the aqueous layer extracted with two 25-ml. portions of ether. The combined ether extracts were washed with 1 *N* sodium carbonate, and dried over anhydrous sodium sulfate. Removal of the ether afforded 16.25 g. (90%) of a mixture of menthol and neomenthol, $[\alpha]^{25}\text{D}$ −28.00° (homog.) (corresponding to 71% *l*-menthol in the mixture[24]). Variation in the molar excess of lithium aluminum hydride produced no appreciable change in the composition of the product. When 10 g. of the above mixture was reoxidized to menthone, 7.0 g. (71%) of III, $[\alpha]^{26}\text{D}$ −24.70° (homog.) was obtained.

Reduction of *d*-Camphor.—*d*-Camphor[25] was recrystallized from ethanol, m. p., 177–178°, $[\alpha]^{25}\text{D}$ 42.8° (*c* 10 in ethanol).

A solution of 15 g. (0.099 mole) of camphor in 50 ml. of anhydrous ether was added over a period of 1 hour to a stirred refluxing suspension of 4.5 g. (0.119 mole) of lithium aluminum hydride in 200 ml. of anhydrous ether. The mixture was allowed to reflux 12 hours to ensure complete reduction, and the excess lithium aluminum hydride dedecomposed with water and 6 *N* hydrochloric acid. The ether layer, dried over sodium sulfate was carefully evaporated to give a mixture of borneol and isoborneol, which was air-dried; 14.10 g. (94%), $[\alpha]^{25}\text{D}$ −26.00° (*c* 10 in ethanol).[26]

Reduction of α-Ethyl-α-butylglutaric Acid (IV).—A solution of 1.8 g. (0.047 mole) of lithium aluminum hydride in 55 ml. of anhydrous ether was added at −15° to 9.18 g. (0.043 mole) of IV dissolved in 200 ml. of anhydrous ether over a period of 40 minutes. After allowing to warm to room temperature, ice and 6 *N* hydrochloric acid were added to decompose any unreacted lithium aluminum hydride and the reduction complex. The separated ether layer was extracted with four 25-ml. portions of 2 *N* sodium hydroxide and concentrated to give 0.88 g. (11%) of crude 2-ethyl-2-butyl-1,5-pentandiol (see below).

Extraction of the acidified sodium hydroxide extracts gave a mixture of recovered IV and α-ethyl-α-butyl-δ-valerolactone, which was further separated by extraction with 1 *N* sodium carbonate solution. In this manner there was obtained 1.30 g. (14%) recovered IV, m. p. 77–80°.

The ether solution of the lactone, dried over sodium sulfate, was fractionated, b. p. 114–115° (4.5 mm.), to give 3.06 g. (39%), d^{25}_4 0.9699, $n^{25}\text{D}$ 1.4620, $M\text{D}$ calcd. 52.3, found 52.2. There was a residue of 0.75 g. (10%) from the distillation.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.74; H, 10.87. Found: C, 72.03; H, 11.01.

Preparation of 2-Ethyl-2-butyl-1,5-pentanediol.—A solution of 10 g. (0.046 mole) of IV in 50 ml. of ether was added slowly to a stirred refluxing suspension of 7.92 g. (0.21 mole) of lithium aluminum hydride in 200 ml. of anhydrous ether. After refluxing overnight, excess lithium aluminum hydride was decomposed with ice and 6 *N* hydrochloric acid. The separated ether layer was washed with 1 *N* sodium carbonate, dried over sodium sulfate, and fractionated. In this manner there was obtained 6.54 g. (75%) of 2-ethyl-2-butyl-1,5-pentanediol, b. p. 146° (4 mm.), $n^{24}\text{D}$ 1.4671, d^{25}_4 0.9414.

Anal. Calcd. for $C_{11}H_{24}O_2$: C, 70.20; H, 12.78. Found: C, 70.12; H, 12.80.

The bis-(3,5-dinitrobenzoate) was prepared in the usual manner.[27] Recrystallized three times from ethanol, m. p. 98.2–98.7°.

Anal. Calcd. for $C_{25}H_{28}N_4O_{12}$: C, 52.08; H, 4.90; N, 9.72. Found: C, 52.08; H, 5.11; N, 9.93.

Summary

Selective reduction with lithium aluminum hydride has been shown to be generally only slightly affected by steric effects, It has also been shown that lithium aluminum hydride does not affect racemizable asymmetric centers.

