

are in reasonable agreement with the observed shifts which in  $\tau$  units are

	II	III	V	VI
Y = H	0.04	-0.09	-0.71	-0.57

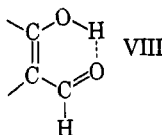
Here, negative values are downfield with respect to positive. These, and the other measurements given later, were made on dilute solutions in tetrachloride using cyclohexane as an internal reference.<sup>3</sup> The shifts were converted to the tetramethylsilane  $\tau$ -scale by using a  $\tau$ -value of 8.51 for cyclohexane.

In the case of the corresponding ketones, Y = CH<sub>3</sub>, prediction of the ring current shifts is complicated by rotation about the C-CH<sub>3</sub> bond, but similar principles hold. The relative chemical shifts, however, will be smaller within this series than in the case of the aldehydes, because the protons of the -CH<sub>3</sub> group are further away from the elementary induced dipoles, and they do not lie in the same plane as the aromatic system. The observed shifts of the -CH<sub>3</sub> absorption peaks in  $\tau$  units are

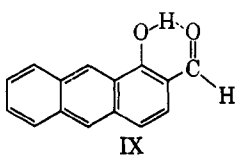
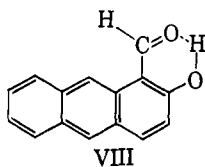
	II	III	IV	V	VI
Y = CH <sub>3</sub>	7.35	7.21	7.23	7.14	7.19

in qualitative agreement with the above arguments.

As an example of the use of these methods in structural determination, consider the position to be assigned to the -CYO groups in an hydroxyanthraldehyde (A) and in an hydroxyanthryl methyl ketone (B) which melt at 167 and 116°, respectively. In the case of the hydroxyanthraldehyde, chemical evidence<sup>6,7</sup> showed that the -OH group was at the 2-position, but it was not known whether the aldehyde group was at the 1- or the 3-position. The -OH proton line of A occurs at  $\tau$  -3.64. This position is about 8.75 p.p.m. downfield from that expected<sup>3</sup> for the -OH position in either 1-hydroxy, or 2-hydroxyanthracene ( $\tau \cong 5.1$ ) and is at the position expected for the chelated system VII



in which the mobile bond order of the C=C bond is 0.745.<sup>3</sup> Hence, it follows that the -OH and aldehyde groups are chelated and that the chelated system must span the 1-2 bond in the anthracene nucleus. It can not span the 2-3 position; *i.e.*, A is either VIII or IX on the basis of the -OH proton shift. Com-

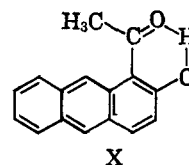


paring the -OH proton shift and chemical evidence, we find VIII to be the correct structure.

The ring current effects enable us to confirm that VIII is the correct structure. The observed position of the -CHO absorption peak, at a  $\tau$ -value of -0.87, is in the range predicted for structure VIII. For structure

IX, the -CHO  $\tau$ -value is predicted to be about -0.1, which differs so greatly from experiment that VIII must be the correct structure. This conclusion supports a structural determination based upon chemical arguments.<sup>6,7</sup>

In a similar way, the -OH and -CH<sub>3</sub> chemical shifts, with  $\tau$ -values of -4.37 and 7.18 p.p.m., respectively, indicate<sup>3</sup> that B is X. In this case, the arguments based upon the -CH<sub>3</sub> group proton shift are not conclusive and the isomeric form with -OH and -COCH<sub>3</sub> groups interchanged was eliminated primarily by chemical evidence<sup>6,7</sup> as to the -OH position.



### Experimental

The samples and experimental procedure, with one exception, were the same in these experiments as described in an earlier report.<sup>3</sup> The exception is the hydroxyanthraldehyde (A), the synthesis of which has been described elsewhere.<sup>6,7</sup> Furthermore, we are indebted to Professor I. Moyer Hunsberger for furnishing the samples and giving us some helpful comments on the manuscript.

