is 0.85 g. (quant.) and after crystallization from methanol–ether, 4-benzamido-3-phenyl-*s*-triazolium benzenesulfonate was obtained as white needles, m.p. 187–188°. The melting point on admixture with a specimen prepared from benzhydrazide benzenesulfonate and dimethylformamide was 186–187°; these specimens had identical infrared spectra.

Anal. Calcd. for $C_{21}H_{18}N_4O_4S$: C, 59.7; H, 4.3; N, 13.3; S, 7.6. Found: C, 59.5; H, 4.4; N, 13.2; S, 7.5.

Replacement of the benzenesulfonic acid in method B above with an equivalent amount of methanesulfonic acid gave an 89% yield of the corresponding methanesulfonate salt, m.p. 164°. It crystallized from methanol–ether as long, white needles, m.p. 164°.

Anal. Calcd. for $C_{16}H_{16}N_4O_4S$: C, 53.3; H, 4.5; N, 15.5; S, 8.9. Found: C, 53.3; H, 4.4; N, 15.1; S, 9.05.

Alkaline Hydrolysis of 4-Benzamido-3-phenyl-*s*-triazolium Benzenesulfonate.—The benzenesulfonate (3.0 g.) was suspended in water (20 ml.) and after the addition of dilute sodium hydroxide solution (20 ml. of 5 *N*) warmed on the water bath for 30 min. After cooling to 0°, concentrated hydrochloric acid was added until the mixture was just acid to litmus. The gum that separated soon crystallized and was collected and washed well with cold water. 1-Benzoyl-4-formamidobenzhydrazidine crystallized from aqueous methanol as white needles, 1.9 g.(90%), m.p. 160–161°, and did not depress the melting point of a sample prepared from benzhydrazide benzenesulfonate as above. It had an identical infrared spectrum with this sample.

Action of Boiling Water on the Above Benzenesulfonate.—The benzenesulfonate (0.2 g.) was heated under reflux in water (30 ml.) for 24 hr. After cooling to 0°, the crystalline precipitate was collected, washed with a small quantity of cold water, and dried, 35 mg., m.p. 158–159°, It crystallized from acetone–ether as white, irregular prisms, m.p. 161°, and was identical in all respects with 1-benzoyl-4-formamidobenzhydrazidine.

1-Benzoyl-4-benzamidoformhydrazidine.—Benzhydrazide (14.8 g.) and diethyl orthoformate (10 g.) were heated together and the alcohol formed in the reaction slowly distilled. Heating was continued until no more alcohol distilled (temperature of mixture, 85°; volume of alcohol collected, 6 ml.) and the contents of the flask suddenly solidified. This material was collected by filtration and, after drying, was extracted with acetone for 30 hr. in a hot Soxhlet extractor. An analytical sample separated as long, fibrous needles from methanol, m.p. 164°.

Anal. Calcd. for $C_{15}H_{14}N_4O_2$: C, 63.8; H, 5.0; N, 19.9; mol. wt., 282.3. Found: C, 63.9; H, 5.2; N, 19.8; mol. wt., 290.

N,N-Diphenylformamidine Benzenesulfonate.—Aniline benzenesulfonate (20 g.) and dimethylformamide (100 ml.) were heated together under reflux overnight. As much as possible of the dimethylformamide was removed by distillation at atmospheric pressure and the residual dark green oil poured onto ice. After standing, the initial gummy product crystallized. The crude material (3 g., 10%) crystallized from acetone (charcoal) and finally from methanol–ether as pale cream needles, m.p. 154°.

Anal. Calcd. for $C_{19}H_{18}N_2O_3S$: C, 64.4; H, 5.1; S, 9.0. Found: C, 64.5; H, 5.2; S, 8.8.

This product was identical (mixed melting point and infrared spectrum) with a sample of authentic N,N′-diphenylformamidine benzenesulfonate prepared from N,N′-diphenylformamidine[34] and benzenesulfonic acid in methanol–ether solution.

3-Phenyl-*s*-triazole.—4-Amino-5-mercapto-3-phenyl-*s*-triazole (1.5 g.) in ethanol (25 ml.) was heated under reflux with alkaline Raney nickel catalyst (*ca.* 6 g.) for 1.5 hr. Effervescence occurred immediately on adding the catalyst and at room temperature. Filter Cel was added and the reaction mixture filtered, the filter cake being washed with hot ethanol (20 ml.). Evaporation of the solvent under reduced pressure on the water bath left a gummy residue that was extracted several times with boiling ethyl acetate, the extract filtered, and concentrated to small bulk. 3-Phenyl-*s*-triazole separated from this ethyl acetate concentrate and crystallized from water as white needles, m.p. 120° (lit.,[35] m.p. 119.5–120°).