BERKELEY 4, CALIFORNIA RECEIVED JUNE 5, 1950

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[24] Simonsen, "The Terpenes," Cambridge Univ. Press, p. 243, lists the properties of the pure isomers.

[25] Purchased from Magnus, Mabee and Reynard, New York.

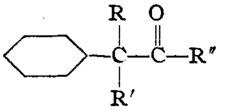
[26] Hückel, *Ann.*, **549**, 183 (1941), reports that the rotation of both borneol and isoborneol are independent of concentration in ethanol. The result above therefore indicated the formation of 90% isoborneol and 10% borneol.

[27] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., p. 138.

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY OF THE UNIVERSITY OF CALIFORNIA]

The Dipole Moments of Some α-Phenyl Ketones[1]

BY EDWARD L. ALPEN[2] AND W. D. KUMLER

In the previous papers[3,4] it was shown that compounds of the general type  $C_6H_5-C(R)(R')-C(=O)-R''$ where the R's can be aliphatic, aromatic or hydrogen, have a band of abnormally high extinction in the region 270–320 mμ, which was interpreted as arising from an interaction between the carbonyl and the phenyl groups. The interaction was considered both as a quantum mechanical perturbation and a no-bond resonance phenomenon. This investigation of the same compounds was undertaken to see whether or not the electronic interactions giving rise to the spectral anomalies also resulted in abnormal dipole moment values.

Measurements of the dipole moments were made in benzene solution at 30°. The moments were calculated by the method of Halverstadt and Kumler[5] using the equations

$$p_{2\infty} = \frac{3\alpha v_1}{(\epsilon_1 + 2)^2} + (v_1 + \beta)\frac{\epsilon_1 - 1}{\epsilon_1 + 2}$$

$$P_{2\infty} = p_{2\infty}M \quad \mu = 0.01281\sqrt{(P_{2\infty} - P_{E_2})T}$$

and the graphical modification for obtaining ϵ_1, v_1, α and β. In Figs. 1 and 2 it is seen that the ϵ_{12}–ω_2 curves are linear in all cases. P_{E_2} values were calculated using the group refractions given by

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[1] Abstracted in part from the dissertation presented by E. L. Alpen in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Pharmaceutical Chemistry.

[2] Fellow American Foundation for Pharmaceutical Education, 1949. Department of Pharmacology, The George Washington University School of Medicine, Washington 5, D. C.

[3] Kumler, Strait and Alpen, THIS JOURNAL, **72**, 1463 (1950).

[4] Alpen, Kumler and Strait, *ibid.*, **72**, 4558 (1950).

[5] Halverstadt and Kumler, *ibid.*, **64**, 2988 (1942).

TABLE I

Compound	ϵ_1	v_1	α	β	P_{20}	P_{E_2}	μ, D
1-Phenylpropanone-2	2.2604	1.15371	5.91	−0.260	186.43	38.17	2.72
1-Phenyl-1,1-dimethylpropanone-2	2.2611	1.15287	4.525	− .1235	188.99	49.41	2.63
1,1-Diphenylbutanone-2	2.2610	1.15285	4.20	− .235	240.07	68.90	2.92
3,3-Diphenylbutanone-2	2.2612	1.15283	3.615	− .2285	215.51	68.90	2.70
1,3-Diphenylpropanone-2	2.2622	1.15170	3.87	− .222	212.38	64.28	2.71[a]
1-Mesitylpropanone-2	2.2611	1.15225	4.72	− .1365	211.07	54.03	2.79
2-Phenylcyclohexanone	2.2620	1.15290	6.08	− .2225	249.37	51.83	3.13
Desoxybenzoin	2.2625	1.15181	4.89	− .252	234.50	59.66	2.95

[a] This compound has been previously measured by O. Hassel and E. Z. Naeshagen, *Physik. Chem.*, **B6**, 152 (1949), who reported a value of 2.65 *D*.

Smyth.[6] Measurements of the refractive index on concentrated solutions of three of the compounds were carried out using the D sodium line and the Pulfrich refractometer. The values calculated therefrom agreed, within the experimental error, with those calculated from the group refractions. In Table I are listed the extrapolated values of ϵ_1 and v, the graphic values of α and β, and the calculated values of P_{20}, P_{E_2} and μ. Six of the eight compounds fall within the usual range for ketones namely 2.7–3.0 *D*. One of the compounds is 0.07 below this range the other 0.13 above. There is thus no large variance in the dipole moments of the compounds compared with other ketones which do not have strong absorption in the 280–320 mμ region.

