the C-2 position will be smaller than the LUMO coefficient (0.474) at the C-3 position for β-nitrostyrene.
 (14) The LUMO coefficients (INDO) for 2-trifluoromethyl-1,3-butadiene are as

- follows: C-1, 0.626; C-2, 0.453; C-3, 0.338; C-4, 0.501.
- (15) The classification of the specific uncatalyzed Diels-Alder reactions into

the three general types was determined from the CNDO/2 and INDO orbital energies.

- (16)
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α -Methyleneoxetane. Study of a Retro-Diels-Alder Reaction

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Received September 3, 1974

As a precursor to α -methyleneoxetane (11), the anthracene adduct 7 was prepared in a four-step sequence from the ketone 2. Pyrolysis of 7 gave α -methyleneoxetane and anthracene, as well as the rearranged ether 8 and the olefin 15. The structure of the rearranged ether 8, also formed from 7 on some chromatography adsorbents or with acid, was determined with the aid of carbon-13 NMR spectroscopy and further confirmed by hydrogenation to the alcohol 9. α -Methyleneoxetane (11) was characterized by spectroscopy and by its reaction with phenyllithium.

 α -Methyleneoxetane (11) has interested us for some time because of the possibility that nucleophilic displacement on the oxetane ring^{1,2} could be used to generate a specific enolate of an unsymmetrical ketone; α -methyleneoxetane might thus serve as a potential 3-ketobutyl group in the Robinson annelation reaction.^{3,4} Substituted compounds having the α -methyleneoxetane ring have been prepared by several methods^{2,5-7} and have been proposed as reaction intermediates.⁸ In 1971, we reported a preliminary account of the first synthesis of α -methyleneoxetane (11),^{9,10} which we obtained in low yield from a retro-Diels-Alder reaction⁹⁻¹⁴ by pyrolysis of the anthracene adduct 7. More recently, Haslouin and Rouessac have obtained 11 in higher yield by pyrolysis of the cyclopentadiene adduct.¹¹

Since the pyrolysis of 7 gave α -methyleneoxetane in low yields only, we have investigated the composition of the nonvolatile residue from the pyrolysis experiments. In the course of this investigation we have also encountered an acid-catalyzed rearrangement of 7. We report here a full account of the pyrolysis and rearrangement of 7.

The anthracene adduct 7 was prepared as shown in Scheme I. Both the tosylate 5 and the mesylate 6 served as precursors to 7. The purity of 7 from both routes was indistinguishable (ir, NMR, TLC, melting point); we obtained higher yields from the mesylate.

The anthracene adduct 7 was always purified by chromatography on Florisil followed by recrystallization from ether. On one occasion, chromatography yielded none of 7 but instead an isomeric compound. The rearrangement of 7 to the isomer was found to take place on only certain batches of Florisil. The same rearrangement also occurred on acidic alumina, but not on silica gel or neutral or basic alumina. In addition, treatment with p-toluenesulfonic acid or sulfuric acid at room temperature caused the rearrangement of 7 to its isomer.

The isomer was assigned structure 8 on the basis of its analytical and spectral data, in particular the carbon-13 NMR data. The structure was further confirmed by catalytic hydrogenation to the alcohol 9. The chemical shifts and coupling constants in the proton NMR of 9 are very analogous to those reported for the related compound 10 prepared by Cristol.^{15,16}

Pyrolyses of the anthracene adduct 7 were carried out on a small scale (50-500 mg) by heating at 330-350° in a slow stream of nitrogen for 5-25 min while collecting the volatile products in a receiver cooled in Dry Ice-acetone. The dis-



tillate, a colorless liquid, was identified as α -methyleneoxetane (11) by its ir, NMR, and mass spectra and its reaction with phenyllithium, which produced, after work-up, 4-phenyl-2-butanone (12),^{17,18} 2-phenyl-3-buten-2-ol (13),^{19,20} and 2,4-diphenyl-2-butanol (14).^{18,21} In some pyrolyses, methyl vinyl ketone was formed as an impurity. On three occasions, the yield of α -methyleneoxetane was determined to be about 10%.²²

The NMR spectra of the nonvolatile residue from the pyrolyses suggested that several compounds were present. In addition to anthracene, the expected product from the retro-Diels-Alder reaction, and recovered 7, column chromatography produced samples of the rearranged isomer 8 and a compound assigned the olefin structure $15.1^{5,23}$ The



structure of the olefin was confirmed by independent synthesis using a Wittig reaction on the ketone 2. In one pyrolysis experiment (giving 10% of 11 and 2% of methyl vinyl ketone) the yields of the nonvolatile products were estimated to be 15% of anthracene, 21% of the olefin 15, 24% of recovered anthracene adduct 7, and 34% of the rearranged isomer 8.

