the partial and total quantum yield profiles shown in Figure 6. The decrease in the quantum yield for the triplet reaction relates to the continual decrease in the intersystem crossing efficiency of fluorenone as the bimolecular complex formation reaction becomes more efficient at higher ketenimine concentrations (eq 13), while the quantum yield for the singlet reaction is expected to linearly increase toward the limiting value of ~0.60. Thus, the quantum yield for the total reaction ($1/\Phi_{\mathrm{total}} = 1/[\Phi_{\mathrm{singlet}} + \Phi_{\mathrm{triplet}}]$) *should not decrease* at the higher ketenimine concentrations.

At this time, we can only speculate on an additional deactivation process that is second order in ketenimine and which may be described by step 5a. When incorporated into eq 12, the kinetic expression for the quantum yield of the singlet reaction becomes

$$1/\Phi_{\mathrm{singlet}} = 1/n' + [k_{\mathrm{d^I}} + k_{\mathrm{e}} + k_{\mathrm{x}} + k_{\mathrm{q^I}}(\mathrm{Q})]/[n'k_{\mathrm{c}}(\mathrm{K})]$$

where $n' = k_{\mathrm{r^I}}/[k_{\mathrm{r^I}} + k_{\mathrm{d^{II}}} + k_{\mathrm{K}}(\mathrm{K})]$ and would lead to a decrease in the quantum yield for the singlet reaction at higher ketenimine concentration as is observed in Figure 4. If step 5a proceeds at the diffusion limit,

$$[\mathrm{complex}]^* + \mathrm{K} \xrightarrow{k_{\mathrm{K}}} \mathrm{F} + 2\mathrm{K} \qquad (5a)$$

$k_{\mathrm{r^I}}$ must be approximately an order of magnitude less than the diffusion limit in order for this deactivation step to be significant. Further work directed toward clarifying this picture is in progress.

Experimental Section

Materials. Dimethyl-N-(cyclohexyl)ketenimine was prepared as previously described.[8] Di-*t*-butylnitroxide was prepared as described by Hoffman and coworkers.[10] The material, purified by distillation through a spinning-band column, gave an extinction coefficient at 465 mμ in excellent agreement with that reported. Benzene (Mallinckrodt, thiophene free) was distilled through a 2-ft glass column packed with glass beads and a center cut was collected. Benzophenone (Matheson Coleman and Bell), fluorenone (Aldrich), and benzhydrol (Eastman) were recrystallized from ether–petroleum ether (bp 30–60°) prior to use.

Kinetic Measurements. All kinetic measurements were made at room temperature on a rotating photochemical assembly as previously described:[8] The light from a 450-W Hanovia lamp was filtered through Corning 7-39 filters. Actinometry was by the benzophenone–benzhydrol system (0.10 *M* benzophenone–1.0 *M* benzhydrol, $\Phi = 0.97$).[13]

Emission Spectra. The instrument employed a xenon light source monochromated to the desired exciting wavelength with an American Instrument Co., Inc. monochromator, Model 4-8400. An identical monochromator, placed at 90° and motorized for continuous scan, picked up the emitted light. The photocurrent from an IP-21 phototube was displayed on an American Instrument Co., Inc. Microphotometer, Model 10-213, and the data were collected with a pen recorder.

All emission spectra were taken at room temperature by irradiating degassed and sealed precision bore square Pyrex ampoules. The Stern–Volmer plots of the quenching of the fluorenone emission by DTBN and the ketenimines in benzene were done on solutions containing 0.1 *M* fluorenone. The exciting light was a narrow band centered at 4000 Å. The pen response near the emission peak was noted after ascertaining that no change in peak shape or position occurred at different concentrations of quencher. Periodic measurements on a standard indicated excellent reproducibility of the pen response throughout the experiments.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, for a grant, No. 2894-A4, in support of this work.

Aromatic Molecules Bearing Substituents within the Cavity of the π-Electron Cloud. Optical Resolution and Thermal Rearrangement Studies[1,2]

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Abstract: *trans*-15,16-Dimethyldihydropyrene (**1**) undergoes a thermal rearrangement at around 200° giving *trans*-13,15-dimethyldihydropyrene (**2**). The structure of **2** has been established from its spectral and chemical properties. The preparation and optical resolution of 4-carboxy-*trans*-15,16-dimethyldihydropyrene (**18**) has been accomplished. When **18** was subjected to a thermal rearrangement and the reaction was stopped at approximately 50% of completion, the unrearranged **18** showed no loss of optical activity, demonstrating that there is no interchange of the interior methyl groups occurring prior to the thermal rearrangement of a methyl group out to the exterior.

Previously, we have described the preparations of *trans*-15,16-dimethyldihydropyrene (**1**)[3] and have reported on certain of its chemical properties.[4] One of the properties of **1** not discussed in the previous report, though, is the instability of **1** toward heat. When **1** is placed in an evacuated melting point tube, the deep emerald green crystals melt without decomposition at 119–120°. But, if the temperature is raised, a rapid transition occurs at around 200–210° in which the green color of the solution turns a pale yellow. The ultraviolet absorption spectrum of the product closely resembles that of pyrene and our first assumption was that the interior methyl groups had simply been ex-

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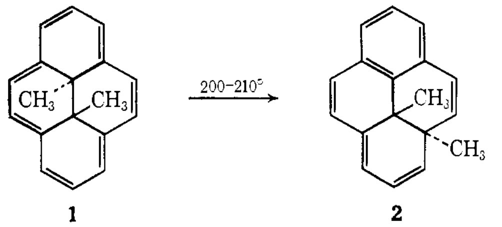
(1) We express our appreciation to the National Science Foundation for their support of this work.

(2) For the preceding communication in this series, see V. Boekelheide and T. Miyasaka, *J. Am. Chem. Soc.*, **89**, 1709 (1967).

(3) V. Boekelheide and J. B. Phillips, *ibid.*, **89**, 1695 (1967).

(4) J. B. Phillips, R. J. Molyneux, E. Sturm, and V. Boekelheide, *ibid.*, **89**, 1704 (1967).

