Mass spectrometric analysis[10] showed that the above material was a mixture.

Reformatsky Reaction of 1,1-Diphenylpropanone (1) with Methyl Bromoacetate. Formation of Methyl 4,4-Diphenyl-3-methyl-3-hydroxybutyrate (11).—This reaction was carried out in an atmosphere of dry nitrogen. To a stirred suspension of 1.96 g. (0.03 g.-atom) of zinc shot (20 mesh) in 10 ml. of ether containing a few crystals of iodine was added at reflux temperature in the course of 30 min. a mixture of 5.25 g. (0.025 mole) of 1,1-diphenylpropanone and 3.83 g. (0.025 mole) of methyl bromoacetate. Reaction commenced after 1.5 hr. of heating and the reaction mixture was held at reflux for an additional 3 hr. The reaction mixture was cooled in an ice bath and hydrolyzed with 50 ml. of 5% aqueous sulfuric acid. The aqueous phase was separated and extracted with three 25-ml. portions of ether. The combined ether solutions were washed with 5% sodium bicarbonate and then with water. Removal of the solvent from the dried solution afforded 6.4 g. of a mobile oil which was evaporatively distilled (210° at 1 mm.). This effected separation of the more volatile, unreacted 1,1-diphenylpropanone (1.50 g., 29% recovery), whose infrared spectrum revealed the presence of a small amount of benzophenone. The nonvolatile residue was chromatographed on a 22 × 3.0 cm. basic alumina packed column using successively hexane, hexane-benzene, benzene, and benzene–ethanol as eluents. Thirty-five fractions were collected. Fractions 28–29 contained 3.59 g. (51%) of methyl 4,4-diphenyl-3-methyl-3-hydroxybutyrate (11), m.p. 54–57°. Two recrystallizations from ligroin gave an analytical sample, m.p. 56.2–57.8°, λ_{max} 2.82 and 5.81 μ.

Anal. Calcd. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 76.27; H, 7.01.

Saponification of 11 to 4,4-Diphenyl-3-methyl-3-hydroxybutyric Acid (12).—Saponification of crude ester 11 was carried out by heating under reflux a 2.95-g. quantity for 4 hr. with 15 ml. of 5% ethanolic potassium hydroxide. The resulting yellow solution was diluted with 15 ml. of water and acidified with dilute hydrochloric acid. The milky suspension was extracted twice with ether and the combined ether extracts were extracted, in turn, with 5% sodium hydroxide. Acidification of the alkaline extract caused a yellow oil to separate. This suspension was extracted with ether and the ether extract was washed with water and dried. Removal of the solvent under reduced pressure afforded 1.46 g. (53%) of 4,4-diphenyl-3-methyl-3-hydroxybutyric acid (12) as an oil, which solidified on standing overnight at room temperature, m.p. 127–130°. Recrystallization of this material from 40 ml. of ligroin containing 2 ml. of ethanol gave, after refrigeration for 48 hr., 990 mg. of white crystals, m.p. 131.0–132.0°, $\lambda_{max}^{CHCl_3}$ 2.87 (broad) and 5.90 μ.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71; neut. equiv., 270.3. Found: C, 75.47; H, 6.64; neut. equiv., 271.0.

Reduction of 12 to 4,4-Diphenyl-3-methylbutyric Acid (7).—A suspension of 200 mg. (0.74 mmole) of hydroxy acid 12, 1.52 g. of red phosphorus, and 550 mg. of iodine in 10 ml. of glacial acetic acid to which 10 drops of water had been added was heated under reflux for 20 hr. The cooled reaction mixture was filtered through Celite and excess iodine was destroyed by treating the orange filtrate with 40 ml. of 2.5% sodium bisulfite. The tan solid which precipitated was collected by filtration, washed with water, and dried (180 mg., m.p. 105–113°). Recrystallization from hexane yielded 130 mg. (69%) of 4,4-diphenyl-3-methylbutyric acid (7), m.p. 115.0–117.5°. A second recrystallization from ethanol–water raised the melting point to 118.2–119.4° (lit.[8] m.p. 113°).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.21; H, 7.15.