The rearrangement of 7 to 8, which occurs as a major pathway with these pyrolysis conditions and as the sole pathway with acid treatment, is similar to carbonium ion rearrangements of several dibenzobicyclo[2.2.2]octadiene derivatives studied by Cristol.²⁴ The C-O bond of 7 is evidently easily broken; the geometry is suitable for neighboring group participation. It is interesting to note that this type of rearrangement is not reported for the cyclopentadiene adduct of 11, where the oxygen atom is endo and neighboring group participation for C-O cleavage is not favorable.¹¹

In the pyrolysis of 7, fragmentation of the oxetane ring to give 15 evidently competes strongly with the retro-Diels-Alder reaction. Although thermal fragmentations of oxetanes are known,²⁵ normally one might not expect a [2 + 2]cycloreversion to compete with a [2 + 4] cycloreversion; oxetanes were stable to retro-Diels-Alder conditions in other systems.^{10,11} This again suggests that the C-O bond of 7 is easily broken. Fragmentation of the oxetane in the other sense (giving ketone 2 and ethylene) was not observed.²⁶

Experimental Section

Commercially available compounds were used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from lithium aluminum hydride. Benzene was freshly distilled; the last half of the distillate was used. Pyridine was distilled from barium oxide. *tert*-Butyl alcohol was distilled from calcium hydride. Methanesulfonyl chloride was distilled (bp 63-64°, 20 mm) before use. *p*-Toluenesulfonyl chloride was decolorized with activated charcoal and was recrystallized (mp 68-68.5°) from hexane. Solutions of *n*-butyllithium and phenyllithium were obtained from Alfa Inorganics.

Unless otherwise specified, reactions were carried out in a nitrogen atmosphere using base-washed glassware. The use of the term "concentrated" refers to evaporation of solvent under reduced pressure (water aspirator) using a rotary evaporator.

Vapor phase chromatographic (VPC) analyses were performed on a Varian Aerograph Model 90-P instrument using helium as the carrier gas at a flow rate of 100 ml/min unless otherwise noted.²⁷ Silica gel G was used for thin layer chromatography (TLC). Florisil (60–100 mesh) used for column chromatography was obtained from Fisher Scientific Co.

Melting points were determined on a Fisher-Johns hot-stage melting point apparatus. Microanalyses were performed by MicroTech Laboratories, Inc., Skokie, Ill., and by Robertson Laboratory, Florham Park, N.J.

Infrared (ir) spectra were obtained using a Perkin-Elmer Model 137 spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained using a Varian T-60 spectrometer unless otherwise noted, using tetramethylsilane as the internal reference. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-7 instrument.

9,10-Dihydro-11-acetoxy-9,10-ethanoanthracene-11-carbonitrile (1). A mixture of 16 g (0.09 mol) of anthracene and 5 g (0.045 mol) of α -acetoxyacrylonitrile²⁸ in 50 ml of p-xylene was heated at 140-150° for 32 hr²⁹ and allowed to cool to room temperature overnight. The reaction mixture was concentrated to remove the xylene, and the residue was stirred with methanol and filtered to partially remove excess anthracene. The filtrate was concentrated and the residue was chromatographed on 67 g of Florisil. Elution with hexane-CH2Cl2 mixtures produced 1 as an oil, homogeneous by tlc $(R_f 0.3, benzene)$.³⁰ The product was partially crystallized with difficulty (CH2Cl2-hexane), producing 6.71 g of white crystals (mp 97.5-99°) and 3.86 g of oil (total 81% yield). The following spectra were obtained from the crystalline material: ir (CHCl₃) 5.71 μ ; NMR (CDCl₃) δ 1.88 (s) partially overlapping with 2.06 (doublet of doublets, J = 14, 2.5 Hz) (total 4.3 H), 2.69 (doublet of doublets, 1.0 H, J = 14, 2.5 Hz), 4.35 (t, 1.0 H, J = 2.5 Hz), 5.08 (s, 1.0 H), 7.25 (m, 8.2 H); mass spectrum m/e 289 (M⁺), 178 (base peak).

