stand in the cold. The bisketo mercurial **35** separated as 1.8 g (28%) of white solid, mp 230–232° dec, ir (Nujol) 1665 cm^{-1} (C=O). We were unsuccessful in obtaining other spectra for this substance because of its insolubility.

Anal. Calcd for $C_{16}H_{24}Cl_2HgO_2$: C, 36.96; H, 4.56; Cl, 13.64; Hg, 38.59. Found: C, 37.21; H, 4.67; Cl, 13.66; Hg, 38.85.

When a sample of the mercurial **35** was thermally decomposed in a sealed melting point tube, the volatile liquid which distilled from the decomposing sample was collected and identified with an authentic sample of the chloro ketone **7** by comparison of ir spectra. No evidence of decomposition was observed when a slurry of the mercurial **35** in cyclohexene was refluxed for 6 hr. After the reaction mixture had been partitioned between pentane and an aqueous solution of NH_4Cl, KI, and HCl, the calculated yield (glpc analysis) of the chloro ketone **7** was quantitative.

The reaction of this bisketo mercurial **35** with excess AcCl yielded a mixture of products containing (glpc, Apiezon L on Chromosorb P) primarily the enol acetate **9** accompanied by lesser amounts of the chloro ketone **7** and several unidentified components. A collected (glpc) sample of this product **9** was identified with an authentic sample by comparison of ir spectra and glpc retention times.

Registry No.—**4**, 31151-32-3; **7**, 1892-09-7; **9**, 311180-45-7; **10**, 31151-34-5; **11**, 31180-46-8; **12**, 31151-35-6; **14**, 31151-36-7; **15**, 31151-37-8; **17**, 3282-32-4; **18**, 31152-14-4; **19**, 31151-39-0; **20**, 959-27-3; **21**, 31151-40-3; **22**, 31152-16-6; **23**, 31152-17-7; **24c** acid, 21448-77-1; **26**, 31151-41-4; **27**, 31152-19-9; **35**, 31151-42-5; **37**, 31151-43-6; **41**, 31152-20-2.

Conformational Analysis. LXXVI. The Perhydrodurenes[1-3]

NORMAN L. ALLINGER*[4] AND NICHOLAS A. PAMPHILIS

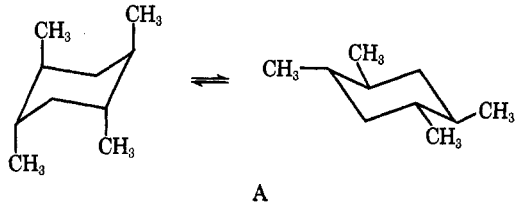
Departments of Chemistry, Wayne State University, Detroit, Michigan 48202, and University of Georgia, Athens, Georgia 30601

Received December 11, 1970

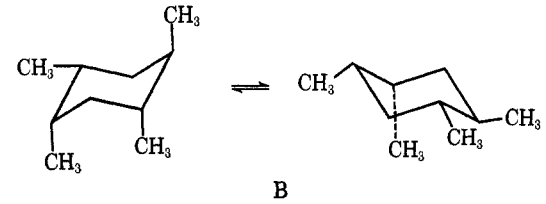
The five stereoisomeric perhydrodurenes (1,2,4,5-tetramethylcyclohexanes) have been prepared and equilibrated over palladium at elevated temperatures, and the thermodynamic quantities for the equilibria have been established. Nmr spectra of the compounds have been recorded, and structures have been assigned for each isomer.

While mono- and disubstituted cyclohexane rings have been extensively studied from the conformational point of view,[5] more highly substituted rings have been rarely examined.[6] It is known that with simple molecules conformational energies in general tend to be additive quantities; so with certain exceptions it is possible to determine *a priori* the relative energies of substituted cyclohexane systems. The present paper is concerned with extending this study experimentally to more complicated systems, specifically to the 1,2,4,5-tetramethylcyclohexane system. This particular ring system was chosen because it is reasonably typical of a polymethylated cyclohexane, there are five stereoisomers which can be individually examined, and each of them has a different energy. Thus it should be possible to assign unambiguously the structures of the isomers by studying the equilibrium between them. Finally, none of the energies is so high that it should not be possible to isolate all of the isomers from equilibrations at elevated temperatures.