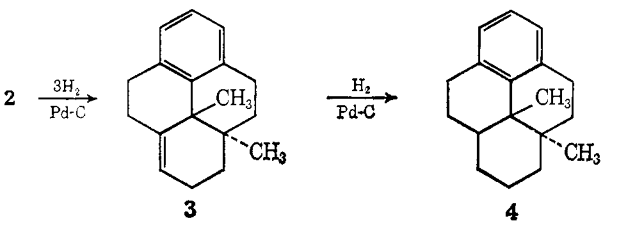
pelled. However, when the experiment was repeated and the reaction tube was broken in an evacuated line joined to a mass spectrometer, it was found that the amount of methane and ethane combined was less than would be expected from 2% of the starting material had the reaction proceeded in this fashion. In a separate experiment the contents of a tube were collected and recrystallized to give, in high yield, pale yellow platelets, mp 56–57°. We now present the evidence leading to an assignment of structure **2** to this thermal rearrangement product.



1 **2**

First of all, elemental analysis proved that the thermal rearrangement product was isomeric with the starting material, **1**. Next, it was clear that the thermal rearrangement had caused loss of the dihydropyrene system, both from the disappearance of the typical emerald green color and the absence of the high-field signal at τ 14.25 observed for the internal methyls of **1**. Instead, the thermal rearrangement product shows a series of absorption bands in the ultraviolet at 382 mμ (ϵ 5540), 368 (5210), 320 (4250), 306 (5300), 293 (4210), 272 (16,450), 260 (22,600), and 251 (23,100); its nmr spectrum exhibits a multiplet centered at τ 3.10 (3 H, ArH), a complex multiplet at 3.55–4.30 (7 H, $-CH{=}C-$), a singlet at 8.63 (3 H, $-CH_3$), and a singlet at 8.87 (3 H, $-CH_3$). Of the structures readily derivable from **1**, the only logical one that would fulfill these spectral requirements is **2**.

The thermal rearrangement product was then subjected to catalytic hydrogenation to determine whether it contained the olefinic unsaturation required by structure **2**. Hydrogenation over a 30% palladium-on-charcoal catalyst in methanol at room temperature and atmospheric pressure led to a rapid uptake of 3 mol of hydrogen. The resultant product has been assigned structure **3** based on its spectral properties. In particular, its nmr spectrum still shows a signal for the three aromatic protons at τ 3.20 but only one vinyl proton at 4.50. The mass spectrum of **3** has the expected parent molecular ion at 238 and the ultraviolet spectrum is in keeping with an alkyl-substituted benzene rather than a styrene. These data are fully in accord with **3** and presumably the reluctance to hydrogenation of the remaining double bond is caused by the steric hindrance of the methyl groups on both sides of the ring.

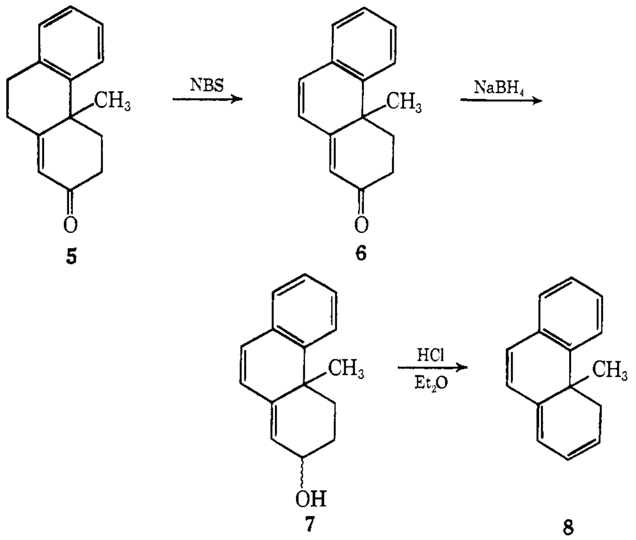


3 **4**

However, when the catalytic hydrogenation of **2** was carried out as before but allowing the reaction to proceed for 15 hr, 4 mol of hydrogen was absorbed saturating all of the olefinic bonds. In accord with structure **4** the product showed only aromatic and saturated protons in its nmr spectrum, and its molecular weight from mass spectral data was 240.

Solution of **1** in trifluoroacetic acid gives a stable carbonium ion whose spectrum has been described.[4] Solution of **2** in trifluoroacetic acid likewise gives a stable carbonium ion but of different spectral properties. Dilution with water led to recovery of **2** with no evidence for an acid-catalyzed rearrangement back to **1** or on to other products.

To provide further support for the conclusions from spectral data a series of model compounds were prepared. The commercially available ketone **5** was treated with N-bromosuccinimide, effecting direct conversion to the dienone **6**.[5] Reduction of **6** with sodium borohydride then gave a diastereoisomeric mixture of alcohols (**7**) which, on treatment with hydrogen chloride in ether, readily yielded the triene **8**.



5 **6** **7** **8**

The structure of **8** follows from its method of synthesis and is supported by elemental analyses and spectral data. The triene **8** has all of the structural features of **2** except the vinyl bridge between the 4 and 5 positions and the angular methyl group at the 5 position. A comparison of its ultraviolet absorption spectrum (maxima at 376 mμ (ϵ 7620), 358 (11,000), 345 (8900), 261 (16,100), 252 (18,500), and 247 (14,700)) with that of **2** shows a close similarity with a small shift to longer wavelengths for **2** as would be expected in view of its more highly substituted chromophore. The signal for the angular methyl of **8** appears at τ 8.90, in very close correspondence to that of the interior methyl of **2** which is observed at τ 8.87. The triene system of **8** would be expected to be less sterically hindered than that of **2** and, in fact, **8** readily absorbs 3 mol of hydrogen. Thus, our assignment of structure **2** is strengthened by the

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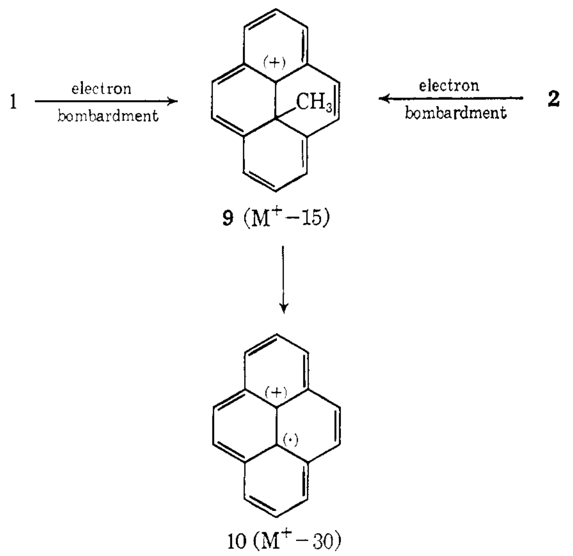
(5) The dienone **6** has been synthesized previously by a different procedure (E. Wenkert and T. E. Stevens, *J. Am. Chem. Soc.*, **78**, 2318 (1956)) and our product was shown to be identical by direct comparison with an authentic sample. We thank Professor Wenkert for his kindness in providing us with this sample.

close correspondence in physical properties and chemical behavior of the analogous compound **8**.

