mm., with a mixture of benzene and petroleum ether gave 0.7 g. (2 mmoles, 0.3%) of a white powder, m.p. 121–122°. Elemental analysis and the infrared spectrum of the solid showed it to be the same as the small amount of material isolated from the reaction of diethyl malonate and diphenyliodonium chloride in *t*-butyl alcohol.[3] The available information suggests the structure *t*-**butyl diethyl 1,2-diphenylethane-1,1,2-tricarboxylate** (II) for this compound.

The infrared spectrum (KBr) of this compound showed bands at 1738, and a shoulder at 1749 cm.$^{-1}$ (ester), 698 cm.$^{-1}$ (phenyl), 1389, 1415, 1449 cm.$^{-1}$ (*o*-ethyl), and 1415, 1365 cm.$^{-1}$ (*t*-butyl).

Acknowledgment.—The support of this research by the Alfred P. Sloan Foundation is gratefully acknowledged.

The Ultraviolet Absorption Spectra of Polyphenyl- and Polybenzylacetones

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Previously proposed statistical equations can be used successfully to predict the ketonic absorption maximum for most phenyl- and benzylacetones, connecting the two series in a useful manner. Other such ketones, not cleanly members of either of these classes, have spectral values which can not be accommodated similarly.

The previous publication in this series[1] suggested that two statistical equations (1 and 2) could be used to correlate the magnitude of the molecular extinction coefficients of the $n - \pi^*$ transitions of, respectively, phenylacetones and benzylacetones in hydrocarbon solvents.

$$\epsilon = 20\,(1 - 1/X^2)^n + k[1 - (1 - 1/X^2)^n] \qquad (1)$$

$$\epsilon = 20\,(1 - 1/2X^3)^m + k[1 - (1 - 1/2X^3)^m] \qquad (2)$$

In these equations, both X and k are constants and have the values of 3 and 810, respectively, n is the number of phenyl groups, and m is the number of benzyl groups.

These equations may be derived utilizing the original proposal of Cookson[2] which suggested that the maximum exaltation of the $n-\pi^*$ transition occurred when the orbitals at C_1 and C_1' (Fig. 1) were directed toward each other as shown. The fact that Cookson has recently modified[3] this early view does not affect the argument; there need only be a position of maximum exaltation. The position shown (in Fig. 1) is maintained here for simplicity and consistency with the earlier writing.[1] It is further assumed, with full recognition of obvious limitations, that the acetyl group and the unsaturated group are both freely rotating about, respectively, the axes C_1-C_2 and C_2-C_1'. Certain events therefore have the following probabilities: atom C-3′ is a minimum distance from C-1, $1/2X$; a π-orbital at C-1′ is directed maximally toward C-1, $1/X$; a π-orbital at C-1 is directed maximally toward C-1′, $1/X$; orbitals at C-1 and C-1′ are directed maximally towards each other, $1/X^2$; and an orbital at C-3 of a γ,δ-unsaturated ketone and an orbital at C-1 are directed maximally toward each other, $1/2X^3$. With a large number of molecules present, these probabilities can be directly equated to fractions of the total molecules. A ketone with one β,γ-unsaturated group thus has a fraction $(1/X^2)$ of molecules with maximum exaltation (k) and a fraction $(1 - 1/X^2)$ with substantially normal (20) $n - \pi^*$ transitions. The total extinction coefficient is then equal to $20\ (1 - 1/X^2) + k\ (1/X^2)$. This relationship can be adapted to the case of a molecule with n unsaturated groups in analogy with the classic combinatorial treatment of coin tossing. If the probability of "no heads" in one toss is 1/2, the probability of "no heads" in n tosses is $(1/2)^n$. Since the probability of no maximum exaltation with one unsaturated group is $(1 - 1/X^2)$, the probability with n equivalent groups is $(1 - 1/X^2)^n$. The final expressions (1 and 2) follow directly from this observation.

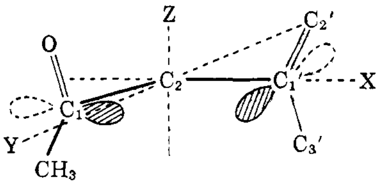

Fig. 1.—A possible position of π-orbitals on carbon atoms in a β,γ-unsaturated ketone.