Oxidative Cleavage of 1,1-Diphenylpropanone (1) to Benzophenone.—Oxygen from a cylinder was passed at the rate of 1 bubble/sec. for 15 hr. through a solution of 300 mg. of 1,1-diphenylpropanone in 6 ml. of 2% ethanolic potassium hydroxide. The solvent was removed under reduced pressure, the residue was taken up in ether, and the resulting solution was washed with water until neutral. Removal of the ether from the dried solution gave 209 mg. of a light yellow oil which was found to contain 111 mg. (42%) of benzophenone by quantitative infrared analysis.[21] The benzophenone was further characterized by conversion to the corresponding 2,4-dinitrophenylhydrazone. Treatment of an ethanolic solution of the oily residue with 2,4-dinitrophenylhydrazine reagent[15] afforded 215 mg. (41%) of the derivative, m.p. 233–239°, which was collected by filtration within 5 min. of its formation in order to avoid contamination by the more slowly formed dinitrophenylhydrazone of 1,1-diphenylpropanone. Recrystallization from glacial acetic acid afforded 190 mg. (37%) of benzophenone 2,4-dinitrophenylhydrazone, m.p. 240–242° (lit.[22] m.p. 238–239°), which was shown to be identical with an authentic specimen by a mixture melting point determination and infrared spectral comparison.

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(21) The analysis was done on a 56.5-mg. aliquot of the crude oily product diluted to a volume of 1.0 ml. with CCl_4. The intensities of the absorption bands characteristic of the ketone at 6.02, 10.63, and 10.88 μ were compared with a calibration curve obtained from the spectra of an authentic sample (2, 5, 10, 20, 35, and 50 mg./ml. of carbon tetrachloride solution) of benzophenone.

(22) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," Order I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 363.

Quantitative Confirmation of the Cookson Rule for α-Phenyl Ketones

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It is suggested that the exaltation of absorption in the region of 280 mμ shown by α-phenyl ketones is unrelated in the main to any orbital overlap between the carbon orbitals of the phenyl ring and the n orbital of the oxygen atom of the carbonyl group. Such exaltations appear to be primarily a result of orbital overlap between the carbon of the carbonyl group and the β-carbon of the β,γ-unsaturated system as previously proposed by Cookson. Data for ketones of fixed geometry and for ketones with groups rotatable to a degree are combined in a single uniform treatment and afford the opportunity of examining the nearest-neighbor suggestion and the accuracy of equations for π and σ overlap of bond orbitals.

After examination of a substantial list of β,γ-unsaturated ketones, Cookson proposed[2] that spectral exaltations in the region of 280–290 mμ arose most significantly when the p orbital on the carbon of the carbonyl group pointed toward the p orbital on the β-carbon of the β,γ-unsaturated system; *i.e.*, S_1 is a maximum in Figure 1. Subsequent to this, Labhart and Wagniere[3] proposed that exalted n–π^* transitions derived their strength from a charge-transfer band, the derivation being proportional to the square of the overlap integral (S_3) of the n orbital on the oxygen of the carbonyl group with the p orbital of the β-carbon of the β,γ-unsaturated system. If only the β- orbital of the β,γ-unsaturated system is involved (the "nearest-

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[1] (a) To whom inquiries should be addressed. (b) From the Ph.D. thesis of S. F. Marsocci. (c) Acting Director, University of Rhode Island Computer Laboratory.

[2] R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956).

[3] H. Labhart and G. Wagniere, *Helv. Chim. Acta*, **42**, 2219 (1959).

$$\epsilon_{n-\pi^*} = AS_1^2 \qquad \text{Cookson} \quad (1)$$

$$\epsilon_{n-\pi^*} = BS_3^2 \qquad \text{Labhart and Wagniere} \quad (2)$$

neighbor" suggestion[4]), one might contrast these two theories with eq. 1 and 2, in which A is merely a constant while B is a function of the magnitude of charge-transfer absorption which is, in turn, a function of the angles of rotation of the two groups. In an exact treatment, of course, the extinction coefficient should be replaced by the oscillator strengths. For the purpose of contrasting these proposals in their application to olefinic ketones of fixed geometry, it was proposed[5] that it was the *charge-transfer* absorption which was proportional, at constant frequency, to S_1^2. Equation 3, in which B' is now a constant, follows from 2. Should each orbital of the carbonyl

$$\epsilon_{n-\pi^*} = B'S_1^2S_3^2 \quad (3)$$

group interact with two orbitals of an olefin or with three orbitals of a phenyl group, eq. 4 might be prefer-

$$\epsilon_{n-\pi^*} = K\Sigma S_c^2 \Sigma S_0^2 \quad (4)$$

able. Although in the previous paper[5] a number of questionable corrections for varying band frequencies had to be made, a measure of support for eq. 4 appeared to result. There was pointed out, however, one hazard. The data tabulated were for molecules which did not have maximum values of $\Sigma S_c^2 \Sigma S_0^2$ and that the range of angular placements was comparatively small.