The five isomers can be given the letters A–E for convenience of discussion. Each of these isomers is in principle an equilibrium mixture of two chair conformations, together with what is assumed to be a minor amount of boat forms. Thus, for isomer A, all of the methyl groups are equatorial, or they are all axial. For isomer B, one methyl is axial and the

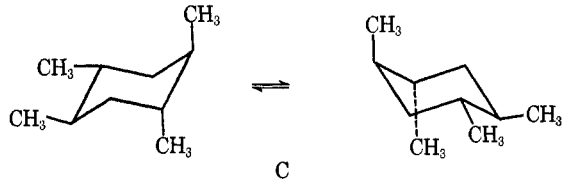


A

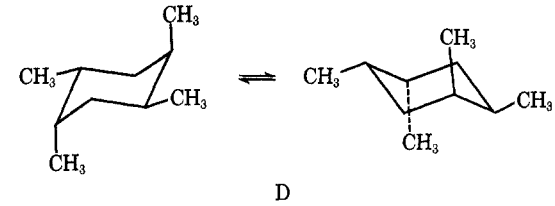


B

rest equatorial, or vice versa. Isomer C has two methyls equatorial and two axial, and the two conformations are superimposable mirror images. For isomer D, again two methyls are axial and two are equatorial in each conformation, and the conformations are in



C



D

fact superimposable. For isomer E, again there are two conformations which are superimposable, each contains two axial and two equatorial methyl groups.

(1) Paper LXXV: N. L. Allinger and J. C. Graham, *J. Org. Chem.*, **36**, 1688 (1971).

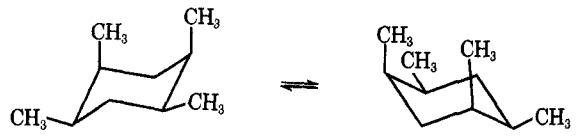
(2) Supported in part by Grant GP-15263 from the National Science Foundation.

(3) Abstracted from the Ph.D. dissertation of N.A.P., submitted to Wayne State University, May 1970.

(4) Correspondence concerning this paper should be addressed to this author at the University of Georgia, Athens, Ga. 30601.

(5) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience–Wiley, New York, N. Y., 1965.

(6) C. J. Egan and W. C. Buss, *J. Phys. Chem.*, **63**, 1887 (1959).



E

With simple methylated cyclohexanes, it is well known that the energy of the system can be estimated (with some exceptions) by adding up the total number of gauche interactions in the system, multiplying by 0.9 kcal/mol, and thus obtaining a relative energy in the liquid phase. One exception which immediately comes to mind is the system which contains a 1,3-syn-diaxial dimethyl interaction. Such an interaction is known experimentally, again in the simple case, to total 5.5 kcal/mol (1.8 kcal/mol for two ordinary gauche interactions, and 3.7 kcal/mol for the methyl–methyl interaction).[7] In Table I, relative enthalpies of the conformations have been calculated in this way.

TABLE I
CONFORMATIONS AND ENTHALPIES OF 1,2,4,5-TETRAMETHYLCYCLOHEXANE[a]

Isomer	Conformation	No. of gauche[b] interactions (1,3-Me–H)	No. of syn-axial di-methyls[c]	Interaction, kcal/mol	ΔH, calcd kcal/mol
A	1a,2a,4a,5a	0	2	11.00	9.20
	1e,2e,4e,5e	2	0	1.80	0
B	1e,2e,4e,5a	4	0	3.60	1.80
	1a,2a,ea,5e	3	1	8.20	6.40
C	1a,2a,4e,5e	5	0	4.50	2.70
D	1a,2e,4a,5e	6	0	5.40	3.60
E	1a,2e,4e,5a	2	1	7.30	5.50

[a] Computed at 0.9 kcal/mol per gauche interaction. [b] Number of gauche butane interactions, excluding those associated with the 1,3-diaxial dimethyl interaction. [c] 5.5 kcal/mol per 1,3-diaxial methyl interaction, including two normal gauche interactions (1.8 kcal/mol) and one methyl–methyl interaction (3.7/kcal/mol).[7]

Since we wish to study equilibria, we must consider entropy differences as well as differences in enthalpy. With the usual assumption[8] that entropy differences between stereoisomers can be ascribed simply to differences in symmetry and mixing, we may calculate the relative entropies expected for isomers A–E. Isomers A and B are in principle mixtures of two conformations; however, the minor conformation has an enthalpy greater than the major one by 9.2 kcal in the first case and by 4.6 kcal in the second case. This means that the minor component will be present to a negligible extent and contribute nothing to the entropy of mixing. Isomers B and C, however, are *dl* mixtures, whereas the others are meso. Hence, there will be entropy due to the mixing of *dl* forms (R ln 2 favoring the *dl* isomer in each case). Finally, the symmetry numbers for isomers B, D, and E are each 1, while the symmetry numbers for isomers A and C are each 2. This means that isomers A and C will have $-R$ ln 2 entropy units contributed by symmetry. The calculated relative entropies thus obtained are given in Table II.

(7) N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, **83**, 2145 (1961).
(8) Reference 5.

