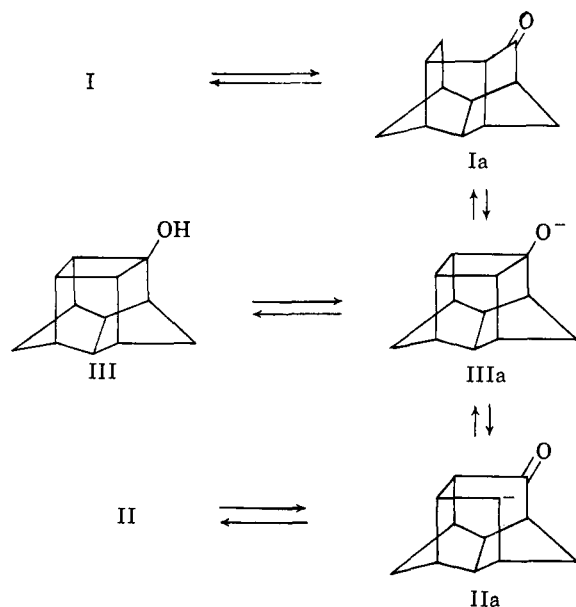


The observed product ratio favoring II can be rationalized, at least qualitatively, in terms of less steric hindrance about the carbonyl groups with respect to solvation, fewer nonbonded hydrogen repulsions, and less ring strain. The steric hindrance about the carbonyl group in I is dramatically demonstrated by its lack of reactivity<sup>6</sup> toward hydroxylamine. In contrast, under normal conditions the ketone II is easily converted to the corresponding oxime,<sup>3</sup> 90% yield, m.p. 135–136°;  $\nu_{\text{Nujol}}$  3226, 3125, and 1667  $\text{cm}^{-1}$ . The n.m.r. spectrum shows a typical C-8 *endo*-proton doublet centered at  $\tau$  8.72,  $J_1 = \sim 13$  c.p.s. and  $J_2 = \sim 4$  c.p.s., and a broad peak at  $\tau$  6.74 (–O–H).

We visualize the isomerization reaction as a transannularly assisted abstraction of a hydrogen atom from C-5 to form the carbanion Ia. Because of the proximity, the anion adds to the carbonyl group to form the bird-cage alkoxide anion IIIa, a *transannular enolate anion*, which is thermally unstable at the reaction temperature with respect to the less strained species Ia and IIa. Protonation of the anions then provides the thermodynamically controlled mixture of the ketones I and II. No alcohol III could be found in the reaction products.



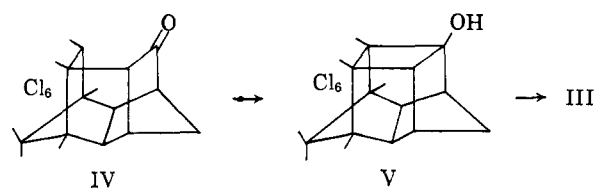
In order to test the intermediacy of the *transannular enolate anion* (IIIa), the bird-cage alcohol III,<sup>3</sup> m.p. 207–208°, was prepared (72% yield) by dechlorination of the hexachloro bird-cage alcohol V<sup>7</sup> with lithium and *t*-butyl alcohol in boiling tetrahydrofuran.<sup>2a</sup> The hexachloro alcohol V was in turn prepared in quantitative yield simply by heating the hexachloro half-cage ketone IV<sup>7</sup> in pyridine.<sup>8</sup>

Treatment of III with potassium *t*-butoxide in *t*-butyl alcohol at 250° readily gave the same mixture of the ketones I and II (*ca.* 4:96). An alternative thermal pathway for the observed isomerization reactions is

(6) For example, no oxime was formed at 10,000 atm., 75°, under which conditions di-*t*-butyl ketone reacted to give the corresponding oxime in 96% yield: W. H. Jones, E. W. Tristram, and W. F. Benning, *J. Am. Chem. Soc.*, **81**, 2151 (1959).

(7) S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *ibid.*, **82**, 5377 (1960).

(8) This reaction was reported in the T. W. Richard Medal Award Lecture by S. Winstein at the Massachusetts Institute of Technology, May 10, 1962.



rejected since, under identical conditions in the absence of base, the ketones I and II and the alcohol III are cleanly recovered.

This reaction thus represents the first example of a transannular keto–enol isomerization involving abstraction of a  $\gamma$ -hydrogen atom<sup>9</sup> by base to give a cyclic *transannular enolate anion*, ketonization of which leads to carbonyl products.<sup>10</sup>

(9) A homoenolization process involving abstraction of a  $\beta$ -hydrogen atom was recently reported: A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962).