To obtain additional information the resultant moments of the molecules were calculated. These are listed in Table II where the symbols refer to the following: μ_{max} is the maximum moment with groups fixed; $\mu_{min.}$ is the minimum moment with groups fixed; $\mu_{f.r.}$ is the moment when all groups are rotating freely.

TABLE II

Compound	$\mu_{obs.}$	$\mu_{f.r.}$	$\mu_{max.}$	$\mu_{min.}$
1-Phenylpropanone-2	2.72	2.70	3.01	2.42
1-Phenyl-1,1-dimethylpropanone-2	2.63	2.70	3.01	2.42
1,1-Diphenylbutanone-2	2.92	2.68	2.85	2.52
3,3-Diphenylbutanone-2	2.70	2.68	2.85	2.52
1,3-Diphenylpropanone-2	2.71	2.68	3.24	1.96
1-Mesitylpropanone-2	2.79	2.70	3.01	2.42
2-Phenylcyclohexanone	3.13	..	3.20[a]	2.60[b]
Desoxybenzoin	2.95	..	2.97	2.89

[a] Phenyl *cis* to carbonyl. [b] Phenyl *trans* to carbonyl.

The latter was calculated by the formula used previously.[7] A group moment of 2.74 *D* was used for the aliphatic carbonyl group, 2.93 *D* for the aro-

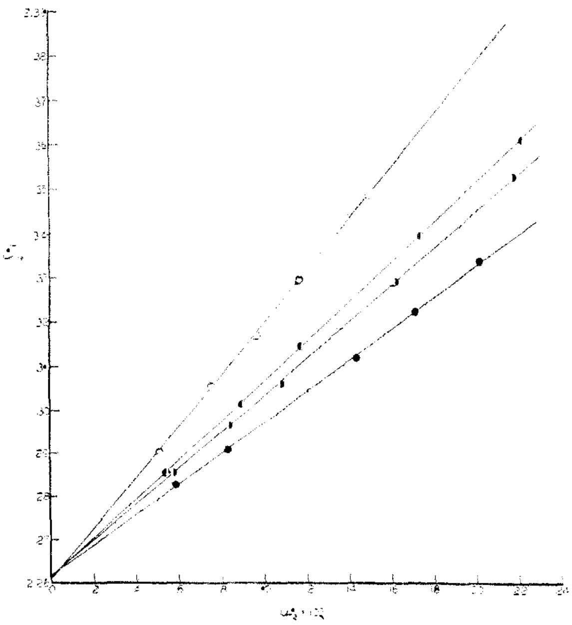

Fig. 1.—○, 1-phenylpropanone-2; ◐, 1-phenyl-1,1-dimethylpropanone-2; ◑, 1,1-diphenylbutanone-2; ●, 3,3-diphenylbutanone-2.

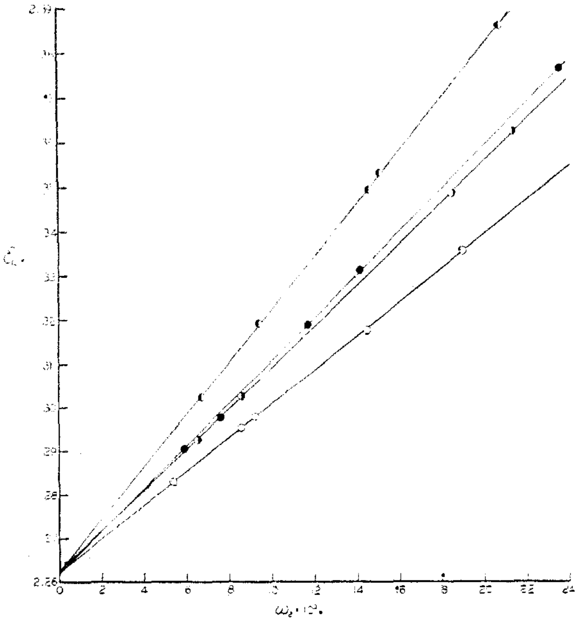

Fig. 2.—○, 1,3-diphenylpropanone-2; ◑, 1-mesitylpropanone-2; ◐, 2-phenylcyclohexanone; ●, α-phenylacetophenone.