Anal. Calcd. for $C_8H_7N_3$: C, 66.2; H, 4.9; N, 28.95. Found: C, 66.3; H, 4.9; N, 29.1.

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Correlation of Computed Overlap Integrals with Exalted n-π* Transitions

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An effort is made to correlate computed overlap integrals with exalted n-π* transitions. The pattern of results is quite encouraging but difficulty is had with data for compounds poorly represented by molecular models.

The abnormally high extinction coefficient exhibited by certain unsaturated, but not conjugated, ketones in the 290 mμ region has received wide attention. Detailed treatment of this phenomenon, particularly with respect to molecules of fixed geometry, has been given by Cookson,[3–5] Labhart and Wagniere,[6] Winstein,[7,8] and Mason.[9]

Part I of this series[10] suggested a simple statistical approach to the problem of predicting exaltations for molecules with free rotation. In a more extensive publication forthcoming,[11] it will be shown that the previously proposed statistical treatment serves well in lengthy series of phenyl- and benzylacetones, connecting the two series in a useful manner. With other compounds, however, the correlation many times fails.

A more uniformly applicable method of predicting these exalted extinction coefficients is currently being sought. Equation I is that presented by Mason[9] and Cookson.[5] Equation II, while never suggested previously in this form, is closely related to an empirical relationship used by Mulliken[12] in a somewhat different context.

$$f_{n-\pi}/f_{ct} = (\nu_{n-\pi}/\nu_{ct})(S_o{}^2P^2)/(\nu_{ct} - \nu_{n-\pi})^2 \qquad \mathrm{I}$$

$$f_{ct}/f_d = (\nu_{ct}/\nu_d)(S_c{}^2P'^2)/(\nu_d - \nu_{ct})^2 \qquad \mathrm{II}[13]$$

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[13] In these equations, f is the appropriate oscillator strength of the n-π* transition, the charge-transfer (ct) transition or the donor (d) transition, P and P' are proportionality constants, S_o is the overlap integral of the nonbonding orbital on oxygen with the orbitals of the donor, S_c is the overlap integral of the orbital on carbon of C=O with the orbital of the donor, and ν is the appropriate frequency, herein always employed in cm.$^{-1}$.

Were the experimental data for all compounds the same (for example, $f_d\cdot$ constant $= \epsilon_d = 10{,}000$, $\lambda_d = 180$ mμ, $\lambda_{ct} = 210$ mμ, and $\lambda_{n\text{-}\pi} = 290$ mμ), equations III and IV could be employed. The qualitative application of this basic idea has been recently discussed.[5]

$$\epsilon_{290} = K_{n-\pi} S_c^2\ S_o^2 \qquad \text{III}$$

$$\epsilon_{210} = K_{ct} S_c^2 \qquad \text{IV}$$

The purpose of the present analysis is to explore the validity of I–IV more quantitatively, allowing the constancy of values of $K_{n\text{-}\pi}$ and K_{ct} to serve as a measure of this validity.

In practice, the calculations were carried out in two stages, the allowance for differences in frequency and ϵ being made first. Replacing f by ϵ throughout, there is obtained equation V.

$$\epsilon_{210}/\epsilon_{180} = (\nu_{210}/\nu_{180})(S_c^2P^2)/(\nu_{180} - \nu_{210})^2 \qquad \text{V}$$

This, divided by II, gives VI.[14]

$$\epsilon_{210} = \epsilon_{ct} \frac{\epsilon_{180}\nu_{210}\nu_d(\nu_d - \nu_{ct})^2}{\epsilon_d\nu_{ct}\nu_{180}(\nu_{180} - \nu_{210})^2} \qquad \text{VI}$$

Likewise obtained is expression VII, in which the constant (−20) is included to minimize the error of background absorption in cases wherein $\epsilon_{n\text{-}\pi}$ is small. Ideally, this term is the extinction coefficient of the corresponding saturated substance.

$$\epsilon_{290} = (\epsilon_{n-\pi} - 20) \frac{\epsilon_{180}\nu_d\nu_{290}(\nu_d - \nu_{ct})^2(\nu_{ct} - \nu_{n\text{-}\pi})^2}{\epsilon_d\nu_{180}\nu_{n\text{-}\pi}(\nu_{180} - \nu_{210})^2(\nu_{210} - \nu_{290})^2} \qquad \text{VII}$$

The values of ϵ_{210} (where pertinent) and ϵ_{290} have been calculated for a series of molecules. Selection of values of S_c^2 and $S_c^2S_o^2$ from extensive tables obtained from computer programs (IBM 1620, Fortran language) has permitted calculation of K_{ct} and $K_{n\text{-}\pi}$.