(10) The same isomerization reaction has been found independently by R. Howe and S. Winstein, *ibid.*, **87**, 915 (1965).

Tadamichi Fukunaga

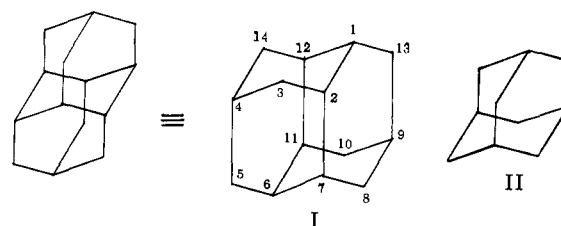
Contribution No. 1027, Central Research Department  
Experimental Station, E. I. du Pont de Nemours and Company  
Wilmington, Delaware

Received November 30, 1964

## Congressane

Sir:

The XIXth International Congress of Pure and Applied Chemistry, held in London on July 10–17, 1963, featured representations of the polycyclic hydrocarbon I as a decoration on the covers of abstracts, programs, and literature.<sup>1</sup> The *Handbook* of the Congress contained the following explanatory foreword: "The Congress Emblem (I) represents a beautifully symmetrical molecule which has not, so far, been described in the literature (*cf.* Prelog<sup>2</sup>). If adamantane (II) be regarded as an "adamantologue" of cyclohexane, then the Congress Emblem is an adamantologue of adamantane. The hypothetical process of adamantolugous expansion would provide a family of compounds all of which contain part of the diamond lattice. Indeed, diamond is an infinite adamantologue of cyclohexane. The synthesis of the Congress Emblem, the correct name of which (kindly supplied by Dr. L. C. Cross) is pentacyclo[7.3.1.1<sup>4,12</sup>.0<sup>2,7</sup>.0<sup>6,11</sup>]tetradecane, is suggested as a challenging objective for the participants in the Congress."



We wish to report the synthesis of "congressane"<sup>3</sup> (I). The method chosen was analogous to the isomeri-

(1) See also endpaper, D. J. Cram and G. S. Hammond, "Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., New York, N. Y., 1964.

(2) V. Prelog, *Bull. soc. chim. France*, 1433 (1960). (However, see cyclitol diborate, A. Weissbach, *J. Org. Chem.*, **23**, 327 (1958)).

(3) V. Prelog, *Pure Appl. Chem.*, **6**, 545 (1963); G. M. Blackburn, D. W. Cameron, A. R. Katritzky, and R. H. Prince, *Chem. Ind. (London)*, 1349 (1963).

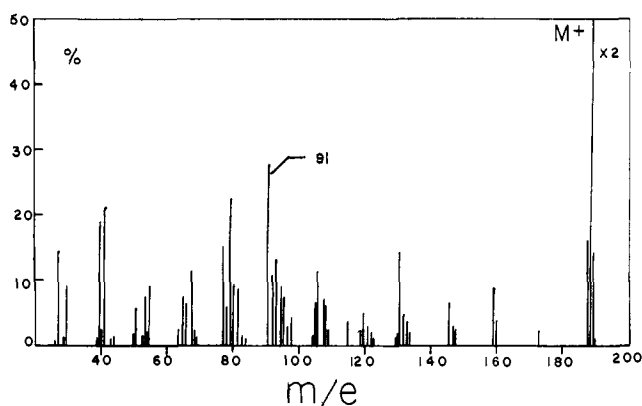
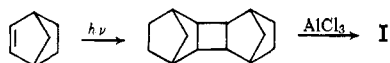


Figure 1. The mass spectrum of congressane.

zation of tetrahydrodicyclopentadiene to adamantane (II),<sup>4,5</sup> by the agency of strong Lewis acid catalysts. Under such conditions, rearrangement pathways available to hydrocarbons are very favorable mechanistically, and extremely complicated transformations can be effected, often in high yields.<sup>5,6</sup>

We felt that congressane (I) might be preparable by a similar rearrangement route. For a starting material, an isomeric pentacyclic alkane was needed, and such molecules have recently become available by the photodimerization of norbornene (III) in the presence of various photosensitizing agents.<sup>7</sup> Samples of two stereoisomeric norbornene dimers (IV) or their mixture were heated with about one-third of their weight of  $\text{AlCl}_3$  to increasingly higher temperatures, while monitoring the reactions by gas chromatography. Unfortunately, large quantities of tar were produced, but in addition small amounts (in these initial nonoptimum experiments, from traces to about 1%) of a high melting substance formed.