Initially, it had been our plan to utilize **8** in an unambiguous synthesis of **2**. However, thus far, attempts to elaborate **8** further have been fruitless.

The remaining, and probably the most conclusive, evidence provided for the structure of **2** is that from mass spectral studies. The mass spectrum of **1** exhibits a small signal for the parent molecular ion (*m/e* 232), a much stronger signal at $M^+ - 15$, and a still stronger signal at $M^+ - 30$. This has been interpreted as a decay of the parent molecular ion to a new ion (**9**) with expulsion of a methyl radical. Subsequent expulsion of a second methyl radical then gives the $M^+ - 30$ ion (*m/e* 202) which corresponds to the parent molecular ion of pyrene (**10**). In accord with this interpretation the fragmentation pattern below the 202 signal is the same as for pyrene.



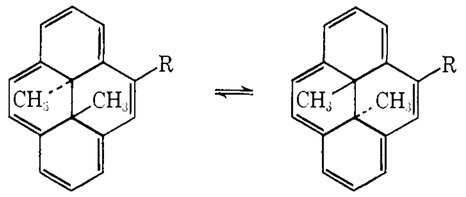
9 (M^+−15)

10 (M^+−30)

It is apparent that the parent molecular ion of **2** can undergo expulsion of a methyl radical to give the same ion **9** which, in turn, would go on to **10** and a further fragmentation similar to pyrene. The mass spectra of **1** and **2** were measured using direct introduction at room temperature to the ion source to avoid the possibility of thermal rearrangement of **1**. It was found that the two spectra were essentially identical, a result predictable for and in accord with structure **2**.

The ease with which **1** undergoes carbon–carbon bond fission thermally is rather surprising. There are two obvious reaction pathways for the conversion of **1** to **2**. A direct 1,3 migration of a methyl group could be involved, or two successive 1,2-methyl shifts would likewise yield **2**.[5a] Experimentally, the task of distinguishing between these two possibilities seems formidable. Although 1,2-methyl shifts under the influence of acid catalysis are well known, it is not obvious that a similar mechanism would be appropriate to thermal rearrangements in neutral solution or in the absence of solvent.

Examination of molecular models of **1**, based on the X-ray crystallographic study of Hanson,[6] shows that the interior methyl attached to carbon 15 is directly over and in good position to enter into bonding with carbon 16. The same is true, of course, in a reverse sense for the methyl attached to carbon 16. Since relatively little is known about the special features of substituent groups within the cavity of an aromatic π cloud and since other studies had suggested the possibility of an unusual degree of methyl hyperconjugation for the interior methyls of **1**,[7] it seemed necessary to consider the possibility that, as the temperature required for thermal rearrangement was approached, the interior methyl groups might rapidly exchange the carbons to which they were attached. Such an exchange is illustrated by the hypothetical equilibrium between structures **11** and **12**.



11 12

With a substituent other than hydrogen present at an unsymmetrical position, such as that shown in **11** and **12**, the two structures are related as object and mirror image. Thus, one possibility for exploring the possible exchange of interior methyl groups was to prepare an optically active derivative such as **11** and see whether it would undergo thermal racemization. We were encouraged to undertake the preparation of such an optically active derivative, since it would be the first example of an optical resolution involving this type of molecular asymmetry and also such optically active derivatives could be useful for other types of mechanistic studies.

One of the problems, though, was the necessity that the substituent be placed at an unsymmetrical position. Direct electrophilic substitution of *trans*-15,16-dimethyldihydropyrene (**1**) places substituents at the 2 and 7 positions, with only minor amounts of 4-substituted derivatives being formed. Thus, a synthetically useful method for preparing a 4-substituted derivatives such as **11** seemed most feasible if introduction of the substituent occurred at an earlier stage. In previous studies on the dehydrogenation of the bisdienone **13** with N-bromosuccinimide,[3] it had been observed that in instances where excess N-bromosuccinimide had been employed that 4-bromo-*trans*-15,16-dimethyldihydropyrene-2,7-quinone (**14**) was a by-product. By a careful reexamination of this reaction it was found that, using 3 mol of N-bromosuccinimide and a more concentrated solution, the yield of **14** could be raised to about 50%.

Presumably, the success of this procedure is due to the fact that bromination on a carbon atom adjacent to one already holding bromine occurs faster than dehydrobromination. That the reaction does not proceed through the quinone **15**, as an intermediate, was established by

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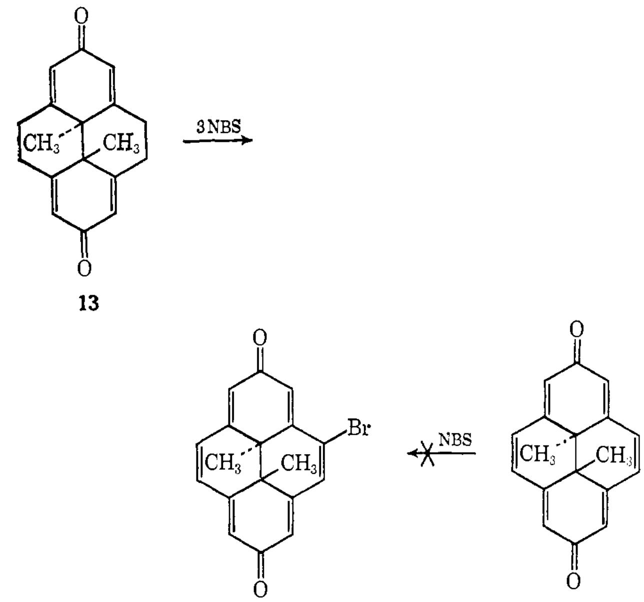
(5a) Note Added in Proof. In this case a 1,3-methyl migration is better described as a 1,5-sigmatropic rearrangement.

(6) A. W. Hanson, *Acta Cryst.*, **18**, 599 (1965).

(7) F. Gerson, E. Heilbronner, and V. Boekelheide, *Helv. Chim. Acta*, **47**, 1123 (1964).