Experimental

Calculations were made utilizing the following values: C—C, 1.54 Å.; C = O, 1.22; C = C, 1.33; C—C—C, 109° 28′; C—CO—C, 120°; and C—C=C, 120°. For the purposes of program construction, the ketone was visualized as lying (Fig. 1) with carbon atoms 1, 2, and 3 in the X-Y plane. As the angle of rotation (ψ) of the C_1–C_2 bond increased from 0 to 90°, the oxygen atom, originally at $Z = 0$ and $X = +$, had a Z coördinate which increased to a maximum. As the angle of rotation (θ) of the C_2–C_3 bond increased from 0 to 90°, the orbital at C-3, originally parallel to the Z-axis and in the $+Z$ direction, reached a $+Y$ position in the X–Y plane and C-4, originally having a coördinate of $Z = 0$, reached its largest negative value of Z. The O–C_4 distance was therefore a maximum at $\psi = 180°$ and $\theta = 180°$ and a minimum at $\psi = 0°$ and $\theta = 0°$.

Each of several programs was divisible roughly into three parts: calculation of the three coördinates of each of the six points involved, resolution of the orbitals, and calculation and utilization of overlap integrals. The resolution was accomplished utilizing a standard equation.[15]

$$S_{ac} = S_{\sigma\sigma} \cos\alpha_1 \cos\alpha_2 + S_{\pi\pi} \sin\alpha_1 \sin\alpha_2 \cos\nu \qquad \text{VIII}$$

For two orbitals, visualized as being of unit length, located respectively at atoms with coōrdinates $X_aY_aZ_a$ and $X_cY_cZ_c$ and terminating, respectively, in the coōrdinate points $X_bY_bZ_b$ and $X_dY_dZ_d$, cos α_1 is given by

$$[(X_d - X_a)^2 + (Y_d - Y_a)^2 + (Z_d - Z_a)^2 - D^2 - 1]/(-2D)$$

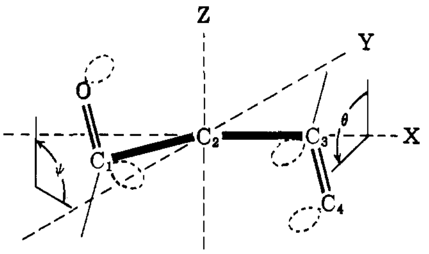

Fig. 1.—Angles of rotation and orbitals for a β,γ-unsaturated ketone.

where D is the distance between the atoms. The quantity sin α_1 sin α_2 cos γ is given by

$$[(X_d - X_b)^2 + (Y_d - Y_b)^2 + (Z_d - Z_b)^2 - (D - \cos\alpha_1 - \cos\alpha_2)^2 - \sin^2\alpha_1 - \sin^2\alpha_2]/(-2).$$

After this latter quantity was found, it, cos α_1 and cos α_2 were, if negative, converted to positive values and utilized in VIII. In this way, only one lobe of each oribital had to be located geometrically.

The quantities $S_{\sigma\sigma}$ and $S_{\pi\pi}$ were calculated as a part of the program from the equations of Mulliken.[16] It was ascertained separately that the equations as written could also be used to calculate either the tabulated coefficients of Kotani[17] or the tabulated values of overlap integrals of Mulliken[16] for selected values of p and t.

Two programs were required for the β, γ-unsaturated ketone. One dealt with O, C-1 and C-3, the second with O, C-1 and C-4. The results were then combined into complete tables (I and II). Thus, at angular values $\psi = 0°$, $\theta = 90°$ there was obtained for C_1–C_3, $S_c^2 = 0$; for C_1–C_4, $S_c^2 = 3.386 \times 10^{-5}$; for O–$C_3$, $S_0^2 = 114.2 \times 10^{-5}$; and for O–$C_4$, $S_0^2 = 5.5 \times 10^{-5}$. Reported in Table I is $\Sigma S_c^2 = 3.386 \times 10^{-5}$ and in Table II, $\Sigma S_c^2\ \Sigma S_0^2 = 405.3 \times 10^{-10}$. Substantial manual checking with five place logarithms accompanied each program. The very simple C_1–C_3 results were easily checked in their entirety, while results for O–C_3, O–C_4, and C_1–C_4 were checked at four scattered values of ψ and θ not equal to 0 or 180°.