While these equations in simplified form appeared to serve well[1] in a number of series [Ar—$(CH_2)_{1-2}$—CO—R, Ar = phenyl or 2-furyl, R = CH_3; and Ar = phenyl, R = phenyl], the number of compounds in any one series was small and it seemed desirable to evaluate the results which would be obtained with a much larger group of ketones.

Discussion

In Table I or Fig. 2 it can be seen that the values for the molecular extinction coefficients of all of the seven benzylacetones[4] (m = 1–4) and of the less symmetrical isomers of each pair in the polyphenylacetone series agree quite well with the predicted values. The observed values for the more symmetrical isomers are generally higher than the calculated, but that for the highly substituted pentaphenylacetone is profoundly lower. In certain cases, therefore, equations 1 and 2 may be helpful in predicting exalted $n-\pi^*$ transitions in other series of unsaturated ketones.

Well known at the time of the previous writing was the fact that certain ketones containing phenyl groups, by virtue of the geometric factors involved, exhibited no exaltation of the $n - \pi^*$ transition. This was cited[1] as one item of proof that the spectral values of benzylacetones, while small, are definite exaltations and are not due, for example, to aryl spectrum tailings. The

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[1] S. F. Marsocci and S. MacKenzie, *J. Am. Chem. Soc.*, **81**, 4513 (1959).

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

[3] R. C. Cookson and J. Hudec, *ibid.*, 429 (1962).

[4] The values for many of these differ considerably from those reported by J. M. Conia and P. Gosselin, *Bull. soc. chim. France*, 836 (1961), although excellent correlation of melting point and infrared spectral values was obtained.

TABLE I

SPECTRAL VALUES OF POLYPHENYL AND POLYBENZYLACETONES (CYCLOHEXANE SOLUTION)

Substituents on 2-propanone	M.p., °C.	Spectral values: Benzenoid	Spectral values: $n-\pi$	$\epsilon_{n-\pi^*}$, Calcd.[a]
Monophenyl		255 mμ (202) 258 (202) 260 (235)	289 mμ (108)[b]	S[c]
1,1-Di		255 (410) 260 (485)	292 (210)[b]	186
1,3-Di		260 (413) 266 (354)	295 (255)[b]	186
1,1,1-Tri[d]	137.5–138.5	261 (870)	300 (261)	255
1,1,3-Tri[e]	82–83	260 (713)	299 (324)	255
1,1,1,3-Tetra[f]	113–115	260 (1140)	304 (320)	317
1,1,3,3-Tetra[g]	133–134	246 (880) 254 (990) 260 (1090)	300 (347)	317
Penta-[g]	178–180	260 (1490)	308 (197)	372
Monobenzyl		260 (223)[h]	281 (32)[b]	S
1,1-Di		260 (440)	285 (51)	48.9
1,3-Di		260 (445)	285 (53)	48.9
1,1,1-Tri	104–105	260 (665)	292 (57)	63.0
1,1,3-Tri	60–61	260 (660)	295 (64)	63.0
1,1,1,3-Tetra	124–125	260 (918)	294 (77)	76.8
1,1,3,3-Tetra	124–125	260 (925)	293 (81)	76.8

[a] By equations 1 and 2. [b] Reported in ref. 1. [c] Standards. [d] By the method of J. L. Greene and H. D. Zook, *J. Am. Chem. Soc.*, **80**, 3629 (1958), who reported m.p. 137.5–138.5°. [e] By the method of A. Orekhoff, *Bull. soc. chim. France*, **25**, 108 (1919), who reported m.p. 80–81°, and by Friedel-Crafts synthesis. [f] A. Orekhoff, *ibid.*, **25**, 179 (1919), reported m.p. 113–113.5°. [g] By the method of S. W. Kantor and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 3290 (1950), who reported 133–134° and 180–181°. [h] In this series, only maximum at 260 mμ is reported.

