sense) as a methyl or ethyl group, and in quite a separate class from the *t*-butyl group.

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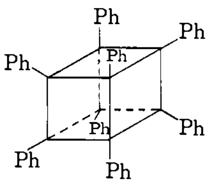
RECEIVED APRIL 19, 1962

TETRAPHENYLCYCLOBUTADIENE DERIVATIVES. IV.[1] "OCTAPHENYLCUBANE"; A DIMER OF TETRAPHENYLCYCLOBUTADIENE

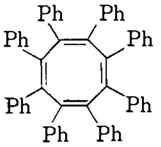
Sir:

We wish to report compelling evidence that the previously reported[2] tetraphenylcyclobutadiene dimer of m.p. 430° is "octaphenylcubane" (I), the first organic compound to incorporate eight carbon atoms bonded to each other symmetrically in the shape of a cube.

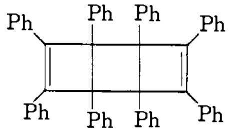


I

Dimerization of the radical intermediate from the thermal decomposition of (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)-dimethyltin bromide leads to I in 85% yield.[2] Its non-identity with hexaphenylbenzene, from which it cannot be distinguished on the basis of analysis or melting point, was established by comparison with an authentic sample prepared by the method of Dilthey.[3] By analogy with the dimerization products of substituted cyclobutadienes obtained by previous workers,[4] the most likely structure for our dimer might be octaphenylcycloöctatetraene[5a] (II) or the octaphenyltricycloöctadiene, III.[5b] However,



II



III

the saturated character of the dimer is unequivocally established by its solid-state Raman spectrum[6] which exhibits a strong phenyl band at 1605 cm.$^{-1}$ (also present in the solid state infrared spectrum at 1603 cm.$^{-1}$) but contains no band reasonably assignable to a double bond stretching mode. In contrast, other unsaturated compounds in this series exhibit a very strong Raman band in the vicinity of 1625–50 cm.$^{-1}$ (see below) and the absence of such a band effectively eliminates II and III as potential candidates.[5] This confirms our previous conclusions, based on preliminary X-ray symmetry considerations.[7]

Further X-ray diffraction experiments on the needle-like single crystals of I have shown the lattice to be body-centered tetragonal, with space group C^6_{4h}–$I4_1/a$, established without ambiguity. Cell constants were derived from single-crystal and from powder data: a = 19.489 ± 0.019 Å.; c = 10.647 ± 0.011 Å. The morphological needle axis is [001]; the only developed faces are [100]. The measured density, by flotation and by displacement, is 1.173 ± 0.008 g. cm.$^{-3}$; the density calculated on the basis of four molecules of $(C_7H_5)_8$ per cell is 1.171 g. cm.$^{-3}$. Reasonably complete three-dimensional diffracted-intensity data have been gathered about both [100] and [001] with the Weissenberg technique, and a full structure determination is in progress by D.R.P. Arguments based upon the X-ray evidence indicate that discrete molecules of formula $C_{56}H_{40}$ exist in the crystalline state, and that each such molecule is at a position of $\bar{4}$ symmetry within the cell. Though the present state of the X-ray investigation does not unequivocally establish the structure of the dimer as I, none of the data is in contradiction to this structure and, in the absence of an equally satisfactory alternative structure, the total body of chemical and physical evidence appears quite compelling.

The extreme insolubility of this dimer precluded normal chemical studies; reasonable solubility was obtained only in refluxing diphenyl ether, solutions of which yield well-formed crystals on cooling and from which its molecular weight was established ebulliometrically[8] in agreement with the X-ray result above. Exposure to hot concentrated sulfuric acid leads to a violet solution which yields a water-soluble ring-sulfonated mixture, and warming with concentrated nitric acid leads to indiscriminate nitration and an intractable mixture of products.

In an attempt to prepare the possible precursors, II and III, of the cubane I, it was found that two unrelated reactions unexpectedly yielded the same new product. Thus, while the reaction of equivalent quantities of 1,4-dilithio-*cis,cis*-tetraphenylbutadiene and 1,4-diiodo-*cis,cis*-tetraphenylbutadiene (route (1)) is expected to produce the D_{2h} ("tub") form of octaphenylcycloöctatetraene (IIa) and the treatment of 3,4-dibromotetraphenylcyclobutene[9] with phenyllithium in ether[10] (route

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(1) Part III, H. H. Freedman, *J. Org. Chem.*, in press.

(2) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2195 (1961).

(3) W. Dilthey and G. Hurtig, *Chem. Ber.*, **67**, 2004 (1934).

