17α-Hydroxycorticosterone.—One gram of 11-desoxy-17α-hydroxycorticosterone (Reichstein's Compound S) was incubated with a mycelium suspension for 16 hours. The effluent fractions from the silica gel column, which contained a compound with the same mobility on paper chromatograms as 17α-hydroxycorticosterone were combined and evaporated to dryness. From a solution of the residue in ethyl acetate there were obtained 410 mg. of crystals, m.p. 208.5–209.5°, $[\alpha]^{25}\text{D}$ +165.7° (95% ethanol), $\lambda^{\text{KBr}}_{\text{max.}}$ 2.95 μ (OH), 5.85 μ (20-ketone); 6.08 and 6.20 μ (Δ^4-3-ketone). (*Anal.* Calcd. for $C_{21}H_{30}O_5$: C, 69.58; H, 8.34. Found: C, 69.42; H, 8.49.) The m.p. and optical rotation are in good agreement with those reported in the literature for 17α-hydroxycorticosterone.[7] In addition to 17α-hydroxycorticosterone, paper chromatograms indicated the presence of three less polar and four more polar transformation products in the extract.

11β,17α-Dihydroxyprogesterone.—Incubation of 1.0 g. of 17α-hydroxyprogesterone for 6 hours with a suspension of *C. lunata* mycelium provided a chloroform extract which yielded, after silica gel partition chromatography, 340 mg. of crystals, m.p. 226–228°, $[\alpha]^{25}\text{D}$ +135.5° (acetone), $\lambda^{\text{KBr}}_{\text{max.}}$ 2.95 and 3.02 μ (OH), 5.94 μ (20-ketone), 6.09 and 6.20 μ (Δ^4-3-ketone). (*Anal.* Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 73.25; H, 8.59.) The m.p. and optical rotation agree with those published for 11β,17α-dihydroxy-Δ^4-pregnene-3,20-dione (21-desoxy compound F).[8] Additional evidence for the presence of an 11β-hydroxy group in the isolated steroid was provided by (1) the failure of the compound to form an acetate with acetic anhydride–pyridine under the usual conditions, and (2) the oxidation of the compound with chromic acid to yield a product,[9] m.p. 231–232.6°, $[\alpha]^{25}\text{D}$ +194° ($CHCl_3$). The properties of the compound agree with those reported for 17α-hydroxy-Δ^4-pregnene-3,11,20-trione.[10] Paper chromatograms indicated that there were four products more polar and one product less polar than 11β,17α-dihydroxyprogesterone also present in the extract.

Corticosterone.—A four-hour fermentation of 11-desoxycorticosterone according to the procedure outlined above produced a conversion product with the same mobility on paper chromatograms as corticosterone. In addition, five other oxygenated products were in evidence on the chromatograms of the broth extract. After silica gel fractionation as in the previous experiments, the effluent fractions containing the compound with a mobility similar to that of corticosterone were combined to yield crystals, m.p. 178–180°, $[\alpha]^{25}\text{D}$ +210.5° (95% ethanol), $\lambda^{\text{KBr}}_{\text{max.}}$ 2.96 μ (OH), 5.93 μ (20-ketone), 6.10 and 6.20 μ (Δ^4-3-ketone). (*Anal.* Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.34; H, 8.61.) The properties of the isolated compound agree with those reported for corticosterone.[11]

11β-Hydroxyprogesterone.—Paper chromatography of a six-hour fermentation of progesterone indicated the formation of 11β-hydroxyprogesterone and four other progesterone transformation products. Fractionation of the broth extract provided crystals, m.p. 185–187°, $[\alpha]^{25}\text{D}$ +213.6° (acetone), $\lambda^{\text{KBr}}_{\text{max.}}$ 2.94 μ (OH), 5.92 μ (20-ketone), 6.08 and 6.20 μ (Δ^4-3-ketone). (*Anal.* Calcd. for $C_{21}H_{30}O_3$: C, 76.32; H, 9.5. Found: C, 76.95; H, 9.13.) The analytical data on the isolated compound are in agreement with those published for 11β-hydroxyprogesterone.[12]

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The Electric Moments and Configurations of Some *cis–trans* Isomers

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Dipole moment studies have been used to prove the configurations of the *cis–trans* isomers of 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene, of 1,-5-dichloro-9,10-dihydro-9,10-anthradiol diacetate and of 1,2-dichloroacenaphthene. The electric moments of 1,8,10-trichloroanthracene and of *trans*-1,2-dibromoacenaphthene also have been determined to establish their structures.

