ture of di-*o*-xylyl trifluoroacetate (XId) and the dibenzocycloheptadiene XII in the ratio of about 1- to -1.

In another experiment *spiro*-di-*o*-xylylene (6 g.) dissolved in heptane (20 cc.) was added slowly to a solution of CF_3CO_2H (50 cc.) and heptane (20 cc.). The two-phase mixture was agitated vigorously at room temperature until a homogeneous slightly green fluorescent solution was obtained. The solution was allowed to remain at room temperature for 2 days. The excess solvent was removed by evaporation and the residue was separated by distillation at 0.45 mm. pressure. The main fraction (4.9 g., b.p. 130–136°) was a mixture of di-*o*-xylyl trifluoroacetate and bis-(*o*-methylbenzyl) ether as indicated by its infrared spectrum (bands at 5.60μ for C=O; 6.23, 7.32, 6.70μ for aromatic grouping; 8.1 to 8.9μ for C—F and C—O of acetate; 13.30μ for *o*-substituents. Small bands at 9.28 and 9.55μ indicate some ether impurity). This was confirmed by its nuclear magnetic resonance spectrum (Table I; τ-values: 7.80 for CH_3, 3.02 for phenyl, 7.14 for ethylene, 2.80 for phenyl, 4.85 for methylene of the ester and 7.70 for CH_3, 2.85 for phenyl, 5.52 for methylene of ether). Elemental analysis (13.3% F) and average molecular weight (293) indicated that the ester to ether ratio in the mixture was about 2.3- to -1. The non-volatile residue (1.5 g.) was poly-(*o*-xylylene) as indicated by its infrared spectrum. The infrared spectrum of the forerun (0.5 g., b.p. < 130°) indicated the presence of some dibenzocycloheptadiene.

Di-*o*-xylyl Methyl Ether (XIe).—Three drops of H_2SO_4 was added to *spiro*-di-*o*-xylylene (7 g.) dissolved in methanol (200 cc.). The mixture was allowed to react at room temperature for 4 days. The excess solvent was removed by evaporation and the residue (6.5 g.) was separated by distillation at 0.15 mm. to afford two main fractions: (1) 5.0 g., b.p. 120–126°; and (2) 0.9 g. residue. The infrared spectrum (bands at 6.29, 6.34, 6.72μ for aromatic structure; 6.88μ for CH_2; 7.27 and 7.38 for the two CH_3 groups; 9.20μ for C–O–C and 13.32μ for *o*-substituted aromatic ring) and nuclear magnetic resonance spectrum (Table I) indicates that fraction 1 is di-*o*-xylyl methyl ether. The molecular weight, as determined by the method of Neumeyer,[15] was 235 (theor. for $C_{16}H_{20}O$, 240).

In a control experiment, *spiro*-di-*o*-xylylene (5.2 g.) dissolved in methanol (75 cc.) was kept at room temperature for 2 weeks. No ether was obtained and only poly-(*o*-xylylene),[11,12] as indicated by its infrared analysis, was isolated instead (1.6 g. as solid polymer, m.p. 110–130°, inherent viscosity 0.676; and 4.0 g. as low molecular weight telomeric oil).

Reaction of *spiro*-Di-*o*-xylylene with Phenol.—*spiro*-Di-*o*-xylylene (10 g.) and phenol (25 g.) dissolved in heptane (500 cc.) were allowed to react at room temperature for 3 days. The excess heptane was removed by distillation at atmospheric pressure. The residue was distilled at 1 mm. pressure to afford four fractions: (1) 14 g. of phenol, b.p. 47°; (2) 4.7 g., b.p. 130–138°, mol. wt. 328; (3) 4.5 g., b.p. 195–196°; (4) 3 g. residue. Fraction 2 was leached with dilute aqueous NaOH leaving 2.0 g. as residue. This residue was identified by infrared analysis as 1-methyldibenzo(a,d)cyclohepta-(1,4)-diene (XII) and was obtained in the form of white crystals (m.p. 68.5–69.5°) after one recrystallization from methanol.