TABLE II
ENTROPY DIFFERENCES IN 1,2,4,5-TETRAMETHYLCYCLOHEXANES[a]

Isomer	Meso or *dl*	Symmetry no., σ	Due to symmetry ($-R$ ln σ)	Due to mixing of *dl* forms (R ln 2)	Total calcd
A	Meso	2	−1.38	0	−1.38
B	dl	1	0	1.38	+1.38
C	dl	2	−1.38	1.38	0
D	Meso	1	0	0	0
E	Meso	1	0	0	0

[a] In eu.

Having now the enthalpies and entropies expected for the isomers A–E, we can calculate from the relationship $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ for a given temperature what the free-energy differences will be, and from the relationship $\Delta G^\circ = -RT \ln K$, we can then calculate the equilibrium constants expected between each pair of isomers, and finally, from these equilibrium constants, we can calculate the percentage composition of an equilibrium mixture. The results are as shown in Table III for a temperature of 250°.

TABLE III
PER CENT ISOMERS AT EQUILIBRIUM (250°)
ESTIMATED LIQUID PHASE

A	51.76
B	36.75
C	7.72
D	3.25
E	0.52

Examination of these numbers shows that there are anticipated very large differences between each isomer, so that from the equilibrium data obtained experimentally, it should be possible to unambiguously assign the structures of these compounds.

Results and Discussion

Perhydrodurene was prepared by the hydrogenation of durene with platinum in acetic acid at room temperature. The equilibration was carried out in a manner similar to that used for other alkylcyclohexanes.[9] The equilibrations were conducted in sealed tubes with small amounts of palladium on carbon at temperatures ranging from 224 to 317°. The tubes were adequately filled (about 70–80% by volume) so that, when the equilibrium temperature was reached, the volume of material in the gas phase was nearly zero. This avoids the problem of the presence of a gas phase in which the equilibrium constant differs from that of the liquid.[9] The equilibrations were then quenched and the mixtures were analyzed by vapor phase chromatography several times. In each run five peaks were detected and labeled 1, 2, 3, 4, 5. These five peaks correspond to the isomers A, C, B, D, and E, respectively, and the data are summarized in Table IV.

The structures can be assigned unambiguously from the percentages present, as indicated in Table IV. The conformational rule suggests that the order of elution of the isomers on vpc should be the same as the order of isomer stability, and, with one exception, this was found to be the case. In addition, the hydrogenation

(9) N. L. Allinger, W. Szkrybalo, and F. A. Van-Catledge, *J. Org. Chem.*, **33**, 784 (1968); N. L. Allinger and J. L. Coke, *J. Amer. Chem. Soc.*, **81**, 4080 (1959).

TABLE IV
EXPERIMENTAL AMOUNTS OF ISOMERS A, B, C, D, AND E AT EQUILIBRIUM

Isomer	Fraction no.	% composition 224°	250°	274°	297°	317°
A	1	62.17	59.23	57.49	54.93	53.58
B	3	31.38	32.90	34.52	35.92	37.21
C	2	5.20	6.11	6.09	6.65	6.90
D	4	1.12	1.59	1.68	2.23	1.99
E	5		0.20	0.15	0.26	0.36

TABLE V
THERMODYNAMIC DATA FOR THE EQUILIBRIA
A ⇌ B, A ⇌ C, A ⇌ D, AND A ⇌ E[a]

Isomers at equilibrium	Calculated $\Delta H°$	Calculated $\Delta G_{298}°$	Calculated $\Delta S°$	Experimental $\Delta H°$	Experimental $\Delta G_{298}°$	Experimental $\Delta S°$
A ⇌ B	1.80	1.00	2.76	2.00 ± 0.04	1.20 ± 0.15	2.67 ± 0.08
A ⇌ C	2.70	2.30	1.38	2.58 ± 0.31	2.49 ± 0.40	0.32 ± 0.56
A ⇌ D	3.60	3.20	1.38	4.78 ± 0.92	4.25 ± 1.2	1.77 ± 1.69
A ⇌ E	5.50	5.10	1.38	6.77 ± 0.62	6.39 ± 1.2	1.26 ± 1.15

[a] Enthalpies and free energies in kcal/mol; entropies in eu.

of durene should yield a mixture of stereoisomers, in which the all-cis (E) product should predominate (von Auwers–Skita rule).[10] It was found that the hydrogenation product was a mixture of E (70.5%), B (24.4%), and D (5.1%).

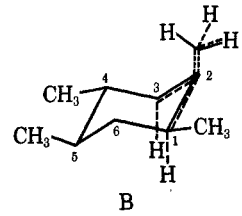
Having the equilibrium constants as a function of temperature, it is now easy to deduce the enthalpy and entropy changes which are experimentally found to relate the isomerizations. These data are summarized in Table V.