Only one program for a γ,δ-unsaturated ketone has thus far been tabulated (γ-orbital). The results are necessarily voluminous and are not presented here. Values were checked at only two positions for the complete program but the initial portion of this which dealt with calculation of orbital positions was extensively checked to avoid sign alteration in a solution of a quadratic equation. Answers presented by the calculator (8 significant figures) were rounded off to four figures, since some simplifying calculations with logarithms were necessary before the machine could accomodate the programs.

In order to evaluate the merit of the present treatment, the bond angles for selected molecules were estimated with Dreiding models.[18] In a few cases, as noted, ball and spring had to be used.

Discussion

Labhart and Wagniere[6] analyzed in detail bicyclo-[2.2.2]octenone. Their results are compared in Table III with those of the present work. These authors used 1.4 Å. for C=C, instead of 1.33 as in the present work and this difference may explain part of the variation in Table III.

If indeed the function $\Sigma S_c^2\ \Sigma S_0^2$, as tabulated in Table II as a function of bond angles, represents a measure of ϵ_{max} (n-π*), a number of interesting suggestions result. If the position $\theta = 0°$, $\psi = 0°$ is called *cis–cis*, the relative position of the *olefin* group being given first, the maximum values of ϵ_{max} (n-π*) are to be sought in the vicinity of the *cis–cis* array and

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(14) Although the alternative, calculation of the term $(f_{ct}/f_d)(\nu_d - \nu_{ct})^2(\nu_d/\nu_{ct})$, appears simpler, the use of VI is preferred since it more clearly presents the effect of shifts of wave length upon ϵ.

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Table I

The Quantity $10^5\ \Sigma S_c{}^2$ as a Function of Bond Angles in a β,γ-Unsaturated Ketone

ψ^a $\theta^b =$	0°	15°	30°	45°	60°	75°	90°	105°	120°	135°	150°	165°	180°
0°	108.3	101.9	83.69	57.63	30.72	10.52	3.386	7.594	20.94	39.89	59.13	73.30	78.51
15°	101.1	109.2	102.2	80.55	51.40	26.05	31.49	52.56	74.65	91.32	97.44	90.91	73.24
30°	81.24	101.9	107.8	95.02	69.09	69.37	101.2	129.7	147.2	147.6	129.5	97.18	58.87
45°	54.16	82.02	99.14	97.15	104.6	153.1	193.8	218.5	219.3	193.6	146.8	90.42	39.25
60°	27.08	54.90	78.47	115.1	186.6	245.4	284.5	295.0	271.4	217.0	144.5	72.45	19.62
75°	7.257	27.78	89.43	182.8	263.6	321.5	349.1	338.9	289.7	211.6	123.4	48.10	5.257
90°	0	42.42	139.3	238.8	314.9	360.9	370.2	338.2	269.2	178.7	89.17	23.87	0
105°	7.254	76.62	179.1	268.0	327.0	353.1	342.0	293.2	215.6	127.3	50.87	15.87	5.260
120°	27.08	108.6	198.2	262.7	296.4	300.2	272.3	216.0	143.0	71.11	47.62	34.39	19.62
135°	54.15	129.7	191.7	224.2	231.5	216.4	179.7	127.2	71.07	63.48	62.83	53.96	39.26
150°	81.23	134.4	161.1	162.9	149.5	124.1	88.96	50.73	47.44	62.78	70.76	69.34	58.88
165°	101.1	121.3	114.6	99.94	77.58	50.23	24.47	16.47	34.77	54.12	69.35	76.39	73.25

[a] Viewed from carbonyl carbon to C_α, the counterclockwise angle of rotation of the ketone group from the extreme *cis–cis* position.
[b] Viewed from C_β to C_α, the corresponding angle, also counterclockwise, for the olefin group.