### *trans*-5-Cyclodecenone<sup>1</sup>

P. S. WHARTON, G. A. HIEGEL, AND R. V. COOMBS

Department of Chemistry, University of Wisconsin,  
Madison 6, Wisconsin

Received May 6, 1963

Although studies of medium carbocycles (C<sub>8-11</sub>) have yielded interesting information on interactions of functional groups with transannular double bonds,<sup>2</sup> the synthetic inaccessibility of the simplest systems has hindered a dissection of the nature of such interactions. One of the most promising methods of generating the exemplary 5-cyclononyl and 5-cyclodecyl systems is the fragmentation of appropriately substituted hydrindane and decalin precursors,<sup>3</sup> two further examples of which we report herewith for the stereospecific synthesis of *trans*-5-cyclodecenone (4).<sup>2c</sup> Allylic alcohol 2<sup>4</sup> prepared *via* photosensitized oxygenation of  $\Delta^9$ -octalin,<sup>4a</sup> was converted to a mixture<sup>5</sup> of 1,10-decalindiols (3a) in 78% yield by the standard procedure using diborane.<sup>6</sup> The oily mixture of

(1) This investigation was supported by a Frederick Gardner Cottrell grant from Research Corporation and by Public Health Service Research Grant GM 09759 from the Division of General Medical Sciences, U. S. Public Health Service.

(2)(a) See J. Sicher, *Progr. Stereochem.*, **3**, 202 (1962), for a review and leading references. Later references include (b) A. C. Cope, S. Moon, and P. E. Peterson, *J. Am. Chem. Soc.*, **84**, 1935 (1962), and (c) H. L. Goering, *et al.*, *ibid.*, **83**, 3507, 3511 (1961).

(3) P. S. Wharton, *J. Org. Chem.*, **26**, 4781 (1961); E. J. Corey, R. B. Mitra, and H. Uda, *J. Am. Chem. Soc.*, **85**, 362 (1963).

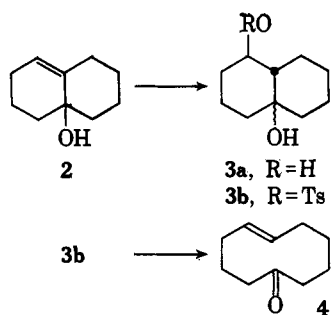
(4) (a) G. O. Schenck and K. Schulte-Elte, *Ann.*, **618**, 185 (1958); (b) S. Dev, *J. Indian Chem. Soc.*, **34**, 121 (1957).

(5) Unpublished work has resulted in the separation of two crystalline *p*-nitrobenzoates of the oily diol mixture in yields of 50 and 20%.

(6) H. C. Brown, *et al.*, *J. Am. Chem. Soc.*, **80**, 1552 (1958); **81**, 6428 (1959); and **84**, 183 (1962).

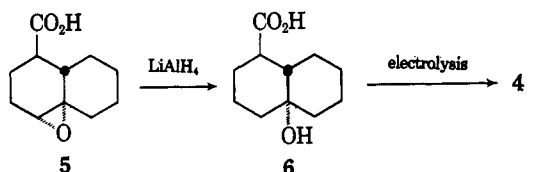
(6) J. L. Ferrari and I. M. Hunsberger, *J. Org. Chem.*, **25**, 485 (1960).

(7) J. L. Ferrari, Ph.D. thesis, Fordham University, 1962.



diols was monotosylated and the crystalline mixture of monotosylates (3b) fragmented by treatment with potassium *t*-butoxide in *t*-butyl alcohol.<sup>7</sup> The distilled product (82% based on diol) was identified as *trans*-5-cyclodecenone from infrared and capillary vapor phase chromatographic data,<sup>8</sup> the latter indicating a purity of 97% and, therefore, 62% over-all yield of 4 from 2. Using literature yields<sup>4a,9</sup> for the preparation of 2 from  $\beta$ -naphthol, it is calculated that 4 is available from  $\beta$ -naphthol by this reported sequence in an over-all yield of 22%.

