pyridine we observed that N-formylalanine (1) produced a yellow, crystalline product, mp 111–112° dec. This compound absorbed in the ultraviolet at 250 mμ (ε 14,000) and exhibited a band in the infrared at 5.65 rather than at 5.55 μ characteristic of the azlactone system. These data as well as the elemental analyses excluded from consideration the possibility of the simple azlactone 2 anticipated. That this substance was a coupled product arising from the anticipated azlactone (2) with N-acetylpyridinium ion became evident on neutral, aqueous hydrolysis. On warming with water the new substance was smoothly cleaved to N-formylalanine (1) isolated as such, together with pyridine identified as its picrate salt, mp 145–150° dec. These findings indicated that the substance at hand most probably had structure 3, the product of γ coupling of azlactone 2 with N-acetylpyridinium ion. The ultraviolet of the new compound, moreover, with λmax 250 mμ excluded a homoannular diene system that would have arisen from α coupling[3] or alternatively a bond rearrangement product of 3. Isolated disposition of the double bonds was further supported by the failure of the coupled product to undergo Diels–Alder addition with either maleic anhydride or N-phenylmaleimide.[3] The nmr spectrum in chloroform-d provided confirmation of 3 exhibiting the acylmethyl singlet at τ 7.8 and the 4-methyl, seen as a doublet centered at τ 7.75 owing to homoallylic coupling with the 2 proton. The vinyl proton pattern with bands at τ 2.73, 3.45, and 5.05 also closely paralleled that reported for 1,1′-diacetyl-1,1′,4,4′-tetrahydro-4,4′-bipyridyl.[4]

Final proof of the point of attachment of the azlactone moiety at the γ position of the pyridine ring was provided by hydrogenation of 3 to the tetrahydro system (4), mp 125–127°, followed by acid hydrolysis to piperidine-4-carboxylic acid (5). The formation of

Scheme I

2-[4-(1-acetyl-1,4-dihydropyridinyl)]-3-oxazolin-5-ones may be a general reaction for simple N-formylamino acids. Although with N-formylphenylalanine, N-formylglycine, and N-formyltryptophane, noncrystalline

products are produced which are correspondingly unstable, nonetheless spectroscopically they conform in large measure to the characteristics determined in the case of 3.

Experimental Section

2-[4-(1-Acetyl-1,4-dihydropyridinyl)]-3-oxazolin-5-one (3).—A 5-g sample of N-formylalanine was dissolved in 20 cc of pyridine, treated with an equal volume of acetic anhydride, and allowed to stand for 24 hr at room temperature. At the end of this period the solvents were evaporated *in vacuo* and the residue was crystallized from acetone–ether to give 3 as yellow needles: mp 110–112°, wt 1.6 g, λmax^CH3OH 250 mμ (ε 14,000); λmax^CHCl3 5.65 μ.

Anal. Calcd for C11H12N2O3: C, 59.95; H, 5.49; N, 12.71. Found: C, 60.10; H, 5.48; N, 12.67.

An additional 0.60 g of 3 was obtained from the mother liquors of crystallization by chromatography on silica gel. Elution was effected with ethyl acetate.

2-[4-(1-Acetylpiperidyl)]-3-oxazolin-5-one (4).—A solution of 500 mg of 3 in 25 cc of ethyl acetate was slurried with 150 mg of 5% rhodium-on-alumina catalyst and filtered. The filtrate was subsequently treated with 250 mg of the same catalyst and hydrogenated. The hydrogen uptake was 2 mole equiv. The reaction mixture was filtered, concentrated, and crystallized from acetone–ether to give 340 mg of 4: ultraviolet showed no maximum; λmax^CHCl3 5.65 μ.

Anal. Calcd for C11H16N2O3: C, 58.90; H, 7.18; N, 12.47. Found: C, 59.18; H, 7.13; N, 12.86.