Table II

The Quantity $10^{10}\ \Sigma S_c{}^2 \Sigma S_0{}^2$ as a Function of Bond Angles[a] in a β,γ-Unsaturated Ketone

ψ $\theta =$	0°	15°	30°	45°	60°	75°	90°	105°	120°	135°	150°	165°	180°
0°	0	6206	11591	8477	4018	1300	405.3	821.7	1803	2282	1689	560.5	0
15°	2070	10610	13133	9545	5633	2787	3171	4465	4570	3443	1631	283.9	176.0
30°	3207	7835	8651	7119	5095	4995	6502	6785	5635	3299	1272	91.75	364.6
45°	1592	3246	3924	3568	4203	5830	6523	6145	4351	2114	547.0	107.2	272.5
60°	367.7	885.5	1336	2074	3385	4098	4492	3823	2418	1019	208.9	109.4	97.43
75°	36.02	164.3	594.5	1303	1842	2274	2327	1842	1072	406.3	69.94	51.37	13.96
90°	0	87.60	333.5	608.0	822.2	1025	998.1	748.4	409.2	142.8	21.79	13.51	0
105°	3.969	53.57	145.5	227.0	339.8	406.1	380.3	272.5	141.0	45.55	6.125	3.831	2.398
120°	4.853	25.09	52.74	86.43	130.4	150.2	134.8	91.78	44.20	12.69	3.213	3.208	3.212
135°	3.975	9.613	16.55	33.90	48.78	53.36	44.98	28.11	11.82	6.418	2.675	1.754	2.153
150°	1.352	2.973	7.295	13.66	17.95	17.88	13.32	6.864	4.967	4.169	2.145	0.6516	0.9539
165°	0.3262	1.068	3.430	5.746	6.550	5.184	2.665	1.650	2.753	2.795	1.725	0.4583	0.2281
180°	0	0.7010	2.101	2.869	2.284	0.9683	0.3325	0.6932	1.533	1.944	1.439	0.4780	0
195°	0.3262	0.7384	2.708	4.367	4.223	2.675	3.476	5.445	6.285	5.215	2.875	0.7875	0.2281
210°	1.353	1.163	3.741	6.973	7.807	9.899	15.65	19.01	17.80	12.40	5.860	2.155	0.9537
225°	3.106	3.232	5.420	11.85	20.10	37.39	51.57	55.67	46.89	29.60	12.72	6.071	2.152
240°	4.853	6.692	8.035	28.51	74.62	124.5	156.3	155.7	122.2	71.94	38.54	16.45	3.210
255°	3.971	10.23	20.33	111.3	263.1	397.4	454.9	420.2	309.7	180.4	99.40	31.83	2.396
270°	0	46.37	83.61	420.3	892.7	1198	1236	1054	725.0	454.8	206.0	43.23	0
285°	36.01	227.8	333.8	1493	2746	3189	2924	2286	1546	892.1	308.2	71.10	13.97
300°	367.7	678.9	1261	4526	6838	6748	5506	3933	2613	1208	659.1	391.7	97.43
315°	1591	921.1	3955	10194	12135	10173	7434	5120	2785	2180	1634	864.4	272.5
330°	3206	938.4	8582	14782	13593	9739	6570	3700	3193	3447	2670	1383	364.7
345°	2070	2945	10935	12972	9379	5550	2631	1687	3075	3568	2755	1262	176.0

[a] For definitions of angles, see text or Table I.

Table III

Comparison of Overlap Integrals for Bicyclo[2.2.2]octenone

	Previous work[a]		Present work		
Atoms	Dist., Å.	Resolved S	Dist., calcd.[b]	Dist., meas.[c]	Resolved S
C_1–C_3	2.46	0.057	2.51	2.5	0.052
C_1–C_4	2.66	.033	3.02	2.8	.017
O–C_3	3.41	.0021	3.44	3.4	.0021
O–C_4	3.77	.0002	4.12	3.9	.00015

[a] Ref. 6. [b] Calculated as part of computer program for angles of 60 and 120°. [c] Measured with centimeter scale in molecular models according to Dreiding.

thereafter in the following: *trans–cis* > *cis–trans* > *trans–trans*. The position of the oxygen atom thus plays a dominant role due to its rapidly changing distance as a bond angles vary. Also noted is the fact that $\Sigma S_c{}^2\ \Sigma S_0{}^2$ is a function which, in many regions, changes rapidly with bond angles. The measurement of exalted n-π^* transitions may, therefore, represent a very sensitive indication of molecular geometry in properly constituted molecules.

