identical with authentic hydrated oxalic acid. The anhydrous acid (m. p. 187° dec.) gave an equiv. wt. by titration of 49.

Analysis of Sodio and Potassio Derivatives.—The solution and suspension of the alkali-metal derivatives were separated from excess metal by decantation or filtration through glass wool in the absence of air, and the alkali formed by decomposition with water titrated: 0.2556 g. of azulene combined with 0.325 g. of sodium. $(C_{15}H_{18}Na)_2$ requires 0.289 g. 0.2387 g. of azulene combined with 0.398 g. of potassium. $(C_{15}H_{18}K)_2$ requires 0.470 g.

Analysis and Oxidation of the Carboxylated Alkali-Metal Derivatives.—0.1058 g. of the carboxylated sodio derivative gave 0.0293 g. of sodium sulfate. Equivalent wt. of corresponding acid, 256. $(C_{15}H_{18}COOH)_2$ requires equiv. wt. 243.

3.5 g. of the potassium salt of the above acid was treated with 4% aqueous potassium permanganate. Acetone was concentrated by distillation, the yield being 0.125 molecular; equiv. wt. of steam volatile acid, 64, and 0.81 g. Ba salt gave 0.2 g. of *p*-phenylphenacyl ester of m. p. 110° identical with a specimen from pure acetic acid. The residue from steam distillation required in the cold 132 cc. of 0.1 *N* potassium permanganate, which would be equiv. to 0.59 g. of oxalic acid, if this were the only reacting substance.

The author extends his thanks to Dr. J. K. H. Inglis for advice and kindly criticism during this investigation, and also to Mr. J. Melville, who arranged for micro-analyses to be done.

Summary

1. Azulene reduced until 2.7 molecules of hydrogen were taken up and then ozonized gave formic acid (in small yield), isobutyric acid, α-methylglutaric acid and the $C_{14}H_{21}COOH$ acid obtained by Melville.[4]

2. A reduced azulene (four molecules of hydrogen absorbed) gave with ozone formic acid (0.6 mole) and in poor yield possibly the same acid $C_{14}H_{21}COOH$ as before.

3. The sesquiterpene guaiene gave on oxidation with permanganate, acetone and oxalic acid in roughly equimolecular proportions and neutral products not investigated.

4. The sodio derivative of azulene probably has the formula $(C_{15}H_{18}Na)_2$ and gives with aqueous ether an unstable crystalline hydrocarbon. The carboxylated potassio derivative, probably $(C_{15}H_{18}COOK)_2$, gives with potassium permanganate, acetone, acetic acid and (probably) oxalic acid.

5. The facts now known regarding the hydrocarbon may best be explained by the formula originally proposed by Ruzicka for elemazulene, although this structure is not free from minor objections.

DUNEDIN, NEW ZEALAND RECEIVED JANUARY 9, 1935

[A COMMUNICATION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

The Michael Condensation. III. The Addition of Simple Ketones[1]

BY DAVID B. ANDREWS AND RALPH CONNOR

In earlier communications[2,3] it has been shown that the order of reactivity of active methylene groups in the Michael condensation is not only a function of the number of labilizing groups attached to them but is dependent also upon other structural influences. This created an interest in the reactivity of simple ketones as representatives of the class of addenda possessing only one activating group. The addition of simple ketones to various acceptors is reported in a number of earlier papers[4,5] but the compounds and conditions used were so varied that no definite comparisons of the influence of structure upon the reactivity of these compounds could be drawn. Therefore a brief investigation of the reaction of a number of ketones with α,β-unsaturated ketones was undertaken with the purpose of comparing the behavior of these substances with the compounds containing two activating groups which have previously been investigated.[3]

In view of the influence[3] of substitution of

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(1) This communication is abstracted from the thesis submitted by David B. Andrews in partial fulfilment of the requirements for the degree of Master of Chemistry at Cornell University in June, 1934.

(2) Connor, THIS JOURNAL, **55**, 4597 (1933).

(3) Connor and Andrews, *ibid.*, **56**, 2713 (1934).

(4) (a) Knoevenagel and Weissgerber, *Ber.*, **26**, **444** (1893); (b) Cornelson and Kostanecki, *ibid.*, **29**, 241 (1896); (c) Kostanecki and Rossbach, *ibid.*, **29**, 1488, 2245 (1896); (d) Stobbe, *ibid.*, **34**, 653 (1901); (e) Abell, *J. Chem. Soc.*, **83**, 360 (1903); (f) Ekeley and Carpenter, THIS JOURNAL, **48**, 2375 (1926); (g) Kostanecki and Podrajansky, *Ber.*, **29**, 2248 (1896).