Hydrolysis of 4 to Piperidine-4-carboxylic Acid 5.—A 100-mg sample of the hydrogenation product (4) in 3 cc of water was treated with potassium bicarbonate until a pH of 8–9 was maintained. The reaction mixture was warmed briefly on the steam bath and then allowed to stand at room temperature for 30 min. At the end of this time the reaction mixture was concentrated to dryness *in vacuo* followed by treatment with 5 cc of 50% aqueous hydrochloric acid and refluxing for 1 hr. The hydrolysate was diluted with water and extracted with chloroform followed by ether. The aqueous layer was evaporated *in vacuo* and the residue was extracted with hot alcohol. The alcohol extract was concentrated to a gum which was redissolved in isopropyl alcohol. Addition of acetone to the isopropyl alcohol solution deposited solid material that was separated and recrystallized to give alanine hydrochloride. The isopropyl alcohol filtrate was concentrated to yield 10–15 mg of piperidine-4-carboxylic acid hydrochloride, mp 255–265° dec. The infrared of this material was identical with that of an authentic specimen.
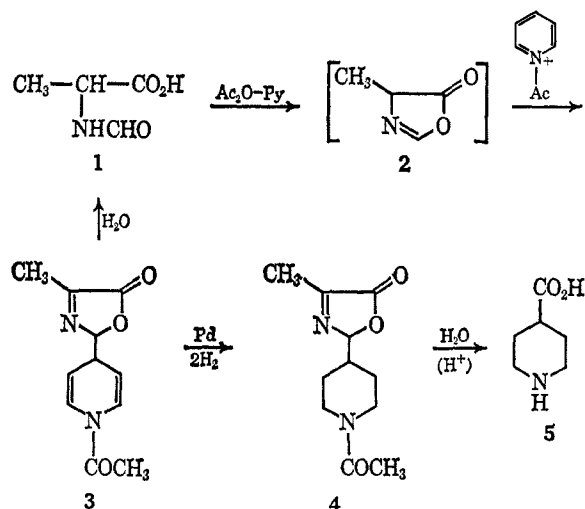
The Acylation of Cyclooctene and 1,5-Cyclooctadiene

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The stannic chloride catalyzed reaction of cyclooctene with acetyl chloride was found by Ruzicka to yield 1-acetylcyclooctene as the major product.[1] Later Jones, Taylor, and Rudd reported that addition of cyclooctene to the aluminum chloride–acetyl chloride complex in methylene chloride at −15° gave 1-acetylcyclooctene in 48% yield.[2] Nenitzescu and co-workers have reported that acetylation of cyclooctene in iso-

(3) M. Saunders and E. Gold, *J. Org. Chem.*, **27**, 1439 (1962).
(4) A. T. Nielsen, D. W. Moore, G. M. Muha, and K. H. Berry, *ibid.*, **29**, 2175 (1964).

(1) L. Ruzicka and H. A. Boekenhoogen, *Helv. Chim. Acta*, **14**, 1319 (1931).
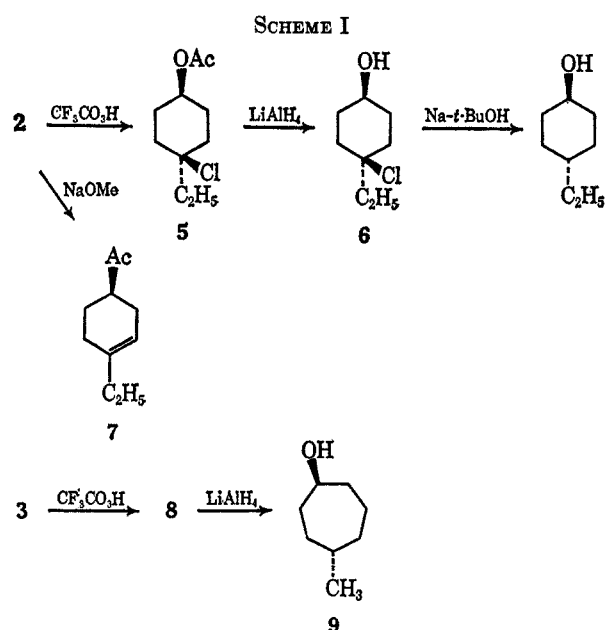(2) N. Jones, H. T. Taylor, and E. Rudd, *J. Chem. Soc.*, 1342 (1961).