The aqueous NaOH extract was acidified with dilute HCl to afford a phenolic oil. Its infrared spectrum (bands at 2.99μ for OH; 6.22, 6.28, 6.63, 6.73μ for aromatic; 6.90μ for CH_2; 7.30μ for CH_3; 8.15μ for aromatic C–O; 12.20, 12.83, 13.34 and 13.54μ for complex aromatic substitution) and its molecular weight indicated that this was a telomeric mixture of *o*- and *p*-isomers of di-*o*-xylyl phenol (XIf). Fractions 3 and 4 were mixtures of telomeric phenols and phenyl ethers as indicated by their respective infrared spectra.

The experiment was repeated in the absence of a mutual solvent and a mixture of telomeric ethers and phenols was again obtained, but no evidence for the formation of the dibenzoheptadiene was detected.

Copolymerization of *spiro*-Di-*o*-xylylene and Formaldehyde.—A mixture of trioxane (5 g.), *spiro*-di-*o*-xylylene (2.5 g.), ether (50 cc.) and a catalytic amount of H_2SO_4 (3 drops) was allowed to react at room temperature for 3 days. The excess solvent was removed by evaporation. The residue was dissolved in a minimum amount of benzene and the solution was added dropwise to a 20-fold by volume excess of methanol to afford 2 g. of insoluble polymer which was separated by filtration. Its infrared spectrum (bands at 2.99μ for OH end-groups; 5.82μ C=O end-group; 6.24, 7.33 and 6.71μ for aromatic; 6.90 for CH_2; broad band 9.0 to 10.5μ for C—OC; 13.35 μ for *o*-substituted aromatic ring) molecular weight (1600) and elemental analysis (77.0% C; C; 6.6% H) indicated that the product was a polyether of formaldehyde and di-*o*-xylylene units having carbonyl or hydroxyl end groups.

Similar results were obtained when formaldehyde vapor, generated by thermal decomposition of paraformaldehyde, was condensed into a solution of *spiro*-di-*o*-xylylene in hexane containing a trace amount of formic acid. Formaldehyde was liberated when the copolymer was subjected to thermal degradation.

Acknowledgments.—The author is indebted to Dr. J. J. McBrady for interpretation of the infrared and nuclear magnetic resonance data.

(15) J. J. Neumeyer, *Anal. Chim. Acta*, **20**, 523 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY, STANFORD, CALIF.]

Relative Inversion and C1 Acetoxy Exchange Rates During Anomerization of Acetylated 2-Deoxy-D-glucose. The Ionic Mechanism[1]

BY WILLIAM A. BONNER

RECEIVED AUGUST 29, 1960

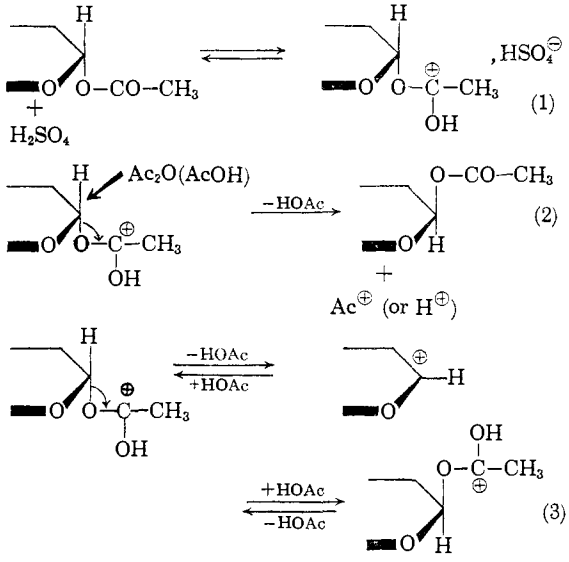
Previous studies of the acid-catalyzed anomerization of acetylated aldopyranoses by both polarimetric and radiochemical techniques have led to an ambiguity, in that the data are amenable to interpretation in terms of either an SN1 or SN2 mechanism. The origin of this ambiguity lies in the participation of the C2 acetoxy group in the anomerization process for all 1,2-*trans* anomers previously studied. A distinction between these two mechanisms should be possible by employing the anomers of tetra-*O*-acetyl-2-deoxy-D-glucopyranose, where such C2 acetoxy participation is precluded. These anomers, labeled in the C1 acetoxy group with carbon-14, have been prepared and subjected to anomerization and C1 acetoxy exchange rate studies under several conditions. In all cases the C1 acetoxy exchange rate exceeded the inversion rate by a factor of 1.8–3.7, an observation which accords with the predictions of an ionic SN1 mechanism and precludes the intervention of an SN2 mechanism.