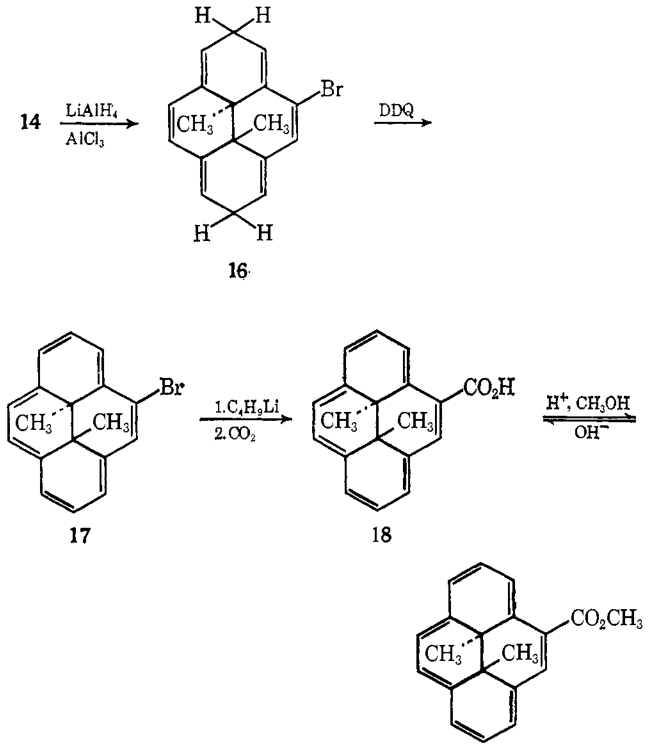
13

14

15

an experiment in which it was shown that **15** does not react with N-bromosuccinimide.

The subsequent steps were patterned after our previous syntheses.[2,3] Reduction of **14** with a mixture of lithium aluminum hydride and aluminum chloride gave the bistriene **16** which, on direct dehydrogenation with 2,3-dichloro-5,6-dicyanoquinone, gave 4-bromo-*trans*-15,16-dimethyldihydropyrene (**17**) in 51% yield. Treatment of **17** with *n*-butyllithium followed by carbonation then gave 4-carboxy-*trans*-15,16-dimethyldihydropyrene (**18**) in 78% yield. For ease of isolation and purification, **18** was converted to its methyl ester **19** and then recovered as the acid **18** through basic hydrolysis.



16

17

18

19

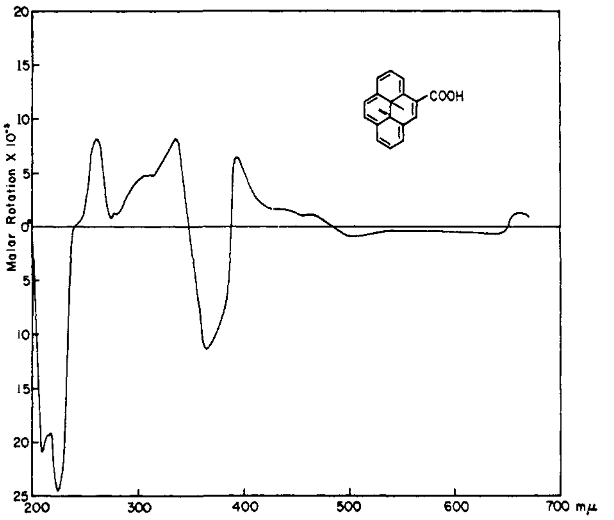


Figure 1. Optical rotatory dispersion curve of the pure enantiomorph of 4-carboxy-*trans*-15,16-dimethyldihydropyrene (**18**) in ethanol.

Optical resolution of **18** was accomplished through fractional crystallization of the cinchonidine salt of **18**. One of the diastereoisomers of the cinchonidine salt of **18** was obtained as sharp-melting, deep green crystals, and recovery of **18** from these crystals gave one of the enantiomorphs in a pure state. Its optical rotatory dispersion curve is presented in Figure 1. A Cotton effect is apparent for each of the five absorption bands starting at 653 mμ in the visible. The values for the molar rotations are surprisingly high ranging from 1200 at 663 mμ to 24,480 at 225 mμ. The other enantiomorph was recovered from the mother liquors of the fractional crystallization experiments and, although not completely pure, it gave an optical rotatory dispersion curve that was essentially a mirror image of the curve in Figure 1.

To test the question of a possible thermally induced racemization of the type illustrated by **11** and **12** was now relatively simple. It could be shown that **18** undergoes a thermal rearrangement similar to that exhibited by **1**, although in the case of **18** four different isomeric rearrangement products of the type shown by **20** are possible and all appear to be formed. Since **18** shows absorption bands in the visible, where the thermal rearrangement products do not absorb, examination of both the absorption and optical rotatory dispersion spectra of solutions of **18** prior to and after heating allow a direct determination of the extent of thermal rearrangement and the extent, if any, of thermal racemization. A solution of optically active **18** in ethanol in an evacuated sealed tube was heated at 180° for 10 min. From the change in extinction coefficients of the visible absorption bands, it was ascertained that a thermal rearrangement had occurred with 47% of **18** still remaining. The optical rotatory dispersion curve of the visible portion of the spectrum for this solution was then taken and it was found to correspond exactly in over-all shape to the original curve with a decrease in the specific rotation of the various peaks and troughs that, within experimental error, was 53%.[8] Thus, the

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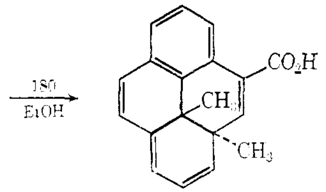
[8] We are indebted to Dr. Thomas Hooker for the optical rotatory dispersion measurements.

evidence is conclusive that no thermal racemization of the type shown by **11** and **12** occurs even at temperatures effecting thermal rearrangement.

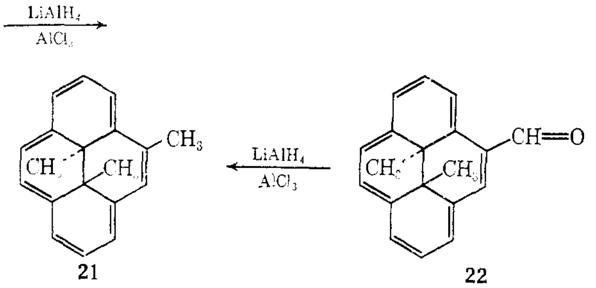
18



20

Since **1** shows very little absorption in the ultraviolet below 337 mμ, it seemed probable that the strong Cotton effect observed at 225 mμ with optically active **18** was related to the carboxylic acid chromophore. To test this, optically active **18** was subjected to reduction with a lithium aluminum hydride–aluminum chloride mixture to convert the carboxylic acid function to a methyl group. Surprisingly, the resulting product, **21**, showed a strong Cotton effect in this same region, indicating the presence of a weak absorption band of high specific rotation.

