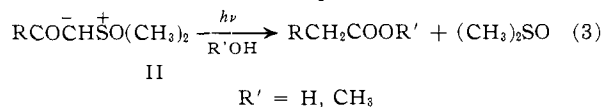
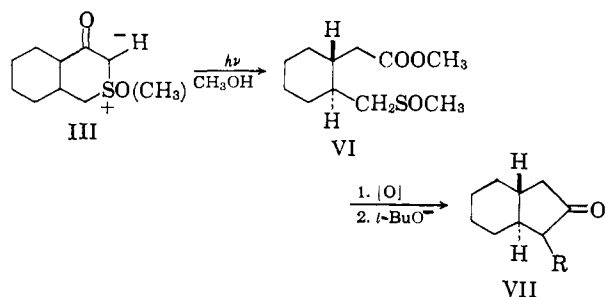


One of the most interesting properties of β -ketosulfoxonium ylides is their susceptibility to photochemical fission of the dipolar S-C bond by ultraviolet irradiation. The ylides II, R = C₆H₅ or cyclo-C₆H₁₁, upon excitation with 253 m μ radiation (low-pressure mercury arc) are transformed smoothly according to eq. 3, presumably *via* keto carbene and ketene intermediates. The combination of (1) and (3) is a process of chain extension



which is analogous to the Arndt-Eistert sequence.

Cyclic β -ketosulfoxonium ylides decompose by a pathway which parallels (3). Irradiation of the cyclic ylide III in methanol at 253 m μ produces the sulfoxide ester VI, infrared maximum 5.74, 9.5 μ , in 80% yield; in water the corresponding carboxylic acid is formed. This reaction opens a new route to carbocycles: oxidation of VI with peracetic acid affords the corresponding sulfone which undergoes cyclization with potassium *t*-butoxide to give the keto sulfone VII, R = SO₂CH₃, and this in turn is converted by treatment with aluminum amalgam⁴ to *trans*-hydrindan-2-one (VII, R = H, 60% over-all yield from III), shown to be the pure



trans isomer by vapor phase chromatography and conversion to known solid derivatives.⁵ The stereospecific formation of *trans*-hydrindan-2-one is of special interest. Preliminary studies indicate that the reaction of I with ethyl esters of Δ^1 -cycloalkenyl carboxylic acids produces *trans*-fused cyclic ylides in preference to the *cis* isomers.

Starting from ethyl cinnamate and I, 3-phenylcyclopentanone⁶ was synthesized *via* the cyclic β -ketosulfoxonium ylide⁷ by a sequence corresponding to III \rightarrow VII in 30% over-all yield.

This new carbocycle synthesis can in some cases be modified to permit the synthesis of *cis*-fused ring systems. For example, the ylide II, R = Δ^1 -cyclopentyl, undergoes cyclization upon heating in methanol at reflux (15 hr.) to give a cyclic product (55%) analogous to III but largely *cis*-fused since it is converted to *cis*-pentalan-2-one by a sequence of the type III \rightarrow VII.

The parent member of the new class of cyclic β -ketosulfoxonium ylides VIII has also been prepared

(4) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **86**, 1639 (1964).

(5) W. Hüchel and H. Friedrich, *Ann.*, **461**, 132 (1926).

(6) W. Borsche and W. Menz, *Chem. Ber.*, **41**, 190 (1908).

(7) E. J. Corey and M. Chaykovsky, *Tetrahedron Letters*, **No. 4**, 169 (1963).

from I and ethyl acrylate; m.p. 181–185° dec., ultraviolet maximum 241 m μ (ϵ 15,800).

The transformations described above are easily carried out and are of practical value in synthesis. The photochemical reactions are especially interesting, and these are being studied further.

(8) National Institutes of Health Postdoctoral Fellow 1962–1964.

DEPARTMENT OF CHEMISTRY

HARVARD UNIVERSITY

CAMBRIDGE 38, MASSACHUSETTS

E. J. COREY

MICHAEL CHAYKOVSKY*

RECEIVED FEBRUARY 4, 1964

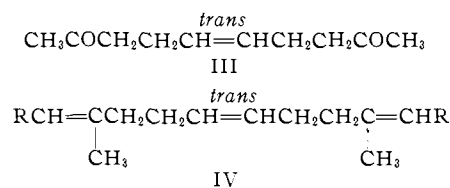
A New Synthetic Approach to Medium-Size Carbocyclic Systems

Sir:

In the first stage of an investigation directed at the total synthesis of the naturally occurring substance humulene (I), a study has been made of the reaction of a doubly allylic α,ω -dihalide with nickel carbonyl as a model cyclization process. This communication describes the results of these experiments¹ and the successful synthesis of 1,6-dimethylcyclododeca-1,5,9-triene (II); the new knowledge which has been obtained suggests simple synthetic routes to humulene and related structures and thus provides a key to these hitherto unsolved problems.