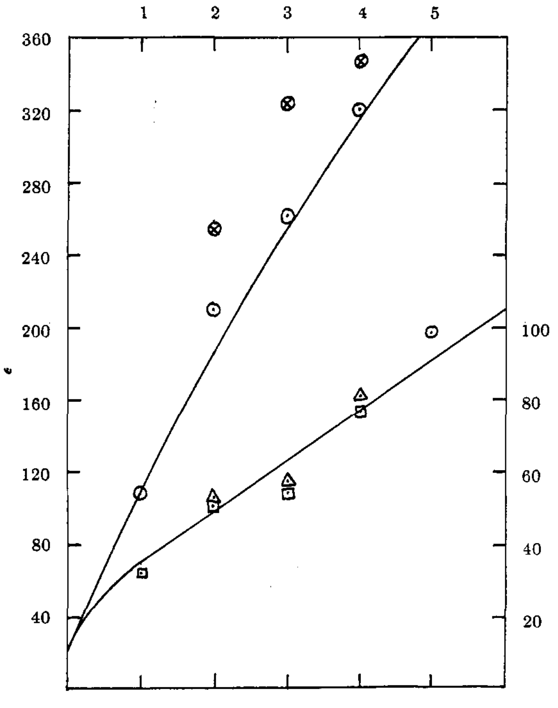


Fig. 2.—ϵ_{max} ($n-\pi^*$) of arylacetones *vs.* number of aryl groups.
Left ordinate: ⊙ less symmetrical polyphenylacetones
⊗ more symmetrical
Right ordinate: ⊡ less symmetrical polybenzylacetones
⚠ more symmetrical

generosity of several other authors has permitted further substantiation of this point (Table II, compounds 1–4).

Benzhydrylacetones, unlike the benzylacetones to which they are most closely related statistically, do not obey equation 2. These were found to have extinction coefficients which were uniformly lower than the predicted values, so much so that the contribution of the second phenyl group of any benzhydryl group could be ignored as a contributing influence (Table II, compounds 5–7).

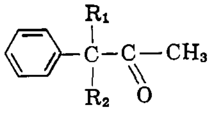
TABLE II

SPECTRAL VALUES OF OTHER PHENYL KETONES (CYCLOHEXANE SOLUTION)

Compounds or Substituents on 2-Propanone	Spectral values: Benzenoid	Spectral values: $n-\pi^*$	$\epsilon_{n-\pi^*}$ Calcd.
4-Phenylcyclohexanone[a]	259 mμ (232)	287 mμ (19.5)	
4-Phenylcycloheptanone[a]	259 (232)	288 (23.6)	
5,5-Diphenylcyclononanone[b]	260 (476)	291 (19.6) infl.	
4,5-Benzcyclohept-4-en-1-one[c]	262 (255)	289 (16)	
Benzhydryl	260 (455)	284 (30)	48.9
1-Benzyl-3-benzhydryl	260 (666)	284 (50)	63.0
1,3-Dibenzhydryl	260 (929)	286 (48)	76.8
1-Benzyl-1-phenyl	260 (460)	288 (245)[d]	120[e]
1,1-Dibenzyl-1-phenyl	260 (648)	299 (217)	139
1-Benzyl-1,3-diphenyl	260 (615)	298 (332)	198
1,3-Dibenzyl-1,3-diphenyl	260 (820)	298 (340)	210
1,1,3-Tribenzyl-1,3-diphenyl	260 (1125)	303 (184)	225

Compounds by courtesy of [a] E. D. Bergmann and S. Yaroslavsky, *J. Am. Chem. Soc.*, **81**, 2772 (1959); [b] A. T. Blomquist and B. F. Hallam, *ibid.*, **676**; and [c] N. L. Allinger and W. Szkrybalo, *J. Org. Chem.*, **27**, 722 (1962). [d] Previously reported, 288 mμ, 502. [e] Last five values calculated with the equation $\epsilon = 20(1 - 1/X^2)^n(1-1/2\,X^3)^m + k\,[1-(1-1/X^2)^n(1-1/2X^3)^m]$.

A second, and much more important, exception to the present statistical treatment was found in substituted phenylacetones, I, containing an α-substituent different from phenyl.