To confirm that all of the structures had been assigned correctly, small amounts of each isomer were isolated from the vapor phase chromatographic studies, and the nmr spectrum of each compound was determined. Since these molecules have various degrees of symmetry, considerable support for the structural assignments should be available from the nmr spectra. Some preliminary discussion of the nmr spectra of the 1,2-dimethylcyclohexanes at this point is appropriate. These compounds have been studied by several investigators.[11] Interestingly, the signal due to the methyl protons of *trans*-1,2-dimethylcyclohexane appears as an unresolved singlet. This fact has been explained in terms of identical chemical shifts for the axial methine proton and for the methyl group protons (the splitting of the methine proton by the adjacent methylene is swamped by the strong methyl singlet which is superimposed on it). This conclusion seems well established. On the other hand, the methyl protons of *cis*-1,2-dimethylcyclohexane are split into a doublet by their adjacent methine protons. In the cis isomer, because of the inversion of one chair form to the other, a given methyl spends half of its time in the axial and half in the equatorial position, and the two methyls become equivalent in the nmr. For comparison, *trans*-1,2-dimethylcyclohexane shows a broad absorption band at δ 1.20–1.80, integrating for 8 protons, and a sharp singlet at δ 0.92, integrating for 8 protons. The cis isomer shows a singlet at δ 1.42, integrating for 10 protons, and a sharp doublet at δ 0.835, integrating for 6 protons and showing a separation of 6.6 Hz.

The nmr spectrum of fraction 1 (assigned the structure of isomer A) consists of a large peak at δ 0.889 and two broad peaks at δ 1.516 and 1.616. The peak at δ 0.889 apparently stems from the methine protons plus the methyl protons and integrates for an area of 16 or 17 protons. The overall spectrum is quite strikingly like that of *trans*-1,2-dimethylcyclohexane, consistent with the assigned structure. Since the axial protons on a simple cyclohexane ring absorb at a higher field than do the equatorial,[12] the broad peak at δ 1.516 is probably due to the axial methylene protons, and the peak at δ 1.616 is due to the equatorial methylene protons.

The nmr spectrum of fraction 3 (Figure 1), assigned the structure of isomer B, consists of a broad region between δ 1.93–0.97, a large doublet (J = 1.5 Hz) at δ 0.853 which integrates for 12–13.5 protons, and a smaller, sharper doublet (J = 1.5 Hz) at δ 0.785 which integrates for 1.5–3 protons. The total integration for the two doublets is 14.5–15 protons.

Our interpretation of this spectrum is as follows. The signal at δ 0.785 represents one-half of the axial methyl doublet ($J \approx$ 6.8 Hz); the other half is under the large peak at δ 0.853, together with the three equatorial methyls and three of the methine protons. From the chemical shifts of the peaks, compared with those of the dimethylcyclohexanes, the nmr is consistent with the structure B. Finally, the 1.5-Hz splittings observed at δ 0.785 and 0.853 can be interpreted by means of long-range coupling. Such coupling requires an "M" type of arrangement of the 4 σ bonds involved,[13] which are as shown by the dashed lines for isomer B. The axial protons at C-1 and at C-3 are



B

both oriented properly to couple with protons in the methyl group at C-2. The proton at C-1 probably has a chemical shift not too different from that of the axial methyl,[12] however, so that probably it is the axial proton at C-3 which is leading to the observed coupling.

(10) Summary and references: R. P. Linstead, W. v. E. Doering, S. B. Davis, P. Levine, and R. R. Whetstone, *J. Amer. Chem. Soc.*, **64**, 1985 (1942).
(11) J. I. Musher, *Spectrochim. Acta*, **16**, 835 (1960); N. Muller and W. C. Tosch, *J. Chem. Phys.*, **37**, 1167 (1962); S. Brownstein and R. Miller, *J. Org. Chem.*, **24**, 1886 (1959).
(12) H. Booth, *Tetrahedron*, **22**, 615 (1966).
(13) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Amer. Chem. Soc.*, **84**, 1594 (1962).

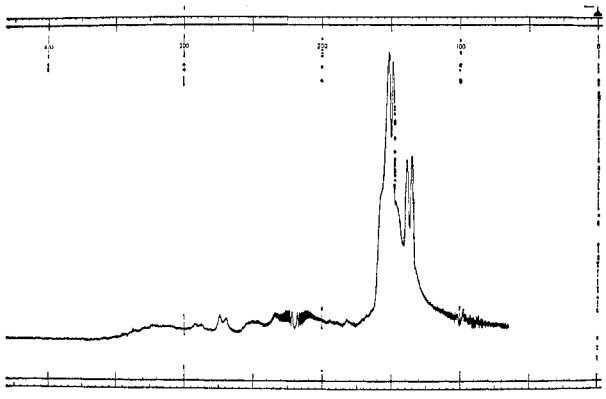


Figure 1.—100-MHz nmr spectrum of isomer B, 250-Hz sweep width.