9,10-Dihydro-9,10-ethanoanthracen-11-one (2). To a solution of 9.57 g of the Diels-Alder adduct 1 (3.86 g of above oil and 5.71 g of above crystals) in 91.5 ml of THF and 16 ml of methanol was added 46 ml of 14% aqueous KOH.³¹ The reaction mixture was stirred at 40° for 4 hr, then part of the solvent was removed under vacuum, and the resulting mixture was partitioned between ether and water. The aqueous layer was extracted twice with ether and the combined ether layers were washed with water, dried (MgSO₄), and concentrated, leaving a white, crystalline residue. Recrystallization from ether-hexane yielded white crystals: 4.23 g, mp 152.5-153°, and 2.42 g, mp 152-152.5° (total 91% yield) (lit.³² mp 152.5-153°); ir (CHCl₃) 5.79 μ ; NMR (CDCl₃) δ 2.30 (d, 1.9 H, J = 3 Hz), 4.52 (t, 1.0 H, J = 3 Hz), 4.80 (s, 1.0 H), 7.27 (m, 8.0 H).

9,10-Dihydro-11-hydroxy-9,10-ethanoanthracene-11-acetic Acid Ethyl Ester (3). A mixture of 13 g of activated zinc,³³ 100 ml of benzene, and 100 ml of anhydrous ether was heated to reflux. A solution of 5.65 g (0.0256 mol) of ketone 2 and 3.5 ml (0.032 mol) of ethyl bromoacetate in 50 ml of benzene was added dropwise. 33 The reaction started (became cloudy) with the addition of a crystal of iodine after about one-half of the ketone-ester solution had been added; the remainder was added over a 15-min period. Three additional 13-g portions of zinc along with a trace of iodine were added after 0.5, 1, and 2 hr; 1 ml (0.009 mol) of ethyl bromoacetate accompanied the last addition. Heating was then continued for 35 min. Acetic acid was added to the reaction mixture to dissolve the solids and the resulting solution was poured into water and extracted twice with ether. The combined ether extracts were washed (10% NH₄OH followed by brine), dried (MgSO₄), concentrated, and placed under oil pump vacuum for several hours. The crystalline residue was chromatographed on 50 g of Florisil. Elution with benzene-CH₂Cl₂ mixtures yielded 7.26 g (92%) of white crystals: mp 119-120°; ir³⁴ (CHCl₃) 2.8, 5.83 μ ; NMR³⁴ (CDCl₃) δ 1.20 (t, 3 H, J = 7 Hz), 1.83 (d; 2 H, J = 3 Hz), 2.28 (s, 2 H), 3.32 (broad s, 1 H), 3.94-4.38 [several peaks which appear to be composed of 4.13 (q, J = 7 Hz) overlapping with 4.20 (crude t) and 4.31 (s) (total 4 H)], 7.18 (m, 8 H).

Three recrystallizations from ether gave white crystals: mp 121.5-122°; mass spectrum m/e 308 (M⁺, small), 290 [(M - H₂O)⁺], 263, 178 (base peak). Anal. Calcd for C₂₀H₂₀O₃: C, 77.90; H, 6.54. Found: C, 77.89; H, 6.74.

9,10-Dihydro-11-hydroxy-9,10-ethanoanthracene-11-ethanol (4). To 3 g (0.08 mol) of lithium aluminum hydride in 75 ml of THF, a solution of 7.43 g (0.024 mol) of hydroxy ester 3 in 30 ml of THF was added dropwise. (Reaction mixture was protected from the atmosphere with a drying tube.) The mixture was heated at reflux for 3 hr, and then cooled in ice. About 20 ml of brine was added dropwise and the mixture was stirred at room temperature until the salts became white. The mixture was filtered (salts washed with ether), and the filtrate was dried (MgSO₄) and concentrated, leaving an oil which crystallized. Recrystallization from ether yielded 4.16 g (65%) of white crystals, mp 87-89.5°.

Three recrystallizations from ether gave white crystals, mp 92.5–93.5°. The spectral and analytical data indicated that 1,4-butanediol was present: ir $(CHCl_3)$ 2.95 μ ; NMR^{35} $(CDCl_3)$ δ 1.4–

2.1 (m, 6.05 H, CCH₂C of 4 and of butanediol), 2.7 (s, 1.08 H, OH), 3.2–4.0 (m, 6.05 H, -CH₂O- of 4 and of butanediol and 2 OH), 4.3 (broad s, 1.95 H, benzylic H of 4), 7.0–7.5 (m, 8.0 H, aromatic H of 4). When the contents of the NMR tube were shaken with several drops of D₂O, the peaks in the general region of δ 1.4–1.6 and 3.2–3.6 were reduced in size (and the singlet at δ 2.7 disappeared and was replaced by a small singlet at lower field). The NMR spectrum of the material having mp 87–89.5° indicated that less 1,4-butanediol was present. The mass spectrum showed m/e 248 [(M – H₂O)⁺], 230 [(M – 2H₂O)⁺], 178 (base peak). Anal. Calcd for C₁₈H₁₈O₂: C, 81.17; H, 6.81. Calcd for C₄₀H₄₆O₆ (2:1 diol 4:1,4-butanediol): C, 77.14; H, 7.45. Found: C, 77.23; H, 7.58.

