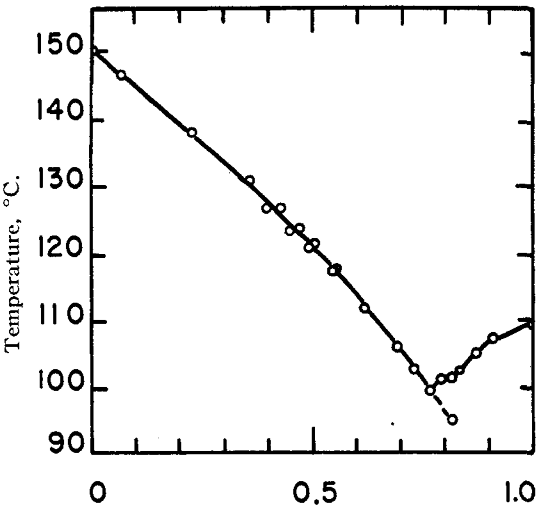
for the binary melting point diagram was very kindly supplied by Professor W. G. Dauben,[26] m.p. 109.9°.

N-(*trans*-2-Methylcyclohexyl)-benzamide (Ib).—2-Methylcyclohexylamine was prepared by the sodium–alcohol reduction of 2-methylcyclohexanone oxime.[27] After conversion to the benzamide in the usual manner with benzoyl chloride, Ib was obtained by three crystallizations from ethanol, m.p. 151.0°.

Mixed Melting Point Behavior of Ia and Ib.—The binary melting point diagram of N-(*trans*-2-methylcyclohexyl)-benzamide was determined using various mixtures in a modified Hershberg melting point apparatus according to the method described in detail by Cason and Winans.[28] The temperature at which the last crystalline material was no longer visible was easily reproducible to 0.1°. The results are shown in Fig. 1.

2-Methylcyclohexylamine by the Leuckart Reaction.—In a 100-ml. round-bottomed flask fitted with a take-off condenser, were placed 10 g. of 2-methylcyclohexanone, 40.4 g. of formamide and 1 g. of magnesium chloride. The mixture was heated at 175–180° for three hours, the water being formed removed periodically, and the ketone codistilling returned to the reaction mixture. The reaction mixture was poured into 100 ml. of water, and extracted continuously with ether. The ethereal solution was concentrated, and to the crude N-2-methylcyclohexylformamide was added 25 ml. of concentrated hydrochloric acid. This mixture was heated under reflux for three hours, cooled, and neutral compounds removed by extraction with ether. The aqueous solution was basified, saturated with sodium chloride, and continuously extracted with ether. After drying over sodium hydroxide, distillation afforded 5.52 g. (55%) of mixed *cis*- and *trans*-2-methylcyclohexylamine, b.p. 74–75° (52 mm.). Skita[29] reports 153° (760 mm.).

N-(2-Methylcyclohexyl)-benzamide.—To a mixture of 6.04 g. of 2-methylcyclohexylamine and 50 ml. of 20% sodium hydroxide was added with shaking 14.0 g. of benzoyl chloride. The precipitate of crude benzamide was ground and thoroughly washed with sodium carbonate and water. The yield of colorless benzamide was 10.2 g. (88.5%), final melting temperature, 113.1°.



Mole fraction N-(*cis*-2-methylcyclohexyl)-benzamide.

Fig. 1.

Anal. Calcd. for $C_{14}H_{19}ON$: C, 77.42; H, 8.76; N, 6.45. Found: C, 77.54; H, 8.77; N, 6.59.

A small sample was sublimed (97% recovery), and the melting point redetermined in the manner used in constructing the binary melting point diagram, m.p. 114.1° (corresponding to 60% *cis* isomer in this mixture).

From Sodium–Alcohol Reduction of the Oxime.—A sample of the amine prepared by sodium–alcohol reduction of 2-methylcyclohexanone oxime[27] was converted to the benzamide as above. It melted at 141.0° (corresponding to 80% *trans* isomer in this mixture).

From Hydrogenation of Aceto-*o*-toluidide.—Aceto-*o*-toluidide was hydrogenated with platinum oxide in acetic acid solution. The 2-methylcyclohexylamine resulting from hydrolysis of the N-(2-methylcyclohexyl)-acetamide was converted to the benzamide as above. It melted at 98.5° (corresponding to 79% *cis* in this mixture).

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[26] See W. G. Dauben and E. Hoerger, THIS JOURNAL, **73**, 1504 (1951).

