Oxidation of the sample of *trans*-4-ethylcyclohexanol with Jones reagent gave 4-ethylcyclohexanone, identical in every respect with an authentic sample.

Dehydrohalogenation of 2.—A solution of **3** (2.8 g, 14 mmoles) and sodium methoxide (1.5 g, 30 mmoles) in methanol (25 ml) was refluxed under nitrogen for 3 hr. The solution was evaporated nearly to dryness and then poured into water. Extraction with ether, drying, evaporation, and distillation gave the olefin, bp 54–57° (0.2 mm). The infrared spectrum of **7** showed a strong band at 1706 cm^{-1}; the nmr spectrum exhibited a one-hydrogen mulitiplet at τ 4.67 and an acetyl singlet at 7.9. A sample was redistilled for analysis [bp 50–51° (0.05 mm)].

Anal. Calcd for $C_{10}H_{16}O$: C, 78.95; H, 10.52. Found: C, 78.66; H, 10.31.

The semicarbazone was prepared and recrystallized from aqueous ethanol; the white prisms thus obtained had mp 156–157.5°.

Reaction of Acetyl Chloride with 1,5-Cyclooctadiene.—A solution of 1,5-cyclooctadiene (108 g, 1.00 mole) in methylene chloride (400 ml) was added over 2 hr to a stirred solution of aluminum chloride (135 g, 1.0 mole) and acetyl chloride (78 g, 1.0 mole) in methylene chloride (100 ml) at −10 to −15°. The solution was stirred for 0.5 hr while warming to 0° and was poured onto ice.

The reaction mixture was worked up in the same manner as described for the cyclooctene–acetyl chloride reaction. Distillation gave the crude product, **8**, as a yellow oil, bp 88–110° (0.05 mm).

Redistillation using a spinning-band column gave pure **8**, *exo*-2-acetyl-6-chloro-*cis*-bicyclo[3.3.0]octane, as a colorless oil, bp 98–100° (0.04 mm) (81 g, 48%).

For analysis, **8** was converted to the semicarbazone, mp 188–189°.

Anal. Calcd for $C_{11}H_{20}ClO$: C, 53.85; H, 8.14. Found: C, 54.10; H, 7.65.

Conversion of 11 to *exo*-2-Acetyl-*cis*-bicyclo[3.3.0]octane.—Sodium (12 g, 0.50 g-atom) was added in small pieces over 5 hr to a solution of 9.0 g (0.05 mole) of **11** to tetrahydrofuran (300 ml) and *t*-butyl alcohol (75 ml).

The reaction mixture was refluxed for 16 hr longer, concentrated to a volume of ~200 ml on a rotary evaporator, and poured into ice water. Extraction with ether, followed by water washing of the ether extracts, drying, and evaporation gave a colorless oil. Some reduction of the carbonyl group had occurred as indicated by broad OH stretching absorption at ~3400 cm^{-1}.

This crude ketone–alcohol mixture (4.0 g) was dissolved in 30 ml of acetone and treated dropwise with Jones reagent at 10–20° until further reagent was not decolorized. Pouring into water, ether extraction, water washing, evaporation, and distillation gave *exo*-2-acetyl-*cis*-bicyclo[3.3.0]octane, bp 46–48° (0.06 mm). The infrared spectrum of this material was identical with that of an authentic sample. The semicarbazone had mp 180–181.5°, undepressed on admixture with the semicarbazone of an authentic sample.[8]

Registry No.—**1,** 931-88-4; **2,** 10126-44-0; semicarbazone of **2,** 10126-45-1; **3,** 10126-46-2; semicarbazone of **3,** 10126-42-8; **5,** 10126-47-3; **6,** 10126-48-4; **7,** 10126-49-5; semicarbazone of **7,** 10126-50-8; **8,** 10126-51-9; **9,** 10126-52-0; phenylurethan of **9,** 10126-53-1; **11,** 10126-54-2; semicarbazone of **11,** 10126-55-3; 1,5-cyclooctadiene, 111-78-4.

(11) E. R. H. Jones, *et al.*, *J. Chem. Soc.*, 39 (1946).