Dec-5-ene-2,9-dione (III)² was synthesized by alkylation of ethyl β -dimethylaminocrotonate with *trans*-



1,4-dibromo-2-butene³ followed by hydrolysis and decarboxylation; m.p. 41–42°, infrared maximum 5.81 μ , n.m.r. peaks at 5.20 δ (2 olefinic H) and 1.98 δ (2 CH₃CO).⁴ The diketone III was converted to diethyl 3,10-dimethyldodeca-2,6,10-triene-1,12-dioate (IV, R = COOC₂H₅) by the procedure of Wadsworth and Emmons,⁵ and this was reduced by lithium aluminum hydride to 1,12-dihydroxy-3,10-dimethyldodeca-2,6,10-triene (IV, R = CH₂OH). The n.m.r. spectrum of the diol IV, R = CH₂OH, so obtained indicated it to be a mixture of 80% all-*trans* isomer and 20% *cis*, *trans*, *trans* isomer⁶; as expected the Wittig process leading to

(1) This approach to cyclization seemed worthy of study because of the known coupling of simple allylic halides by nickel carbonyl to give 1,5-dienes [I. D. Webb and G. T. Borchardt, *J. Am. Chem. Soc.*, **73**, 2654 (1951)] and the catalytic action of low-valent nickel compounds in the trimerization of 1,3-butadiene to 1,5,9-cyclododecatrienes [G. Wilke, *Angew. Chem.*, **75**, 10 (1963)]. More recently the coupling of allylic acetates has been reported [N. L. Bauld, *Tetrahedron Letters*, **No. 19**, 859 (1962)].

(2) Satisfactory analytical and spectroscopic data were obtained for all new compounds reported.

(3) See (a) S. A. Glickman and A. C. Cope, *J. Am. Chem. Soc.*, **67**, 1017 (1945); (b) G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3052 (1953).

(4) N.m.r. chemical shifts expressed as p.p.m. downfield displacement from tetramethylsilane as internal standard and measured at 60 Mc.

(5) W. S. Wadsworth and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

(6) See R. B. Bates and D. M. Gale, *ibid.*, **82**, 5749 (1960), for the n.m.r. methodology.

IV, R = COOC₂H₅, was not stereospecific. The all-*trans* isomer of the diol IV, R = CH₂OH, was obtained in pure condition (as a colorless oil) *via* the crystalline 3,5-dinitrobenzoate derivative, m.p. 136–137°. The pure diol IV, R = CH₂OH, and the 4:1 mixture of stereoisomeric diols were transformed into 1,12-dibromo-3,10-dimethyldodeca-2,6,10-triene (IV, R = CH₂Br) by reaction with phosphorus tribromide and pyridine in ethereal solution at –15°; the two products had essentially identical infrared and n.m.r. spectra. Slow addition of the dibromide IV, R = CH₂Br, to a stirred solution of nickel carbonyl (excess) in 1,2-dimethoxyethane at 78° followed by continued heating for 12 hr., removal of solvent under reduced pressure, partitioning between ether and water, and distillation of the product from the organic layer at 100° bath temperature (6 mm.) gave 63–68% yield of II as a colorless oil, appearing homogeneous in vapor phase chromatography using fluorosilicone, tris(β-cyanoethoxy)propane, and diethylene glycol succinate columns. The product showed a parent peak in the mass spectrum at *m/e* = 190 and absorbed 3.16 molar equivalents of hydrogen based on molecular weight 190 using prerduced platinum oxide catalyst in acetic acid. Ozonolysis⁷ of the triene followed by reduction of the total mixture with sodium borohydride and acetylation gave a liquid product which was shown by v.p.c. and spectral analysis to be a 16:7.5 mixture of pentane-1,4-diol diacetate and butane-1,4-diol diacetate (91% of the theoretical yield). These facts clearly establish that the product from the reaction of dibromide IV, R = CH₂Br, with nickel carbonyl must be 1,6-dimethylcyclododeca-1,5,9-triene.

Analysis of the triene so produced by thin layer chromatography (on silica gel–silver nitrate) and n.m.r. analysis indicated that the material was, in fact, a mixture of two isomers in a ratio of *ca.* 2:1. The same mixture was obtained starting from the pure all-*trans* diol IV, R = CH₂OH, or the 4:1 mixture described above. Although it is clear that one or both of the last two steps in the synthesis of the cyclic triene may be nonstereospecific, we are inclined to believe that most of the isomerization occurs at the last stage. Further work is in progress on this point. The major isomer, which can be separated from the mixture by column chromatography using 10% silver nitrate on silica gel, is probably the all-*trans* structure II; the n.m.r. spectrum shows two sharp methyl peaks (6H) at 1.39 and 1.42 δ,⁸ a peak at 1.9 δ (12H), and broad olefinic proton absorption at 4.3–4.9 δ (4H). The minor isomer, presumably the *cis*, *trans*, *trans* form of II, shows methyl absorption at 1.58 p.p.m., closer to a normal value for C=C–CH₃.