pentane, using an aluminum chloride catalyst, yields dimethylacetylcyclohexenes.[3]

We have recently investigated the acetylation of cyclooctene and 1,5-cyclooctadiene. We find, in agreement with Ruzicka, that cyclooctene, when treated with acetyl chloride in the presence of stannic chloride, gives 1-acetylcyclooctene as the major product. Use of aluminum chloride in methylene chloride, as described by Rudd, *et al.*, gave no 1-acetylcyclooctene, but instead a mixture of 1-acetyl-4-chloro-4-ethylcyclohexane (**2**, 45–53%), semicarbazone mp 188°, and *trans*-1-acetyl-4-methylcycloheptane (**3**, 12–14%), semicarbazone mp 140°, and small amounts of an acetylchlorocyclooctane (**4**, 3–5%) (eq 1).

(1)
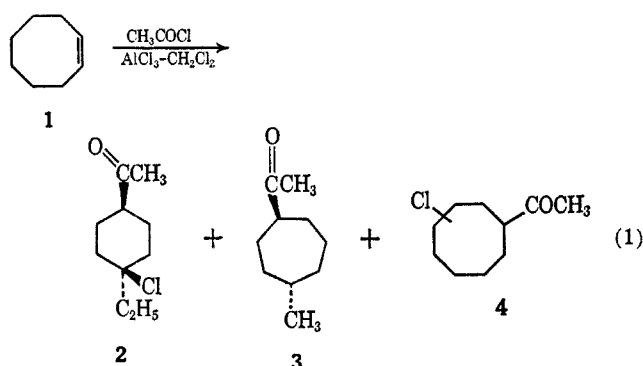
Baeyer–Villiger oxidation of **2** gave the acetate **5** which was cleaved to the chloro alcohol **6** by lithium aluminum hydride. Reductive dechlorination with sodium–*t*-butanol gave *trans*-4-ethylcyclohexanol, identical with an authentic sample.[4] Dehydrochlorination of **2** (Scheme I) with methanolic sodium methoxide gave an acetylethylcyclohexene (**7**) whose nuclear magnetic resonance (nmr) spectrum showed the presence of *one* vinyl hydrogen. This information, together with the observation that the carbonyl group of **7** is not conjugated with the double bond, indicates that **7** is 1-ethyl-4-acetylcyclohexene and that the chlorine in **2** must be either at C-3 or C-4. If the chlorine were located at C-3, the nmr spectrum of **2** should exhibit a signal due to the hydrogen on C-3 downfield from the rest of the signals. The absence of any absorption below τ 7.5 indicates that the chlorine is instead at C-4 and that **2** possesses the structure shown.

Baeyer–Villiger oxidation of **3**, followed by cleavage with lithium aluminum hydride, gave *trans*-4-methylcycloheptanol, identical with a sample prepared by reduction of 4-methylcycloheptanone with lithium aluminum hydride. The assignment of the *trans* stereochemistry to **9** was made on the basis of the observation that **9** was the predominant epimer formed in the reduction of 4-methylcycloheptanone with both lithium aluminum hydride and aluminum isopropoxide-isopropyl alcohol. It has been shown that the thermodynamically more stable *trans* alcohols are the major products of the reduction of 2-methylcyclohexanone and 4-methylcyclohexanone by both reagents,[5a] as well

(3) C. D. Nenitzescu, in "Friedel–Crafts and Related Reactions," G. A. Olah, Ed., Vol. III, Part 2, Interscience Publishers, Inc., New York, N. Y., 1964, p 1125. See also, C. D. Nenitzescu, *et al.*, *Acad. Rep. Populare Romine, Studii Cercetari Chim.*, **6**, 375 (1958); *Chem. Abstr.*, **53**, 18885g (1959).

(4) S. Winstein and A. H. Lewin, *J. Am. Chem. Soc.*, **84**, 2464 (1962). We are indebted to Dr. Winstein for furnishing a sample of this alcohol.