The purpose of the present work was to examine the utility of these equations in an analysis of α-phenyl ketones. The data for these have the advantage that very little change of the "ketonic" band position occurs but offer the disadvantage that most of the ketones having exalted spectral values are those which have ketone and phenyl groups which are, to a degree, rotatable. In the present paper, these are treated in the form of population tables or data decks, each consisting of 325 fractions, the sum of which is equal to 1. For certain ketones with elements of symmetry, the data deck was reduced in size appropriately. The collection of such decks, along with the data for a few α-phenyl ketones of fixed geometry, was used to examine the validity of certain "intensity decks" which represented, for example, $\Sigma S_c^2 \Sigma S_0^2$, $S_1^2S_3^2$, or S_1^2.

Experimental Section

Preparative Work.—The 1-cyano-1-phenylcycloalkanes, having 3-, 4-, 5-, and 6-membered rings, were prepared from the sodamide-catalyzed reactions of benzyl cyanide and the appropriate dibromides in yields of 79, 25, 80, and 37%, respectively. Only the cyclobutane compound was reached with difficulty and only this procedure is given

1-Cyano-1-phenylcyclobutane—To a three-necked, round-bottomed flask (A), with condenser, mechanical stirrer, dropping funnel, and a drain-off at the bottom, was added 300 ml. of liquid ammonia and 20 g. (0.9 g.-atom) of sodium. After the formation of sodamide was complete, there was added 88.0 g. (0.75 mole) of benzyl cyanide dissolved in 50 ml. of anhydrous ether. The solution was allowed to stir for 1 hr. and the ammonia was allowed to evaporate as an equal volume of anhydrous ether was added. The ethereal solution was then refluxed for 2 hr. by means of a heating lamp. To a 2-l., three-necked, round-bottomed flask (B), equipped with condenser, mechanical stirrer, and a connection by Tygon tubing to flask A, was added 1 l. of anhydrous ether and 108.0 g. (0.53 mole) of trimethylene bromide. The ether solution in flask A was added to flask B with stirring over a 2-hr. period. The final mixture was refluxed 4 hr. After the addition of water, the ether was separated, dried, and evaporated. The residual oil was separated into three fractions by distillation: (1) trimethylene bromide, 10 ml., 30–35° (0.5 mm.); (2) benzyl cyanide, 25 ml., 72° (0.5 mm.); (3) 1-cyano-1-phenylcyclobutane, 23 g., 80–94° (0.3 mm.). Analysis by gas chromatography showed that the last fraction contained some benzyl cyanide. It was boiled 24 hr. with 400 ml. of 48% hydrobromic acid and thus converted, in 85% yield, to 1-phenyl-1-cyclobutanecarboxylic acid, m.p. 106–107.5° (lit. m.p. 106–107°).[6]

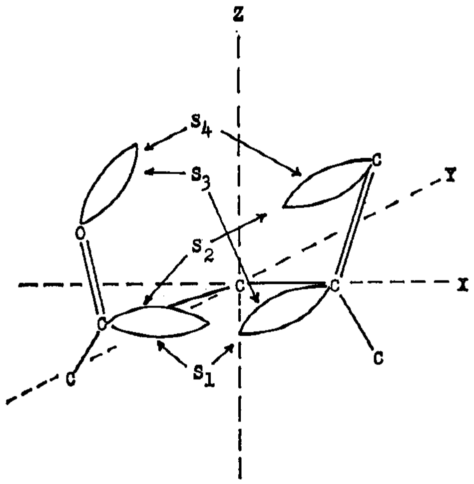

Figure 1.—The relationship of bond orbitals in an α-phenyl ketone. For clarity, the third orbital of the phenyl ring and the p orbital of the oxygen atom are omitted. The phenyl group is shown perpendicular to the X–Y plane ($\theta = 90°$), and the oxygen atom has its maximum value of Z ($\psi = 90°$).

1-Cyano-1-phenylcyclopropane[7] was converted to the amide,[8] m.p. 99–100°, in 61% yield by the action of alkaline hydrogen peroxide. Reaction with an excess of methylmagnesium iodide gave 1-acetyl-1-phenylcyclopropane[9] in 82% yield. 1-Cyano-1-phenylcyclopentane[10] reacted with methylmagnesium iodide prepared from 3 molar equiv. of methyl iodide and magnesium to give the methyl ketone[9] in good yield. 1-Cyano-1-phenylcyclohexane[7] failed to react under the same conditions; it was converted to 1-phenyl-1-cyclohexanecarboxylic acid, m.p. 123.5–125°,[11] in 79% yield by boiling with 48% hydrobromic acid. Both 1-phenyl-1-cyclobutane- and 1-phenyl-1-cyclohexanecarboxylic acids were converted, by reaction with excess ethereal methyllithium,[12] into the corresponding methyl ketones in yields of 74 and 53%, respectively. A specimen of 1-acetyl-1-phenylcyclobutane, b.p. 56–57° (0.2 mm.), was analyzed.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.75; H, 8.05. Found: C, 82.94; H, 8.04.

