and 7.09 (q, 4, $J = 9$ Hz, aromatic). The nmr spectra displayed a considerable reduction of the methyl singlet while other portions of the spectra remained constant.

exo-2-*p*-Anisyl-3,3-dimethyl-*endo*-2-norbornanol (20) (*p*-Anisyl-camphenilol).—Alcohol 20 was prepared by the method of Bartlett, *et al.*, from (−)-camphenilone: mp 138–140° (lit.[12] mp 143.5–144.5°); [α]D −24.72° (c 6.22 benzene) [lit.[12] [α]D −25.7° (c 4.2, benzene)]; nmr (concentrated H₂SO₄) δ 1.3–2.9 (complex m, CH₂'s) and C₄H), 1.72 (broad s, 6, −CH₃'s), 4.35 (broad s, C₁ H), 4.37 (broad s, −OCH₃), and 8.02 (m, aromatic); uv max (concentrated H₂SO₄) 385.2 nm (log ε 4.6).

endo-2-*p*-Anisyl-*exo*-methyl-3-methylenenorbornane (2) (*p*-Anisylapocamphene).—Olefin 2 was prepared according to the procedure of Bartlett, *et al.*:[12] nmr (CDCl₃) δ 0.85–2.00 (complex m, CH₂'s), 1.38 (s, 3, −CH₃), 2.22 and 2.75 (m, 2, bridgehead H), 3.65 (s, 3, OCH₃), 4.65 and 5.10 (d, 2, =CH₂), and 6.99 (q, 4, aromatic).

Carbonium Ion Trapping Experiments. *endo*-2-*p*-Anisyl-3,3-dimethyl-*exo*-2-norbornanol (21) (Iso-*p*-anisylcamphenilol). **A. General Procedure.**—The starting substrate (450–550 mg) was dissolved in concentrated sulfuric acid or deuteriosulfuric acid by swirling. The resulting orange solution was allowed to stand at room temperature for the specified time. This was then rapidly and with stirring poured into 200 ml of ice water, and the resulting aqueous solution was extracted with 2 × 100 ml of ether. The ether extracts were combined and washed with 100 ml of 5% sodium bicarbonate and 100 ml of saturated sodium chloride, dried (anhydrous magnesium sulfate), and concentrated to yield a yellow oil which crystallized after standing at room temperature for several hours. Two recrystallizations from heptane yielded white needles of 21. The physical constants found for 21 from the various starting substrates are listed in Table III.

B. Specific Procedure.—The alcohol 20 (1.0 g, 0.04 mol) was dissolved in 10 ml of concentrated sulfuric acid by swirling. The orange solution, after standing at room temperature for 30 min, was poured into 200 ml of ice water with stirring. The aqueous mixture was extracted with 2 × 100 ml of ether, and the ether extracts were combined and washed with 100 ml of 5% sodium bicarbonate and 100 ml of saturated sodium chloride, dried (anhydrous magnesium sulfate), and concentrated to yield a yellow oil which solidified after standing at room temperature for 2 hr to give 820 mg (82%) of crude 21, mp 66–76°. Recrystallization from 10 ml of hot heptane gave 478 mg (48%) of 21 as white needles: mp 77.4–78.4° (lit.[12] mp 76–78°); ir (KBr) 3455 (-OH), 2940 (CH), 1515, and 1245 cm⁻¹; nmr (CDCl₃) δ 0.80 (s, 3, −CH₃), 1.10–1.90 (complex m, CH₂'s and -OH), 1.29 (s, −CH₃), 2.15–2.63 (complex m, 2, bridgehead H), 3.79 (s, 3, −OCH₃), and 7.10 (q, 4, $J = 9$ Hz, aromatic); nmr [CDCl₃ and Eu(DPM)₃] δ 1.68 (s, 3, −CH₃), 1.76–2.76 (complex m, 6, CH₂'s), 3.18 (s, 3, −CH₃), 3.50 (s, 1, −OH), 3.88 (s, 3, -OCH₃), 4.34–4.98 (m, 2, C₁ H and syn 7-H), and 7.80 (q, 4, aromatic).

Anal. Calcd for C₁₆H₂₂O₂: C, 78.01; H, 9.00. Found: C, 77.99; H, 8.94.