Index of Free Valence

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One of the useful bits of information derivable from the Hückel molecular orbital (HMO) calculations is the index of free valence, F_i.[1] The index of free valence may be defined as[2]

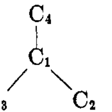
$$F_i = N_{\max} - N_r \qquad (1)$$

where N_r is the sum of the bond orders of all bonds, π and σ, between the rth atom and all adjacent atoms; and $N_{\max}$ is the maximum possible value of N_r. According to Coulson,[3] Moffett has proven that the maximum possible bond order, $N_{\max}$, is 4.732 although no proof is shown. While no restrictions are placed on this statement, it is obvious from further writings by Coulson and others[4] that some restrictions may be necessary. Coulson says, "Now it may be shown that for a carbon atom (excluding triple bonds) the greatest possible value of N is $N_{\max} = 3 + \sqrt{3} = 4.732$."[4a] and, "It can be shown that for a trigonal carbon atom $N_{\max}$ has the value $3 + \sqrt{3}$, $3 + \sqrt{2}$, or $3 + \sqrt{1}$ according as the atom in question is attached to three, two, or one other trigonal carbon atoms."[4b]

Unfortunately many authors[5,6a] have overlooked this necessary condition of trigonality. Their statements are exemplified by Roberts[5a] who states, concerning $N_{\max}$, that "...the theoretical maximum is easily shown to be 4.732" and by Dowd,[6a] "Trimethylenemethane I is important in theoretical chemistry by virtue of the fact that the central carbon atom of this molecule attains the maximum π-bond order possible for any carbon atom. The magnitude of the bond order thus obtained (4.732)...." In both cases the authors refer to the central atom of the trimethylenemethane molecule[7] and leave the impression that no carbon atom may have a greater maximum bond order. (See Chart I).

CHART I

TRIMETHYLENEMETHANE AND PROPARGYLENE



I

$$C_1{\equiv}C_2{-}(C{\equiv}C)_{n-1}{-}C_{2n+1}$$

II

The fallacy of this conclusion came to our attention while preforming "back of the envelope" type of calculations on the Hückel MO parameters of propargylene (II, $n = 1$).[9] Since this is simply two orthogonal

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(1) B. Pullman and A. Pullman, *Progr. Org. Chem.*, **4**, 37 (1958).

(2) C. A. Coulson, *Discussions Faraday Soc.*, **2**, 9 (1947).

(3) C. A. Coulson, *J. Chim. Phys.*, **45**, 243 (1948), footnote *.

(4) (a) C. A. Coulson, "Valence," Oxford University Press, London, 1961, p 271; (b) F. H. Burkitt, C. A. Coulson, and H. C. Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 554 (1951); (c) H. H. Greenwood, *ibid.*, **48**, 677 (1952).

(5) (a) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Inc., New York, N. Y., 1962, p 56; (b) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 93; (c) C. Sandorfy, "Electronic Spectra and Quantum Chemistry," Prentice-Hall Co., Inc., Englewood Cliffs, N. J., 1964, p 41; (d) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 56; (e) D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, **14**, 220 (1953); (f) M. S. de Giambiagi, M. Giambiagi, and R. Ferreira, *J. Chim. Phys.*, **61**, 697 (1964).

(6) (a) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966); (b) R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966).

(7) Recent literature[6] claims the observance of trimethylenemethane by means of esr as an intermediate in the decomposition of 4-methylene-1-pyrazoline. Another author[8] has reported the iron carbonyl complex of trimethylenemethane.

(8) G. F. Emerson, K. Ehrlich, W. P. Giering, and P. C. Lauterbur, *ibid.*, **88**, 3172 (1966).

(9) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 69.

allyl radicals, the π-bond order of atom 2 must be four times the p_{12} of the allyl radical.[10] Thus N_2 for propargylene is found to be

$$N_2 = 2 + 4(\sqrt{2}/2) = 4.828 \qquad (2)$$

This value is considerably larger than the bond order of the central atom of trimethylenemethane.[10a] This observation prompted further exploration of this point to see what the trend would be in the higher homologs. The N_2 and $N_{(N+1)/2}$ were calculated[11] for the homologous series $C_{2n+1}H_2$, of which propargylene is the first member. The results of the calculation of the mobile bond order of the central atom and the second atom of this series are shown in Table I. It will be noted that the maximum bonding appears at the second atom of the chain and that it gradually drops off with increasing chain length. Bonding at the central carbon varies with values considerably less than trimethylenemethane with the exception of propargylene, in which case the central carbon and the second carbon atoms are identical.