For further purification, the methyl ketones with 3- 4- 5-, and 6-membered rings were converted into semicarbazones having melting points, respectively, of 169–171, 206–208, 228–230, and 210–211°. The reported values of these melting points are, respectively, 172–172.5°,[13] . . . ., 228.5–231°,[13] and 217–218°.[14] The ketones were regenerated by boiling the recrystallized semicarbazones with aqueous pyruvic acid. Only 1-acetyl-1-phenylcyclohexane was solid. The melting point of 34–35° was in good

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[4] A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerrassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962). In the present paper, the β-carbon is always assumed to be the "nearest neighbor."

[5] S. MacKenzie, S. B. Saila, and R. A. Shappy, *J. Org. Chem.*, **28**, 548 (1963).

[6] F. H. Case, *J. Am. Chem. Soc.*, **56**, 715 (1934).

[7] A. W. Weston, *ibid.*, **68**, 2345 (1946).

[8] E. C. Knowles and J. B. Cloke [*ibid.*, **54**, 2028 (1932)] reported m.p. 100–101°.

[9] P. A. S. Smith, D. R. Baer, and S. N. Ege, *ibid.*, **76**, 4564 (1954).

[10] C. H. Tilford, M. G. VanCampen, and R. S. Shelton, *ibid.*, **69**, 2092 (1947).

[11] M. Rubin and H. Wishinsky [*ibid.*, **68**, 828 (1946)] reported m.p. 123–124°.

[12] This is the method of C. Tegner [*Acta Chem. Scand.*, **6**, 782 (1952)] and F. J. Impastatio and H. M. Walborsky [*J. Am. Chem. Soc.*, **84**, 4839 (1962)].

[13] S. C. Bunce and J. B. Cloke, *ibid.*, **56**, 715 (1934).

[14] G. G. Lyle, R. A. Covey, and R. E. Lyle, *ibid.*, **76**, 2713 (1954).

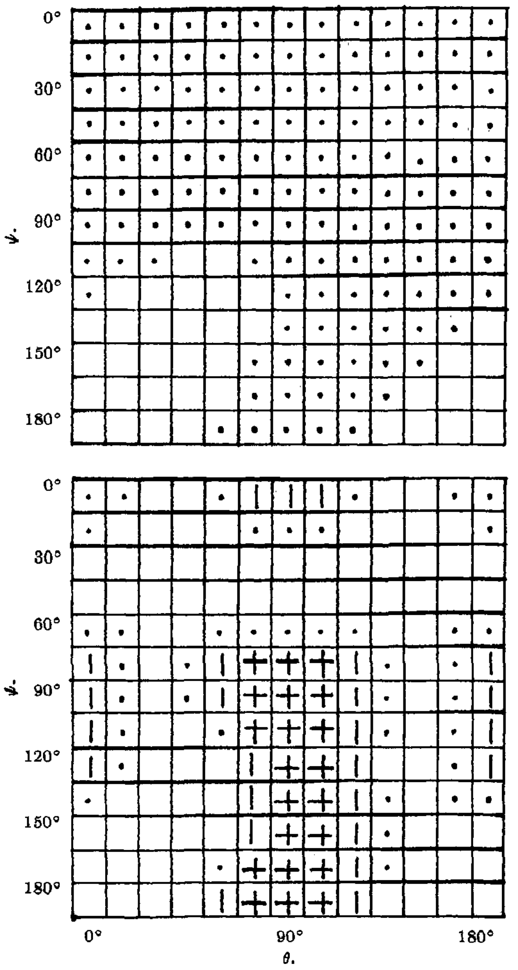

Figure 2.—Conformational populations of two ketones as a function of H–H repulsions. Lower figure is for 1-acetyl-1-phenylcyclopropane and the upper for phenylacetone (without hyperconjugation term). Populations are indicated as follows: each • is 0.1–0.5%, each | is 0.5–1.0%, and each + is 1.0–2.0%. Both angles are counterclockwise viewed from the end of the bond serving as the axis of rotation. The angle ψ is for Ac and θ is for Ph.

agreement with the reported value, 33–35°.[14] The four ketones were homogeneous to gas chromatography. Further, n.m.r. spectra taken at 60 Mc. showed the absence, in all four cases, of benzyl or vinyl hydrogens.