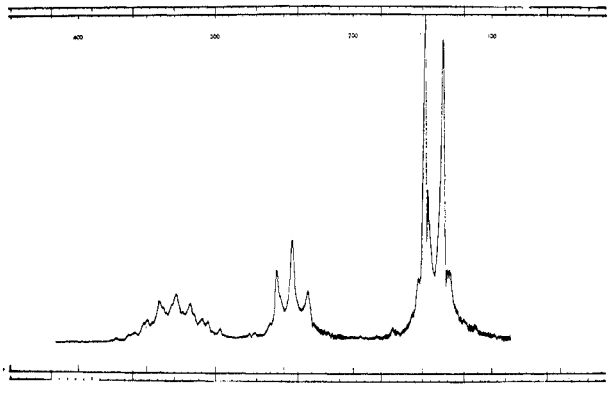


Figure 2.—100-MHz nmr spectrum of isomer D, 250-Hz sweep width.

Inspection of the structures of isomers C, D, and E shows that they have a good deal of similarity. Because of the high symmetry, each has many equivalent protons, and the differences between them are rather subtle. Therefore, all we are able to do here is show that the three spectra from fractions 2, 4, and 5 are consistent with the structures C, D, and E and thus consistent with the assignment of structure as determined from the energy relationships. The nmr spectra themselves are insufficient to prove which of these structures is which.

The nmr spectrum of fraction 4 (assigned structure D) consists of a doublet at δ 0.818 separated by 6.9 Hz, a triplet at δ 1.330 separated by 5.6 Hz, and a complex multiplet at δ 1.780 (Figure 2). These three absorptions integrate for 12, 4, and 4 protons, respectively. The first is clearly the methyl peak, which is split by coupling with the adjacent methine hydrogen. When D inverts, the axial and equatorial methyls are interchanged and so are the methine hydrogens. Hence the methyls are all equivalent. Similarly, the 4 methine protons are equivalent, and the 4 methylene protons are equivalent. There is more to the situation than that, however, because of the couplings between the protons.

The actual nmr spectrum at 100 MHz for isomer D is recorded in Figure 2. The detailed interpretation is as follows. The chemical shifts for the methyl, methylene, and methine protons are taken to be the values indicated respectively in the downfield direction.

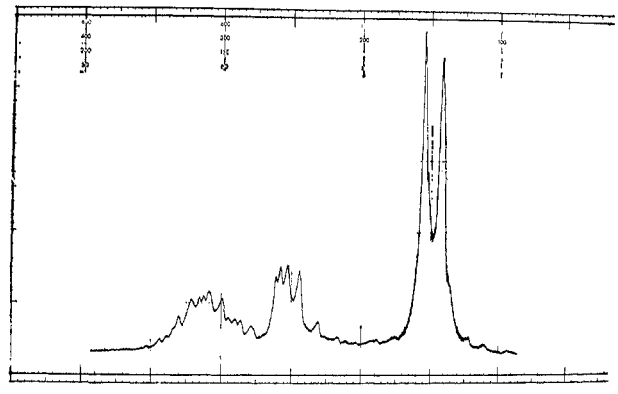


Figure 3.—100-MHz nmr spectrum of isomer E, 250-Hz sweep width.

Coupling constants (in hertz) are estimated by analogies, considering the dihedral angles from models, as follows.

$$J_{\text{methine-methine}} = 5.1$$
$$J_{\text{methylene-geminal}} = -12.0$$
$$J_{\text{methine-methylene-}trans} = 6.2$$
$$J_{\text{methylene-methine-}cis} = 5.0$$

These coupling constants and chemical shifts give a calculated spectrum for the methyl group which shows a large doublet, the downfield peak being slightly taller, separated by 6.9 Hz and each component of the doublet is split into a triplet, with about 80% of the intensity being in the center part. This is consistent with the rather broad base of the methylene doublet. Again, the calculations for the methylene part of the spectrum show a triplet with the center component being the largest, and the downfield component being larger than the upfield component, and then each of these components is further split, the center one into a triplet, and the other two into doublets. The overall separation between the components is 5.6 Hz, and the separation of the smaller peaks are of the order of 0.5 Hz. This is all quite consistent with the observed spectrum, where the resolution does not permit one to detect the fine structure.