We also have observed the formation of *trans*-5-cyclodecenone from electrolytic fragmentation of a type commented on recently.<sup>10</sup> Epoxide 5, of established stereochemistry,<sup>11</sup> was reduced to  $\gamma$ -hydroxy acid 6 with lithium aluminum hydride. Fragmentation of 6 was realized under arbitrary (and presumably nonideal) conditions. A methanol solution in a non-



compartmented cell was subjected to 40 volts applied to two immersed platinum electrodes. Short-path distillation of the neutral product yielded a volatile material (80% based on unrecovered acid), the infrared spectrum of which differed little from that of authentic<sup>8</sup> 4. Comparison with the spectrum of authentic *cis*-5-cyclodecenone showed, by the absence of absorption at 14.2  $\mu$ , that an undetectable amount (less than 5%) of the *cis* isomer was present, a result consistent with stereospecificity of the fragmentation and subsequent nonisomerization of the double bond. Assay of 4 in the distillate was effected by capillary v.p.c. (55%) and semicarbazone formation (56%). Several attempts to separate pure 4 from the remaining unidentified multicomponent 45% by chromatography on alumina and silica gel were unsuccessful (lack of separation combined with decomposition on the columns) and were not pursued when the sequence 2  $\rightarrow$  4 was developed.

(7) Cf. R. B. Clayton, H. B. Henbest, and M. Smith, *J. Chem. Soc.*, 1982 (1957).

(8) Authentic samples were generously supplied by Professor H. L. Goering.

(9) W. P. Campbell and C. G. Harris, *J. Am. Chem. Soc.*, **63**, 2721 (1941).

(10) E. J. Corey, *et al.*, *ibid.*, **81**, 1743 (1959); **82**, 2645 (1960).

(11) V. F. Kucherov, *et al.*, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 559 (1956); 367 (1958); 673 (1959); *Chem. Abstr.*, **51**, 1929 (1957); **52**, 12813 (1958); and **54**, 442 (1960).

## Experimental<sup>12</sup>

The published<sup>4a</sup> procedure for the preparation of 2 was modified slightly as recorded herewith.

**10-Hydroperoxy- $\Delta^{1(9)}$ -octalin (1).**<sup>4a</sup>—A mixture of octalins<sup>9</sup> (100 g. of *ca.* 70%  $\Delta^9$ ) in 1000 ml. of isopropyl alcohol containing 5 g. of rose bengal was irradiated with a Hanovia Type L lamp, using a Vycor immersion well and Corex sleeve.<sup>13</sup> By using a diaphragm pump,<sup>14</sup> oxygen was bubbled rapidly through the system while maintaining a closed system, thus enabling gas consumption to be measured volumetrically.<sup>15</sup> The rate of uptake fell from an initial value of 166 to 26 ml. per minute after 2 hr. at which time 11.37 l. (60%) had been absorbed and the reaction was stopped.<sup>16</sup> The solvent was evaporated at room temperature, hexane and Filter Cel added to the residue, and the resulting suspension filtered. Concentration and cooling ( $-20^\circ$ ) of the red hexane solution yielded 24.2 g. (19%) of 1, m.p. 55–59° (lit. m.p. 59–60°).

**$\Delta^{1(9)}$ -10-Octalol (2).**<sup>4a</sup> A.—To a solution of 59.2 g. of 1, m.p. 49–60°, in 300 ml. of refluxing cyclohexene<sup>17</sup> was added dropwise 50 ml. of hydrazine hydrate. Heating was continued until gas evolution ceased. After cooling, the cyclohexene solution was washed well with water and then dried. Evaporation of solvent yielded 52.5 g. (98%) of crude 2, m.p. 70–80° (lit.<sup>4a</sup> 87–88°), crystallization of which from ether at  $-20^\circ$  gave 32.4 g., m.p. 84–85.5°, and further crops from the filtrate.

**B.**—A cyclohexene solution of evaporated mother liquors (*ca.* 210 g.) from crystallization of 1 was similarly reduced with hydrazine hydrate. After removal of the solvent the crude product was distilled at oil pump pressure and unchanged octalins (83 g., b.p. *ca.* 40°) separated from 2 (77 g., b.p. *ca.* 70°). The crude 2 solidified in the receiver, m.p. 41–75°, and could be purified by crystallization from ether or 2-methylbutane at  $-20^\circ$ .