(5) (a) D. S. Noyce and D. B. Denney, *ibid.*, **72**, 5743 (1950). (b) W. Huckel and J. Wachter, *Ann.*, **672**, 62 (1963).

Scheme I

as in the reduction of 2-methylcycloheptanone by lithium aluminum hydride.[5b] By analogy with the above cases, we assign the *trans* configuration to **9**.

The chloroacetylcyclooctane (**4**) was identified as such by the absence of C-methyl signals in its nmr spectrum, and by its dehydrohalogenation by potassium *t*-butoxide to an acetylcyclooctene. The latter compound has a nonconjugated carbonyl group, suggesting that **4** is 3-, 5-, or 5-chloro-1-acetylcyclooctane. We favor the 4-chloro structure on the basis of mechanistic considerations (*vide infra*).

The formation of **2**, **3**, and **4** may be envisaged as proceeding *via* several carbonium ion processes, as shown in Scheme II. The 2-acetylcyclooctyl cation

Scheme II
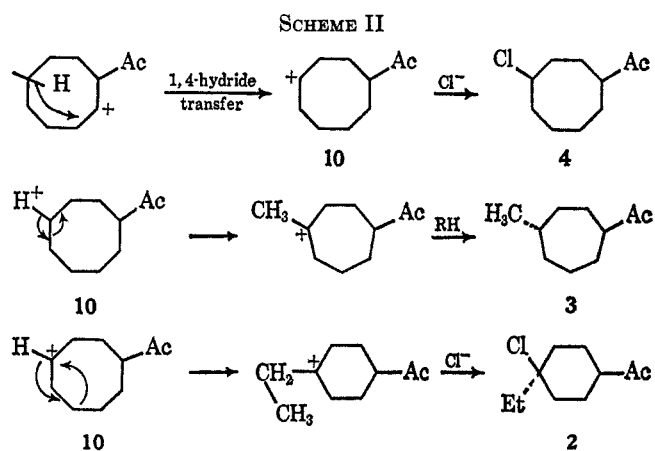
undergoes 1,5-hydride transfer, a well-documented process,[6] to give 4-acetylcyclooctyl cation. Rearrangement to the tertiary ion, with a 1,2-hydride ion shift, followed by hydride transfer from the solvent would give **3**. A similar route has been proposed recently by Rand and Dolinski to explain the formation of 2-methyl-1-acetylcyclohexene and 2-methyl-3-acetylcyclohexene in the reaction of cycloheptene with acetic acid in polyphosphoric acid.[7] A similar rearrangement in-

(6) V. Prelog and J. G. Traynham, in "Molecular Rearrangements," P. De Mayo, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 9.

(7) L. Rand and R. J. Dolinski, *J. Org. Chem.*, **31**, 3063 (1966).

volving a 1,3-hydride ion shift, or alternatively, two 1,2 shifts, could give 4-acetyl-1-ethylcyclohexyl cation, leading to 2 by combination with chloride ion. The possibility that ring contraction occurs by rearrangement of cyclooctene before reaction with acetyl chloride was eliminated by the observation that, when only 0.5 equiv of acetyl chloride was used, the recovered C_8 hydrocarbon fraction was over 98% cyclooctene. No methylcycloheptene or ethylcyclohexenes were found. The intermediate 4-acetylcyclooctyl cation (10) could be chlorinated to give 4-acetylchlorocyclooctane; other isomers of the acetylcyclooctyl cation could be produced by successive 1,2-hydride ion shifts, but this possibility seems less likely.