The action of a Lewis acid catalyst in acetic anhydride and acetic acid on pure anomers of acetylated aldopyranoses induces equilibration of the latter to a mixture in which the α-anomer usually predominates.[2] This anomerization reaction, which is of considerable preparative utility, has been studied mechanistically in recent years by

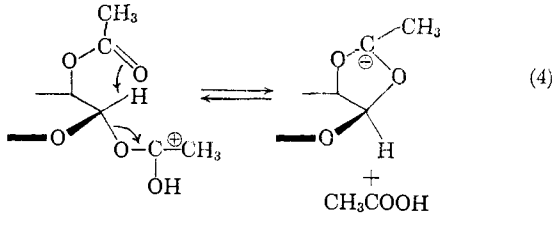
(1) The author is indebted to the National Science Foundation for its generous support of a portion of this investigation.

(2) W. A. Bonner, *J. Am. Chem. Soc.*, **81**, 1448 (1959).

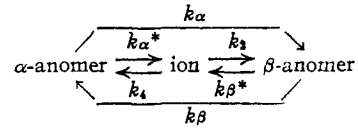
both kinetic[3,4] and radiochemical[5-7] techniques. Such investigations have to date led to a mechanistic ambituity in that both the kinetic and radiochemical data so far available are in accord with either a concerted SN2 mechanism (2) or an ionic SN1 mechanism (3), following preliminary formation (1) of the conjugate acid at the anomeric acetoxy group of the acetylated aldose[5a] or formation of the conjugate acid of the acetic anhydride solvent.[3] This ambiguity may be illustrated by considering the data pertaining to the penta-*O*-acetyl-D-glucopyranoses. The polarimetrically determined inversion rate[5a] for the α-anomer in 1:1 acetic acid–acetic anhydride solvent at 25° using 0.5 *M* sulfuric acid catalyst is 0.0041 min.$^{-1}$; the



radiochemically determined Cl acetoxy exchange rate[5a] under the same conditions is 0.00422 min.$^{-1}$ The essential identity of these two rates argues strongly for an SN2 process such as 2. On the other hand, the inversion rate for penta-*O*-acetyl-β-D-glucopyranose under these conditions is 0.0296 min.$^{-1}$, while its Cl acetoxy exchange rate is 0.433 min.$^{-1}$ This 14.6-fold enhancement of the exchange rate over the inversion rate for the β-anomer has been explained[6,7] in terms of C2-acetoxy participation (4), a process which might compete[5a] with the accompanying SN2 inversion.



Alternatively, a simple ionic mechanism such as 5 both qualitatively and quantitatively explains the inversion and Cl acetoxy exchange data for