The available program will not deal with a number of protons involved in calculation of the methine spectrum, but a first-order calculation, allowing for the coupling constants used predicts a quite complicated spectrum with 16 peaks, 8 of them being more intense than the other 8, and a detailed calculation would doubtlessly give an even more complex spectrum. Hence this calculation does not appear to be inconsistent with the observed spectrum, and the total spectrum is therefore taken to be consistent with the structure assigned.

For the spectrum which is assigned to compound E (Figure 3), the interpretation is rather similar to that given for the compound D. The methyl group appears as a doublet at δ 0.856, with a separation of 6.6 Hz. The methylene group appears as a multiplet, not very different from the triplet of isomer D. The geminal methylene protons are not necessarily identical in this case, but it looks as though they are nearly, but perhaps not quite, equivalent, which complicates the spectrum further.

Finally, the methine protons appear as a very com-

plex multiplet at δ 1.687. Again, this portion of the spectrum is beyond our ability to analyze. However, it is not inconsistent with what has been deduced up to this point. We may note that the methine protons are equivalent to one another, and there are only two kinds, of methylene protons: the pair which is cis to the adjacent methyls and the pair which is trans.

It is concluded that insofar as we can interpret the spectrum, it is consistent with the structure E. This spectrum should be similar to that of isomer D, but more complicated, due to the two sets of methylene protons instead of only one set.[14]

The spectrum assigned to isomer C (Figure 4) is quite different from the others. There is a doublet at δ 0.93 with a separation of 5.5 Hz, which integrates for 12 protons, and there is a poorly resolved doublet with peaks at δ 1.332 and 1.345 which integrates for 8 protons. The methyl groups are all equivalent in isomer C; so the chemical shift, splitting, and area of the peak at δ 0.923 is consistent with the methyl groups of this compound. The methylene and methine protons must by chance have almost identical chemical shifts. The methine protons are all equivalent to one another, and also the methylene protons are all equivalent to one another. This is conveniently seen using the postulate of Mislow and Raban and imagining deuterium substituted in turn for an axial and for an equatorial methylene proton at the same carbon. External rotations of the molecule together with ring inversion permit the two forms to be superimposed.[15]

If the chemical shifts of the methylene and methine protons in isomer C are accidentally equivalent (or almost so) in addition, then the very simple spectrum obtained is accounted for.

Experimental Section

1,2,4,5-Tetramethylcyclohexane (Mixture of Isomers).—To a 200-ml round-bottomed flask containing 13.4 g of durene dissolved in 75 ml of glacial acetic acid, 1.34 g of platinum oxide was added. The mixture was hydrogenated in an atmospheric hydrogenating apparatus. When the absorption of hydrogen became sluggish, the catalyst was removed and a fresh batch was added (1.34 g). This was repeated once or twice until the theoretical amount of hydrogen (7400 ml) was consumed, the sample was then diluted with 200 ml of water and extracted three times with three 50-ml portions of pentane. The pentane extracts were combined, washed with 10% sodium bicarbonate water, and dried over magnesium sulfate. The pentane was removed and the residue was distilled as a colorless liquid, bp 166–167.5°, wt 12.5 g (89.2%). Infrared analysis showed no C=C stretching but did show methyl bending at 1370 cm^{-1}. The tetranitromethane test for olefins was negative.

Anal. Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37. Found: C, 85.50; H, 14.61.

Vpc Conditions for the Separation and Identification of Isomers. Procedure A.—(1) Varian Autoprep (Model 700); (2) a 20 ft × $^3/_8$ in. aluminum column containing 30% SE-30 on Chromosorb W (45–60 mesh); (3) flow rate, 200 ml/min; (4) temperature, 120°; (5) relative areas of isomers were determined by the half-band width technique.

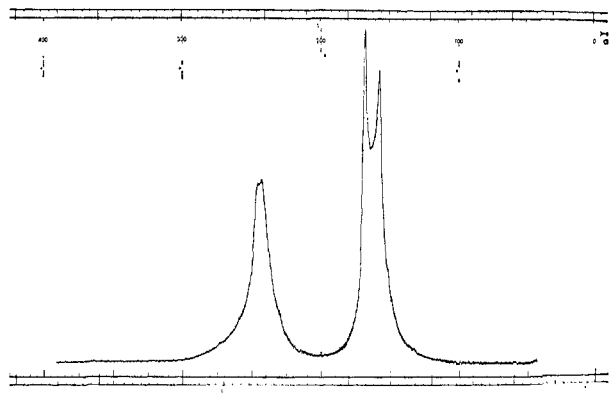


Figure 4.—100-MHz nmr spectrum of isomer C, 250-Hz sweep width.

Procedure B.—(1) F & M (Model 800); (2) a 39 ft × 0.25 in. aluminum column containing 30% SE-30 on Chromosorb W (60–80 mesh); (3) flow rate, 25 ml/min; (4) temperature, 175°; (5) relative areas of isomers were determined by the half-band-width technique.