The aluminum chloride catalyzed reaction of 1,5-cyclooctadiene with acetyl chloride in methylene chloride at −20° gave exo-2-acetyl-6-chloro-cis-bicyclo-[3.3.0]octane (11, 48%) (eq 2). Reductive removal of

$$\bigcirc + CH_3COCl \xrightarrow[CH_2Cl_2]{AlCl_3} \text{(structure)} \quad (2)$$
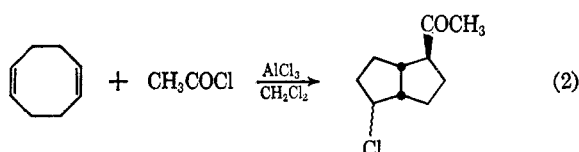
the chlorine atom with sodium and t-butyl alcohol caused partial reduction of the carbonyl group. Oxidation of the dechlorinated material with Jones reagent gave exo-2-acetylbicyclo[3.3.0]octane, identical with an authentic sample.[8] Although the formation of bicyclo[3.3.0]octanes in free-radical reactions of 1,5-cyclooctadiene is well established,[8] the only reported reaction of this diene which probably involves carbonium ions is the addition of sulfur dichloride which also proceeds via 1,5 bridging.[9]

Experimental Section

Reaction of Cyclooctene with Acetyl Chloride.—Cyclooctene (110 g, 1 mole) was added dropwise to a stirred solution of aluminum chloride (150 g, 1.05 moles) and acetyl chloride (78 g, 1 mole) in methylene chloride (1200 ml) at −15 to −20°. After completion of the addition, which required 2 hr, the solution was stirred warming to 0° and then poured into crushed ice. The methylene chloride layer was washed five times with water, dried (MgSO₄), and concentrated under reduced pressure. The residue was distilled without fractionation to give a pale yellow oil, bp 68–125° (0.5 mm) (116 g). Distillation on a spinning-band column gave the following fractions. Fraction I, 1-acetyl-4-methylcycloheptane (3) [bp 34–36° (0.03 mm), $n^{25}D$ 1.4328], was obtained as a colorless oil (17.0 g, 11%). Conversion of 3 to the semicarbazone was accomplished using a standard procedure;[10] the derivative was obtained after recrystallization from aqueous ethanol as white needles, mp 138–140° dec.

Anal. Calcd for $C_{11}H_{21}N_3O$: C, 62.56; H, 9.95. Found: C, 62.31; H, 9.93.

Fraction 2 [bp 37–53° (0.04 mm), 2.1 g] was a mixture of 2 and 3.

Fraction 3 [bp 54–55° (0.04 mm), 68 g, 36%] consisted of almost pure 1-acetyl-4-chloro-4-ethylcyclohexane (2), a yellow oil which darkened on standing. For analysis III was converted to the semicarbazone by the usual procedure. There was thus obtained colorless leaflets, mp 188° dec.

Anal. Calcd for $C_{11}H_{20}ClN_3O$: C, 53.83; H, 8.14. Found: C, 54.11; H, 8.14.

The nmr spectrum of 2 consisted of a three-hydrogen triplet at τ 9.06 (methyl on 4-ethyl), a three-hydrogen singlet at τ 7.98, and complex absorption at τ 7.5–8.6.

Fraction 4 [bp 86–95° (0.04 mm), 7.5 g, 4%] appeared to consist of isomeric monochloroacetylcyclooctanes; the 2-chloro structure is eliminated by the observation that the product of dehydrochlorination shows an infrared band at 1710 cm⁻¹, characteristic of nonconjugated carbonyl groups. The nmr spectrum showed no C-methyl signals; a one-hydrogen multiplet attributable to the hydrogen on the chlorine-bearing carbon was present at τ 6.67. Attempts at purification by vapor phase chromatography (vpc) and fractional distillation proved fruitless and this fraction was not investigated further.

Baeyer–Villiger Oxidation of 3.—A solution of pertrifluoroacetic acid (prepared from 0.11 mole of trifluoroacetic anhydride and 0.11 mole of 90% hydrogen peroxide) in methylene chloride (200 ml) was added to a vigorously stirred slurry of ketone 3 (15.2 g, 0.1 mole) and disodium phosphate (80 g) in methylene chloride (200 ml). The solution was stirred and refluxed for 1 hr more and then filtered. The solid was washed twice with methylene chloride and the combined methylene chloride solutions were washed three times with water and dried. Evaporation of solvent followed by distillation gave 1-acetoxy-4-methylcycloheptane (8), bp 54–58° (0.2 mm) (12.3 g, 71%).