[27] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 318.

[28] J. Cason and W. Robert Winans, *J. Org. Chem.*, **15**, 148 (1950).

[29] A. Skita, *Ber.*, **56**, 1014 (1923).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Small-Ring Compounds. X. Molecular Orbital Calculations of Properties of Some Small-Ring Hydrocarbons and Free Radicals[1]

BY JOHN D. ROBERTS, ANDREW STREITWIESER, JR.,[2] AND CLARE M. REGAN

RECEIVED MARCH 17, 1952

The molecular orbital (LCAO) method has been used to calculate the electron delocalization energies, bond orders and free-valence indexes of some cyclic small-ring hydrocarbons and free radicals including a number of cyclobutadiene derivatives. It is concluded that the $(4n + 2)$ π-electron rule of aromatic stability can only be justified by the simple molecular orbital treatment for monocyclic conjugated polyolefins.

One of the substantial successes of the simple molecular orbital theory as developed by Hückel[3] is the prediction that, of the completely-conjugated planar monocyclic polyolefins as cyclobutadiene, benzene, etc., those which possess $(4n + 2)$ π-electrons ($n = 0, 1, 2, 3, \ldots$) will be peculiarly stable by virtue of having fully-filled molecular orbitals with substantial electron delocalization (resonance) energies as compared to the classical valence bond structures. The same rule may be applied[3,4] without known exceptions, to the cyclopropenyl, cyclopentadienyl, cycloheptatrienyl, etc., cations, anions and free radicals although but few quantitative cal-

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[1] Supported in part by the program of research of the United States Atomic Energy Commission under Contract AT(30-1)-905.

[2] U. S. Atomic Energy Commission Post-Doctoral Fellow, 1951–1952.

[3] E. Hückel, *Z. Physik*, **70**, 204 (1931); "Grundzüge der Theorie ungesättiger and aromatischer Verbindungen," Verlag Chemie, Berlin, 1938, pp. 77–85.

[4] (a) H. J. Dauben, Jr., and H. J. Ringold, THIS JOURNAL, **73**, 876 (1951); (b) W. v. E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).

culations[3,5] on such species have been published previously. It has been sometimes assumed[6] without proof that the $(4n + 2)$ π-electron rule holds for polycyclic as well as monocyclic conjugated polyolefins despite the fact that a number of seemingly anomalous stable substances are known; *e.g.*, dibenzcyclobutadiene (diphenylene), acenaphthylene, pyrene, fluoranthene, etc. In the present work, the general applicability of the rule has been considered as part of a search for new cyclic conjugated systems, particularly derivatives of cyclobutadiene which might be predicted on theoretical grounds to be reasonably stable. Cyclobutadiene itself has been well studied from the standpoint of the molecular orbital theory[3,5,7] and has been predicted to have an unstable triplet ground state. Cyclobutadiene is of course highly symmetrical and it has been of interest to determine whether the simple molecular orbital theory predicts that less-symmetrical substituted cyclobutadienes would be more stable and have triplet ground states.

All of the calculations in the present paper have been made by the simple molecular orbital method[3,8,9] with neglect of resonance integrals between non-adjacent atoms and of non-orthogonality of atomic orbitals on different nuclei. Wherever possible the secular determinants were factored by group theory procedures.[9] The results must be regarded as being uncertain and essentially qualitative by virtue of the known limitations of the method, including not only the general difficulties discussed by Coulson and Dewar[10] but also the uncertainties introduced by non-self-consistent fields in other than "alternant" hydrocarbons.[11] For each compound, we have calculated the delocalization (resonance) energy (*DE*) in units of β (about 17 kcal.), the bond orders[8,12] and the "free-valence" indexes.[13] The results are given in Fig. 1. Where the simple molecular orbital theory predicts a triplet ground state, the compounds in Fig. 1 are marked with a T following the figures for *DE*.