several pairs of poly-*O*-acetylaldopyranose anomers,[5a] at least when k_β^* (the Cl acetoxy exchange rate for the 1,2-*trans* anomer) is (due to participation such as 4) appreciably larger than the inversion rate k_β for this anomer, and when k_α^* (the exchange rate for the 1,2-*cis* anomer) approximately equals the inversion rate k_α. Application of the usual steady-state equations to 5, followed by introduction of equilibrium restrictions, leads to 6, from whence 7 and 8 are derivable.[5a] With the aid of 7 and 8 it is possible to test the quantitative applicability of ionic mechanism 5 by predicting the ratio of the Cl acetoxy exchange rate (k^*) to inversion rate (k) for either anomer, knowing only the numerical values of the anomerization equilibrium constant and the exchange rates for each anomer. With the acetylated D-glucose anomers[5a] the predicted value for k_α^*/k_α is 1.07 whereas the observed ratio is 1.03, while the predicted value for k_β^*/k_β is 15.06 *versus* an observed ratio of 14.60. Thus in addition to the SN2 mechanism 2, the ionic mechanism 5 explains with equal adequacy the inversion–exchange rate relationships during anomerization of the acetylated glucoses as well as other aldoses. Accordingly, a distinction between the two mechanisms cannot be made on the basis of the available kinetic data, due to the complication of C2 acetoxy participation inherent in all of the aldoses so far investigated.

$$k_2/k_4 = K_e k_\beta^*/k_\alpha^* \quad (6)$$

$$k^*_\alpha/k_\alpha = 1 + K_e k_\beta^*/k_\alpha^* \quad (7)$$

$$k^*_\alpha/k_\alpha = 1 + k_\alpha^*/K_e k_\beta^* \quad (8)$$

It has seemed to us that an unambiguous distinction between an SN1 and SN2 mechanism for anomerization might be made on the basis of Cl acetoxy exchange and inversion rate data for aldoses where C2 acetoxy participation was structurally unlikely or impossible. Our initial attempt to prepare the anomers of 2-*O*-methyl-1,3,4,6-tetra-*O*-acetyl-D-glucose[8] for this purpose by methylation of the anomers of 1,3,4,6-tetra-*O*-acetyl-D-glucose was frustrated by a Cl → C2 acetyl migration during the methylation step. Accordingly, we turned our attention to the theoretically more suitable but hitherto unknown anomers of 1,3,4,6-tetra-*O*-acetyl-2-deoxy-D-glucose,[9] labeled in the Cl acetoxy group with carbon-14, for similar purposes.

Since participation of type 4 by the C6 acetoxy group of an acetylated aldohexose has been demonstrated specifically not to occur[5a] and since there has been no evidence for similar participation by any acetoxy group save that at C2, the anomers of an acetylated 2-deoxyaldose should permit a clear distinction between mechanisms 2 and 3. Lacking C2 participation, mechanism 2 predicts an identity of inversion and Cl acetoxy exchange rates for *both* anomers of such an acetylated 2-deoxyaldose. Mechanism 3, however, requires qualita-

(3) W. A. Bonner, *J. Am. Chem. Soc.*, **73**, 2659 (1951).
(4) E. B. Painter, *ibid.*, **75**, 1137 (1953).
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(9) W. A. Bonner, *ibid.*, **26**, in press (1961).

TABLE I

C1 ACETOXY EXCHANGE AND INVERSION RATE RATIOS IN THE ACID-CATALYZED ANOMERIZATION OF THE ANOMERS OF TETRA-O-ACETYL-2-DEOXY-D-GLUCOPYRANOSE

Solvent	$[H_2SO_4]$, M	$k\alpha^*$, min.$^{-1}$	$k\beta^*$, min.$^{-1}$	$k^*\alpha/k\alpha$ Calcd. from 8	Obsd.	$k\beta^*/k\beta$ Calcd. from 7	Obsd.
1:1 Ac_2O–AcOH	0.001	0.0300	0.141	2.72	3.66	1.58	2.14
AcOH	0.002	0.0292	0.218	2.04	1.83	1.96	1.80

TABLE II

ANOMERIZATION RATE DATA FOR TETRA-O-ACETYL-2-DEOXY-D-GLUCOSE SAMPLES

Solvent	$[H_2SO_4]$, M	$k\alpha + k\beta$, min.$^{-1}$	K_e[c]	$k\alpha$, min.$^{-1}$	$k\beta$,[d] min.$^{-1}$
1:1 Ac_2O–AcOH	0.001	0.0740[a]	0.124	0.0082	0.0658
AcOH	0.002	0.137[b]	0.129	0.016	0.121

[a] Average of values extrapolated to t_0 for α-anomer (0.0720 min.$^{-1}$) and β-anomer (0.0760 min.$^{-1}$). [b] Average of values calculated at 12 time intervals during anomerization; average deviation, 0.001 min.$^{-1}$. [c] Calculated from the observed rotation of the equilibrated anomerization mixture. [d] Calculated from the relation $k\beta = (k\alpha + k\beta)/(1 + K_e)$.