Calculation of Intensity Tables.—In the present work, the term ΣS_c^2 is equal to $S_1^2 + S_2^2 + S_5^2$, in which S_5^2 is the square of the overlap integral of the p orbital on the carbon atom of the carbonyl group with the third orbital (not shown in Figure 1) of the phenyl ring. The term ΣS_o^2 is equal to $S_3^2 + S_4^2 + S_6^2$, in which S_6 is the overlap integral of the n orbital of the oxygen atom with the third orbital of the phenyl ring. The method of calculation of these terms in a computer program has already been described.[5] Separate tables of ΣS_c^2 and $\Sigma S_c^2 \Sigma S_o^2$ were required for the cyclobutane and cyclopropane compounds, owing to the difference in the Ph–C–Ac bond angles. Tables for bond angles[15] of 109° 28′, 112′, and 118° 12′ were calculated. The C–H bond distance in aldehydes was taken[16] as 1.09 Å. The C–C bond distance in the phenyl ring was taken[17] as 1.39 Å, The calculation of other intensity tables, such as S_1^2, $S_1^2S_3^2$, $\sin^2\theta \sin^2\psi$, was far simpler and utilized the same bond angles and distances.

Calculation of Population Tables.—In some early programs not described herein, populations were evaluated as a function of H–H, C–H, and C–C repulsions. It was found that the latter two repulsions resulted in minor refinements of the population tables and, accordingly, the policy of using only the H–H repulsion was adopted. The equation of Hendrickson[18] was used. Some calculations (not described) were done with Haigh's equation[19] but little change resulted. Unfortunately, use of the equation of Simmons[20] was not explored. The sum of the energies of repulsion at any angular position was converted to a population term by Boltzmann's equation and each of these terms was divided by the sum of such terms so that the final population table had a sum equal to unity. In Figure 2, two such population tables are compared graphically.

Selection of Conformations.—The conformations of certain of the ring systems were viewed as being open to experimental selection. A number of possible ring conformations were considered throughout the calculations for a number of the ketones. The structures evaluated and those finally chosen for this report are presented in Table I.

Table I

Conformations and Structures Evaluated

Compd.	Conformation or structure[a]
1-Acetyl-1-phenyl-cyclopropane	. . .
-cyclobutane	1. Cyclobutane ring flat
	2. Puckered to phenyl side
	3. Rapidly oscillating pucker*
-cyclopentane	1. Cyclopentane ring flat
	2. Puckered to phenyl side
	3. Rapidly oscillating pucker*
-cyclohexane	1. Ph is equatorial
	2. Ph is axial*
	3. Rapidly oscillating chair
2-Formyl- or 2-Acetyl-2-phenyl-A-norcholestane[b]	1. Ph is α
	2. Ph is β*

[a] Under this heading, the asterisk designates the conformation or structure selected. [b] R. C. Cookson and J. Hudec, *J. Chem. Soc.*, 429 (1962).

The angle of pucker (26° 45′) for cyclobutane was obtained from the work of Roberts.[21] The conformation selected for 1-acetyl-1-phenylcyclobutane involved rapid oscillation of C-3 to both sides of the plane made by the other three carbons, the total angle of oscillation being 2 × 26° 45′ = 53° 30′. The hydrogen atoms at C-2 and C-4 were viewed as being in the same position that they would occupy in a flat cyclobutane molecule. 1-Acetyl-1-phenylcyclopentane was not viewed as having a pucker which involved all carbons of the cyclopentane ring, such a condition being too complex for programming. Instead, the pucker was seen as involving only C-1. The angle of pucker selected experimentally (37° 16′) was equivalent to an out-of-plane distance for C-1 of 0.5384 Å. Brutcher[22] suggested a distance of 0.5 Å. The final conformation selected for the cyclopentane compound involved the oscillation of C-3 and C-4 to both sides of the plane made by the other three carbons, the angle of oscillation being 2 × 37° 16′ = 74° 32′. The population pattern obtained was very sensitive to this choice. The hydrogen atoms at C-2 and C-5 were regarded as having the same positions that they would occupy in a flat cyclopentane molecule. For 2-formyl- or 2-acetyl-2-phenyl-A-norcholestane, the pucker was viewed as stationary at the carbon (9) bearing the methyl group, this choice being suggested by Dreiding models.

The methyl group of the acetyl group was maintained by the program in a conformation such that one hydrogen remained coplanar and "*cis*" with the Ac–C bond. Such a position was most often one of maximum interference. It offered the advantage of necessitating the calculation of fewer H–H interactions. In retrospect, the coplanar "*trans*" position, usually one of minimum interference, might well have been preferable. This position, however, doubles the number of H–H interactions

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[15] A. I. Kitaygorodsky, *Tetrahedron*, **9**, 183 (1960).

[16] D. P. Stevenson, J. E. LuValle, and V. Schomaker, *J. Am. Chem. Soc.*, **61**, 2508 (1939).

[17] A. Maccoll, "Progress in Stereochemistry," Vol. I, Butterworth (Publishers) and Co. Ltd., London, 1954.