A 13 C NMR³⁶ (CDCl₃) was taken of a sample (mp 91.5–93.5°) from a similar experiment: δ 29.84 (C-2 of 1,4-butanediol), 41.98 (C-1'), 44.59 (C-10 or C-12), 44.89 (C-12 or C-10), 56.33 (C-9), 59.61 (C-2'), 62.57 (C-1 of 1,4-butanediol), 78.11 (weak, C-11).

Monotosylate (5) of 9,10-Dihydro-11-hydroxy-9,10-ethanoanthracene-11-ethanol. To an ice-cooled solution of 297.9 mg (1.1 mmol) of the diol 4 (mp 87–89.5°) in 3 ml of pyridine was added a solution of 500 mg (2.6 mmol) of p-toluenesulfonyl chloride in 3 ml of pyridine. (Reaction vessel was protected from the atmosphere with a drying tube.) The solution was stirred at ice temperature for 0.5 hr and was placed in a refrigerator overnight. The resulting mixture was poured into ice water and extracted with ether; the ether extract was washed twice with cold 1N HCl, followed by saturated NaHCO₃. The ether layer was dried (Na₂SO₄-K₂CO₃-MgSO₄) and concentrated; the residue was chromatographed on 5 g of Florisil. Elution with benzene followed by 2% CH₂Cl₂ in benzene produced 252.7 mg of oil, TLC R_f 0.23 (CH₂Cl₂). The major peaks of the NMR spectrum³⁴ (CCl₄) were a singlet at δ 2.38 and multiplets centered approximately about δ 1.5, 4.1, and 7.1 with a doublet at δ 7.7 (J = 8 Hz) (part of tosylate aromatic protons).

Monomesylate (6) of 9,10-Dihydro-11-hydroxy-9,10-ethanoanthracene-11-ethanol. Most of the benzene was distilled from a solution of 0.5 g (1.9 mmol) of the diol 4 (mp 85-90°) in 10 ml of benzene, to remove traces of water. Pyridine (3 ml) was added, the solution was cooled in ice, and 0.22 ml (2.9 mmol) of methanesulfonyl chloride was added dropwise. (Reaction vessel was protected from the atmosphere with a drying tube.) The solution was stirred at ice temperature for 30 min and placed in a refrigerator for 16 hr. The resulting mixture was poured into ice water and was extracted with ether. The ether extract was washed with two portions of cold 1N HCl followed by two portions of brine. (The second brine wash was neutral to pH paper.) The organic layer was dried (Na₂SO₄-MgSO₄) and concentrated, and the residue was placed under oil pump vacuum, leaving 0.65 g of a viscous, colorless oil, ir (CHCl₃ mull) 2.8, 7.4, 8.5 μ . The major peaks of the NMR (CDCl₃) spectrum were a sharp singlet (δ 2.86, 2.9 H) and multiplets centered approximately about δ 1.7 (5.3 H), 4.3 (3.8 H), and 7.2 (8.0 H). The TLC (1% CH₃OH in CHCl₃) showed one spot (R_f 0.22). The R_f value of 4 under the same conditions was 0.08.

9,10-Dihydrospiro[9,10-ethanoanthracene-11,2'-oxetane] (7). A mixture of 5 g of potassium in 80 ml of tert-butyl alcohol was heated at reflux until all the potassium dissolved. A solution of the entire crude mesylate 6 (0.65 g) from the above experiment in 4 ml of benzene was added dropwise at 50-60° and the reaction mixture was stirred for 2 hr at 60-70°. After cooling to room temperature, the reaction mixture was poured into saturated NaHCO3 and extracted twice with ether. The combined ether extracts were dried (Na₂SO₄-MgSO₄), concentrated, and placed under oil pump vacuum. The oily residue was chromatographed on 10 g of Florisil. Elution with hexane-benzene mixtures produced material which was recrystallized from ether, yielding 0.34 g (73% from 4) of white crystals: mp 129–130°; ir³⁴ (CHCl₃) 10.4 μ (strong, broad); NMR³⁴ $(CDCl_3)$ δ 2.13 (d, J = 2.5 Hz) overlapping with 2.1-2.9 (m) (total 4.0 H), 4.1–4.8 (m, 3.9 H), 6.9–7.6 (m, 8.1 H); ¹³C NMR (CDCl₃)^{34,36} δ 34.63 (t, C-1'), 44.59 (d, C-10 or C-9), 46.40 (t, C-12), 56.50 (d, C-9 or C-10), 64.26 (t, C-2'), 87.74 (weak, s, C-11).