TABLE III

C1 ACETOXY EXCHANGE DATA FOR LABELED TETRA-O-ACETYL-2-DEOXY-D-GLUCOSE SAMPLES

Anomer	Solvent	$[H_2SO_4]$, M	t, min.	Assay, mc./mole	k_{exch},[a] min.$^{-1}$
α	1:1 Ac_2O–AcOH	0.001	4	1.591	0.0464
			8	1.061	.0739
			12	0.638	.0917
			16	.311	.1137
			20	.147	.1284
			Extrapolated value		0.0300
β[b]	1:1 Ac_2O–AcOH	0.001	4	1.025	0.143
			8	0.575	.144
			12	.317	.146
			16	.127	.166
			20	.057	.173
			Extrapolated value		0.141
α	AcOH	0.002	0.5	1.888	0.0276
			2	1.807	.0291
			5	1.638	.0312
			8	1.519	.0290
			11	1.387	.0293
			Average value		0.0292
β	AcOH	0.002	0.5	7.074	0.216
			5	6.100	.204
			8	5.813	.100
			11	5.622	.193
			Extrapolated value		0.218

[a] Calculated from the relationship $k = (2.303/t) \log (a/a-x)$, where a is the original radioactivity and $a-x$ that remaining after time t. For the C1 labeled anomer a = 1.915 mc./mole, and a-x = the radioactivity assay at time t. For the randomly labeled β-anomer $a = 0.25 \times 7.260$ = 1.815 mc./mole, and a-x = assay at time $t - 0.75 \times 7.260$ = assay -5.445 mc./mole. [b] After anomerization equilibrium had been reached the β-anomer had an assay of 5.444 mc./mole, indicating that only the C1 acetoxy of the randomly labeled sample had undergone exchange. This observation emphasizes again[2,5] the failure of acetoxy groups other than that at C1 to undergo exchange under anomerization conditions.

tively that the C1 acetoxy exchange rate should be *greater* than the inversion rate in the case of both anomers. Furthermore, the simple scheme 5 and its derived relationships 7 and 8, if applicable, should permit prediction of the numerical value of $k_{exchange}/k_{inversion}$ for each anomer, again in the manner outlined above.

The anomers of tetra-*O*-acetyl-2-deoxy-D-glucopyranose labeled in the C1 acetoxy group with carbon-14 were prepared and subjected to sulfuric acid-catalyzed anomerization at 25° in two different solvent systems under the conditions indicated in Tables I, II and III. Polarimetric inversion rate data are indicated in Table II, while C1 acetoxy exchange rates for both anomers are summarized in Table III. Comparison of the data in Tables II and III indicates that the $k_{exchange}/k_{inversion} > 1$ relationship required qualitatively of each anomer by mechanism 3 is in fact encountered. The numerical values for $k_{exchange}/k_{inversion}$ for each anomer, predicted by application of 7 and 8, are compared with the observed k^*/k ratios for each anomer in Table I. It is seen that the quantitative predictions of these ratios, based on the simple ionic mechanism 5, agree with the observed ratios reasonably well. The disagreement in the calculated and observed k^*/k values in Table I probably arises both from the mechanistic oversimplification inherent in the simple scheme 5 as well as the fact that the first-order rate data for both anomerization and C1 acetoxy exchange in the case of the acetylated 2-deoxy-D-glucose anomers were neither as reproducible nor free from drift as were the data for anomerization reactions previously studied.[5] In any case the inversion and exchange data in Tables I, II and III appear to us qualitatively and semiquantitatively to support an ionic mechanism such as 3 or 5 for the anomerization process, and once and for all to exclude an SN2 mechanism such as 2.