[18] J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

[19] For a discussion of these equations, see I. Fisher-Hjalmars, *Tetrahedron*, **19**, 1805 (1963).

[20] H. E. Simmons and J. K. Williams, *J. Am. Chem. Soc.*, **86**, 3222 (1964).

[21] J. B. Lambert and J. D. Roberts *ibid.*, **85**, 3710 (1963).

[22] F. V. Brutcher and W. Bauer, *ibid.*, **84**, 2233 (1962).

experienced by the methyl group, although the total interaction energy is somewhat less.

In α,α-dimethyl-α-phenylacetone, the α-methyl groups were visualized as occupying minimum interference positions; *i.e.*, there is a planar, W-shaped system, H–C–C–C–H.

For phenylacetone there was utilized in addition an attraction term

$$-\cos^2(\psi - 30) - \cos^2(\psi + 30) = -0.5 - \cos^2\psi$$

based on the suggestion of Cotterill and Robinson[23] that the energy of hyperconjugation of a ketone group with an axial hydrogen is 1.0 kcal.

Ultraviolet Spectra.—The spectral values discussed in this work are those for ethanol solutions only unless otherwise stipulated. New values reported are given in Table II.

TABLE II

ULTRAVIOLET SPECTRAL VALUES

	λ^{EtOH}, mμ (ϵ)		$\lambda^{C_6H_{12}}$, mμ (ϵ)	
Subst.[a]	Benzenoid[b]	Ketonic	Benzenoid	Ketonic
$n = 3$	260 (245)	289 (75)[c,d]	260 (205)	284–285 (50)[d]
$n = 4$	261 (294)	289 (355)[c]	261 (238)	295 (252)
$n = 5$	260 (252)	291 (292)[c]	260 (220)	296 (217)
$n = 6$	260 (250)	290 (314)[c]	260 (208)	298 (230)
e	258 (193)	No absorp.		
f	258 (192)	No absorp.		

[a] 1-Acetyl-1-phenylcycloalkane with n carbons in the alicyclic ring. [b] The highest maximum only. [c] An average of three separate determinations. [d] Inflection. [e] 1-Cyano-1-phenylcyclopentane. [f] 1-Phenyl-1-cyclohexanecarboxylic acid.

Discussion of Results

It will be seen from Table III that the quantity $\Sigma S_c{}^2\Sigma S_o{}^2$ is grossly unsatisfactory for predicting the exaltation of n–π^* transitions when the assumption is made that the conformations of ketones are a function of H–H repulsions only. Two principal organizational reasons suggested themselves: (a) some of the conformations are wrong, or (b) the quantity $\Sigma S_c{}^2\Sigma S_o{}^2$ is wrong. A very substantial amount of computer time has gone into the exploration of both of these alternatives. In the computation, these possibilities were considered in the order given. However, the latter should be discussed first since it is simpler.

If the assumption is made that the intensity pattern $\Sigma S_c{}^2\Sigma S_o{}^2$ is wrong, the question immediately arises as to what the true intensity pattern should be. In the present work it soon became apparent that a degree of conformity was shown using the pattern $\Sigma S_c{}^2$. There was next examined the possibility of omitting from consideration the second and third orbitals of the phenyl ring, *i.e.*, of using $S_1{}^2$. Correspondence with a straight line was improved (figure not shown). Next was used the function $KS_{\sigma\sigma}{}^2 \sin^2\psi \sin^2\theta$ which contains only the sigma portion of the overlap integral, the factor K being less than unity for the cyclobutane ring (0.938) and the cyclopropane ring (0.791) owing to the constantly smaller portion of σ contribution following the expansion of the Ph–C–Ac bond angle. The quantity $S_{\sigma\sigma}{}^2$ is, of course, also less by virtue of the increase in interaction distance. The relative values for cyclobutane and cyclopropane are, respectively, 0.8896 and 0.6744. A plot of the values of $KS_{\sigma\sigma}{}^2 \sin^2\psi \sin^2\theta$, a function which is regarded as the precise mathematical embodiment of the Cookson rule, against the values of ϵ is shown in Figure 3. In spite of one serious discrepancy, the plot suggests that there is a high degree of correlation between these variables. The large error for 1-acetyl-1-phenylcyclopropane might be interpreted as arising from two causes:

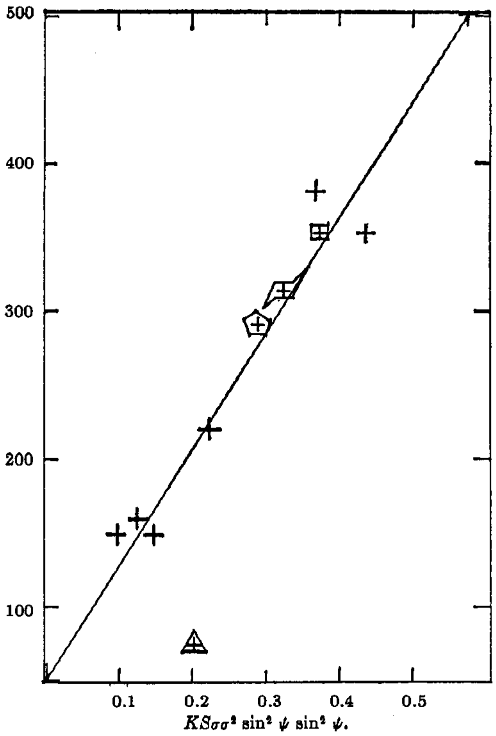

Figure 3.—Analysis of ketone populations calculated without repulsion.

TABLE III

THE SUMS OF THE POINT-BY-POINT PRODUCTS OF INTENSITY PATTERNS AND POPULATION PATTERNS

		Intensity pattern[b]			
Subst.[a]	ϵ (EtOH)	A	B	C	D
I	50	5092.0	71.6	0	0
II, $n = 3$	75[c]	166.2	79.8	0.202	0.063
III	150[d]	10.6	163.1	0.094	0.012
$PhCH_2Ac$	150	3950.7	102.6	0.145	0.079
$PhCMe_2Ac$	160	2122.8	90.3	0.120	0.062
IV	220	31.7	80.7	0.219	0.068
II, $n = 5$	292	15.5	33.0	0.285	0.176
II, $n = 6$	314	1194.2	127.4	0.320	0.170
V, R = CHO	353	2690.9	180.1	0.434	0.264
II, $n = 4$	355	190.2	146.6	0.369	0.173
V, R = Ac	380	952.4	147.3	0.362	0.252
VI	505	300.5	135.9	0.562	0.369

[a] I, 2-phenylcyclopentanone [K. Mislow and A. K. Lazurus, *J. Am. Chem. Soc.*, **77**, 6383 (1955)]; II, 1-acetyl-1-phenylcycloalkanes with n carbons in the alicyclic ring; III, 1,1-dimethyl-2-tetralone [values taken were $\psi = 150°$ and $\theta = 37.5°$; the spectrum in isooctane was kindly furnished by R. D. Campbell and N. H. Cromwell, *ibid.*, **79**, 3458 (1957). It showed a maximum at 282 mμ (ϵ 108.3) and was judged similar to phenylacetone]; IV, 3α-phenylcholestan-2-one [R. C. Cookson and J. Hudec, *J. Chem. Soc.*, 429 (1962); only θ varies; ψ was chosen as 105°]; V, 2β-Phenyl-2α-R-norcholestane-A (R. C. Cookson and J. Hudec); VI, dimethyl 5,6-benzo[2.2.2]bicyclo-5-octen-7-on-2,3-endodicarboxylate [R. C. Cookson and N. S. Wariyar, *ibid.*, 2302 (1956)]; $PhCMe_2Ac$ (R. C. Cookson and N. S. Wariyar); $PhCH_2Ac$ [S. F. Marsocci and S. MacKenzie, *J. Am. Chem. Soc.*, **81**, 4513 (1959)]. [b] Intensity patterns are as follows: A, $10^{10}\text{-}\Sigma S_c{}^2\Sigma S_0{}^2$; B, $10^5\Sigma S_c{}^2$; C, $KS_{\sigma\sigma}{}^2 \sin^2\psi \sin^2\theta$ in which $KS_{\sigma\sigma}$ is set equal to unity for a Ph–C–Ac bond angle of 109° 28′; D, $KS_{\sigma\sigma}{}^2 \sin^2\psi \sin^2\theta\,(1 - \cos\psi)S_3{}^2$ which must use population patterns with a strong repulsion term. [c] Inflection. [d] Estimated.

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(23) W. D. Cotterill and M. J. T. Robinson, *Tetrahedron Letters*, 1833 (1963).