18



21 **22**

For purposes of correlation racemic **21** was prepared in an independent fashion. Careful examination of the formylation of **1** by the Rieche procedure revealed that, in addition to the main product, 2-formyl-15,16-dimethyldihydropyrene, as reported before,[4] there could also be isolated the 4-formyl derivative (**22**) in 18% yield. Reduction of **22** with a lithium aluminum hydride–aluminum chloride mixture gave racemic **21** whose spectral properties in solution were identical in all respects with those of the specimen of **21** obtained from optically active **18**.

Experimental Section[9]

Thermal Rearrangement of *trans*-15,16-Dimethyldihydropyrene (1) to *trans*-13,15-Dimethyldihydropyrene (2). An evacuated sealed tube containing 110 mg of **1** was heated at 210° in an oil bath until the green color of the molten mass disappeared (5–6 min). The tube was then cooled and opened and the contents dissolved in a 20:1 pentane–ether mixture. Chromatography of the solution over alumina (Woelm, activity 1) gave one main eluate fraction. After concentration, the oily residue of 88 mg (80%) crystallized. Recrystallization from a methanol–water mixture yielded pale yellow platelets: mp 56–57°; uv $\lambda_{\max}^{n\text{-hexane}}$ 251 mμ (ε 23,100), 260 (22,600), 272 (16,450), 293 (4210), 306 (5300), 320 (4250), 368 (5210), 382 (5540), and 402 (sh, 3530); nmr (CCl$_4$), multiplet at τ 3.10 (3 H, Ar*H*), multiplet at 3.55–4.30 (7 H, -C*H*=C-), singlet at 8.63 (3 H, -C*H*$_3$), and a singlet at 8.87 (3 H, -C*H*$_3$); mass spectrum, *m/e* at 232 with much stronger signals at 217 and 202.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.30; H, 6.97.

Hydrogenation of *trans*-13,15-Dimethyldihydropyrene (2). A. To the Hexahydro Derivative 3. A mixture of 93 mg of **2** and 100 mg of a 30% palladium-on-charcoal catalyst in 20 ml of methanol was subjected to hydrogenation at room temperature and atmospheric pressure. Absorption of 3 mol of hydrogen was complete in 3 min. After removal of the catalyst and solvent, the residual oil was taken up in carbon tetrachloride and chromatographed over alumina (Woelm, activity 1). The main eluate fraction gave 82 mg of a colorless oil: nmr (CCl$_4$), multiplet at τ 3.20 (3 H, Ar*H*), broad signal (1 H, -C*H*=C-), multiplet at 6.70–8.60 (12 H, -C*H*$_2$-), singlet at 8.76 (3 H, -C*H*$_3$), and a singlet at 9.38 (3 H, -C*H*$_3$); mass spectrum, *m/e* 238. An analytical sample was prepared by vapor phase chromatography using a 20% SE 30 on chromsorb column, retention time 10.5 min.

Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.28; H, 9.30.

B. To the Octahydro Derivative 4. A mixture of 80 mg of **2** and 100 mg of a 30% palladium-on-charcoal catalyst in 20 ml of methanol was subjected to hydrogenation at atmospheric pressure and room temperature for 15 hr. After removal of the catalyst and solvent, the residual oil was taken up in carbon tetrachloride and chromatographed over alumina (Woelm, activity 1). The main eluate fraction gave 80 mg of a colorless oil; nmr (CCl$_4$), multiplet at τ 3.25 (3 H, Ar*H*), broad multiplet at 7.15 (4 H, ArC*H*$_2$), a complex multiplet at 7.8–9.3 (11 H, -C*H*$_2$-), a singlet at 8.97 (3 H, -C*H*$_3$), and a singlet at 9.14 (3 H, -C*H*$_3$); mass spectrum, *m/e* 240. An analytical sample was prepared by vapor phase chromatography as described in A but with the retention time being 12 min.

Anal. Calcd for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 89.65; H, 9.89.

Reaction of *trans*-13,15-Dimethyldihydropyrene (2) with Trifluoroacetic Acid. A solution of 25 mg of **2** in trifluoroacetic acid showed the following spectra: uv, $\lambda_{\max}$ 360 mμ (ε 3700) and 460 (21,300); nmr, doublet at τ 0.96 (1 H, *J* = 8 cps), multiplet at 1.80–2.65 (6 H), doublets at 3.15 (1 H, *J* = 10 cps) and 3.80 (1 H, *J* = 10 cps), multiplet at 6.90 (2 H), and singlets at 8.18 (3 H, -C*H*$_3$) and 9.03 (3 H, -C*H*$_3$). Dilution with water led to recovery of **2** in good yield.

7-Keto-13-methyl-5,6,7,13-tetrahydrophenanthrene (6). A mixture of 1.0 g of **5** (Aldrich Chemical Co.), 850 mg of N-bromosuccinimide, and a trace of azobisisobutyronitrile in 200 ml of carbon tetrachloride was boiled under reflux for 4 hr. After removal of the succinimide by filtration, the filtrate was concentrated. The residual yellow oil was taken up in methylene chloride and chromatographed over alumina (Woelm, activity 2). The main eluate fraction gave 895 mg of a yellow oil which crystallized in the cold. Recrystallization from petroleum ether (bp 30–60°) yielded pale yellow prisms, mp 67–68°. However, when the supersaturated solution was seeded with an authentic specimen from Professor Wenkert,[5] there formed long needles, mp 97.0–97.5°. The spectral properties of **6** were identical with those found for the authentic sample and as reported by Wenkert.[5]

5,13-Dihydro-13-methylphenanthrene (8). A solution of 470 mg of **6** and 100 mg of sodium borohydride in 60 ml of methanol was stirred at 0° for 5 hr. The solution was then concentrated to a small volume and water was added. After extraction of the milky suspension with methylene chloride, the methylene chloride extract was washed with water, dried, and concentrated. This gave 440 mg (90%) of a clear, gummy oil; ir, ν_{Nujol} 3410 cm^{-1} (-O*H*); nmr (CDCl$_3$), multiplet at τ 2.85 (4 H, Ar*H*), doublets at 3.65 (1 H, -C*H*=C, *J* = 10 cps) and 3.85 (1 H, -C*H*=C-, *J* = 10 cps), broad signal at 4.45 (1 H, -C*H*=C-), broad signal at 5.62 (1 H, -C*H*OH-), multiplet at 7.60–8.20 (5 H, -C*H*$_2$- and -O*H*), and a singlet at 8.67 (3 H, -C*H*$_3$). This oil could not be crystallized and is presumably a mixture of the two diastereoisomers corresponding to **7**. It was, therefore, dissolved directly in 100 ml of absolute ether previously saturated with dry hydrogen chloride and allowed to stand at 0° for 24 hr. The solution was then boiled under reflux briefly to expel hydrogen chloride before being washed successively with water, aqueous sodium bicarbonate solution, and water. After the ether solution had been dried, it was concentrated to give a yellow oil. This was taken up in a 2:1 pentane–ether mixture and chromato-