Selected molecules of relatively fixed geometry were represented with Dreiding models and the bond angles estimated with eye and large transparent protractor. In order to minimize the effects of variations in ϵ (donor) and λ (donor), disubstituted olefins have been kept separate from trisubstituted olefins.

It was unfortunately necessary in the present treatment to propose values for ν_d and ν_{ct} when these had not been reported. These frequencies, appearing in equations VI and VII in terms involving squares of differences, are of singular importance and can cause major variations in values for ϵ_{210} and ϵ_{290}. Far less important are terms such as ν_d/ν_{180} and even $10{,}000/\epsilon_d$. Deviations of the latter term from unity have been ignored even though ϵ_d is susceptible to some variation certainly.

Values of ν_d and ν_{ct} which have been estimated are italicized in Tables IV and V. The method used for

TABLE IV

ANALYSIS OF SPECTRAL VALUES FOR RIGID DISUBSTITUTED OLEFINIC KETONES, ETHANOL SOLUTION

Compound	Spectral values,[a] reported and *assigned*	ϵ_{210}	ϵ_{290}	Assigned angles			$10^5 \times \Sigma S_0^2$	$10^{10} \times \Sigma S_0^2 \Sigma S_0^2$	K_{ct}	$K_{n-\pi}$
				θ		ψ				
II	186.7 (11,240); 214 (1810); 297 (43)	1215	23	135°	0°	135°[b]	415.0	1.125	2.93	20
[c]	*189;* 214 (1500); 285 (24)	833	...	Separate calcn.			292		2.85	
[d]	*187; 216;* 302 (84)		53.3	60°		120°	296.4	130.4		0.41
III	*195;* 224 (1250); 313 (63)	861.4	32	165°	60°	285°[g]	338.6	113.1	2.55	.28
IV	*180; 210;* 290 (400)		380	90°		270°	370.2	1236		.31
[e]	*187;* 219 (820); 303 (174)	798	141	112°		90°[g]	303.7	578.8	2.63	.25
[f]	*195; 224;* 300.5 (292)		137.7	75°		105°[g]	353.1	406.1		.34

[a] Wave length in mμ, intensity is (ε). [b] For γ,δ-unsaturated ketones, the last angle given is ψ, the second is the clockwise rotation of C_α–C_β from the *cis* position and the first is that angle taken in a counterclockwise manner from an orbital position parallel to the *X-Y* plane of Fig. 1 and farthest from oxygen. [c] 3-Methylenecyclobutanone-1, F. F. Caserio and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5837 (1958). [d] Dimethyl 7-dichloromethyl-7-methyl-8-oxobicyclo[2.2.2]oct-5-en-2,3-dicarboxylate, Cookson and Wariyar, ref. 3. [e] 1,4,4-Trimethylbicyclo[3.2.0]hept-6-en-2-one, G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960). [f] Bicyclo[2.2.1]-hept-2-en-5-one (norbornenone), P. D. Bartlett and B. E. Tate, *ibid.*, **78**, 2473 (1956). [g] These angles measured using ball and spring models. II, Ref. 8. III, R. C. Cookson, R. R. Hill, and J. Hudec, *Chem. Ind.* (London), 589 (1961). IV, K. Weisner, *et al.*, *ibid.*, 173 (1957).

TABLE V

ANALYSIS OF SPECTRAL VALUES FOR RIGID TRISUBSTITUTED OLEFINIC KETONES, ETHANOL SOLUTION

Compound	Spectral values,[a] reported and *assigned*	ϵ_{210}	ϵ_{290}	Assigned angles			$10^5 \times \Sigma S_c^2$	$10^{10} \times \Sigma S_c^2 \Sigma S_0^2$	K_{ct}	$K_{n-\pi}$
				θ		ψ				
I	187.6 (11,450); 224 (1455); 297 (33)	1774	13	135°	0°	135°[b]	415.0	1.125	4.28	12
[c]	*187;* 219 (1730); 303 (230)	1685	192	112°		90°[d]	303.7	578.8	5.55	0.33
[e]	*187; 216;* 300 (120)		80	60°		120°	296.4	130.4		.61
[f]	*180; 210;* 294 (76)		60	30°		112°	188.6	99.12		.61
[g]	*180; 210;* 287 (55)		33	30°		120°	198.2	52.74		.62
[h]	*180; 210;* 290 (120)		100	60°		120°	296.4	130.4		.77
V	*185; 214;* 295 (120)		81	142°		240°	180.7	55.24		1.47