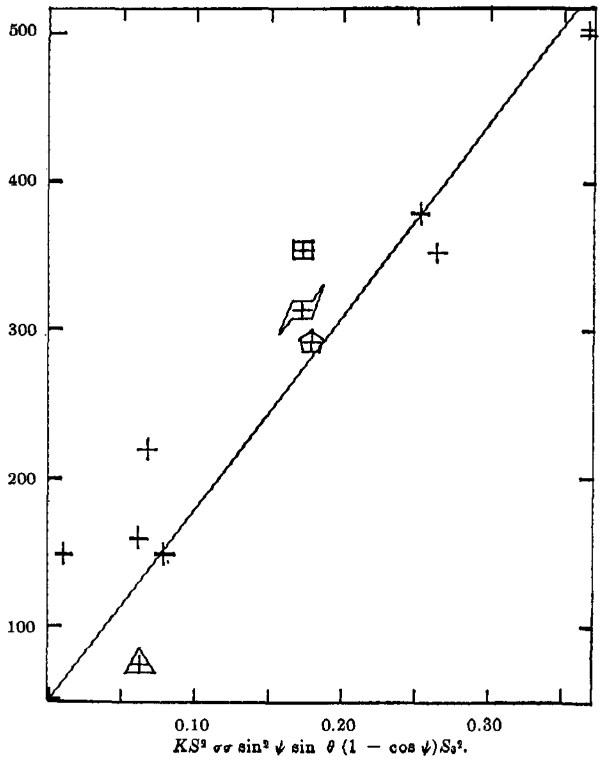

Figure 4.—Analysis of ketone populations calculated with repulsion.

the uncertainty inherent in estimating ϵ at inflection points and principally from the fact that bond-orbital interactions seem to decrease in energy faster with distance than the equations of Mulliken suggest. *For this reason, results of the present paper must be considered to present arguments pertaining only to the factor of geometry; they do not substantiate in any other way that bond orbitals are actually involved.* Two other errors also appear: predicted values of ϵ for phenylacetone are higher than those for the dimethyl derivative, and the predicted values for the aldehyde V are higher than those for the ketone V. These persistent difficulties, however, may arise as a result of a poor choice of conformation for the methyl group of the acetyl. Future work, it is hoped, will clarify this question.

If the assumption is made that the intensity pattern $\Sigma S_0{}^2 \Sigma S_0{}^2$, or a function akin to it containing an oxygen n orbital overlap term, is correct, then the population patterns based only on H–H repulsions must be wrong. The largest portion of computer time was spent addressing this alternative. Suggestions in the literature concerning repulsive forces[24] between orbitals admitted the possibility of the existence of a force operating, at least in gross aspect, as if it were between the oxygen of the carbonyl group and the phenyl ring. Figure 4, which gives the most successful correlation thus far obtained, utilizes an intensity pattern

$$KS_{\sigma\sigma}{}^2 \sin^2 \psi \sin^2 \theta (1 - \cos \psi) S_3{}^2$$

and population patterns which are functions of H–H repulsions and another force of repulsion equal, in kilocalories, to 1.6 (1 + cos ψ).[3] The latter function gives values of repulsion which are clearly outside physical possibility in the region near $\psi = 0°$ but within possibility in the region $\psi = 75–180°$. However, the patterns of population could equally well have been obtained with a function which is, throughout, admissible: repulsion = 3 kcal. (ψ = 0–75°) and $1.6(1 + \cos \psi)^3$ kcal. (ψ = 90–180°). As far as the population patterns are concerned, the two statements of repulsive force are the same. Figure 4, then, admits the possibility of the validity of the oxygen overlap expression, *if* there is a strong repulsion between the oxygen of the carbonyl group and the phenyl ring, and further *if* the use of the empirical term (1 − cos ψ) is justified. Even with these conditions, however, the scatter of points in Figure 4 is greater than that in Figure 3.

The interpretation based on the Cookson rule is preferred. The strong repulsive force, used to obtain the population patterns for Figure 4, and the empirical term (1 − cos ψ), used in the intensity pattern, are regarded as mere inventions which have the effect of deleting the effect of the term $S_3{}^2$. This term, increasing rapidly by a factor of 2–2.5 for each 15° of ψ from $\psi = 180°$ to $\psi = 30°$, and thereafter decreasing slightly or remaining nearly constant, is clearly opposite to the effects of the above two assumptions. Moreover, a telling, if qualitative, argument against a strong repulsive force as herein depicted is found in the spectral values of phenylated acetones.[25] If, to avoid large values of $S_3{}^2$, the acetyl group turns away from the phenyl group, one would expect an unusual increase of spectral value for 1,1,1-triphenyl-2-propanone. In fact, the increase of ϵ is merely statistical.

Endorsement of the Cookson rule for phenyl ketones raises the question at once as to whether or not β,γ-olefinic ketones have values of ϵ also predictable by this method. The data, on close scrutiny, are fewer but suggest that they are *not* in accord with this rule. Whether this means that for phenyl ketones involvement of the n orbital of oxygen can take place *via* an interaction S_1 is not known. The argument seems too highly speculative at the present time.

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[24] N. L. Owens and N. Sheppard, *Proc. Chem. Soc.*, 264 (1963).

[25] S. MacKenzie, S. F. Marsocci, and P. R. Santurri, *J. Org. Chem.*, **28**, 717 (1963).