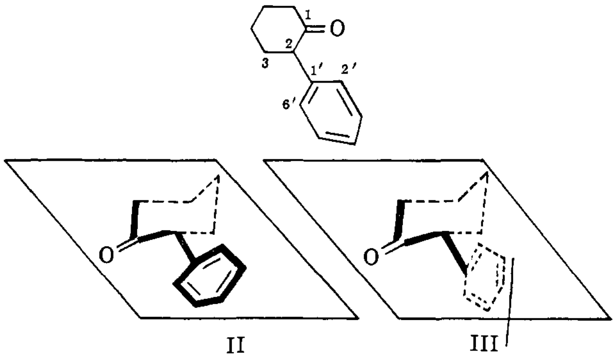


I

Such an effect has been seen previously and tabulation of the results of Kumler,[5] Cram,[6] and DeMoen,[7] as already done in large part by Cookson,[2] suggested that a major increase in $\epsilon_{\max}$ ($n - \pi^*$) resulted when $R_1 = CH_3$ and R_2 = Et but not when $R_1 = R_2 = CH_3$. On the other hand, in the diphenylacetone series (R_1 = phenyl), the presence of a methyl group ($R_2 = CH_3$) caused a major increase, although lengthening R_2 caused little additional increase. These results, unfortunately for our purpose obtained in polar solvents, have now been supplemented with work in cyclohexane solutions (Table II, compounds 8–12). Confirmed is the fact that a large group (R_1), added to the phenylacetone moiety, can profoundly alter $\epsilon_{\max}$ ($n - \pi^*$). Addition of a second group equal in size, however, reversed this trend to an extent.

Clearly, equations 1 and 2 are not uniformly applicable with success. Extensive computation, in line with recent theoretical developments,[8–11] has been[12] and is currently being undertaken to provide a more uniformly successful method of prediction. While the portion of this program dealing with conformations and atomic interactions is still far from complete, it is possible to set forth qualitatively some aspects of this.

In any reconciliation of conformations and these exaltations, key substances to be considered are 2-phenylcyclopentanone (293 mμ, 50, EtOH)[13] and 2-phenylcyclohexanone (295 mμ, 40, hexane[5] or 290 mμ, 17, EtOH[14]). The latter substance is more realistically approximated with models and only it will be discussed. Two extreme conformations can be visualized: planar (II) and perpendicular (III). Because of the low exaltation of $\epsilon_{\max}$ ($n - \pi^*$), one of these two should represent the major contributing form. Favoring II is the fact that a small hydrogen bonding tendency may exist between the 2′ hydrogen atom and the oxygen atom; the distance, *ca.* 1.4 Å., is favorable.[15] Further, the 6′-hydrogen straddles nicely the *cis* hydrogen atoms at carbons 2 and 3. In III, on the other hand, some repulsion between the 2′ hydrogen atom and those axial on carbons 2 and 3 is likely. The angles for the two forms are $\psi = 0°$, $\theta = 0°$ and $\psi = 0°$, $\theta = 90°$, respectively, where ψ is the angle made by the carbonyl group and the equatorial bond to phenyl and θ is that made by the phenyl ring and the C_1—C_2—C_3 plane. Both of these positions are minima in tabulated values[12] of $\Sigma\ S_c^2\ \Sigma\ S_o^2$. The individual squared overlap integrals are tabulated in Table III.



II III

TABLE III

SQUARED OVERLAP INTEGRALS FOR CONFORMATIONS OF PHENYLCYCLOHEXANONE

Atoms	10^5 S_o^2 (II)	10^5 S_c^2 (III)	Atoms	10^5 S_o^2 (II)	10^5 S_o^2 (III)
1–1′	78.25	0	0–1′	0	114.2
1–2′	30.06	3.386	0–2′	0	5.5
1–6′	.30	3.386	0–6′	0	5.5
	108.3	6.772		0	125.2

Comparison of the products, which should indicate the magnitude of the $n - \pi^*$ exaltation, again suggests that II (0.0) is preferable to III (847.8). The alternate to this conclusion would require assumption that the squares of overlap integrals can not be added in this fashion. This would seem contrary to the experience thus far accumulated, but the present case (III) is certainly a more extreme one than any previously analyzed. Great interest attaches to it for that reason. A preference for single atom interactions (nearest neighbor) has indeed been expressed.[16] Under this latter assumption, the values of $10^{10}\ S_c^2\ S_o^2$ would be 0.0 (for II) and 18.62 (for III), either of which would be pretty much in accord with the facts.