Compounds I–XIII are cyclobutadiene derivatives of various types. Cyclobutadiene itself (I) is predicted to have zero *DE*, a triplet ground state[7b,e] (*cf.* however, Craig[7f,g]), but not unusual free-valence indexes (*F*).[14] The apparent instability of the substance might be ascribed to the triplet ground state[7e] on the basis of the molecular orbital treatment since the known cyclopropene should have comparable or greater angular strain. It is interesting that various types of substituted cyclobutadienes without fused rings (II–VI) are predicted to have moderate *DE*-values but also triplet ground states arising from accidental degeneracies. The vinyl derivatives (II–IV) show quite high *F*-values at the terminal positions of the double bonds. VII–XI are benzcyclobutadienes, the calculations for which indicate clearly the lack of theoretical justification for the $(4n + 2)$ π-electron rule when applied to other than monocyclic systems. VII, VIII[15] and XI violate the rule, but are predicted to have singlet ground states, substantial *DE*-values (particularly for VIII which has actually been shown to be quite stable[16]) and *F*-figures at all positions lower than those of ethylene. On the other hand, IX which is an isomer of naphthalene with ten π-electrons is predicted to have a triplet ground state although its position isomer X should have a singlet ground state. IX is particularly interesting as an example of a possible "aromatic"[7g] "alternant"[11] hydrocarbon with a predicted triplet ground state.

Comparisons of XII and XIII with cyclobutadiene (I) are very interesting. Classical valence theory can only predict that fusion of double bonds onto I would result in considerably less stable substances. However, the simple molecular orbital treatment suggests that XII and XIII would be very different from I in having singlet ground states with substantial *DE*- and low *F*-values. If XII could be prepared,[17] studies of its bond distances would be of considerable importance since they would provide an excellent competitive test of the predictions of the simple valence bond and molecular orbital treatments. The valence bond method predicts the order of the central bond to be 1.33 corresponding to a C–C distance of about 1.42 Å. as in graphite while the molecular orbital approach, with a calculated bond order of 1.00, predicts a bond distance of about 1.54 Å. as in normal single bonds.

XIV–XVII are cross-conjugated polymethylene-substituted systems which irrespective of symmetry and number of π-electrons are predicted to

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(5) G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

(6) *Cf.*, (a) V. Boekelheide, W. E. Langeland and C. T. Liu, THIS JOURNAL, **73**, 2432 (1951); (b) J. D. Roberts and W. F. Gorham, *ibid.*, **74**, 2278 (1952); (c) W. v. E. Doering, Abstracts of American Chemical Society Meeting, New York, September, 1951, p. 24M.

(7) (a) W. G. Penney, *Proc. Roy. Soc. (London)*, **A146,** 223 (1934); (b) G. W. Wheland, *ibid.*, **A164,** 397 (1938); (c) C. A. Coulson, *ibid.*, **A169**, 413 (1939); (d) G. W. Wheland, THIS JOURNAL, **63,** 2025 (1941); (e) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, [7] **40,** 1 (1949); (f) D. P. Craig, *Proc. Roy. Soc. (London)*, **A202,** 498 (1950); (g) D. P. Craig, *J. Chem. Soc.*, 3175 (1951).

(8) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A191,** 39 (1947).

(9) H. Eyring, J. Walter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, New York, N. Y., 1944, Chap. XIII.

(10) C. A. Coulson and M. J. S. Dewar, *Discussions of the Faraday Soc.*, **2**, 54 (1947).

(11) (a) C. A. Coulson and G. S. Rushbrooke, *Proc. Camb. Phil. Soc.*, **36,** 193 (1940); (b) D. P. Craig and A. Maccoll, *J. Chem. Soc.*, 964 (1949); (c) Craig[7f,g] has recently indicated that neither the simple molecular orbital or valence bond treatment is likely to be reliable for calculation of the properties of cyclobutadiene or other conjugated cyclic polyolefins (designated as "pseudoaromatic" compounds) in which configuration interaction is important; (d) Prof. C. A. Coulson (private communication) suggests that in many of our small-ring examples (Fig. 1) the neglected π–σ-interactions are possibly of comparable importance to the π-π-interactions.

(12) C. A. Coulson, *Proc. Roy. Soc. (London)*, **A164,** 383 (1938).

(13) (a) C. A. Coulson, *Trans. Faraday Soc.*, **42,** 265 (1946); *Discussions of Faraday Soc.*, **2, 7** (1947); *J. chim. phys.*, **45,** 243 (1948); (b) in our calculations, we need $N_{\max}$ equal to 4.732 since the value 4.698 used by Coulson gives a negative value of *F* for $C(CH_2)_3$.

(14) Typical calculated *F*-values for different types of carbon atoms are as follows: methyl radical, 1.73; α-position of a benzyl radical, 1.04; α-positions in *p*-quinodimethane which is apparently stable in the vapor state but which polymerizes rapidly in condensed phases, 0.92 (singlet state); *cf.* C. A. Coulson, D. P. Craig, A. Maccoll and A. Pullman, *Discussions of the Faraday Soc.*, **2,** 36 (1947); ethylene, 0.73; benzene, 0.23; central carbon of $C(CH_2)_3$, 0.00.