A portion of the product prepared from 5 in a similar experiment was recrystallized three times from ether, giving white crystals: mp 130-130.5°; mass spectrum m/e 248 (M⁺), 178 (base peak). Anal. Calcd for C₁₈H₁₆O: C, 87.06; H, 6.50. Found: C, 87.03; H, 6.59.

2,3,8,12b-Tetrahydro-3a,8-methano-3aH-dibenzo[3,4:6,7]cyclohepta[1,2-b]furan (8). In an experiment similar to that described above, a mixture of 1.0 g (3.8 mmol) of the diol 4 (mp 91.5-93.5°) (dried as above by distilling benzene from a solution), 5 ml of pyridine, and 0.45 ml (0.68 g, 5.9 mmol) of methanesulfonyl chloride was stirred at 0° for 2 hr and placed in a refrigerator for 18 hr. The resulting mixture was poured into ice water; a white precipitate formed immediately. The mixture was filtered and the precipitate was dried under oil pump vacuum, leaving 0.302 g of white, crystalline material, mp 113–114°. The crystalline material had ir and NMR spectra identical with those of an authentic sample of 1,4-di(methanesulfonyloxy)butane, mp 115–115.5° (lit.³⁷ mp 116°), prepared from 1,4-butanediol and methanesulfonyl chloride by a procedure similar to that of Haggis and Owen.³⁷

The filtrate was extracted with two 30-ml portions of ether. The combined ether extracts were washed with two portions of 1N HCl followed by two portions of brine, and were dried (MgSO₄) and concentrated, yielding 0.864 g of the oily monomesylate 6. A solution of 0.85 g of this oil in 4 ml of benzene was added to a refluxing solution of potassium tert-butoxide in tert-butyl alcohol [prepared from 1.5 g (38 mmol) of potassium in 40 ml of tert-butyl alcohol]. The reaction mixture was heated at 70° for 2 hr, cooled to room temperature, poured into saturated NaHCO₃, and extracted three times with ether. The combined ether extracts were dried (Na₂SO₄-MgSO₄) and concentrated to give 0.73 g of residue which was chromatographed on 70 g of Florisil. Elution with CH₂Cl₂ gave 0.645 g of colorless oil which was crystallized with ether and recrystallized from ether, yielding 450 mg (49% from 4) of white crystals of 8: mp 91-91.5°; ir (CHCl₃) 3.32, 3.35, 3.46, 6.72, 6.80, 6.85, 9.78, 9.82, 10.15 μ ; NMR (CDCl₃) δ 1.88-3.12 (m) overlapping with 2.30 (d, J = 2.5 Hz (total 4.1 H), 3.92-4.48 (m, 3.9 H), 7.04-7.50 (m, 8 H); ¹³C NMR³⁶ (CDCl₃) δ 32.52 (t, C-1'), 45.11 (t, C-8), 46.69 (d, C-1), 54.09 (weak, s, C-5), 67.29 (t, C-2'), 81.83 (d, C-4); mass spectrum m/e 248 (M⁺), 247, 246, 202, 178, 105.

A portion of the product was further recrystallized from ether, yielding white crystals, mp 93–93.5°. Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.84; H, 6.52.

Rearrangement of 7 to 8 on Chromatography Adsorbents.³⁸ In a typical experiment, a solution of 10 mg of 7 was adsorbed on 3 g of Florisil and allowed to stand for 24 hr. Elution with CH_2Cl_2 gave 10 mg of an oil having NMR spectrum (CDCl₃) identical with that of 8.

This rearrangement was found to occur on only certain batches of Florisil and also on acidic alumina. Compound 7 was recovered unchanged after standing on basic alumina, neutral alumina, or silica gel.

Rearrangement of 7 to 8 with Acid. To a solution of 50 mg of the anthracene adduct 7 in 0.3 ml of $CDCl_3$ in an NMR tube (having the NMR spectrum reported above for 7) was added 3 mg of *p*-toluenesulfonic acid. After standing for 1 hr at room temperature, the NMR spectrum was taken and was identical with that of the rearranged product 8 (above).

To a solution of 50 mg of 7 in 5 ml of CHCl₃ was added 10 ml of 6M H₂SO₄. After standing at room temperature for 16 hr in a covered flask, the reaction mixture was extracted with ether, and the ether extract was dried (MgSO₄) and concentrated, yielding 44 mg of pale, yellow oil. The NMR spectrum (CDCl₃) was identical with that of the rearranged product 8.