**Hydroboration of  $\Delta^{1(9)}$ -10-Octalol.**—Diborane, generated by dropwise addition of a solution of 34.2 g. (0.90 mole) sodium borohydride in 650 ml. of diglyme to a mixture of 227 ml. (1.8 mole) of boron trifluoride etherate and 100 ml. of diglyme, was passed, with a stream of nitrogen, through a solution of 32.4 g. (0.213 mole) of 2, m.p. 84–85.5°, in 100 ml. of tetrahydrofuran. Sodium hydroxide solution (56 ml. of 3 *N*) was then added dropwise with stirring followed by dropwise addition of 20.5 ml. of 30% hydrogen peroxide with cooling and stirring. After stirring overnight at room temperature, the water layer was saturated with potassium carbonate, separated, and extracted several times with tetrahydrofuran. The combined organic solutions were washed with saturated sodium chloride solution, treated with a small amount of 10% palladium on charcoal, and dried. Evaporation of solvent yielded a residue of 33.6 g. which was distilled, giving 24.7 g. (78%) of an oily mixture of 1,10-decalindiol (3a), b.p. 103° (0.2 mm.).

***trans*-5-Cyclodecenone (4).**—A solution of 0.989 g. (5.8 mmoles) of distilled 3a and 1.438 g. (7.5 mmoles) of tosyl chloride in 10 ml. of dry pyridine was stirred at 0° for 9 hr. Water was added (a small amount followed by excess after 5 min.) and the mixture extracted with ether. The combined ether solutions were extracted with dilute acid, washed with salt solution, and dried. Evaporation of the solvent yielded 2.56 g. of crystalline residue (still containing some solvent), a portion of which, 1.87 g., was dissolved in 45 ml. of *t*-butyl alcohol. To this solution was added 12 ml. of 1 *N* potassium *t*-butoxide in *t*-butyl alcohol and the mixture maintained at 35° for 45 min. (a white precipitate formed immediately after mixing). Addition of water and extraction with ether gave, after further work-up, 0.650 g. of a yellow oil, 0.589 g. of which was subjected to short-path distillation; bath temperature, 45–65° (0.1 mm.); yield, 0.483 g. (82%);

(12) Melting points are uncorrected. Analytical data were recorded using a Perkin-Elmer Infracord spectrophotometer, Model 137, a Cary spectrophotometer, Model 11, and a Perkin-Elmer vapor phase refractometer, Model 154D, with flame ionization detection and disk integration.

(13) Engelhard Hanovia, Inc., Newark, N. J.

(14) Fisher Scientific Co., 1-092-10.

(15) The apparatus was basically the same as described by G. O. Schenck, K. G. Kinkel, and H. J. Mertens, *Ann.*, **584**, 125 (1953), without automatic leveling and recording.

(16)  $\Delta^9$ -Octalin is reported to be oxygenated 25 times as fast as the  $\Delta^{1(9)}$ -octalin, which is also present in the octalin mixture: G. O. Schenck, *Angew. Chem.*, **69**, 579 (1957).

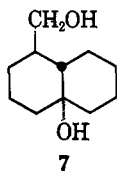
(17) Cyclohexene was used as solvent to prevent the reduction of 2 by any diimide formed; for references to diimide reductions see E. E. van Tamelen and R. J. Timmons, *J. Am. Chem. Soc.*, **84**, 1067 (1962).

$n_D^{25}$  1.4957 (lit.<sup>18</sup> for 4,  $n_D^{25}$  1.4982);  $\lambda_{\max}^{\text{nat}}$  5.88 and 10.2  $\mu$ ; no indication of *cis* isomer at 14.2  $\mu$ . Capillary v.p.c. on a 150-ft. Ucon Polar column at 169° showed 97% of a single component with retention time the same as authentic 4 (20.8 min.), and 3% of a minor component (21.2 min.).