TABLE III

PHYSICAL CONSTANTS FOR 21 ISOLATED FROM VARIOUS STARTING MATERIALS

Substrate	Acid	Time, min	Mp, °C	$\alpha^{26.0}$D
20	H₂SO₄	30	77.4–78.4	
2	D₂SO₄	10	77.0–78.5	
1	D₂SO₄	10	74.5–75.5	
20	D₂SO₄	10	79.0–79.5	
1-CH₃-*d*	H₂SO₄	10	71.0–74.5	
(−)-20	H₂SO₄	2	79.0–79.5	−0.10°
(−)-20	H₂SO₄	21	79.0–80.5	−0.08°
(−)-20	H₂SO₄	30	77.8–79.5	

Hydrogenation of 9,10-Dimethylanthracene with Cobalt Hydrocarbonyl

PAUL D. TAYLOR AND MILTON ORCHIN*

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

The hydrogenation of 9,10-dimethylanthracene can be achieved with cobalt hydrocarbonyl at room conditions. Although the product consists of a mixture of *cis*- and *trans*-9,10-dihydro-9,10-dimethylanthracenes, a mechanism consistent with exclusive cis addition is suggested.

The catalytic homogeneous hydrogenation of a variety of polynuclear hydrocarbons is reported[1] to proceed smoothly in the presence of Co₂(CO)₈ and synthesis gas (CO + H₂) at elevated temperatures and pressures. The hydrogenation is reported to be quantitative and to lead exclusively to dihydro and tetrahydro products. With anthracene, for example, 9,10-dihydroanthracene is the sole product. Since under these reaction conditions the catalytic species is unquestionably HCo(CO)₄, or HCo(CO)₃ with which it is in equilibrium, it was of interest to learn whether

such aromatic compounds could be reduced at room conditions with stoichiometric quantities of HCo(CO)₄. We have now found that such is the case; *e.g.*, 9,10-dimethylanthracene (1) is converted essentially completely into the corresponding 9,10-dihydro derivative. This reaction provided a further opportunity to study the stereochemistry of HCo(CO)₄ reactions. Although the stereochemistry of the hydroformylation of olefins has not been ascertained conclusively, the hydrogenation[2] and the isomerization[3] of olefins with HCo(CO)₄

(1) S. Friedman, S. Metlin, A. Svedi, and I. Wender, *J. Org. Chem.*, **24**, 1287 (1959).

(2) W. L. Fichteman and M. Orchin, *ibid.*, **33**, 1281 (1968).

(3) F. Piacenti, S. Pucci, M. Bianchi, R. Lazzaroni, and P. Pino, *J. Amer. Chem. Soc.*, **90**, 6847 (1968); R. Casey and C. Cyr, *ibid.*, **93**, 1280 (1971), P. Taylor and M. Orchin, *ibid.*, **93**, 6504 (1971).

have been shown to proceed *via* a cis process. In the present study we have found that the reduction of **1** with HCo(CO)₄ leads to a mixture of *cis-* and *trans-* 9,10-dihydro products **2** and **3**; however, as will be shown, this fact is not necessarily inconsistent with exclusive cis addition.

Experimental Section

Analysis.—Analysis of the products from the reaction with anthracene and with **1** was performed on an F & M gas chromatograph equipped with a 10 ft × ¹/₁₆ in. stainless steel column packed with silicone XE-60 (5 wt %) supported on Ana-Chrome ABS 90–120 mesh using helium (38 ml/min) as the carrier gas. At a column temperature of 200°, 9,10-dihydroanthracene is eluted before anthracene, and *cis*-9,10-dihydro-9,10-dimethylanthracene (**2**) is eluted before the trans compound, **3**. After **2** and **3** were eluted, the column was programmed to 250° at 30° min to elute **1**. Concentrations were determined by measuring the peak areas by the method of triangulation. No other products, other than those reported, were detected.

Materials.—Anthracene (Matheson Coleman and Bell) was recrystallized three times from acetone and dried under vacuum (1 mm) for 4 hr at 25°, mp 220–222° (uncor). 9,10-Dimethylanthracene (Aldrich-Puriss. Grade) was used without further purification, mp 175–179° (uncor). Reagent grade benzene was dried over a molecular sieve before use. Tri-*n*-butylphosphine (Carlisle Chemical Co.) was vacuum-distilled and stored under nitrogen at −20°. Co₂(CO)₈ was prepared in the usual way.[4] The crystalline carbonyl was collected and stored at −20° under a carbon monoxide atmosphere. Synthesis gas was prepared by mixing equal amounts of carbon monoxide and hydrogen.