Experimental

Acetic-1-C^{14} Anhydride.—2 Millicuries (32.6 mg.) of sodium acetate-1-C^{14} was rinsed into acetic anhydride (10 ml.). The mixture was treated with sulfuric acid (0.5 ml.), allowed to stand 6 hours and then distilled to dryness in a slight vacuum, "scavenging" the residue by distillation therefrom of additional acetic anhydride (4–5-ml. portions). The product was redistilled, b.p. 128–135°, specific activity 3.844 mc./mole (as determined by the assay of its product below).

Tri-O-acetyl-2-deoxy-α-D-glucopyranosyl Acetate-1-C^{14}.—Sulfuric acid (0.014 ml.) was added to acetic-1-C^{14} anhydride (5 ml.), giving a solution approximately 0.05 M. To this was added tetra-*O*-acetyl-2-deoxy-β-D-glucopyranose (2.5 g.), stirring to dissolve. After 10 minutes the solution was poured into ice-water (30 ml.) whereupon the mixture was stirred for 40 minutes and then extracted 4 times with chloroform. Customary processing yielded a crude sirup (3.1 g.) which quickly crystallized. Two recrystallizations from a mixture of ethanol (5 ml.) and ligroin (4 ml.) afforded 1.89 g. of pure C1 acetoxy labeled tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose, m.p. 110.2–110.7°, $[\alpha]^{25}D$ + 110.3° (*c* 0.9, $CHCl_3$), specific radioactivity 1.915 ± 0.008 mc./mole.

Tetra-O-(acetyl-1-C^{14})-2-deoxy-β-D-glucopyranose.—Since pilot attempts to prepare C1 acetoxy labeled 2-deoxy-β-D-glucose tetraacetate were unsuccessful, a randomly labeled sample was prepared instead. 2-Deoxy-D-glucose

was acetylated using pyridine (20 ml.) and the above acetic-1-C^{14} anhydride (15 ml.) in the manner previously described,[9] and the desired β-anomer was separated as before by fractional crystallization of the crude product from 2-propanol. The final material had m.p. 92.2–93.0°, $[\alpha]^{25}D$ −3.04° (*c* 1.0, $CHCl_3$) and a specific radioactivity of 7.260 ± 0.006 mc./mole.

Anomerization and C1 Acetoxy Exchange Experiments.—Since the kinetic data obtained in consecutive individual anomerization and C1 acetoxy exchange experiments were, for unknown reasons, not as reproducible as might be desired, we have wherever feasible obtained both anomerization and exchange data on the *same* reaction mixture, thus eliminating the uncontrollable errors attending separate experiments. Two series of experiments were conducted, one employing a 1:1 mixture of acetic anhydride and acetic acid 0.001 *M* in sulfuric acid as the anomerizing solvent, and the other employing absolute acetic acid (containing 1% acetic anhydride) 0.002 *M* in sulfuric acid. The same solvent and catalyst solution was employed in all of the experiments in each series. All solutions were thermostated at 25 ± 0.2° prior to and during each experiment. The procedure for a typical experiment was: The above randomly labeled tetra-*O*-(acetyl-1-C^{14})-2-deoxy-β-D-glucose (0.6646 g.) was dissolved in 18.0 ml. of 1:1 acetic acid–acetic anhydride, and the solution was treated at time zero with 2.0 ml. of freshly prepared catalyst solution consisting of the same solvent 0.01 *M* in sulfuric acid. Half of the resulting solution, 0.1 *M* in solute and 0.001 *M* in catalyst, was placed in a 2-dcm. jacketed polarimeter tube for polarimetric observations and the remaining half was sampled for residual radioactivity at the indicated time intervals, isolating the product from each aliquot as previously described.[5a] The crude product in each case was dried for several days *in vacuo* over P_2O_5 and NaOH, then assayed as usual[10] for its radioactivity. The C1 acetoxy exchange data pertaining to these experiments are summarized in Table III. The corresponding anomerization rate data, obtained as fully described previously,[2,3,5] are given in Table II.