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[9] Analyses by Microtech Laboratories and A. Bernhardt Microanalytical Laboratories. Ultraviolet and visible spectra were measured with a Cary Model 15, infrared spectra with a Beckman IR-5, nmr spectra with a Varian A-60, and optical rotatory dispersion spectra with a Cary Model 60. Mass spectra were determined by the Morgan and Schaffer Corp. We thank the National Science Foundation for funds for the purchase of the Varian A-60.

graphed over alumina (Woelm, activity 1). The main eluate fraction was concentrated under nitrogen and the residual yellow oil was distilled in a short-path still at 90–100° (0.05 mm). This gave 220 mg of a fragrant, pale yellow oil: uv, $\lambda_{\max}^{\text{cyclohexane}}$ 247 mμ (sh, ε 14,700), 252 (18,500), 261 (16,100), 345 (sh, 8900), 358 (11,000), 376 (7620); nmr ($CDCl_3$), multiplet at τ 2.90 (4 H, Ar*H*), doublets at 3.70 (1 H, –C*H*=C*H*–, *J* = 10 cps) and 3.82 (1 H, –C*H*=C*H*–, *J* = 10 cps), multiplet at 4.20 (3 H, –C*H*=), doublet at 7.26 (2 H, $-CH_2-$), and a singlet at 8.90 (3 H, $-CH_3$). The oil was unstable and prone to react with oxygen.

Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.03; H, 7.64.

Hydrogenation of 5,13-Dihydro-13-methylphenanthrene (8). A mixture of 184 mg of **8** and 100 mg of a 30% palladium-on-charcoal catalyst in 20 ml of methanol was subjected to hydrogenation at room temperature and atmospheric pressure. Hydrogen uptake corresponding to 3 mol of hydrogen was complete in 30 min. After removal of the catalyst and solvent, the residual oil was taken up in ether and chromatographed over alumina (Woelm, activity 1). After concentration of the main eluate fraction the residue was subjected to short-path distillation at 70° (0.05 mm), giving 175 mg of a colorless oil: nmr ($CDCl_3$), multiplet at τ 2.9 (4 H, Ar*H*), multiplet at 7.2 (2 H, $ArCH_2-$), broad multiplet at 7.6–8.8 (11 H, $-CH_2-$), and a singlet at 8.95 (3 H, $-CH_3$); mass spectrum, *m/e* 200.

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 90.39; H, 9.62.

4-Bromo-*trans*-15,16-dimethyldihydropyrene-2,7-quinone (14). A mixture of 1.435 g of **13**,[3] 2.40 g of N-bromosuccinimide, and 20 mg of azobisisobutyronitrile in 450 ml of carbon tetrachloride was boiled under reflux for 4 hr. Reaction began within 5 min and the solution turned from orange-red to a reddish brown as free bromine became evident. At the end of the period of heating, the solution was much lighter and hydrogen bromide was no longer being evolved. After the solution had been concentrated, the residue was taken up in chloroform and passed over a short column of alumina (Woelm, activity 3) to remove succinimide and tar. Concentration of the eluate yielded 1.58 g of a crude mixture of quinones, **14** and **15**. This was dissolved in methylene chloride and carefully chromatographed over alumina (Woelm, activity 2). A series of eluate fractions were collected which gave first 870 mg (50%) of **14**, then 68 mg of a mixture of **14** and **15**, and finally 700 mg (47%) of the unsubstituted quinone, **15**. The sample of **14** was contaminated with a small amount of dibromoquinones and to effect their removal repeated chromatography over alumina was carried out, eventually yielding 605 mg (33%) of pure **14**. This, after recrystallization from petroleum ether (bp 65–110°), gave yellow crystals: mp 240–245° dec; ir, $\nu_{\max}^{CHCl_3}$ 1610 and 1630 cm^{-1} (–C=O); nmr ($CDCl_3$), singlet at τ 3.17 (1 H), doublet at 3.40 (2 H), singlet at 3.60 (2 H), multiplet at 3.85 (3 H), and a singlet at 8.13 (6 H).

Anal. Calcd for $C_{18}H_{13}BrO_2$: C, 63.34; H, 3.81. Found: C, 63.01; H, 3.60.

4-Bromo-*trans*-15,16-dimethyldihydropyrene (17). A solution of 3.0 g of lithium aluminum hydride and 10.5 g of aluminum chloride in 180 ml of ether was cooled to −78°, and a solution of 600 mg of **14** in 20 ml of benzene and 400 ml of ether was added dropwise with stirring over a period of 4 hr. The reaction mixture was then allowed to warm to room temperature with stirring and to stand overnight. The excess lithium aluminum hydride was destroyed by adding ethyl acetate and then water. The green ether extract was separated, washed with water, dried, and concentrated. The nmr spectrum of the residue indicated it was mostly the bistriene **16** but with some **17** already present. Rather than attempt a separation, the mixture was dissolved in 150 ml of benzene containing 500 mg of 2,3-dichloro-5,6-dicyanoquinone and stirred at room temperature for 10 hr. The dark brown solution was then filtered through a Florisil column. Concentration of the green eluate fraction gave almost pure **17**. This was taken up in a 20:1 pentane–ether mixture and chromatographed over alumina (Woelm, activity 1). The main eluate fraction gave 281 mg (51%) of green crystals, mp 123–125°. A sample recrystallized from aqueous methanol yielded long green needles: mp 124–126°; uv, $\lambda_{\max}^{\text{cyclohexane}}$ 342 mμ (ε 89,000), 356 (24,400), 382 (47,800), 431 (sh, 4660), 454 (6270), 470 (6700), 531 (85), 539 (75), 582 (sh, 118), 589 (sh, 135), 601 (175), 614 (244), 630 (sh, 290), 638 (sh, 325), and 644 (488); nmr ($CDCl_3$), multiplet at τ 1.05–2.05 (9 H, Ar*H*), and a singlet showing incipient splitting at 14.15 (6 H, $-CH_3$).