(15) VIII has been treated by the molecular orbital method previously by other workers whose calculations are given here for comparison purposes; *cf.* C. A. Coulson, *Nature*, **150,** 577 (1942), and J. Waser and V. Schomaker, THIS JOURNAL, **65, 1451** (1943).

(16) W. C. Lothrop, *ibid.*, **63**, 1187 (1941); **64**, 1698 (1942); see also Waser and Schomaker.[15]

(17) Experiments directed toward synthesis of simple derivatives of XII are currently in progress.

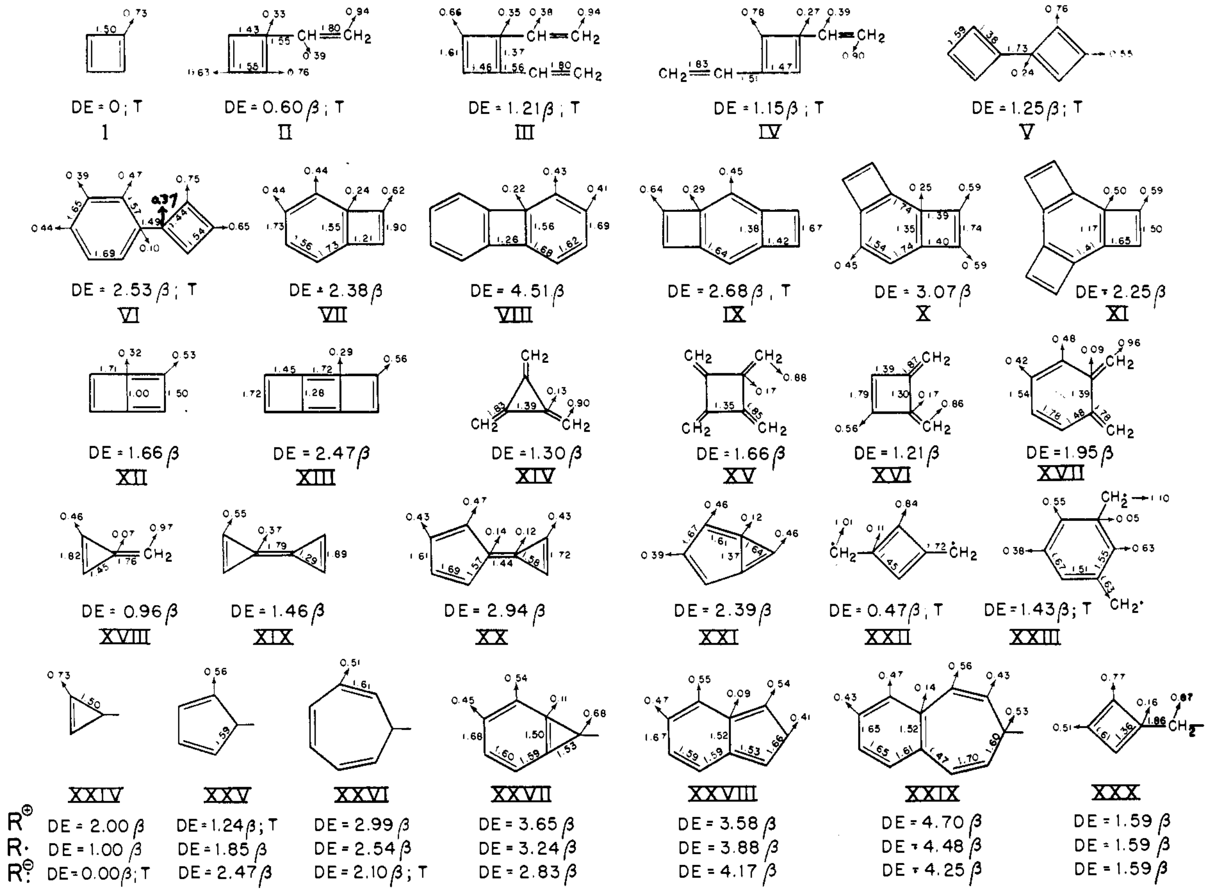
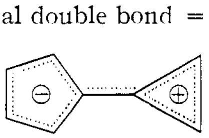


Fig. 1.—Calculations by molecular orbital method. Delocalization energies (DE) are given below each formula, the bond orders (p) are shown by figures near each bond and the free-valence indexes (F) for each position are placed at arrow points. The letter T denotes a predicted triplet ground state. The free valence indexes given for XXIV–XXX are those calculated for the free radicals.