**10 $\alpha$ -Hydroxy-*trans*-decalin-1 $\beta$ -carboxylic Acid (6).**—To a solution of 2.00 g. (10.2 mmoles) of epoxide 5,<sup>11</sup> m.p. 132.5–133.5°, in 50 ml. of ether was added 0.589 g. (15.5 mmoles) of lithium aluminum hydride. Work-up, after stirring for 3 hr. at room temperature, gave 1.42 g. (70%) of crude acid 6, m.p. 119–125°, and 0.546 g. of neutral material. An analytical sample of 6 was obtained from the crude acid after four recrystallizations from chloroform, m.p. 133–134.5°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>16</sub>O<sub>3</sub>: C, 66.67; H, 9.09. Found: C, 66.96; H, 9.39.

Crystallization on a larger scale presented a problem as no satisfactory solvent was found. A single stage, high-yield purification to material of m.p. 127–130° could be effected with ether as solvent but the melting point could not be raised by further crystallization.



7

The neutral fraction yielded analytically pure diol 7, m.p. 114–115°, on crystallization from ether.

*Anal.* Calcd. for C<sub>11</sub>H<sub>20</sub>O<sub>2</sub>: C, 71.74; H, 10.87. Found: C, 71.92; H, 11.06.

**Electrolysis of 6.**—To a 300-ml. beaker fitted with a cold-finger spiral condenser and two platinum electrodes separated by 2–3 mm., each 5 cm.<sup>2</sup>, was added a solution of 4.76 g. of crude<sup>19</sup> 6, m.p. 119–125°, in 150 ml. of boiled methanol. A nitrogen atmosphere was maintained over the solution throughout the electrolysis. Sufficient sodium hydride was added to produce a current of ca. 0.5 amp. at constant applied voltage, 41 v. The current was stopped after the passage of 2.2 times the theoretical amount,<sup>20</sup> the methanol evaporated, and the residue worked up normally. Recovered crystalline 6 amounted to 0.37 g. (7%); the remainder was a neutral oil, 3.37 g. (92%, based on loss of carbon dioxide), which was subjected to short-path distillation. The yield of clear colorless liquid was 2.70 g. (80%); bath temperature, 85–110° (0.3 mm.);  $\lambda_{\max}^{\text{nat}}$  5.88 and 10.2  $\mu$  (no absorption at 14.2  $\mu$ ). V.p.c. of the distilled product (168° on a 150-ft. capillary column with a Ucon Polar coating) showed the presence of the following components<sup>21</sup> (retention time in minutes, area): 1.8, 6%; 18.0, 7%; 22.3, 55%; 25.1, 7%; 39.5, 4%; 54.7, 4%. Treatment of 81 mg. of the distillate with a solution of 65 mg. of semicarbazide hydrochloride and 90 mg. of sodium acetate in 0.8 of ml. water, 20 min. at 70° and 48 hr. at room temperature, gave white crystals of the semicarbazone which were filtered from the solution and dried, 63 mg. (56%), m.p. 176–178°. Recrystallization from acetonitrile raised the m.p. to 182–183° (authentic<sup>8</sup> m.p. 183–184°, m.m.p. 182–183°); ultraviolet spectrum superimposable on that of authentic semicarbazone,  $\lambda_{\max}^{\text{EtOH}}$  232 m $\mu$  ( $\epsilon$  11,000).

(18) E. M. Kosower, W. D. Closson, H. L. Goering, and J. C. Gross, *J. Am. Chem. Soc.*, **83**, 2013 (1961).

(19) Similar results were obtained using purified 6 on a smaller scale.

(20) The approximate quantity of electricity required to give high conversion without overelectrolysing was determined in trial runs.

(21) Numerous minor peaks, each less than 3%, constituted the remaining 17%.