Dibenzobicyclo[3.2.1]octadiene-5-ethanol (9). To a solution of 125 mg of the rearranged product 8 in 40 ml of absolute ethanol was added 34 mg of 10% Pd/C and 1 drop of 60% perchloric acid. The mixture was stirred under a hydrogen atmosphere for 92 hr at room temperature and atmospheric pressure. Filtration and concentration yielded 125 mg of colorless oil. A portion (115 mg) of the oil was purified by column chromatography on 20 g of Florisil. Elution with CH₂Cl₂ gave 105 mg of oil which was crystallized with ether and recrystallized from ether, yielding 98 mg of white crystals: mp 61.5–63°; ir (CHCl₃) 2.70, 2.82, 3.30, 3.36, 9.30, 9.98 μ ; $NMR^{39}~(CDCl_3)~\delta$ 1.53 (s, disappears with addition of $D_2O),$ 1.95 (d, J = 10 Hz), 2.15 (t, J = 7 Hz), 2.33 (m, appearing as a doublet, J = 10 Hz, split into doublets, J = 4.5 Hz, split further into doublets, $J \approx 1.4$ Hz), 2.52 (doublet of doublets, J = 16.5, 1.4 Hz), 3.04 (d, J = 16.5 Hz), 3.72 (t, J = 7 Hz) overlapping with 3.79 (d, J = 4Hz), 6.6-7.0 (m). The relative areas upon integration are as follows: δ 1.53 (1.4 H), 1.8–2.7 (5 H), 2.9–3.2 (1 H), 3.6–3.9 (3 H), 6.6–7.0 (8.3 H). A ¹³C NMR³⁶ (CDCl₃) was taken: δ 39.56 (C-1' or C-4), 40.32 (C-4 or C-1'), 44.79 (C-8), 46.09 (weak, C-5), 46.71 (C-1), 59.56 (C-2').

The product was recrystallized again from ether, yielding white crystals, mp 65-66.5°. The mass spectrum showed m/e 250 (M⁺), 232, 231, 219, 206. Anal. Calcd for C₁₈H₁₈O: C, 86.36; H, 7.25. Found: C, 86.00; H, 7.56.

Pyrolysis of the Anthracene Adduct 7.40 A 193.6-mg sample of the anthracene adduct 7 was placed in one arm of an all-glass apparatus consisting of two connecting U tubes. A slow stream of nitrogen was initiated; the receiving arm was cooled in a Dry Ice-acetone bath, then the arm containing 7 was immersed for 5 min in

a Wood's metal bath held at 340-350°. White crystals deposited on the tube immediately above the Wood's metal bath, and a small amount of a colorless liquid collected in the receiver. A 2-µl sample of cyclohexane (internal NMR integration standard) was added to the distillate, which was then transferred to a NMR tube with tetrachloroethylene: NMR⁴¹ (C₂Cl₄) δ 1.43 (cyclohexane), 2.17 (methyl vinyl ketone), 3.16 (m, 2 H, appearing as triplet, J = 6.5Hz, split into triplets, $J \approx 2$ Hz, allylic H of 11), 3.63 (m, 1 H, appearing as doublet, J = 3.5 Hz, split into overlapping triplets, J =1.8 Hz, vinyl H of 11 trans to O), 4.03 (m, 1 H, appearing as doublet, J = 3.5 Hz, split into overlapping triplets, J = 2.4 Hz, vinyl H of 11 cis to O), 4.50 (t, 2 H, J = 6.5 Hz, $-CH_2O-$ of 11), 5.6–6.5 (methyl vinyl ketone). The yield of α -methyleneoxetane (11) (by NMR integration) was 10%, and that of methyl vinyl ketone was 2%. VPC analysis (SF-96, 49°)^{27a} showed (in addition to solvent) peaks at 5.7 (major), 5.4 (shoulder) and 9.1 min (cyclohexane).42

The nonvolatile residue from the above pyrolysis was chromatographed⁴³ on 21 g of Florisil. Elution with hexane-benzene mixtures gave (1) 52.8 mg of white crystals and (2) 4.5 mg of white crystals. Further elution with benzene gave (3) 99.5 mg of oil, and elution with CH2Cl2 gave (4) 19.8 mg of oil. The integrated nmr spectrum (CDCl₃) of fraction 1 indicated that it consisted of a 5:6 molar ratio of anthracene:olefin 15 (see below). The ir and NMR spectra of fraction 2 indicated that it was pure olefin 15. The NMR spectrum of fraction 3 indicated that it consisted of a mixture of recovered anthracene adduct 7 and the rearranged product 8^{44} (see below) in approximately a 1:2 ratio. The NMR spectrum of fraction 4 indicated that it consisted primarily of 7 with unknown impurities (estimated purity >75%). From these data, the yields of compounds in the nonvolatile residue were estimated at anthracene (15%), olefin 15 (21%), rearranged product 8 (34%), and recovered anthracene adduct 7 (24%).