[a] Wave length in mμ, intensity (ε). [b] For definitions of angles for γ,δ-unsaturated ketones, see Table IV, footnote *b*. [c] 4,4,6-Trimethylbicyclo[3.2.0]hept-6-en-2-one, ref. *e*, Table IV. [d] Angles estimated with ball and spring models; other with Dreiding models. [e] 2,2,4-Triethyl-1-hydroxy-6-methylbicyclo[2.2.2]oct-5-en-3-one, T. J. Kealey and D. D. Coffman, *J. Org. Chem.*, **26**, 987 (1961). [f] Ethyl 4-methylbicyclo[3.2.1]oct-3-en-8-one-1-carboxylate, W. G. Dauben and J. W. McFarland, *J. Am. Chem. Soc.*, **82**, 4245 (1960). [g] Ethyl 4-methylbicyclo[3.3.1]non-3-en-9-one-1-carboxylate, W. G. Dauben and J. W. McFarland, *ibid.*, **82**, 4245 (1960). [h] 1,5,5-Trimethylbicyclo[3.1.1]hept-1-en-7-one (chrysanthenone), J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 2864 (1960).

this estimation is based on only a very few pieces of selected data and probably has very limited validity. A plot of ν_d for cyclohexene (180 mμ),[19] methylenecyclohexane (185 mμ),[8] and norbornene (195 mμ)[7] against the square root of ν_{str} (the heat of hydrogenation of the analogously strained olefin less 27.1 kcal. and converted to cm.$^{-1}$) is linear and is given by the equation $\nu_d = 55555 - 93.03\ (\nu_{str})^{1/2}$. From the heats of hydrogenation[20] of methylenecyclobutane (29.40), methylcyclobutene (28.50) and bicyclo[2.2.2]octene (28.30) are obtained the respective values for ν_d (189, 187, 187 mμ). These last values are based on data for cyclohexane solutions but for the donor molecules there is probably little change with solvent. Estimation of the position of charge-transfer bands (ethanol solution) was effected similarly. The best straight line corresponding to the points given by the four pieces of data in Table IV gave the equation $\nu_{ct} = 47619 - 64.79\ (\nu_{str})^{1/2}$. This equation, which again accommodated best the data for the ketones involving the methylenecyclohexane and norbornene systems, suggested that the charge-transfer bands for unstrained olefinic ketones would be found at 210 mμ, that for bicyclo[2.2.2]octenone at 216 mμ, and that for ergostadienone, like that for methylenecyclohexanone, at 214 mμ. It is to be emphasized that, in assigning values to trisubstituted ketones, the same values were taken as were used for the disubstituted ketones, since such changes as are produced by alkylation were, by definition, to be absorbed in alterations of the values for *K*. This was done even for compound I, Table IV. A value of 214 mμ was taken for the charge-transfer band (only in calculation of $K_{n-\pi}$) even though it is known to be at 224 mμ. Although the point for compound I is an exceedingly minor one, due to the much greater error in estimation of background absorption, it deserves emphasis.

The positions of reference bands are quite critical and the present calculations are limited strictly to data reported for ethanol solutions when dealing with positions of charge–transfer bands. The data for such bands are known to vary markedly with solvent.

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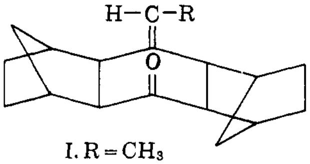
(19) R. A. Micheli and T. H. Applewhite, *J. Org. Chem.*, **27**, 345 (1962).

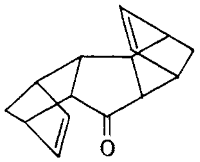
(20) R. B. Turner in "Theoretical Organic Chemistry," IUPAC Kekulé Symposium, Butterworth's Scientific Publications, London, 1959.

In spite of the numerous assumptions which have had to be made during the execution of the present analysis (the applicability of equation II, the constancy of f_d and the very questionable validity of equations for predicting ν_d and ν_{ct}), it is concluded that Tables IV and V suggest very concretely that there is value in this correlation method. Highly gratifying is the easy accommodation of data for three γ,δ-unsaturated ketones. This observation should help dispel any lingering preference for a hyperconjugation mechanism of interaction. Harmonious also is the data for the highly strained ketone, norbornenone, which, while having a relative small value of S_0, has a large value of ϵ.