(4) (a) R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957); (b) R. Criegee, *et al.*, *ibid.*, **93**, 1553 (1960); (c) M. Avram, *et al.*, *Tetrahedron Letters*, **1**, 21 (1961); (d) E. H. White and H. C. Dunathan, Abstracts of the 134th A.C.S. Meeting, Chicago, Ill., 1958, p. 41-P; (e) M. Avram, *et al.*, *Chem. Ber.*, **93**, 1789 (1960).

(5) (a) A recent publication (E. H. Braye, W. Hubel and I. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961)), reports the formation of a hydrocarbon $(C_{14}H_{10})x$ of m.p. 421° which appears to be identical with our dimer and, on the basis of its method of formation and ultraviolet spectrum, is assumed by the authors to be II. (b) Structure III has been assigned to the dimer by M. Tsutsui (*Chem. and Ind.*, 780 (1962).

(6) The authors are greatly indebted to Dr. John Evans for supplying the Raman data.

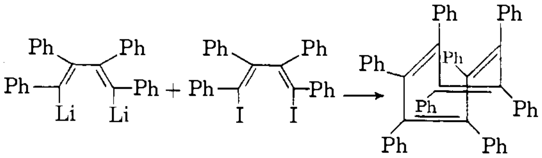
(7) Private communication by D. R. Petersen, cited by H. H. Freedman.[2]

(8) We are indebted to Dr. D. R. Stull for this determination and for the observation that the molecular weight tended to decrease with prolonged boiling in diphenyl ether. It is also of interest that the solution of I in this solvent is bright yellow and on cooling returns to its original colorless condition.

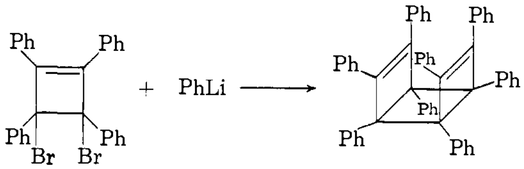
(9) H. H. Freedman and A. M. Frantz, Jr., paper presented before the Organic Division at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, Abstracts p. 26-O.

(10) The possibility that tetraphenylcyclobutadiene itself is an intermediate in this reaction is being currently investigated.

(2)) reasonably could be expected to produce the octaphenyltricyclooctadiene (IIIa, written as the *exo* isomer), there was obtained in 40 and 80% yield, respectively, the same new colorless hydrocarbon.



IIa



IIIa

This new compound is distinguished by its tendency to isomerize to I even in the solid state at room temperature, and preliminary attempts at its characterization have led only to the quantitative recovery of I. However, it is stable at $-25°$ and is readily distinguished from I by the X-ray powder pattern and by the solid state infrared and, in particular, the Raman spectrum, which has a strong band at 1650 cm.$^{-1}$. This latter band is assignable only to a C═C stretching mode and could fit equally well for IIa or IIIa.[11]

Though the exact identity of this unstable compound must be deferred pending the completion of studies now in progress, it is clear that a choice between IIa and IIIa cannot be made by analogy with the established chemistry of similar compounds. Structural considerations suggest that IIIa would be the logical precursor of I, but the production of IIIa by route (1) is unlikely and the isomerization of a cycloöctatetraene to a tricyclooctadiene (in contrast to the reverse isomerization[4]) is unknown. It has been calculated that unsubstituted cycloöctatetraene is more stable than its cubic tautomer by about 80 cal.[12]; based on their thermal behavior, the reverse seems to be true for the octaphenyl derivatives and it is tempting to explain this remarkable reversal of thermal stability as a consequence of the steric requirements of the eight phenyl groups.

Acknowledgments.—H. H. F. is indebted to Dr. Frederick Leavitt for the initial preparation of the unstable dimer and to Angus Frantz, Jr., for experimental assistance.

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RECEIVED MAY 16, 1962

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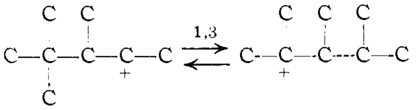
[11] 3,4-Dibromotetraphenylcyclobutene has a strong band at 1627 cm.$^{-1}$ in the Raman. Steric interference between the opposing phenyls on the double bonds of IIIa might well raise this stretching frequency to 1650 cm.$^{-1}$.

[12] W. Weltner, Jr., *J. Am. Chem. Soc.*, **75**, 4224 (1953).