Nmr Data Specifications.—The nmr spectra of the perhydrodurene isomers were taken with the Varian HA-100 (100 MHz) unless otherwise specified, although integrations were done on the A-60 (60 MHz) instrument. All perhydrodurene sample were diluted with carbon tetrachloride to make a 20% solution and were run at room temperature with TMS as the internal standard. The dimethylcyclohexane samples were diluted to 20% in chloroform with TMS as the internal standard.

Separation of a Hydrogenated Mixture of 1,2,4,5-Tetramethylcyclohexane Isomers.—The 1,2,4,5-tetramethylcyclohexane isomers obtained from the hydrogenation of durene were subjected to vpc analysis (procedure A). Three peaks were detected and isolated as fractions 1A, 2A, and 3A with retention times of 45.4 min (24.4% of the total), 54.0 min (5.1% of the total), and 57.0 min (70.5% of the total), respectively. These fractions were identified both by comparison of their retention times with those from the equilibrated samples and also by a comparison of the corresponding nmr spectra. The same perhydrodurenes were subjected to vpc analysis by procedure B. Three peaks were again detected with retention times of 140, 160, and 171 min.

Equilibration of 1,2,4,5-Tetramethylcyclohexane Isomers.—In a capillary tube, neat 1,2,4,5-tetramethylcyclohexane (mixture of isomers) was added along with 10% by weight of 10% palladium on carbon. The total amount of hydrocarbon was about 250 μl and occupied approximately 70–80% of the capillary's volume. The glass tube was sealed, immersed in a long stainless tube, and heated in an oven at the desired temperature for the desired length of time. Immediately upon removal from the oven, the stainless tube containing the sealed tube was quenched in ice water. The contents of the ampoule were analyzed by vpc (procedure B).

For each equilibration temperature, four sealed capillary tubes containing the hydrocarbon and catalyst were prepared and heated simultaneously. This was done so that the course of the equilibration could be followed by removal and vpc analysis of the contents of any of the four ampoules. Equilibrium was considered to have been reached when the amount of the main fraction detected by vpc did not change by more than 0.5% after 48 hr of heating.

In each run, five peaks were detected and labeled as fractions 1, 2, 3, 4, and 5, with retention times of 126, 136, 140, 160, and 171 min, respectively. Each sample was analyzed at least four times and the average value was taken, the average deviation being between 0.1–0.2% in each case. In Table IV, the relative amounts of all five fractions are tabulated for each equilibration temperature.

In order to illustrate reproducibility, a typical analysis of an equilibrated sample (12 days at 250°) monitored through the vpc several times is shown in Table VI. The thermocouple of the oven where the equilibrations were carried out was calibrated against three National Bureau of Standards thermometers.

(14) A referee has suggested that the energies of isomers D and E are sufficiently high that twist-boat forms may contribute significantly to the populations, since they would allow elimination of the severe 1,3-diaxial dimethyl interaction. This is correct. However, the entropies of the isomers are as calculated (to within the large experimental error, Table V), and other compounds that had to choose between the twist-boat or the 1,3-diaxial dimethyl interaction seem to have chosen the latter [ref 7, and B. L. Shapiro, *et al.*, *Tetrahedron Lett.*, 219 (1971)]. In any case, our arguments concerning the nmr spectra are unchanged. We assume rapid chair $\rightleftharpoons$ chair interchange, and pseudorotation will lead to the same result as far as proton equivalencies are concerned.

(15) K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

Calculated Spectra.—The calculated methyl and methylene nmr spectra of the perhydrodurene isomers were obtained through the use of a greatly modified version of the program by Stanley, Marquardt, and Ferguson, as modified by Scherr.[16]

TABLE VI

	% isomers				
Run no.	1	2	3	4	5[a]
1	59.13	6.12	32.97	1.78	
2	59.23	6.19	32.32	1.26	
3	59.52	6.06	32.62	1.80	
4	59.13	6.17	33.21	1.49	(0.20)
5	59.74	6.09	32.77	1.40	
6	59.25	6.10	32.84	1.81	
Av	59.33	6.12	32.96	1.59	

[a] The percentage of fraction 5 is an average value and is not totaled in with the percent of the other fractions.

Registry No.—A, 19899-39-9; B, 31328-42-4; C, 31328-43-5; D, 19899-42-4; E, 19903-06-1.

Acknowledgments.—The authors are greatly indebted to Dr. Paul Scherr, for the use of his program and for his advice and help in the calculation of nmr spectra to compare with the experimental spectra obtained in the present work; and to Dr. G. Karabatsos, for his kindness in helping us to obtain the 100-Hz nmr spectra.