The properties of the new material were consistent with those expected of congressane and were so similar to those of adamantane (II)<sup>5</sup> that we were encouraged to favor the hoped for structure, I.<sup>8</sup> The melting point of congressane, 236–237°, was almost as high as that of adamantane, m.p. 268–269°. The empirical formula was  $\text{C}_{14}\text{H}_{20}$  (Anal. Calcd. for  $\text{C}_{14}\text{H}_{20}$ : C, 89.29; H, 10.71. Found: C, 89.17; H, 10.74), and the expected molecular weight was confirmed dramatically in the mass spectrum of congressane (Figure 1). The parent peak at  $m/e$  188 not only was the base peak, but its intensity was more than three times greater than that of any other ion. The fragmentation tendency of hydrocarbons in the mass spectrograph is very high, even for low molecular weight materials, but with congressane (as with adamantane)<sup>5</sup> the interlocking system of rings ensures unusual

(4) P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960); P. von R. Schleyer, *ibid.*, **79**, 3292 (1957).

(5) For a review, see R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).

(6) A. Schneider, R. Warren, and E. J. Janoski, *J. Am. Chem. Soc.*, **86**, 5365 (1964).

(7) (a) D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963); (b) R. D. Arnold, D. J. Trecker, and E. B. Whipple, to be published.

(8) P. von R. Schleyer and C. Cupas, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, Abstracts, p. 8U.

stability of the molecular ion. The second most intense peak in the mass spectrum, at  $m/e$  91, is suggestive of the tropylium  $\text{C}_7\text{H}_7^+$  ion<sup>9</sup> which might be produced by splitting of the congressane molecular ion symmetrically down the middle, rearrangement, and loss of three hydrogens. The n.m.r. spectrum also was interesting, since only a single relatively sharp ( $w_h \cong 3$  c.p.s.) signal at  $\tau$  8.32 was observed. The chemical shifts of the two kinds of protons of adamantane fortuitously are almost identical ( $\tau$  8.22)<sup>5</sup> and the same is true for the three kinds of protons of congressane. Finally, the very simple infrared spectrum of I indicated a highly symmetrical structure. Besides the CH stretching bands (at 2908, 2878, and 2851  $\text{cm}^{-1}$ ) and  $\text{CH}_2$  deformations (at 1442 and 1457  $\text{cm}^{-1}$ ) there was only one other absorption of more than very weak intensity (at 1047  $\text{cm}^{-1}$ ) out to 16  $\mu$ . The Raman spectrum had bands at 2926, 2907, 2880, 2851, 1444, 1308, 1233, 1179, 1086, 1072, 1039, 982, 935, and 708  $\text{cm}^{-1}$  ( $\text{CCl}_4$  solution).

None of these data, however, proves the congressane structure. This was done by X-ray analysis, reported separately.<sup>10</sup>

The chemistry of adamantane has now been well worked out,<sup>5</sup> and congressane should behave in much the same way, with the added complication that there are now two kinds of bridgehead positions readily substitutable under ionic conditions. We will report on the chemistry of congressane subsequently, as well as on attempts to prepare congressane homologs by rearrangement.

**Acknowledgments.** We wish to thank the Petroleum Research Fund, administered by the American Chemical Society, for support of this research at Princeton University. We appreciate especially the efforts of Drs. I. L. Karle and J. Karle, who determined the X-ray structure of congressane.<sup>10</sup>

(9) See S. Meyerson, J. D. McCollum, and P. N. Rylander, *J. Am. Chem. Soc.*, **83**, 1401 (1961); F. Meyer and A. G. Harrison, *ibid.*, **84**, 4757 (1964).

(10) I. L. Karle and J. Karle, *ibid.*, **87**, 918 (1965).

(11) Alfred P. Sloan Foundation Fellow, 1962–1966; Fulbright Research Fellow and J. S. Guggenheim Fellow at the Institute of Organic Chemistry of the University of Munich, Munich, Germany, 1964–1965

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## The Crystal and Molecular Structure of Congressane, $\text{C}_{14}\text{H}_{20}$ , by X-Ray Diffraction

Sir:

A structure analysis by X-ray diffraction of the material described in the accompanying communication by Cupas, Schleyer, and Trecker<sup>1</sup> has verified that the material is congressane (I).

A fragment of a large octahedron grown from petroleum ether was mounted on the  $a$  axis and was used to take eight layers of equi-inclination Weissenberg photographs with  $\text{Cu K}\alpha$  radiation. Visual estimates were

(1) C. Cupas, P. von R. Schleyer, and D. J. Trecker, *J. Am. Chem. Soc.*, **87**, 917 (1965).