Anal. Calcd for $C_{18}H_{15}Br$: C, 69.47; H, 4.86; Br, 25.68; mol wt, 311. Found: C, 68.87; H, 4.73; Br, 25.72; mol wt (vapor phase osmometric), 307.

4-Carboxy-*trans*-15,16-dimethyldihydropyrene (18). To a solution of 230 mg of **17** in 75 ml of ether held at −40° under a nitrogen atmosphere there was added through a syringe 3.0 ml of a 1.6 *N* solution of *n*-butyllithium in hexane. After the mixture had been stirred at −40° for 1 hr, it was added to a suspension of Dry Ice in ether at −78°. After the mixture had warmed to room temperature, it was shaken twice with 200-ml portions of an aqueous 10% solution of sodium carbonate. The combined aqueous extracts were acidified with dilute sulfuric acid and extracted with ether. The ether extract was washed with water, dried, and concentrated, leaving 160 mg (78%) of a green-black solid. Since chromatography did not seem practical with the acid, the green-black solid was dissolved in a mixture of 50 ml of methanol and 200 ml of ether to which an excess of an ethereal diazomethane solution was added. After the solution had been allowed to stand at room temperature for 2 hr, it was concentrated under reduced pressure. The residual green oil was taken up in a 20:1 pentane–ether mixture and chromatographed over alumina (Woelm, activity 1). From the main eluate fraction there was isolated 165 mg of a green gum which showed no tendency to crystallize. Its spectral properties (ir, $\nu_{\max}^{CHCl_3}$ 1705 cm^{-1} (C=O); nmr ($CDCl_3$), doublet at τ 0.14 (1 H, Ar*H*), singlet at 0.65 (1 H, Ar*H*), multiplet at 1.18–2.0 (7 H, Ar*H*), singlets at 5.82 (3 H, $-OCH_3$) and 14.14 (6 H, $-CH_3$)) are in full accord with structure **19**. Tlc showed a single spot.

The green gum was then dissolved in 100 ml of methanol containing 3 ml of a 40% aqueous solution of potassium hydroxide, and the resulting solution was boiled under reflux for 15 hr. The solution was then concentrated to a small volume and diluted with 500 ml of water. This was then extracted with ether to remove any neutral impurities. Acidification of the green aqueous solution precipitated a solid which was removed by ether extraction. The ether extract, after drying, was concentrated to give 140 mg of green crystals. These were sublimed by heating at 130° (10^{-3} mm) and the sublimate was recrystallized from a benzene–hexane mixture to give 125 mg of green-black crystals: mp 206–208°; ir, $\nu_{\max}^{CHCl_3}$ 1660 cm^{-1} (C=O); uv, $\lambda_{\max}^{\text{ethanol}}$ 343 mμ (ε 46,400), 384 (41,100), 460 (5650), 472 (5650), 538 (235), 593 (332), 640 (sh, 860), 651 (1550); nmr ($CDCl_3$), broad signal at τ −1.00 (1 H, $-CO_2H$), doublet at 0.00 (1 H, Ar*H*), singlet at 0.50 (1 H, Ar*H*), multiplet at 0.85–2.00 (7 H, Ar*H*), and a singlet at 14.05 (6 H, $-CH_3$).

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.64; H, 5.83.

Optical Resolution of 4-Carboxy-*trans*-15,16-dimethyldihydropyrene (18). To a solution of 200 mg of **18** in 20 ml of hot acetone there was added 216 mg of cinchonidine in a minimum of acetone for solution. The hot solution was filtered and allowed to stand in the cold. After 24 hr, 73 mg of green crystals, mp 194–196°, had separated and were collected. These were recrystallized several times from an acetone–hexane mixture to give 40 mg of green crystals, mp 198–200°, corresponding to the cinchonidine salt of one enantiomorph of **18**.

Anal. Calcd for $C_{38}H_{38}N_2O_3$: C, 79.97; H, 6.71. Found: C, 79.79; H, 6.89.

A solution of 40 mg of the cinchonidine salt of **18**, as described above, was dissolved in 50 ml of ether and shaken with aqueous dilute hydrochloric acid. The ether layer was separated, dried, and concentrated to give nice green crystals. These, after recrystallization from a benzene–hexane mixture, gave 16 mg of green-black crystals, mp 197–198°, corresponding to the levorotatory enantiomorph of **18**. The spectral properties of these crystals were identical with those described for racemic **18**. The optical rotatory dispersion curve was taken with a solution containing 1.150 mg of the above sample in 5 ml of ethanol. The specific rotations of the peaks and troughs at the various wavelengths were 660 mμ (+438°), 651 (0°), 637.5 (−244°), 550 (−128°), 505 (348°), 480 (0°), 393 (+230°), 388 (0°), 365 (−4132°), 346 (0°), 277 (−113°), 275 (0°), 261 (+2969°), 240 (0°), 225 (−8874°), 210 (−7586°), and 200 (0°).

To isolate the dextrorotatory enantiomorph the mother liquor from the cinchonidine salt recrystallization was concentrated causing the separation of an additional 20 mg of crystals which were collected. The mother liquor was then concentrated to dryness, and the crystalline residue was recrystallized from a hexane–acetone mixture to separate 60 mg of crystals, mp 184–188°. The mother liquor from this crystallization was concentrated; the residue was dissolved in ether and treated with dilute aqueous hydrochloric acid, as before, to recover the free acid. This gave 110 mg of green crystals, mp 180–184°. Fractional crystallization of these from a petroleum ether–benzene mixture gave 60 mg of dark green crystals, mp 195–197°. Solution spectra of these crystals were the same as those described for racemic **18**. That these crystals were the dextrorotatory enantiomorph of **18** containing a small impurity of the levorotatory isomer was demonstrated by its optical rotatory dispersion curve taken on a solution of 1.13 mg of these crystals in 5 ml of ethanol. The specific rotations of the peaks and troughs at the various wavelengths were 660 mμ (−305°), 651 (0°), 637 (+243°), 550 (+120°), 503 (+340°), 480 (0°), 393 (−182°), 387 (0°), 365 (+3000°), 348 (0°), 278 (+222°), 275 (0°), 261 (−2120°), 240 (0°), 227 (+7150°), 213 (+6450°), and 200 (0°).