### *cis*- and *trans*-1,2,3-Tricyanocyclopropanes

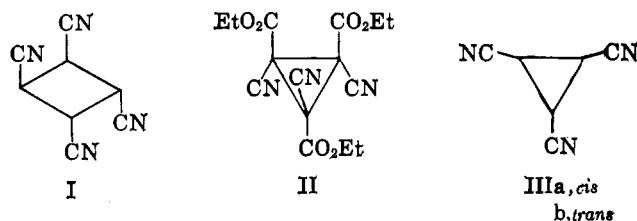
G. W. GRIFFIN AND L. I. PETERSON

Department of Chemistry, Yale University, New Haven, Connecticut  
and Department of Chemistry, Tulane University,  
New Orleans, Louisiana

Received July 8, 1963

In 1958, Sadeh and Berger<sup>1</sup> reportedly obtained tetracyanocyclobutane (I) while attempting to synthe-

size ethyl cyanoacetoxycetate from ethyl bromocyanacetate and potassium acetate. The properties of their product were in no way similar to those of the solid state photodimer of fumaronitrile which we have shown has structure I.<sup>2</sup> However, it did not appear unreasonable that Sadeh and Berger's product might actually be the "all-*trans*" isomer of I in view of the possibility for thermodynamic equilibration under the reaction conditions. A structure proof was, therefore, undertaken.



An initial literature survey revealed that, in 1900, Errera and Perciabosco<sup>3</sup> had obtained *trans*-1,2,3-tricyano-1,2,3-tricarboethoxycyclopropane (II)<sup>4</sup> on treating the anion of ethyl cyanoacetate with bromine. Subsequent hydrolysis of II with cold, dilute barium hydroxide afforded small amounts of a substance whose elemental analysis was consistent with that expected for a 1,2,3-tricyanocyclopropane (III). In view of the similarity of the reaction conditions and reagents employed by the two groups, it seemed reasonable that Sadeh and Berger's product, in reality, might be either *cis*- or *trans*-1,2,3-tricyanocyclopropane.

Preliminary investigations on a sample of Sadeh and Berger's nitrile<sup>5</sup> indicated that indeed it was a 1,2,3-tricyanocyclopropane and not a tetracyanocyclobutane. The infrared spectrum of the nitrile has a strong absorption band at 3063 cm.<sup>-1</sup> which may be attributed to the cyclopropyl C–H stretching<sup>6</sup> as well as a doublet at 2261 and 2278 cm.<sup>-1</sup> in the characteristic region for nitriles.<sup>6</sup> Hydrolysis with aqueous sodium hydroxide and subsequent esterification with diazomethane provided a material whose infrared and n.m.r. spectra are identical to those of an authentic sample of *trans*-1,2,3-tricarboethoxycyclopropane.<sup>7</sup> The stereochemistry of the original nitrile, of course, cannot be inferred from these results.

It is noteworthy, that in our attempts to reproduce Sadeh and Berger's experiments, we obtained not one but two products (in a 1.2:1 ratio) which could be separated by chromatography on neutral alumina. Although infrared spectra of the two compounds possessed features in common, they were not identical. The major product (m.p. 201°) was identical in all respects with Sadeh and Berger's nitrile. The elemental analyses and ebullioscopic molecular weight determina-

(1) T. Sadeh and A. Berger, *Bull. Res. Council Israel*, **7A**, 98 (1958).

(2) G. W. Griffin, J. E. Basinski, and L. I. Peterson, *J. Am. Chem. Soc.*, **84**, 1012 (1962).

(3) G. Errera and F. Perciabosco, *Chem. Ber.*, **33**, 2976 (1900).

(4) The infrared and n.m.r. spectra of II confirm Errera and Perciabosco's structural assignment. The stereochemistry was clearly established as *trans* from the n.m.r. spectrum which shows two equivalent and one non-equivalent ethyl groups.

(5) We wish to thank Dr. T. Sadeh for samples of his nitrile (*cis*-1,2,3-tricyanocyclopropane) and *trans*-1,2,3-tricarboethoxy-1,2,3-tricyanocyclopropane for purposes of comparison.

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

(7) Prepared according to the method of E. Buchner, *Chem. Ber.*, **21**, 2637 (1888).