The pentane-soluble portion of fraction 1 was rechromatographed on Florisil, yielding 12.8 mg of white crystals homogeneous by TLC (R_f 0.13, hexane) which were combined with fraction 2. Recrystallization twice from pentane (-22°) produced white crystals of 15: mp 104.5-105° (lit.^{23a} mp 103.5-104°); mass spectrum m/e 218 (M⁺), 178 (base peak).

In a separate pyrolysis experiment (330-340°), the distillate was transferred to an ir cell and to an NMR tube with CCl₄: ir (CCl₄) 5.92, 8.44, 10.45 μ . The NMR was similar to that reported for 11 in C_2Cl_4 ; the corresponding chemical shifts were at δ 3.18, 3.60, 3.96, and 4.53. The NMR indicated that very little if any methyl vinyl ketone was present.

In a separate pyrolysis experiment (330-340°), the distillate was taken up in ether and analyzed by GC-MS:⁴⁵ m/e 70 (M⁺), 55, 42, -39

9,10-Dihydro-11-methylene-9,10-ethanoanthracene (15). A 320-mg sample of methyltriphenylphosphonium bromide was added in small portions to a solution of 0.34 ml of *n*-butyllithium (2.67 M in hexane) in 4 ml of anhydrous ether.⁴⁶ The reaction mixture was stirred at room temperature for 2.5 hr; then an additional 0.1 ml of n-butyllithium (2.67 M in hexane) was added (because much solid remained) and the stirring was continued for an additional 1.5 hr. A solution of 189.6 mg of ketone 2 in 8 ml of ether was added and the mixture was stirred for 0.5 hr at room temperature and overnight at reflux. After cooling to room temperature, the reaction mixture was filtered (precipitate washed with ether), and the filtrate was shaken with water, dried (MgSO₄), and concentrated. The residue was chromatographed on 17 g of Florisil. Elution with hexane produced 94 mg (50%) of white crystals having essentially identical ir and NMR spectra to those of the olefin 15 obtained from the pyrolysis of 7 (above). The spectra were equivalent to the reported spectra of this compound.²³ One recrystallization from pentane (-22°) produced 50 mg of white crystals, mp 103.5-104.5° (lit.^{23a} mp 103.5–104°).

Treatment of α -Methyleneoxetane with Phenyllithium. A 200-mg sample of the anthracene adduct 7 was pyrolyzed at 330-340° in the apparatus described above. The distillate was transferred in 1 ml of THF to a nitrogen-filled flask and was cooled in ice. Phenyllithium (0.8 ml, 2.2 M in 70:30 benzene-ether) was added dropwise and the reaction mixture was heated at 30-40° for 1 hr and at 80° for 4 hr. The mixture was cooled in ice; saturated NH₄Cl was added; the resulting mixture was extracted twice with ether. The combined ether extracts were dried (Na₂SO₄-MgSO₄) and concentrated. VPC analysis (SF-96, 125°)^{27c} of the residue showed three major peaks at 2.9, 4.0, and 8.1 min in an area ratio of 1:1.7:4. The three components were separated by preparative VPC. The first component had ir and NMR spectra and VPC retention time essentially identical with those of a sample of 2-phe-

nvl-3-buten-2-ol (13)¹⁹ which was prepared from methyl vinvl ketone and phenyllithium, essentially the procedure of Buchta.^{19a} The second component had ir and NMR spectra and VPC retention time essentially identical with those of a sample of 4-phenyl-2-butanone $(12)^{17,18}$ prepared by catalytic hydrogenation¹⁷ (PtO₂, ethyl acetate) of benzalacetone.⁴⁷ The third component was identified as biphenyl by ir, NMR, and VPC.⁴⁸ At a higher temperature, VPC analysis (SF-96, 172°)^{27c} of the crude product showed (in addition to early retention time peaks) peaks at 1.7 (corresponding in retention time to biphenyl) and 9.2 min in an area ratio of 2:1. From a separate experiment, the component representing the latter peak was purified by preparative VPC,⁴⁹ and had ir and NMR spectra and VPC retention time essentially identical with those of a sample of 2,4-diphenyl-2-butanol (14).^{18,21} This sample was prepared from 4-phenyl-2-butanone (12) by the procedure of Stoermer¹⁸ except that phenyllithium was used in place of phenylmagnesium bromide. The ir and NMR spectra of this sample were equivalent to the reported spectra.²¹

Acknowledgments. We thank the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the Research Council of Rutgers University for their support of this research. We thank Dr. D. Z. Denney for obtaining the 100-MHz proton NMR spectrum of 11, and Mr. L. R. Rudnick for obtaining the carbon-13 NMR spectra.