Table I

Maximum Bond Order

$2n + 1$	Middle atom	Second atom
3	4.82842702	4.82842702
5	4.30940092	4.73205078
7	4.61312556	4.72077644
9	4.46124646	4.71802250
11	4.57580119	4.71708256
13	4.50359154	4.71669075
15	4.56291401	4.71650353
17	4.52056789	4.71640506
19	4.55697888	4.71634921
21	4.52914387	4.71631563
23	4.55376321	4.71629447

F_1 for II is 1.318 while F_2 for I is only 1.155. Both of these are greater than the 1.04 for the benzyl radical but less than the 1.73 for the methyl radical.[14] Caution should, however, be exercised since HMO theory does not recognize differences in multiplicity. Therefore the value of F_1 for II does not depend upon whether we consider a singlet or a triplet propargylene. Since singlet–triplet inversions are forbidden, the singlet and the triplet are two different species which should react differently with respect to "...neutral nonpolar reagents, such as free radicals...."[15] The calculations do not show any difference in the F_1 between singlets and triplets.

The F_2 for propargylene is greater by 0.096 bond order unit than for atom 1 of I. The literature accepts 4.732 as the maximum possible bond order. This was chosen so that all F_i would be positive. It should be noted from this definition that F_2 for II is -0.096. However, in order to avoid confusion in the future as to what value of $N_{\max}$ is being used, perhaps it might be best to accept 4.732 as a standard reference point. This would serve index of free valence much as TMS serves nmr. In both instances species exist on both sides of the reference.[16]

Registry No.—Trimethylenemethane, 10316-06-0; propargylene, 2008-19-7.

Acknowledgment.—The author wishes to thank Dr. W. M. Jones for the helpful suggestions and discussions which he has offered during the writing of this paper.

[10] C. A. Coulson and A. Streitwieser, "Dictionary of π-Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965, p 183.

[10a] Note Added in Proof.—After submission of our paper it was discovered that the same conclusions were reached by W. M. A. Smit and D. H. N. den Boer, *Theoret. Chim. Acta*, **6**, 358 (1966).

[11] N_r was calculated by computer[12] using the following equations:[13]

$$C_{ir} = \frac{\sqrt{2}}{n+1} \sin \frac{i\pi}{n+1} r$$

$$P_{rs} = \sum_j N_i C_{ir} C_{is}$$

where r and s are neighbors, and

$$N_r = \Sigma P_{rs}$$

over all neighbors s.

[12] We wish to express our thanks to the University of Florida Computing Center for the use of its computer.

[13] A. Streitwieser, Jr., ref 5d, pp 50, 55.

[14] J. D. Roberts, ref 5a, p 58.

[15] J. D. Roberts, ref 5a, p 57.

[16] A referee has suggested doing away with F_i completely and using instead N_r as a stability index. This would have the advantage of not having to worry about maxima.

1,2- and 1,4-Addition Products from the Reaction of Benzylmagnesium Chloride and *trans*-α-Phenylchalcone

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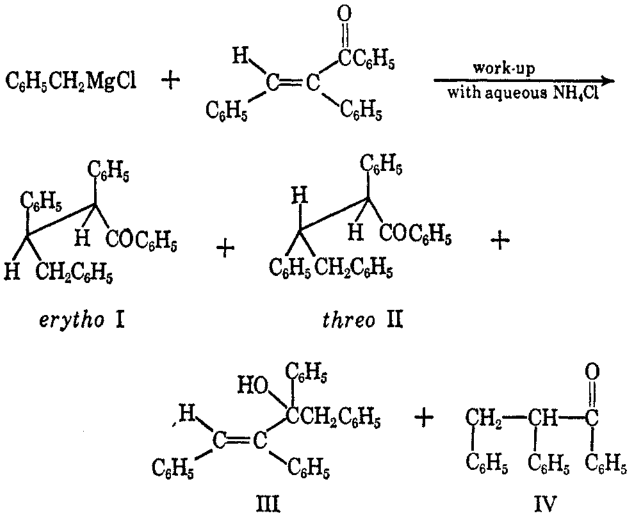
In the hope of photochemically synthesizing 1,2,3,4-tetraphenylcyclobutanol we have had occasion to synthesize the stereoisomers of 1,2,3,4-tetraphenylbutanone (Scheme I). Bergmann, Winter, and Schreiber[1] originally reported that the reaction of *trans*-α-phenylchalcone with benzylmagnesium chloride results in the formation of only one 1,4-addition diastereoisomer in 26% yield having a melting point of 178–179°. No 1,2-addition product was reported. When

Scheme I



[1] E. Bergmann, D. Winter, and W. Schreiber, *Ann.*, **500**, 122 (1933).