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[6] Smyth, "Dielectric Constant and Molecular Structure," (Chemical Catalog Co.) Reinhold Publishing Corp., New York, N. Y., 1931, p. 150.

[7] Kumler and Halverstadt, THIS JOURNAL, **63**, 2182 (1941).

matic carbonyl group, 2.90 D[8] for the cyclic aliphatic ketone, 0.4 D for the benzyl group and 0.24 D[9] for the diphenyl methyl group.

Of the six compounds where free rotation is involved three have moments within 0.03 D of that calculated for free rotation, two differ by 0.07 and 0.09 D and one by 0.24 D. The possibilities to account for the near identity of the $\mu_{\text{obs.}}$ and $\mu_{\text{f.r.}}$ for three of the compounds are: firstly, the molecules have free rotation; secondly, the groups may be held in, or oscillate about, such positions that they by chance happen to have a moment near or equal to that for free rotation; thirdly, the contributions from the no-bond resonance structures may in part determine the observed moment. The Fischer–Hirschfelder–Taylor models of these compounds indicate the presence of considerable hindrance to free rotation so the first possibiltiy is unlikely. The second and third possibilities are probably both operating and it is only by chance that the observed moment in three cases turns out to be very close to that for free rotation.

The moment of 1,1-diphenyl-butanone-2, 2.92 D, is higher than $\mu_{\text{max.}}$, 2.85 D. This apparently anomalous situation may be due to taking the moment of the diphenyl methyl group in this compound to be equal to that of diphenylmethane. The angle between the phenyl groups is 115° in diphenylmethane[9] but is likely to be near the tetrahedral angle in 1,1-diphenylbutanone-2 which would cause the moment contributed by the diphenylmethyl group to be larger than 0.24 D, the value used in the calculation. The appreciable difference between the $\mu_{\text{f.r.}}$ and the $\mu_{\text{obs.}}$ indicated this compound does not have free rotation.

An interesting conclusion can be drawn from the data in regard to the structure of 2-phenylcyclohexanone. Taking the cyclohexanone ring to be in the more stable *trans* or chair configuration there are two possibilities: one with the phenyl group replacing an equatorial hydrogen and *cis* to the carbonyl; the other with the phenyl group replacing a polar hydrogen and *trans* to the carbonyl. In Table II, it is seen that the observed moment, 3.13 D, is near that for the *cis* structure, 3.20 D, and quite different from that for the *trans* structure, 2.60 D. In view of the improbability of the no-bond resonance forms being of much significance with this compound,[4] the above evidence is considered fairly conclusive that this compound has the *cis* structure. It is significant that the models also indicate the *cis* compound is less hindered than the *trans*.

Experimental

Apparatus.—The dielectric constants were measured in an apparatus similar to that described elsewhere.[7] Matching of the beat frequency was accomplished by placing the radio speaker input voltage in the vertical plates of a cathode-ray oscilloscope, while the output voltage from a 1000 cycle Leeds and Northrup tuning-fork was placed on the horizontal plates. When the vertical and horizontal frequencies are equal, a circular Lissajou's figure results.

Material

Benzene.—This solvent was purified by shaking the Mallinckrodt thiophene-free material three times with one-tenth its volume of concd. sulfuric acid, then washing with distilled water until neutral to litmus. The benzene was then dried several days over anhydrous calcium sulfate. After drying, it was refluxed over sodium for several hours. Just before use the solvent was fractionally distilled from phosphorus pentoxide through a 30-inch Widmer column. A small forerun was discarded, then the benzene was collected in clean dry 1-liter glass stoppered bottles which were filled completely. No solvent was used from one day to the next without redistillation.

The preparation of all other materials has been described elsewhere.[3,4]

Summary

The dipole moments of eight α-phenyl carbonyl compounds have been measured in benzene solution. The moments of the compounds are normal falling in the range 2.63 to 3.13 D and are not greatly different from the moments of simple aliphatic carbonyl compounds. There is thus no appreciable evidence from the dipole moment values of the electronic interactions which give rise to the high extinction band at 280–320 mμ. The observed moments are compared with those calculated for free rotation and with the maximum and minimum moments. Evidence is presented that the phenyl group in 2-phenylcyclohexanone replaces an equatorial hydrogen, and is *cis* to the carbonyl group.

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[8] Halverstadt and Kumler, *ibid.*, **64**, 1982 (1942).

[9] Hampson, Farmer and Sutton, *Proc. Roy. Soc.* (*London*), **A143**, 147 (1933).