In the course of a study of the mechanisms of elimination reactions, the *cis* and *trans* isomers of 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene were prepared by the Diels–Alder addition of anthracene and the isomeric 1,2-dichloroethylenes.[2] The structures of the products may be presumed from the Alder rule of *cis* addition.[3] However, the lower melting *trans* compound, which has the hydrogen and chlorine atoms *cis*, was found to react with sodium hydroxide in ethanol–dioxane to give the chloroölefin at a rate approximately eight times as fast as the higher melting *cis* isomer. In most other cases of second-order elimination which have been studied,[2,4] *trans* elimination is significantly[1] faster than *cis* elimination; as these compounds disobey the normal rule, it seemed desirable to have some physical data to substantiate the presumed structures. Therefore, the electric dipole moments of the isomers have been measured in benzene solution at 25°.

If the carbon–chlorine bond moment in aliphatic halides is taken to be 2.0 Debye units, and the bond angles for the bonds involving the bridge carbon atoms are assumed to have normal tetrahedral values, then the electric moments calculated for the *cis* and *trans* isomers are 3.77 and 1.89 *D*, respectively. The observed moments are 3.16 ± 0.12 and 2.17 ± 0.12 *D*, in fair agreement with the calculated values; the isomer with the higher dipole moment is the one assigned the *cis* configuration on the basis of the Alder rule. It is evident that the Alder rule leads to the correct assignment of configuration and the rates of elimination are anomalous.[2] The moment observed for the *cis* isomer is lower by 0.6 *D* than the calculated value—a lowering comparable to the difference between observed and calculated values for *o*-dichlorobenzene. This may indicate that there is some twisting about the 11–12 carbon–carbon bond so that the chlorine atoms are not directly opposed or it may result from interaction of the carbon–chlorine dipoles as in *o*-dichlorobenzene. A twist of 60° about

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the 11–12 carbon–carbon bond would be required to give quantitative agreement with the observed data for the *cis* compound, and this seems unreasonable.

The moments of the 1,2-dichloroacenaphthenes are similar to those of the 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracenes. As before, the higher melting isomer is assigned the *cis* configuration (as it has the higher electric moment 2.97 *D*), and the lower melting isomer, with dipole moment 2.04 *D*, is *trans*. The calculated values would be 3.77 and 1.89 *D*, respectively, if the groups on the 1- and 2-carbon atoms are directly opposed. The higher melting isomer was prepared by the addition of chlorine to acenaphthalene and the lower melting isomer by reaction of acenaphthalene with iodobenzene dichloride; it was expected, on this basis, that the higher melting isomer would be *trans*.[5] Since the dipole moment results were the reverse of expectation, resolution of the isomers was undertaken[6]; partial resolution of the lower melting isomer by treatment with brucine in dioxane showed that it was the *dl-trans* modification, whereas the higher melting isomer must have the *meso-cis* structure since it was not resolved by this procedure.

Only the 124° melting isomer of 1,2-dibromoacenaphthene is known and its observed electric moment, 1.63 *D*, is close to that calculated for the *trans* isomer (about 1.75 *D*). Partial resolution by treatment with brucine in dioxane confirms the *dl-trans* structure for this compound.

The lower melting 1,5-dichloro-9,10-dihydro-9,10-anthradiol diacetate has been assigned the *cis* configuration on the basis of its larger dipole moment. However, because of the possibility of interactions between the two acetate groups, which might appreciably affect the dipole moments, this assignment is not as certain as the others. It is in agreement with the structures assigned to the corresponding diols.[7]

The single trichloroanthracene[8,9] obtained by dehydrohalogenation of the known isomer (*trans*) of 1,8,9,10-tetrachloro-9,10-dihydroanthracene[7] is shown to be 1,8,10-trichloroanthracene. The electric moments calculated for 1,8,10-trichloroanthracene and 1,8,9-trichloroanthracene are, respectively, 1.5 and 4.5 *D*.