In an effort to obtain evidence favoring a planar, or weakly hydrogen-bonded, form, a previous solvent study[1] has been evaluated to see if the spectacular increase in ϵ found for phenylacetone and diphenylacetone on change to more polar solvents could be attributed to disruption of this conformation. For this purpose, it was necessary to calculate by equation 3[17] that increase in ϵ which could be expected to result when a change to a polar solvent produced a bathochromic shift of λ_{ct} and a hypsochromic shift of $\lambda_{n - \pi^*}$.

$$\frac{\epsilon_{n - \pi^*}}{\epsilon'_{n - \pi^*}} = \frac{\epsilon_{ct}(v'_{ct} - v'_{n - \pi^*})^2}{\epsilon'_{ct}\,(v_{ct} - v_{n - \pi^*})^2} \tag{3}$$

The values of $\epsilon'_{n - \pi^*}$, $\nu'_{n - \pi^*}$, and $\nu_{n - \pi^*}$ are available from the previous report. A value of ν'_{ct} of 45,662 cm.$^{-1}$ (219 mμ.)[9] is taken based on the assumption that this value is largely determined by the ionization potential[18] of the donor; toluene and trimethylethylene have about the same[19] ionization potential. The terms $\epsilon_{ct}/\epsilon'_{ct}$ and ν_{ct} are not available, since the charge–transfer band for these phenyl ketones is buried in stronger absorption. These terms are estimated by assuming that *alterations* in charge–transfer band values follow *alterations* for the $\pi - \pi^*$ transformation of mesityl oxide,[20] which has been particularly well studied. Results are shown in Table IV.

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[5] W. D. Kumler, L. A. Strait, and E. L. Alpen, *J. Am. Chem. Soc.*, **72**, 1463, 4558 (1950).

[6] D. J. Cram and J. D. Knight, *ibid.*, **74**, 5835 (1952).

[7] P. J. A. DeMoen, P. A. J. Janssen, and J. L. M. Loomans, *ibid.*, **81**, 6286 (1959).

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

[9] S. Winstein, L. de Vries, and R. Orloski, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

[10] R. C. Cookson and S. MacKenzie, *Proc. Chem. Soc.*, 423 (1961).

[11] S. F. Mason, *Quart. Rev.*, 287 (1961).

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

[13] K. Mislow and A. K. Lazurus, *J. Am. Chem. Soc.*, **77**, 6383 (1955).

[14] W. C. Wildman and R. B. Wildman, *J. Org. Chem.*, **17**, 581 (1952).

[15] L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952).

[16] A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *ibid.*, **84**, 1945 (1962).

[17] Obtained by simple division from equation of ref. 3, 11, and 12.

[18] For example, R. Foster, *Tetrahedron*, **10**, 96 (1960).

[19] K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957); W. C. Price, R. Bralsford, R. G. Ridley, and P. V. Harris, *Spectro. Acta.*, **14**, 45 (1959); A. Streitwieser, *J. Am. Chem. Soc.*, **82**, 4123 (1960).

[20] E. M. Kosower, *ibid.*, **80**, 3261 (1958).

Table IV

Interpretation of Solvent-induced Changes in $\epsilon_{\max}$, $(n - \pi^*)$

Solvent	Phenylacetone Calcd.[a]	Phenylacetone Found	1,1-Diphenyl-2-propanone Calcd.	1,1-Diphenyl-2-propanone Found
C_6H_{12}		108		210
MeCN	92	97	177	180
$CHCl_3$	132	178	247	219
EtOH, 95%	132	150	254	230

[a] Values are $\epsilon_{\max}$, calculated by equation 3.

Striking is the fact that many of the solvent-induced changes were outstandingly well explained by the calculations. The only instance, therefore, which admitted the strong possibility of conformational change was that of phenylacetone in chloroform. Little support for the planar conformation (II) resulted.

Computer programs involving separately the assumptions implicit in conformation 2 and those implicit in 3 have also failed to be conclusive. Detailed analysis of these phenyl ketones is therefore deferred.

Experimental

All spectra were obtained using solutions in purified cyclohexane unless otherwise specified. The same spectrophotomer (Beckman DU) was used as in the previous work so that values would be strictly comparable. Liquid ketones were purified by recrystallization of the semicarbazones.

t-Butyl acetoacetate was benzylated as follows: (a) 2 moles of potassium *t*-butoxide and benzyl chloride gave a liquid which decomposed on distillation to 1,1-dibenzylacetone, 68%; (b) 2 moles of sodamide and benzyl chloride followed by 1 mole of potassium *t*-butoxide and benzyl chloride gave analogously 1,1,3-tribenzyl-2-propanone, 11%; (c) 2 moles of sodamide and benzyl chloride followed by a second such treatment gave analogously 1,1,3,3-tetrabenzyl-2-propanone,[21] 7.3%. These procedures gave materials more easily purified than those obtained by (a) the cleavage of ethyl dibenzylacetoacetate with hydrogen iodide in acetic acid,[22] (b) the hydrogenation of 1,1-dibenzyl-3-benzal-2-propanone,[23] or (c) the dibenzylation of 1,3-dibenzyl-2-propanone.