(10) W. A. Bonner, *J. Am. Chem. Soc.*, **80**, 3378 (1958); O. K. Neville, *ibid.*, **70**, 3501 (1948); V. A. Raaen and G. A. Ropp, *Anal. Chem.*, **25**, 174 (1953).

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE, RENSSELAER, N. Y.]

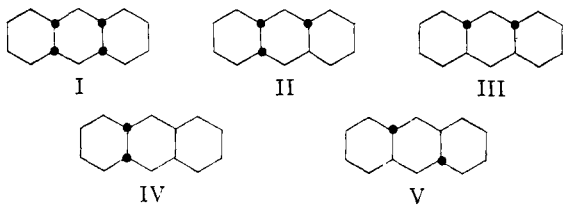
The Preparation of *trans-anti-trans*-Perhydroanthracene

BY ROBERT L. CLARKE

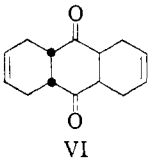
RECEIVED OCTOBER 21, 1960

The preparation of the fifth and last of the perhydroanthracene isomers, a *chair-boat-chair* form, is described.

Of the five possible perhydrogenated anthracenes, the *cis-syn-cis* isomer I, m.p. 61°; the *cis-trans* isomer II, m.p. 40°; and the *trans-syn-trans* isomer III, m.p. 90°; have been known for several years.[1] Recently, Hill and Martin,[2] Crossley and Henbest,[3] and Clarke and Johnson[4] independently isolated the *cis-anti-cis* isomer IV, m.p. 122°. The last and possibly the most interesting of these hydrocarbons, *trans-anti-trans*-perhydroanthracene (V), m.p. 48.5–49.7°, is reported in the present paper. This compound has been isolated also by Hill and Martin.[5] The considerable interest in this isomer stems from the fact that its central ring is forced into a boat or *stretched*[6] conformation. It constitutes one of the simplest structures containing such a system and a comparison of this isomer with the all-chair, *trans-syn-trans* isomer by combustion calorimetry should afford an estimate of the difference in energy between the boat and the chair forms of cyclohexane. The first such determination of this energy difference by this method was recently reported by Johnson, Margrave, Bauer, Frisch, Dreger and Hubbard.[7]



When earlier investigations in our laboratory had led to the isolation of *cis-anti-cis*-perhydroanthracene (IV),[4] substantiation of its structure was sought through the addition of two equivalents of 1,3-butadiene to one equivalent of benzoquinone, the required *cis-anti-cis* skeleton presumably being formed; *cf.* structure VI. As an ancillary experiment, the hydroanthraquinone VI was isomerized (KOH) and hydrogenated as described by Alder and Stein[8] to give the *trans-trans*-decahydro-9,10-anthraquinone of m.p. 253–256° and this diketone was subjected to modified Wolff–Kishner conditions for reduction. The Huang-Minlon modification[9] did not give satisfactory results but the Barton, Ives and Thomas modification[10] produced a 64% yield of hydrocarbon products. Separation of this mixture of hydrocarbons was not accomplished by adsorption chromatography on silica gel or alumina with pentane as a solvent and was poorly accomplished by fractional crystallization. However, separation of the mixture into two distinct



VI

(1) *Cf.* J. W. Cook, N. A. McGinnis and S. Mitchell, *J. Chem. Soc.*, 286 (1944).

(2) R. K. Hill and J. G. Martin, *Proc. Chem. Soc.*, 390 (1959).

(3) N. S. Crossley and H. B. Henbest, *J. Chem. Soc.*, 4413 (1960).

(4) R. L. Clarke and W. S. Johnson, *J. Am. Chem. Soc.*, **81**, 5706 (1959).

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(7) W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger and W. N. Hubbard, *J. Am. Chem. Soc.*, **82**, 1255 (1960).

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(9) Huang-Minlon, *J. Am. Chem. Soc.*, **71**, 3301 (1949).

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