Experimental

Materials.—The synthesis and properties for the compounds studied are given elsewhere: the *cis–trans* isomers of 11,12-dichloro-9,10-dihydro-9,10-ethanoanthracene[2]; the *cis–trans* isomers of 1,5-dichloro-9,10-dihydro-9,10-anthradiol diacetate[10]; the *cis–trans* isomers of 1,2-dichloroacenaphthene[6]; the *trans* isomer of 1,2-dibromoacenaphthene[6] and 1,8,10-trichloroanthracene.[9] The melting points of the isomers are listed in Table I.

Benzene was fractionally crystallized twice, distilled and dried over sodium: $n^{25}{}_D$ 1.4979, $d^{25}{}_4$ 0.87350.

Measurements and Calculations.—The electric moments were determined in benzene solution at 25°. By use of apparatus and technique described previously,[11] dielectric constants and densities of from five to ten solutions, ranging in mole fraction from 0.0001 to 0.005, were measured for each compound. The molar polarizations and dipole moments were calculated by the method of Halverstadt and Kumler.[12] The constants of their equation are shown in Table I along with the calculated molar polarizations, molar refractions and dipole moments. The probable error in molar polarizations is ±4%, and the probable error in dipole moments about ±0.12 *D*.

TABLE I

EMPIRICAL CONSTANTS,[a] MOLAR REFRACTIONS,[b] MOLAR POLARIZATIONS AND DIPOLE MOMENTS AT 25° IN BENZENE SOLUTION

ϵ_{10}	α^1	V_{10}	β^1	$P_2\infty$	MR_D	μ
cis-11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene (m.p. 203–204°)						
2.2737	14.77	1.14495	−1.38	278.73	74.03	3.16
trans-11,12-Dichloro-9,10-dihydro-9,10-ethanoanthracene (m.p. 113.6–114°)						
2.2714	7.268	1.14488	−1.307	170.26	74.03	2.17
cis-1,5-Dichloro-9,10-dihydro-9,10-anthradiol diacetate (m.p. 246°)						
2.2725	3.65	1.14487	−1.91	133.73	88.78	1.48
trans-1,5-Dichloro-9,10-dihydro-9,10-anthradiol diacetate (m.p. 265°)						
2.2725	2.9	1.14484	−2.10	118.30	88.78	1.20
cis-1,2-Dichloroacenaphthene (m.p. 113–114°)						
2.2734	12.12	1.14474	−1.156	242.06	61.14	2.97
trans-1,2-Dichloroacenaphthene (m.p. 67–68°)						
2.2723	6.61	1.14480	−1.148	146.69	61.14	2.04
1,8,10-Trichloroanthracene (m.p. 191°)						
2.2725	4.50	1.14485	−1.59	125.15	71.58	1.62
trans-1,2-Dibromoacenaphthene (m.p. 124–125°)						
2.2732	4.60	1.14488	−2.370	118.86	64.21	1.63

[a] The observed dielectric constants ϵ_{12}, and specific volumes, V_{12}, of the solutions were plotted graphically against mole fraction of solute. The points fall, within experimental error, on straight lines with slopes α^1 and β^1, respectively, and the intercepts at zero mole fraction are ϵ_{10} and V_{10}, respectively. The molar polarizations are infinite dilution $P_2\infty$, and the dipole moments μ, expressed in Debye units, were calculated from these constants. [b] Molar refractions were calculated from empirical atomic refractions.

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The Preparation of O-Phenylcarbamyl Benzohydroxamate Through the Lossen Rearrangement

BY MARVIN A. STOLBERG, ROBERT C. TWEIT, GEORGE M. STEINBERG AND THEODOR WAGNER-JAUREGG

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In May, 1954, Hurd and Bauer[1] reported the formation of substituted O-carbamyl hydroxamates by treatment of sodium salts of hydroxamic acids with aromatic sulfonyl chlorides

$$2\ \mathrm{RCONHONa} + \mathrm{RSO_2Cl} = \mathrm{RCONHOCONHR} + \mathrm{RSO_2ONa} + \mathrm{NaCl}$$

At the time of this publication we were in the

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