Catalytic Hydrogenations.—The catalytic hydrogenations were carried out in 30-ml, well-agitated high-pressure vessels. The catalyst was weighed accurately and placed in the reactor, which was then purged with CO, and 10 ml of a benzene solution of anthracene or **1** was added before sealing the vessel. The reactor was purged with carbon monoxide before pressuring with the desired amount of carbon monoxide and hydrogen. The reactors were heated (30 min) to the reaction temperature with agitation, kept at this temperature (±2°) for a specified period of time, and cooled (45 min) to room temperature before releasing the pressure. The solutions were withdrawn and analyzed by vpc.

A solution of 15.4 mg of **1** in 10 ml of dry benzene was added to 27.8 mg of Co₂(CO)₈ and the solution treated with H₂/CO (1:1) at 3000 psi and 150° for 90 min. Vpc of the solution indicated a 99% yield of a mixture consisting of **2** (48%) and **3** (52%). Similar treatment of anthracene gave a 99% yield of 9,10-dihydroanthracene.

A solution of 15.4 mg of **1** in 10 ml of dry benzene was added to 31.9 mg of Co₂(CO)₈ and 0.146 g of tributylphosphine and the solution treated at 1600 psi and 150° for 90 min. Vpc of the solution indicated a 68% yield of a mixture consisting of **2** (44%) and **3** (56%).

A solution of 20.6 mg of **2** (containing 4% **3** as impurity) in 10 ml of dry benzene was added to 17.9 mg of Co₂(CO)₈ and the solution treated at 3000 psi and 150° as above. Vpc indicated a mixture of **2** (94%) and **3** (6%).

Stoichiometric Hydrogenations with Cobalt Hydrocarbonyl.— HCo(CO)₄ was prepared as described in the literature.[5] Its concentration was determined by addition of excess standardized NaOH solution and back titration with HCl using phenolphthalein as an indicator. Anthracene (or 9,10-dimethylanthracene) was dissolved in the appropriate solvent and treated with a solution of HCo(CO)₄ at 25° under an atmosphere of CO. The reaction mixture was worked up by adding 3 ml of dimethylformamide (DMF) to 10 ml of the product solution and stirring the mixture until the Co₂(CO)₈ color disappeared. Water (5 ml) was then added and the lower layer withdrawn using a syringe. The organic layer was washed twice with 5 ml portions of water and dried over Na₂SO₄ before analyzing by vpc.

A 20-ml solution of toluene containing 6.8 mmol of HCo(CO)₄ was added with stirring to 200 mg (1.12 mmol) of anthracene

(4) I. Wender, H. W. Sternberg, S. Metlin, and M. Orchin, *Inorg. Syn.*, **5**, 190 (1957).

(5) L. Kirch and M. Orchin, *J. Amer. Chem. Soc.*, **80**, 4428 (1958).

dissolved in 20 ml of toluene in a round bottom flask purged with carbon monoxide. The solution was stirred for 24 hr before being worked up as described above. Vpc indicated a 25% yield of 9,10-dihydroanthracene.

A 10-ml solution of toluene containing 4.74 mmol of HCo(CO)₄ was added with stirring to 46.4 mg of **2** dissolved in 20 ml of toluene as described above. The solution was stirred for 48 hr. Vpc of the solution indicated a 99% yield of a mixture consisting of **2** (35%) and **3** (65%).

A solution of 1.06 g of 1,1-diphenylethylene (Eastman) in 15 ml of pentane (spectroscopy grade) was injected into a 50-ml round bottom flask previously purged with CO. Then 10 ml of a cold solution of pentane containing 5.9 mmol of HCo(CO)₄ was injected into the flask with stirring. Within 10 min the solution turned dark, and after 1 hr it was very dark. The solution was stirred for 12 hr and then treated with 3 ml of DMF. The solution was washed three times with 5-ml portions of water, and the pentane layer was dried over sodium sulfate and then evaporated on a rotovap at 25°. The resulting liquid was analyzed by nmr and found to be 99% 1,1-diphenylethane.