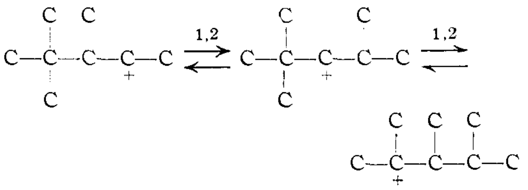
CARBONIUM ION REARRANGEMENTS. V.[1] 1,3-HYDRIDE SHIFTS IN THE 1-PROPYL CATION

Sir:

The occurrence of Wagner–Meerwein 1,3-shifts in *open chain systems* has eluded unambiguous confirmation. Such shifts have been proposed[2] in mechanistic interpretations of product formation in carbonium ion reactions, *e.g.*, (1) has been suggested.[2a] However, the products can always be rationalized equally well by postulating successive 1,2-shifts, *e.g.* (2), and the acceptance or rejection of 1,3-shifts in open chain systems remains at best a matter of personal taste.[3]


(1)

$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}\overset{C}{C}{-}\underset{+}{C}{-}C} \;\overset{1,3}{\rightleftarrows}\; \mathrm{C{-}\underset{+}{\overset{C}{C}}{-}\overset{C}{C}{-}\overset{C}{C}{-}C} \qquad (1)$$


(2)

$$\mathrm{C{-}\underset{C}{\overset{C}{C}}{-}\overset{C}{C}{-}\underset{+}{C}{-}C} \;\overset{1,2}{\rightleftarrows}\; \mathrm{C{-}\underset{C}{\overset{C}{C}}{-}\underset{+}{C}{-}\overset{C}{C}{-}C} \;\overset{1,2}{\rightleftarrows}\; \mathrm{C{-}\underset{+}{\overset{C}{C}}{-}\overset{C}{C}{-}\overset{C}{C}{-}C} \qquad (2)$$

Our interests in carbonium ion rearrangements and, from a mechanistic point of view, the obvious importance of settling unambiguously the question of 1,3-shifts have led us to undertake a thorough examination of the problem. We shall discuss in this communication 1,3-hydride shifts.

It has been shown[4,5] that the nitrous acid deamination of the perchlorate salt of 1-propylamine-1-C^{14} leads to labeled 1-propanol and 2-propanol, the label in 1-propanol being at C-1 and C-3 only.[5] As pointed out[5] the formation of 1-propanol-3-C^{14} can result from either a 1,3-hydride shift, according to (3), or from successive 1,2-shifts, according to (4). We wish to present evidence that (3) represents the correct mechanism of the rearrangement.[6]

$$\mathrm{CH_3{-}CH_2{-}\underset{+}{\overset{14}{C}}H_2} \xrightarrow{1,3} \mathrm{\underset{+}{C}H_2{-}CH_2{-}\overset{14}{C}H_3} \qquad (3)$$

$$\mathrm{CH_3{-}CH_2{-}\underset{+}{\overset{14}{C}}H_2} \;\overset{1,2}{\rightleftarrows}\; \mathrm{CH_3{-}\underset{+}{C}H{-}\overset{14}{C}H_3} \;\overset{1,2}{\rightleftarrows}\; \mathrm{\underset{+}{C}H_2{-}CH_2{-}\overset{14}{C}H_3} \qquad (4)$$

Differentiation between (3) and (4) is possible by use of the perchlorate salt of 1-propylamine-1,1,2,2-d_4, since (3) leads to I and (4) to II. Proton n.m.r. can distinguish between I and II as follows: I should show a broad singlet or quintet around 6.6

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[1] Papers III and IV in this series, in press.

[2] (a) F. C. Whitmore, K. C. Laughlin, J. F. Matuszeski and J. D. Surmatis, *J. Am. Chem. Soc.*, **63**, 756 (1941); (*b*) F. C. Whitmore and W. A. Mosher, *ibid.*, **68**, 281 (1946); (c) W. A. Mosher and J. C. Cox, *ibid.*, **72**, 3701 (1950).

[3] W. H. Saunders and C. J. Carges, *ibid.*, **82**, 3582 (1960), have shown that during the dehydration of 3,4,4-trimethyl-2-pentanol, under irreversible conditions, no appreciable 1,3-shifts occur.

[4] J. D. Roberts and M. Halman, *ibid.*, **75**, 5759 (1953).

[5] O. A. Reutov and T. N. Shatkina, *Dokl. Akad. Nauk S.S.S.R.*, **133**, 606 (1960); *Tetrahedron*, **18**, 237 (1962).

[6] The assumption is made that the carbonium ion is the intermediate and that the products do not arise from direct reactions of the diazonium salt with solvent.