Registry No.-1, 33988-20-4; 2, 6372-63-0; 3, 33190-01-1; 4, 33084-39-8; 2:1 4-butanediol, 54119-94-7; 5, 54119-95-8; 6, 33988-19-1; 7, 32869-16-2; 8, 54119-96-9; 9, 54119-97-0; 11, 32869-14-0; 19978-14-4; anthracene, 120-12-7; α -acetoxyacrylonitrile, 15. 3061-65-2; 1,4-di(methanesulfonyloxy)butane, 55-98-1.

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- ment; chemical shifts of the nonaromatic carbon atoms are reported in parts per million relative to tetramethylsilane (δ 0) as an internal reference, followed by the multiplicity observed with off-noise decoupling, and assignments. For consistency, compounds 4 and 7 are both numbered as shown below for compound 7, and compounds 8 and 9 are both numbered as shown below for compound 8.



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- The NMR spectrum was taken on a Jeol MH-100 instrument.
- (40) A number of pyrolyses were also carried out by dropping crystals of 7 (100-200 mg) directly through a 2.2 × 35 cm Vycor tube packed with short lengths of 5-mm Vycor tubing, at temperatures from 400 to 800° and 0.18-1-mm pressures. Anthracene, recovered 7, 8, 15, allene, and formaldehyde were among the products detected in these pyrolyses, but little or no α -methyleneoxetane was formed.
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- (43) An NMR spectrum was taken before chromatography to ascertain that the products isolated were not formed during the chromatography.
- (44) From separate pyrolyses, careful chromatography of the nonvolatile residue produced samples of the rearranged product 8 as an oil, having essentially identical ir and NMR spectra with those of the crystalline sample of 8 prepared earlier. Pure crystalline samples of anthracene and 7 were similarly isolated. (45) The mass spectrum of 11 was obtained on a Hitachi Perkin-Elmer Model
- RMU-7 instrument in conjunction with a Perkin-Elmer Model 881 gas chromatograph using a 10% SE-30 column (10 ft \times 0.25 in.) at 68°, helium flow about 78 ml/min. VPC analysis showed peaks at 4.7 (corresponding in retention time to the ether solvent) and 9.1 min. The mass spectrum was taken of the material represented by the 9.1-min peak. THF under these conditions had a retention time of 9.7 min.
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Carbon-13 Spectra of Methoxyflavones

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Received July 26, 1974

Assignments of NMR chemical shifts for carbon of flavone, chromone, and seven methoxyflavones are reported. Qualitatively, the upfield shift induced by the methoxyl substituent is similar to that indicated by the shielding relationships given in major texts. However, the effect of methoxyl appears to be larger in compounds where important resonance forms can be written indicative of a high degree of double-bond character. The use of ¹³C-H splittings of the various carbons to elucidate the position of substitution is covered. Splittings due to a proton meta to a given carbon are quite large (\sim 8 Hz) and are very useful, but splittings due to ortho and para protons are irregular and of little use.

One great advantage of ¹³C NMR spectroscopy has been in the characterization of aromatic and pseudoaromatic compounds, whose proton spectra are not well differentiated. This work is concerned with the application of ¹³C spectroscopy to structure elucidation in a common class of naturally occurring compounds, namely, the flavones.

Proton NMR spectra of flavanoids have been studied in many laboratories since the first extensive correlation of aromatic proton signals in 1962.¹ Other studies described the use of deuterated dimethyl sulfoxide as a solvent for

polyhydroxyflavones,² and trimethylsilylation as solubilization techniques for NMR analysis of flavanoids.³ Several aspects of flavone NMR spectra have continued to be of interest, including an extensive study of the effect of acidic media.4a Solvent-induced shifts are a valuable technique for study of polysubstituted flavones.^{4b} Detailed reviews of flavone NMR spectra are available.⁵ Apparently no systematic ¹³C NMR studies of the flavanoids have appeared, however.⁶ The ¹³C correlations reported herein complement these other techniques and should provide future in-