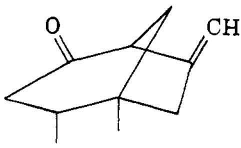
There are instances of difficulty, however. In Table IV the value of $K_{n\text{-}\pi}$ for bicyclo[3.2.0]hept-6-en-2-one is low and this is confirmed by the data of the analogous compound in Table V. This discrepancy is probably related, not only to the impossibility of adequate model representation of four-membered rings, but also to a similar failure for five-membered rings. The latter system, seen in models as rigid, is known to be flexible and groups depicted as largely axial are often largely equatorial.[21] Analysis of such substances by observation of bond angles is obviously severely inaccurate.



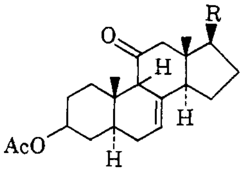
I. R = CH_3
II. R = H



III



IV. Napellonine, partial formula



V. R = C_9H_{17}
VI. R = OAc
VII. R = C_8H_{17}

The only serious problem is found in Table V, substance V. 3-β-Acetoxy-9-β-ergosta-7,22-dien-11-one,[22] represented by Dreiding models as completely rigid, exhibited an absorption band at 295 mμ, (120),[22] values well substantiated by other workers.[23] However, it was also shown by this latter group that the values for compound VII were similar but those for VI were noticeably different (298 mμ, 95.5). Reported also was the high residual absorption of Δ^{22}-3-β-acetoxy-7,8-oxido-11-keto-9-β-ergostene (295 mμ, 42). For construction of Table V, a problem of selection was involved; it was decided that the most unfavorable case should be included. Had there been selected instead substance VI, with the assumption of a background absorption of 42,[24] the calculations would have appeared as follows: VI, *185; 214;* 298 (95.5)—43.5 142.5° 240° 180.7 55.24—0.79. In these substances, V–VII, the size of R may be a factor which influences the relative dispositions of the ketone and olefin groups.

Attention is called to the fact that, unfortunately, all of the compounds discussed in this report have bond angles falling in the region ψ = 90–270° and θ = 60–142°. The treatment therefore makes no comment concerning the validity of I at larger values of S_0. Nor does the favorable report concerning the validity of II carry great weight, since the variations in S_c in the restricted region are comparatively minor.

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[21] Some earlier literature on this point is given in ref. 10.

[22] P. Bladon, *et al.*, *J. Chem. Soc.*, 2921 (1953).

[23] K. Heusler and A. Wettstein, *Helv. Chim. Acta*, **36**, 398 (1953).

[24] A similar correction would be necessary for a completely successful treatment of compounds I and II.

Potentially Cyclic Difunctional Compounds Containing Substituent Methyl Groups

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A β,β-dimethyl-δ-keto acid behaves similarly to the unsubstituted compound, in that the acid chloride exists as the cyclic structure, but the pseudo ester could not be obtained. Unsubstituted ϵ-keto acids gave only the open-chain acid chloride. 2,3-Dimethyl-4-oxo acids, in contrast with the unsubstituted γ-keto acids, exist partly in the cyclic (lactol) form in solution. The cyclic acid chloride may be converted to the pseudo ester, but the pseudo ester is converted to the normal ester with acid catalysis, as in the case of the unsubstituted compounds. Both the acid chloride and pseudo ester crack readily to yield the α,β-unsaturated butenolide (double bond migration), and this butenolide is also obtained readily by treatment of the normal keto ester with methoxide.

In previous publications,[2,3] it has been reported that, although succinyl and glutaryl dichlorides exist as normal open-chain structures, unsubstituted γ- and δ-keto acid chlorides exist only as cyclic structures (chloro lactones), even at 0°. In view of the well recognized tendency of substitution, especially *gem*-disubstitution (the "*gem*-dimethyl effect"), to promote cyclization,[4,5] it is somewhat surprising that the infrared

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[1] Recipient of a National Science Foundation Summer Fellowship, 1960; a U. S. Rubber Co. predoctoral Fellowship, 1959–1960; a Procter and Gamble Co. predoctoral Fellowship, 1960–1961.

[2] J. Cason and E. J. Reist, *J. Org. Chem.*, **23**, 1492 (1958).

[3] J. Cason and E. J. Reist, *ibid.*, **23**, 1675 (1958).

[4] R. F. Brown and N. M. van Gulick, *ibid.*, **21**, 1046 (1956).

[5] N. L. Allinger and V. Zalkow, *ibid.*, **25**, 701 (1960).