A solution of 12 g of the acetate 3 in 15 ml of ether was added to a slurry of 2.0 g of lithium aluminum hydride on 50 ml of ether and the reaction mixture was stirred for 0.5 hr at room temperature. The excess hydride was destroyed by adding ethanol and the solution was poured onto cold aqueous ammonium chloride. The ether layer was washed twice with water and dried (MgSO₄). Removal of the ether under reduced pressure gave an oil which was distilled to give trans-4-methylcycloheptanol (9), bp 40–42° (0.2 mm).

The phenylurethan, prepared in the usual manner, was obtained after crystallization from hexane as white needles, mp 68–69°.

Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.90; H, 8.91. Found: C, 72.74; H, 8.97.

Reduction of 4-methylcycloheptanone with lithium aluminum hydride gave a mixture of alcohols which was shown by vpc on a Carbowax column to consist essentially of two components in the ratio 65:35. Meerwein–Ponndorf–Verley reduction gave the same two components in a 61:39 ratio. The major isomer was identical in every respect with the alcohol obtained by degradation of 3. It has been reported[5a] that reduction of 2- and 4-methylcyclohexanone by these two methods gives predominantly the more stable trans-alkylcyclohexanols, and that reduction of 2-methylcycloheptanone gives mainly trans-2-methylcycloheptanol. Since the relative stabilities of 1,4-disubstituted cycloheptanes should parallel those of the cyclohexanes, we assign the configuration of trans by analogy.

Baeyer–Villiger Oxidation of 2.—A solution of peroxytrifluoroacetic acid (prepared from 4.2 g of 90% hydrogen peroxide and 31 g of trifluoroacetic anhydride) in 300 ml of methylene chloride was slowly added to a stirred suspension of 22 g (12 moles) of 2 and 120 g of disodium phosphate in methylene chloride (300 ml). The reaction mixture was worked up as described in the oxidation of 3, above, to give 16.8 g (68%) of the chloroacetate 5, bp 71–73° (0.4 mm).

The chloroacetate was reduced with lithium aluminum hydride in the manner described for reduction of 8 to give the chloro alcohol 6 in 60% yield, bp 59–63° (0.3 mm).

Dechlorination of 6.—Sodium (8 g, 0.33 g-atom) was added in small pieces to a stirred, refluxing, solution of 6 (4.0 g, 0.25 mole) and t-butyl alcohol (75 ml) in tetrahydrofuran (300 ml). The solution was stirred and refluxed until all the sodium had dissolved (18 hr). The bulk of the solvent was removed under reduced pressure and the residue was poured into an ice–water slush. Extraction of the resulting suspension with ether, washing with water, drying, and evaporation, followed by vacuum distillation of the residue, gave trans-4-ethylcyclohexanol, a colorless oil, bp 51–53° (0.3 mm). The infrared spectrum was superimposable on that of an authentic sample. The phenylurethan, prepared in the usual manner, crystallized from hexane as white needles, mp 111–112°, undepressed on admixture with the phenylurethan of authentic trans-4-ethylcyclohexanol.

Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.90; H, 8.91. Found: C, 73.16; H, 9.07.

(8) (a) We are grateful to Dr. R. Dowbenko for providing a sample of this material. (b) R. Dowbenko, *Tetrahedron*, **20**, 1843 (1964).

(9) (a) E. J. Corey and E. Block, *J. Org. Chem.*, **31**, 1663 (1966). (b) E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, 1669.

(10) R. Shriner, R. Fuson, and D. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 253.

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]

$$F_i = N_{max} - N_r \tag{1}$$

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

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

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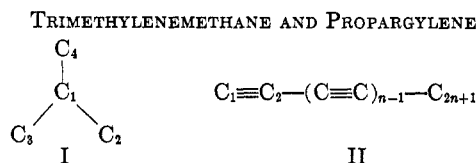
The fallacy of this conclusion came to our attention while preforming "back of the envelope" type of calculations on the Hückel MO parameters of propargylene (II, $n = 1$).[9] Since this is simply two orthogonal

(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.