have singlet ground states. Although the calculated DE-values[18] are substantial, the F's at the CH_2 positions are quite high and suggest that these substances should polymerize readily like p-quinodimethane.[14]

XVIII–XXI are possible fulvene-like substances and are predicted to have singlet ground states and quite stable π-electron systems.[19,20] XX is particularly interesting since the three- and five-membered unsaturated rings might be qualitatively expected to accommodate well positive and negative charges, respectively, to give a charge distribution as in XXXI. The calculated DE is high (fulvalene with an additional double bond = 2.80 β[20]) and as would be expected for the postulated charge separation, the computed bond order of the bond linking the two rings is quite low compared to the corresponding bonds in XIX and fulvalene (1.67).[20] XXI has interest as a possible non-pseudoaromatic[7g] analog of azulene and pentalene with a substantial predicted resonance energy.



XXXI

XXII and XXIII represent diradical isomers of XVI and XVII. Here, the molecular orbital treatment agrees with the classical valence theory in predicting that these substances should be diradicals with high F-values. Both substances have low DE's compared with their isomers.

XXIV–XXIX represent series of cyclic conjugated cations, free radicals and anions. With XXIV–XXVI, the calculated stabilities of the various ionic species alternate with ring size in a remarkable manner. It seems significant that no experimental exceptions have been found to the predicted behavior.[3,4,21] The calculations for XXVII–XXIX show that benz-substitution of XXIV–XXVI does not alter the relative ionic stability sequences predicted for the unsubstituted

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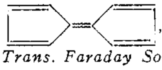
[18] (a) J. Syrkin and M. Diatkina, *Acta Physiochem.* (*USSR*), **21**, 641 (1946) give DE = 1.20 β for XVI; (b) A. J. Namiot, M. E. Diatkina and Y. K. Syrkin, *Compt. rend. acad. sci.* (*USSR*), **48**, 233 (1945); *C. A.*, **40**, 4927 (1946) give DE = 1.92 β for XVII. In neither case were the bond orders or F-values calculated.

[19] A related molecule, fulvalene , has been analyzed thoroughly by R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); **46**, 146 (1950).

[20] J. Syrkin and M. Dyatkina[18] give DE = 0.96 β for XVIII.

[21] While no published evidence is available on the species corresponding to XXIV, preliminary qualitative experiments in this Laboratory indicate that cyclopropene may not react with Grignard reagents under conditions where cyclopentadiene is converted to cyclopentadienylmagnesium compounds.

species, although the differences in *DE* are considerably smaller. With the benz-derivatives none of the ionic species is predicted to have a lowest triplet state.

The cyclobutadienylcarbinyl radical (XXX) is interesting in that it is calculated to have a *DE* more than twice that of the benzyl radical. The difference between the radicals is particularly striking when it is remembered that methylcyclobutadiene would have a *DE* of 2 β less than that of toluene. The calculations suggest that methylenecyclobutene XXXII should be readily attacked by free-radical, anionic or cationic reagents at the 4-position.

XXXII

Acknowledgment.—We are much indebted to Professor W. G. McMillan, Jr., for advice on methods of calculation and to Professors C. A. Coulson and G. W. Wheland for helpful suggestions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF TUSKEGEE INSTITUTE]

An Interesting Side-Reaction in the Preparation of Triphenylvinylsilane[1a]

BY LOUIS F. CASON AND HOUSTON G. BROOKS[1b]

RECEIVED MAY 8, 1952

When vinyltrichlorosilane was allowed to react with phenyllithium in ether, the expected coupling product, triphenylvinylsilane (I) and triphenyl-(β-phenylethyl)-silane (II) resulted. (II) was obtained when phenyllithium was added to (I) in ether, and likewise, triphenyl-*n*-hexylsilane (III) was formed from (I) and *n*-butyllithium. The configurations of (II) and (III) were established by alternate syntheses.