Attempted Thermal Racemization of Optically Active 4-Carboxy-*trans*-15,16-dimethyldihydropyrene (18). A solution of 1.46 mg of the dextrorotatory enantiomorph of **18** in 1.0 ml of ethanol was placed in a small tube, the solution was degassed, and the tube was sealed. The tube was then totally immersed in a constant-temperature bath at 180° for 10 min. After removal from the bath, the tube was cooled and opened and its contents washed into a volumetric flask diluting in volume to exactly 5.0 ml. The absorption spectrum in the visible region showed λ_{max} at 651 mμ (ϵ 720), 593 (160), and 472 (2650) corresponding to an average of 47% of the original extinction coefficients. The optical rotatory dispersion curve in the visible showed the following specific rotations: 660 mμ (−154°), 651 (0°), 637 (+115°), 550 (+59°), and 505 (+151°). Again, within experimental error this corresponds to an average of 47% of the values of the original specific rotations.

Reduction of the Optically Active 4-Carboxy-*trans*-15,16-dimethyldihydropyrene (18) to Optically Active 4-Methyl-*trans*-15,16-dimethyldihydropyrene (21). A solution of 30 mg of the dextrorotatory enantiomorph of **18** in 50 ml of ether was added dropwise with stirring to a solution of 0.2 g of lithium aluminum hydride and 0.7 g of aluminum chloride in 50 ml of ether held at −70°. After the addition was complete, the mixture was allowed to warm to room temperature with stirring over a 12-hr period. Moist ether was then added, followed by water itself. The green ether layer was separated, dried, and concentrated. The residue was taken up in a 20:1 pentane–ether mixture and chromatographed over alumina (Woelm, activity 1). The emerald green eluate fraction was concentrated to yield 20 mg of green crystals. Recrystallization from 5% aqueous methanol gave fine, green needles: mp 110–115°; uv, λ_{max}^{hexane} 643 mμ (ϵ 354), 629 (224), 613 (198), 598 (155), 538 (80), 468 (6190), 453 (sh, 5610), 429 (sh, 3900), 379 (42,100), 353 (sh, 22,400), and 339 (86,500); nmr (CCl_4), multiplet at τ 1.50 (7 H, Ar*H*), triplet at 2.00 (2 H, Ar*H*), doublet at 6.74 (3 H, $ArCH_3$), and two singlets at 14.18 and 14.20 (3 H each, $-CH_3$); mass spectrum, M^+ − 246; ORD (hexane, *c* 1.074 mg/15 ml), 559 mμ (−160°), 485 (−1720°), 417.5 (+885°), 387 (0°), 380 (−1210°), 378 (0°), 375 (+1860°), 265 (+1670), 252.5 (0°), 234 (+27,000°), 224 (+1720), 210 (+6800), and 207 (0°).

Anal. Calcd for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.42; H, 7.51.

4-Formyl-*trans*-15,16-dimethyldihydropyrene (22). To a solution of 200 mg of **1** in 40 ml of methylene chloride at 0°, there was added with stirring a mixture of 0.20 ml of stannic chloride and 180 mg of *n*-butyl dichloromethyl ether in 5 ml of methylene chloride. After the mixture had been allowed to stir for an additional 2 hr, it was poured onto 100 ml of ice water. The aqueous layer was separated and extracted with methylene chloride. The methylene chloride extracts were combined, washed with water, dried, and concentrated. The residue was taken up in methylene chloride and chromatographed over silica gel. The main purple eluate fraction was collected and rechromatographed twice more in the same way. This effected separation into a green band and a purple band. The purple fraction on concentration gave 162 mg (72%) of reddish purple plates, mp 129–131°, identical with the 2-formyl-*trans*-15,16-dimethyldihydropyrene described previously.[4] The green eluate, on concentration, gave 40 mg (18%) of green crystals which, after recrystallization from aqueous methanol, yielded long, green needles: mp 107–108°; uv, $\lambda_{max}^{cyclohexane}$ 679 mμ (ϵ 2130), 670 (1550), 613 (485), 559 (263), 470 (3740), 447 (7000), 429 (7250), 394 (21,800), and 369 (67,100); ir, $\nu_{max}^{CHCl_3}$ 1668 cm^{-1} (C═O); nmr ($CDCl_3$), singlet at τ −1.20 (1 H, −C*H*═O), doublet at 0.20 (1 H, Ar*H*), multiplet at 1.35 (7 H, Ar*H*), triplet at 1.85 (1 H, Ar*H*), and singlets at 14.00 (3 H, $-CH_3$) and 14.05 (3 H, $-CH_3$)

Anal. Calcd for $C_{19}H_{16}O$: C, 87.06; H, 6.19. Found: C, 87.76; H, 6.31.

A solution of 25 mg of **22** in 100 ml of ether was added dropwise with stirring at −70° to a solution of 100 mg of lithium aluminum hydride and 350 mg of aluminum chloride in 20 ml of ether. After the addition was complete, the solution was allowed to warm to room temperature and stir for 5 hr. After addition of water, the ether layer was separated, dried, and concentrated. The residue was taken up in a 20:1 pentane–ether mixture and chromatographed over alumina (Woelm, activity 1). The bright green eluate fraction was concentrated to give 14 mg of crystals. Recrystallization from aqueous methanol gave long green needles, mp 80–81°. The solution spectra of these crystals were essentially identical with those described previously for the optically active sample of **21**.

Base-Catalyzed β-Elimination Reactions in Aqueous Solution. II. ElcB Elimination from β-Methoxy Ketones

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Abstract: β elimination of methoxide ion from 4-methoxy-2-butanone and from 4-methoxy-4-methyl-2-pentanone to give the respective α,β-unsaturated ketones is kinetically specific base catalyzed. The reactions likely proceed *via* rapid general base catalyzed enolate anion formation, as determined by α-methylene proton exchange in deuterium oxide, followed by rate-determining loss of methoxide ion from the enolate anion. Deuterium solvent kinetic isotope effects as well as Arrhenius activation parameters provide additional support for the postulated mechanism.

Previously, general base catalysis in β-elimination reactions of β-acetoxy ketones was established.[1] Similarly, general base catalysis in β-elimination reactions of β-acetoxy thiol esters as well as in β-phenoxy ketones and β-thiophenoxy ketones has been established.[2,3] Thus for these particular cases general base catalysis in elimination reactions is observed when good leaving groups are involved. It could be anticipated

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[1] L. R. Fedor, *J. Am. Chem. Soc.*, **89**, 4479 (1967).

[2] L. R. Fedor, to be published.

[3] See ref 1 for references to studies involving general base catalysis in elimination reactions of compounds structurally dissimilar to β-substituted ketones and thiol esters.