A pentane solution containing 2.0 g of *cis*-stilbene was treated with 3 ml of a solution of pentane containing 5.91 mmol of HCo(CO)₄. The solution was stirred for 60 hr at 26° and worked up as above. The liquid product was analyzed by nmr spectroscopy and found to consist of 7% *trans*-stilbene, about 2% 1,2-diphenylethane, and 91% of unchanged material.

Results and Discussion

The reduction of **1** gives a mixture of **2** and **3**, respectively. The mixture which results under various
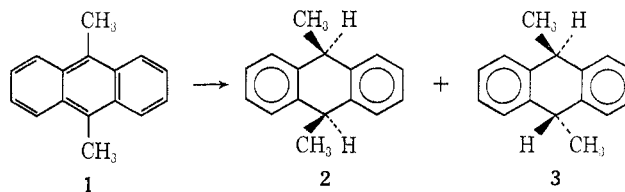
oxo conditions is shown in Table I. That the cis isomer is not a precursor to the trans isomer was shown when the cis isomer was treated under catalytic oxo conditions with Co₂(CO)₈ and it was found to be inert to such treatment.

TABLE I
REDUCTION OF 9,10-DIMETHYLANTHRACENE (1)

Catalyst	Temp. °C	% cis (2)	% trans (3)
Co₂(CO)₈	150	48	52
Co₂(CO)₆(Bu₃P)₂	150	44	56
HCo(CO)₄	25	35	65

Addition to anthracene is usually thought to proceed by 1,4-conjugate addition at the meso positions. If addition of the H and Co(CO)₄ moieties occurs simultaneously, or if addition of the two moieties is from the same side, cis product should be formed exclusively. Most of the available evidence dealing with reactions of HCo(CO)₄ indicate that the addition is simultaneous. The failure to obtain cis product exclusively in the hydrogenation of **1** leads us to propose Scheme I. This scheme requires that compound **5** be present, at least at low concentration, as free olefin so that subsequent attack of HCo(CO)₄ can occur at either face of the olefin and thus produce both cis and trans isomers. This scheme also requires that the hydrogenolysis of **4** proceed slowly enough to permit competitive elimination to **5**. It is, of course, not necessary that the reaction of **5** with HCo(CO)₄ produce **4** again; anti-

SCHEME I

4

$\xrightarrow{2HCo(CO)_4}$ 2 + 3

5
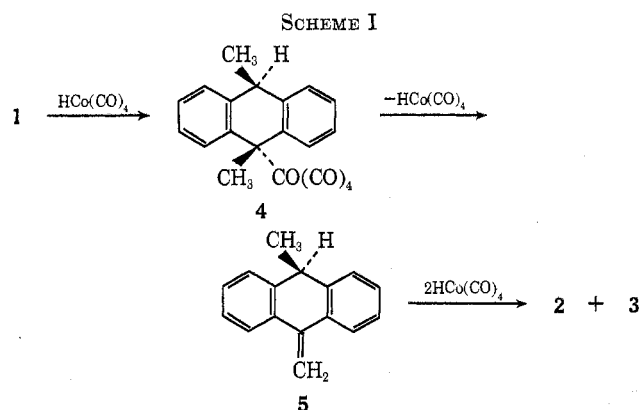
Markovnikov addition is also possible. In an experiment with the structurally related 1,1-diphenylethene, it was shown that the reaction proceeds smoothly and relatively rapidly with $HCo(CO)_4$ to give 1,1-diphenylethane. It is likely that this reaction proceeds by anti-Markovnikov addition

$$Ph_2C{=}CH_2 \longrightarrow Ph_2CHCH_2Co(CO)_4 \longrightarrow Ph_2CHCH_3$$

The reaction with **5** may proceed similarly. Preliminary results with $DCo(CO)_4$ showed, as expected, the presence of D_3 in both **2** and **3**. However, in addition to D_3 ($\sim$10%), there was substantial D_1 and D_2 present; the deuterium experiments are not clear-cut and need further investigation.