Benzylation with benzyl chloride and alkali metal amides effected the following conversions: (a) 1,1-dibenzyl-2-propanone to 1,1,1-tribenzyl-2-propanone,[23] 55%, the simultaneously formed 1,1,3-tribenzyl being removed by recrystallization; (b) 1,1,1-tri- to 1,1,1,3-tetrabenzyl-2-propanone,[23] 25% using diglyme as solvent; (c) 1,3-diphenyl-2-propanone to 1-benzyl-1,3-diphenyl-2-propanone[24] and 1,3-dibenzyl-1,3-diphenyl-2-propanone,[25] m.p. 118–119°, 58%. Benzylation with benzyl chloride and potassium *t*-butoxide converted phenylacetone to 1-benzyl-1-phenyl-2-propanone, as previously reported,[26] and the latter to 1,1-dibenzyl-1-phenyl-2-propanone,[27] 59%.

1,1,3-Tribenzyl-1,3-diphenyl-2-propanone.—To 0.1 mole of potassium amide and 0.05 mole of 1,3-dibenzyl-1,3-diphenyl-2 propanone was added 0.05 mole of benzyl chloride. The solid product, 15.0 g., 61%, m.p. 160–160.5°, was recrystallized from benzene and alcohol.

Anal. Calcd. for $C_{36}H_{32}O$: C, 89.95; H, 6.72; Found: C, 90.29; H, 6.75.

Although the production of benzylated ketones by hydrogenation of benzal ketones often gave products contaminated with starting material with consequent invalidation of spectral results, this synthesis was successfully applied in two instances. Dibenzylideneacetone was reduced in ethylene dichloride[28] solution with Raney nickel catalyst and the distilled liquid purified through the semicarbazone.

1-Benzyl-3-benzhydryl-2-propanone was prepared by hydrogenation of 1-benzylidene-3-benzhydryl-2-propanone in ethylene dichloride solution with Raney nickel at 40–50°. Six recrystallizations from ethanol gave the final product, m.p. 71.5–72.5°.

Anal. Calcd. for $C_{23}H_{22}O$: C, 87.86; H, 7.05; Found: C, 88.04; H, 7.08.

Benzhydryl- and 1,3-dibenzhydryl-2-propanone were prepared by the Friedel-Crafts methods.[29]

1,1,3-Triphenyl-2-propanone.—Into a gently boiling mixture of 150 ml. of dry benzene and 37.5 g. (0.28 mole) of anhydrous aluminum chloride was added, over a period of 1 hr., a solution of 39.0 g. (0.135 mole) of recrystallized 1-bromo-1,3-diphenyl-2-propanone in 100 ml. of dry benzene. The final yield was 78%.[30]

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(21) H. Leuchs, J. Wutke, and E. Gieseler, *Ber.*, **46**, 2207 (1914).

(22) H. Leuchs, A. Heller, and A. Hoffmann, *ibid.*, **62B**, 817 (1929).

(23) J. M. Conia and P. Gosselin, *Bull. soc. chim. France*, 836 (1961).

(24) Procedure of C. R. Hauser and T. M. Harris, *J. Am. Chem. Soc.*, **81**, 1154 (1959).

(25) Hauser and Harris reported m.p. 120.5–122° and did not investigate the structure of this compound. The present assignment is supported by the n.m.r. spectrum which exhibited twelve peaks in addition to that for phenyl hydrogens.

(26) T. Ando and N. Tokura, *Bull. Chem. Soc. Japan.*, **31**, 1026 (1958); *Chem. Abstr.*, **53**, 19966 (1959).

(27) T. Ando and N. Tokura, *Bull. Chem. Soc. Japan.*, **31**, 351 (1958); *Chem. Abstr.*, **53**, 289 (1959).

(28) R. Cornubert and H. G. Eggert, *Bull. soc. chim. France*, 522 (1954).

(29) C. F. Woodward, G. T. Borcherdt, and R. C. Fuson, *J. Am. Chem. Soc.*, **56**, 2103 (1934).

(30) Using bromo ketone prepared *in situ*, A. C. B. Smith and W. Wilson, *J. Chem. Soc.*, 1342 (1955), obtained 17%.