(16) R. N. Stanley, O. W. Marquardt, and R. C. Ferguson, IBM Scherr Systems-SDA 3165 OPE NMR.

An Aminocyanoketenimine, Aminomalononitrile, and Aminocyanoimidazole from Diisobutene, Hydrogen Cyanide, and Hydrogen Fluoride. Preparation of Novel Diaminoethylenes and Diiminoethanes

L. DE VRIES

Chevron Research Company, Richmond, California 94802

Received January 18, 1971

Reaction of 2,4,4-trimethylpentene-2 (TMP), with HCN and HF gave three novel products $(TMP)_n(HCN)_m$: (1) *tert*-octylaminocyanoketen-*N*-*tert*-octylimine (**1**) ($n = 2$, $m = 3$); (2) *tert*-octylaminomalononitrile (**12**) ($n = 1$, $m = 3$); and (3) 4-cyano-5-*tert*-octylaminoimidazole (**14**) ($n = 1$, $m = 4$). Reaction of **1** with $(CN)^-$ or HCN gave di-*tert*-octylaminomaleonitrile (**4**). Compound **4** was dehydrogenated by benzoyl peroxide to give di-*tert*-octyliminosuccinonitrile (**7**). With diethylamine **1** gave 2,3-di-*tert*-octylamino-3-diethylaminoacrylonitrile (**3**), which autoxidized to give 2,3-di-*tert*-octylimino-3-diethylaminopropionitrile (**6**). It is proposed that protonated **1**, **12**, and **14** are the end products of a thermodynamically controlled process in which *tert*-octylisonitrile is an intermediate. Biological and prebiological implications are discussed.

The following investigation is concerned with the mechanism and the novel products of the reaction of 2,4,4-trimethylpentene-2 (TMP), a diisobutene isomer, with hydrogen cyanide and hydrogen fluoride in the absence of additional nucleophiles.

These products are quite different from those obtained in the related Ritter reaction.[1] In that reaction, olefins are allowed to react with nitriles and nucleophiles, such as water in sulfuric acid medium.

A patent[2a] and two recent articles[2b] describe the use of HF in the Ritter reaction. In this modification HCN may be used as the nitrile. Depending on the nature of the olefin and the reaction conditions, formamides, imidoylfluorides, or trialkyl-substituted aminomalonamides were obtained.

Results and Discussion

The reaction consisted of an initial stage in which TMP was allowed to react with hydrogen cyanide and hydrogen fluoride. This stage was followed by a work-up stage in which unreacted hydrogen cyanide and hydrogen fluoride were removed, and the residue was added to a dipotassium hydrogen phosphate solution. The product was separated into three fractions: (1) the main fraction obtained from the pentane extracts of the crude reaction mixture; (2) a base-soluble by-product; (3) a crystalline high melting by-product.

The product composition was highly dependent upon reaction variables. No attempt was made to establish conditions for optimum yields of specific products.

Treatment of the main fraction with methanesulfonic acid resulted in the precipitation of a colorless salt. Treatment of this salt with concentrated aqueous KOH gave pure **1**. Elemental analysis and spectral data were consistent with *tert*-octylaminocyanoketen-*N*-*tert*-octylimine (Scheme I), $C_{19}H_{35}N_3$. The infrared spectrum showed a very strong band at 2025 cm^{-1} which is diagnostic of only the ketenimine group (>C=C=N–).[3]

The nitrile band is located at an anomalously low frequency (2180 cm^{-1}). A similarly displaced nitrile band is found in enaminonitriles[4] ($N{\equiv}CC{=}C\ddot{N}R_2$) and is ascribed to a considerable contribution of a charge-separated structure ($^-{:}\ddot{N}{=}C{=}CC{=}\overset{+}{N}R_2$) to the ground-state resonance hybrid. In the case of **1** the low frequency is probably due to analogous delocalization, involving a charge-separated structure $^-{:}\ddot{N}{=}C{=}C\overset{+}{C}{\equiv}NR$.

In the absence of protic reagents, **1** was stable at room temperature as judged by the constancy of the infrared spectrum.

Treatment of **1** with concentrated aqueous sodium cyanide gave a crystalline compound **4**.

(1) L. J. Krimen and D. J. Cota, "The Ritter Reaction," Wiley, New York, N. Y., 1969, Chapter 3.

(2) (a) R. H. Potts, E. J. Miller, and A. Mais, British Patent 1,121,094 (1968); (b) J. R. Norell, *J. Org. Chem.*, **35**, 1611, 1619 (1970).

(3) C. L. Stevens and J. C. French, *J. Amer. Chem. Soc.*, **77**, 3491 (1955).

(4) S. Baldwin, *J. Org. Chem.*, **26**, 3288 (1961).