At this time we have no firm explanation for the differences in cis/trans ratio found under the different conditions shown in Table I. The intermediate **5**, if indeed it does exist, may be present in isomeric[6] form

5a   5b
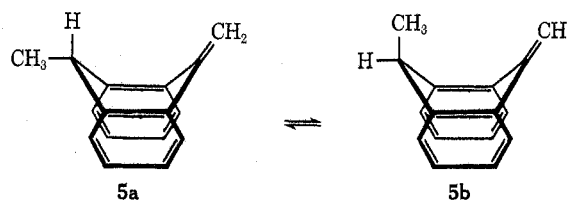
The equilibrium concentration of these isomers may change with temperature and the ratio of exo/endo attack by $HCo(CO)_4$ may be different for each isomer and also be affected by temperature.

Registry No.—**1**, 781-43-1; **2**, 13417-34-0; **3**, 13417-35-1; cobalt hydrocarbonyl, 16842-03-8.

(6) S. J. Cristol, *Accounts Chem. Res.*, **4**, 393 (1971).

The Polar and Steric Substituent Constants for an Alkylperoxy Group and Related Ether Groups

W. H. RICHARDSON,* R. S. SMITH, G. SNYDER, B. ANDERSON,[1] AND G. L. KRANZ

Department of Chemistry, California State University, San Diego, San Diego, California 92115

Rates of acid-catalyzed esterification were measured for 2-*tert*-butylperoxy-2-methylpropanoic acid (**1a**), 2,2-dimethyl-3-*tert*-butoxypropanoic acid (**2a**), and 2-methyl-2-neopentoxypropanoic acid (**3a**). Rates of the basic hydrolysis of the methyl esters of these acids were obtained and from the kinetic data from these two types of reactions σ^* and E_s values were calculated. The σ^* and E_s values for the substituents $(CH_3)_3COOC(CH_3)_2$, $(CH_3)_2COCH_2C(CH_3)_2$, and $(CH_3)_3CCH_2OC(CH_3)_2$ are +0.520 and −1.96, −0.166 and −1.57, and +0.178 and −1.43, respectively. These values are discussed with relationship to each other and to analogous groups that are reported in the literature. The basic hydrolysis of methyl 2-*tert*-butylperoxy-2-methylpropanoate (**1b**) yields *tert*-butyl alcohol and acetone. The origin of these fragmentation products is discussed by considering the rate of *tert*-butyl alcohol formation from **1b**, the rate of disappearance of **1b**, and the rate of disappearance of ethyl 2-*tert*-butylperoxy-2-methylpropanoate (**5**) in 85% ethanol. The basic hydrolysis of **1b** was considered as a possible source of excited-state carbonyl products. However, the lack of light emission from an acceptor (fluorescein) added to the reaction mixture indicates that excited-state carbonyl species are not produced.

As part of a program to evaluate neighboring peroxide group reactions[2] it was necessary to determine the polar substituent constant[3,4] σ^* for an alkylperoxy group. To our knowledge there are no previous re-

ports of such a substituent constant. Polar substituent constants for stereochemically similar ether groups were required as well and they are reported here. The σ^* values were obtained from the rates of acid-catalyzed esterification of 2-*tert*-butylperoxy-2-methylpropanoic acid (**1a**), 2,2-dimethyl-3-*tert*-butoxy-propanoic acid (**2a**), and 2-methyl-2-neopentoxypropa-

(1) National Science Foundation Undergraduate Research Participant, summer, 1969.

(2) (a) W. H. Richardson and V. F. Hodge, *J. Amer. Chem. Soc.*, **93**, 3996 (1971); (b) W. H. Richardson, J. W. Peters, and W. P. Konopka, *Tetrahedron Lett.*, 5531 (1966).

(3) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

(4) We have retained the σ^* symbol for convenience in estimating our neighboring peroxide group rate data, which will be reported later. It has been suggested that the σ^* constant should be replaced by other substituent constants such as σ_I[5] and field and resonance constants.[6]

(5) C. D. Ritchie and W. F. Sager, "Progress in Physical Organic Chemistry," Vol. 2, S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Jr., Ed., Interscience, New York, N. Y., 1964, p 323.

(6) C. G. Swain and E. C. Lupton, *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

noic acid (**2a**), and 2-methyl-2-neopentoxypropa-

1a, R = H
b, R = CH_3

2a, R = H
b, R = CH_3

3a, R = H
b, R = CH_3