Further work on the reactions of nickel carbonyl with dihalides and related substances is in progress with the object of investigating the scope and mechanism of this process and applying the ring closure to the synthesis of natural products.⁹

(7) Procedure of A. J. Hubert, *J. Chem. Soc.*, 4055 (1963).

(8) See ref. 6 and also E. J. Corey and A. G. Hortmann, *J. Am. Chem. Soc.*, 85, 4033 (1963), for analogous cases.

(9) This work was partially supported by the National Science Foundation (Grant GP-1955).

(10) Elmer Peter Kohler Fellow, Harvard University, 1963–1964.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE 38, MASSACHUSETTS

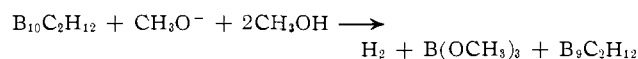
E. J. COREY
ERNEST HAMANAKA¹⁰

RECEIVED FEBRUARY 4, 1964

Dicarbaundecaborane(13) and Derivatives

Sir:

Carborane [1,2-dicarbaundecaborane(12)] and its derivatives, prepared from the reaction of B₁₀H₁₂-(ligand)₂ compounds and acetylenes,^{1,2} have been selectively degraded by methanolic potassium hydroxide at 40°. The degradation reaction is described by the equation



One mole each of hydrogen and boric ester were produced and 1 equiv. of base was consumed per mole of carborane employed. The B₉C₂H₁₂ anion was precipitated as its tetramethylammonium salt I (98% yield) upon the addition of aqueous tetramethylammonium chloride. *Anal.* Calcd. for B₉C₂H₂₄N: B, 46.90; C, 34.70; H, 11.65; N, 6.74. Found: B, 46.90; C, 35.61; H, 12.30; N, 6.60. The corresponding salts were prepared from C-methyl- and C-phenylcarboranes. The infrared spectra of the B₉C₂H₁₂ anion exhibited a sharp C–H stretching band at 3.35 μ and B–H stretching centered at 4.0 μ. No absorptions which could be attributed to B–H–B bridge stretching were observed.

Acidification of a diethyl ether slurry of I with anhydrous hydrogen chloride followed by sublimation (40°) of the product retained in the ethereal solvent produced dicarbaundecaborane(13) (II) in 89% yield. Elemental analysis of B₉C₂H₁₃ was thwarted by its low stability and hydroscopic nature, m.p. 110° dec. However, II was titrated as a monoprotic acid (equiv. wt. 137; theory 134) with an apparent pK_A of 2.95 in 33% (volume) methanol–water. A cryoscopic molecular weight of 147 was observed in benzene solution. The infrared spectrum of II displayed a C–H stretching band at 3.30 μ and a B–H stretching band at 3.85 μ. A weak absorption at 5.10 μ could be reasonably attributed to a B–H–B bridge absorption although the H¹ n.m.r. spectrum of II did not reveal clean evidence for such an interaction.

The degradation reaction was examined kinetically with hydroxide ion in 50% volume aqueous ethanol at 75° and with C-phenylcarborane as the substrate. Hydrogen evolution was employed to monitor the reaction. The reaction was first order in both hydroxide ion and C-phenylcarborane with a second-order rate constant of 1.48 ± 0.03 × 10⁻⁴ l. mole⁻¹ sec.⁻¹. The similar reaction of C-phenylcarborane labeled in the 8, 9, 10, and 12 positions² with deuterium produced an identical rate constant and 97% pure hydrogen was evolved. These results clearly indicate that the 8, 9, 10,

(1) C. C. Clark, U. S. Patent 3,062,756 (Nov. 6, 1962); T. L. Heying, J. W. Ager, Jr., S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, 2, 1089 (1963); H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, 2, 1092 (1963); T. L. Heying, J. W. Ager, Jr., S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, 2, 1097 (1963); S. Papetti and T. L. Heying, *ibid.*, 2, 1105 (1963); R. P. Alexander and H. Schroeder, *ibid.*, 2, 1107 (1963); M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, 2, 1111 (1963); M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *ibid.*, 2, 1115 (1963); D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, 2, 1120 (1963); D. Grafstein, J. Bobinski, J. Dvorak, J. E. Paustian, H. F. Smith, S. Karlan, C. Vogel, and M. M. Fein, *ibid.*, 2, 1125 (1963); D. Grafstein and J. Dvorak, *ibid.*, 2, 1128 (1963).

(2) Carborane(12) is reasonably assumed to have an icosahedral structure with two near-neighbor carbon atoms placed at positions 1 and 2. The numbering system employed was adopted by the Nomenclature Committee of the Inorganic Division of the American Chemical Society. See R. Adams, *Inorg. Chem.*, 2, 1087 (1963).