In connection with investigations on the syntheses and properties of some triarylalkenylsilanes, it was observed that on treatment of vinyltrichlorosilane with an excess of phenyllithium in ether, two principal products are formed in addition to considerable amounts of polymer: the expected coupling product, triphenylvinylsilane (I) and triphenyl-(β-phenylethyl)-silane (II). Convincing evidence for the structures of (I) and (II) was achieved through analysis and molecular weight determination, and speculations as to how (II) was formed in the reaction ultimately led to a hypothesis suggesting the addition of the organometallic compounds to the unsaturated silane.

$$3C_6H_5Li + CH_2{=}CHSiCl_3 \longrightarrow (C_6H_5)_3SiCH{=}CH_2\,(I) + LiCl \quad (1)$$

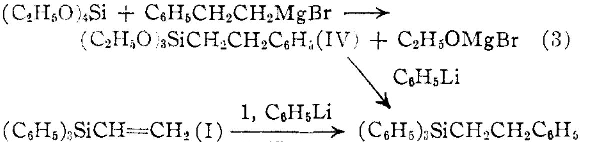
$$(C_6H_5)_3SiCH{=}CH_2 + C_6H_5Li \longrightarrow [(C_6H_5)_3SiCH(Li)CH_2C_6H_5] \quad (2)$$

$$\xrightarrow{H_2O} (C_6H_5)_3SiCH_2CH_2C_6H_5 \quad (II)$$

Organolithium compounds are known to undergo addition to the carbon–carbon double bonds of highly conjugated molecules like 1,1-diphenylethylene, the fulvenes, and $\Delta^{9,9'}$-bifluorene and to simple conjugated dienes in the initiation of polymerization.[2] Recently it has been reported that cyclooctatetraene undergoes a similar reaction with certain organolithium compounds.[3]

As far as we have been able to ascertain, the addition of alkyl and aryl lithium compounds to comparatively simple olefins is a relatively rare phenomenon. Thus, in order to test our hypothesis, triphenylvinylsilane was stirred at room temperature for six hours with an equivalent amount of phenyllithium in ether. Subsequent to hydrolysis and purification (II) was isolated in 84% yield. In addition, triphenyl-*n*-hexylsilane (III) was formed in 67% yield when the procedure was repeated with *n*-butyllithium.

Although, at present, it has not been positively demonstrated that a new organometallic compound is formed as an intermediate in this reaction, the structures of (II) and (III) have been confirmed through unequivocal syntheses. First, triethoxy-(β-phenylethyl)-silane (IV) was formed from tetraethoxysilane and β-phenylethylmagnesium bromide. Refluxing (IV) with three equivalents of phenyllithium in ether produced (II).

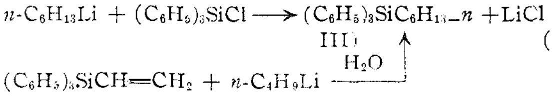


$$(C_2H_5O)_4Si + C_6H_5CH_2CH_2MgBr \longrightarrow (C_2H_5O)_3SiCH_2CH_2C_6H_5\,(IV) + C_2H_5OMgBr \quad (3)$$

$$(IV) \xrightarrow{C_6H_5Li} (II)$$

$$(C_6H_5)_3SiCH{=}CH_2\,(I) \xrightarrow[2,\ H_2O]{1,\ C_6H_5Li} (C_6H_5)_3SiCH_2CH_2C_6H_5\ (II)$$

Then, on treatment of triphenylchlorosilane with *n*-hexyllithium in ether, an excellent yield of (III) resulted. The identity of the addition products was established by mixed melting point determinations with the authentic samples.



$$n\text{-}C_6H_{13}Li + (C_6H_5)_3SiCl \longrightarrow (C_6H_5)_3SiC_6H_{13}\text{-}n\ (III) + LiCl \quad (4)$$

$$(C_6H_5)_3SiCH{=}CH_2 + n\text{-}C_4H_9Li \xrightarrow{H_2O} (III)$$

It is of interest to note that the formation of (I) from vinyltrichlorosilane and phenylmagnesium bromide required more drastic conditions and, apparently, without the addition of the Grignard reagent to the ethylenic linkage. On the other hand,

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[1] (a) Abstracted from a thesis submitted to the graduate faculty of Tuskegee Institute by H. G. Brooks in partial fulfillment of the requirement for the Master of Science Degree. (b) Frederick Gardner Cottrell Fellow, George Washington Carver Foundation, Tuskegee Institute, Alabama.

[2] H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943, Chap. V. Wittig (translated and revised by J. R. Thirtle) in "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 585. See also E. Krause and A. von Grosse, "Die Chemie der Metall-organischen Verbindungen," Photo-lithoprint Reproduction, Edwards Brothers, Inc., Ann Arbor, Mich., 1943, pp. 82, 94-96.

[3] A. C. Cope and M. R. Kintner, THIS JOURNAL, **73**, 3424 (1951).