(5) (a) Stobbe, *J. prakt. Chem.*, [2] **86**, 209, 218 (1912); (b) Stobbe and Rosenburg, *ibid.*, **86**, 226 (1912); (c) Georgi, *ibid.*, **86**, 232 (1912); (d) Striegler, *ibid.*, **86**, 241, 257 (1912); (e) Rosenburg, *ibid.*, **86**, 250 (1912); (f) Cruikshanks, *ibid.*, **86**, 269 (1912); (g) Georgi and Schwyzer, *ibid.*, **86**, 273 (1912); (h) Stobbe, *ibid.*, **89**, 184 (1914); (i) Schwyzer and Cruikshanks, *ibid.*, **89**, 189 (1914); (j) Cruikshanks, *ibid.*, **89**, 194 (1914); (k) Allen and Sallans, *Can. J. Research*, **9**, 574 (1933).

methyl and ethyl groups upon the reactivity of malonic, phenylacetic and acetoacetic esters, the correspondingly ω-substituted acetophenones were selected as addenda. Isobutyrophenone was included because it, like the substituted active methylene compounds previously studied,[3] has only one hydrogen on the reactive carbon. The influence of other tertiary groups in both addendum and acceptor was compared with phenyl by replacing the latter with *t*-butyl and furyl groups. Cyclohexanone was also used as the addendum because previous work[5] indicated that cyclic ketones were very reactive in the condensation. The conditions used for the reactions were selected (after a preliminary study of the influence of conditions upon the reaction of acetophenone with benzalacetophenone) so that both dimolecular and trimolecular products would probably be formed, thus affording a comparison of both the amount and nature of the products from the various reactants.

The results obtained are summarized in Table I. If the influences of substituting methyl and ethyl groups in acetophenone are similar to those observed[3] when these groups are substituted in malonic ester, it would be predicted that acetophenone and propiophenone would have approximately the same reactivity and that butyrophenone would be less reactive. The total yields of condensation products obtained are too close to be significant but the ratio of the products obtained confirms this prediction. In the dimolecular compound (II) formed from propiophenone and benzalacetophenone, there is present only *one* phenacyl group. Since the carbon of the other active methylene group in II bears only one hydrogen, one would expect that it would be quite unreactive (by analogy to isobutyrophenone) and that therefore (if the assumption that acetophenone and propiophenone have approximately the same reactivity is correct) any differences in the behavior of these compounds would be due to differences arising from the fact that propiophenone competes with II for benzalacetophenone while acetophenone competes with I—a compound with *two* phenacyl groups and possessing double the possibility for reaction found in II. This is confirmed by the isolation of two times as much trimolecular compound and half as much dimolecular compound from acetophenone as from propiophenone.

$C_6H_5CH(CH_2COC_6H_5)_2$ I

$C_6H_5COCH(CH_3)CH(C_6H_5)CH_2COC_6H_5$ II

$C_6H_5COCH(C_2H_5)CH(C_6H_5)CH_2COC_6H_5$ III

Inasmuch as the dimolecular compound (III) from *n*-butyrophenone also has one phenacyl group, its reactivity should not vary greatly from that of II and any variation in the products should be due to a difference in the reactivity of the ketones with which they compete for the acceptor. The fact that more trimolecular product is formed in the reaction of *n*-butyrophenone with benzalacetophenone than when propiophenone is the addendum would indicate that propiophenone is the more reactive of these addenda.

The effect of increased branching in the addendum is shown by a comparison of *n*-butyrophenone and isobutyrophenone. The latter was so unreactive that more drastic conditions were necessary to bring about an appreciable amount of condensation than was the case with the other ketones. The fact that only trimolecular compounds were formed in the reaction of isobutyrophenone is doubtless due to the fact that the dimolecular compound (IV) contains a phenacyl group which is more reactive than the more highly substituted structure in isobutyrophenone.

$C_6H_5COC(CH_3)_2CH(C_6H_5)CH_2COC_6H_5$ IV

$(CH_3)_3CCOCH_2CH(C_6H_5)CH_2COC_6H_5$ V

A comparison of the addition of pinacolone to benzalacetophenone with the addition of acetophenone to benzalpinacolone is interesting since the reactions should give the same dimolecular compound (V) but different trimolecular compounds. Actually, the first pair of reactants gave only a trimolecular product and the latter pair gave exclusively a dimolecular product. This difference in the nature of the products from these two reactions is readily understandable from a consideration of the reactivities of the addenda and acceptors. To form the trimolecular products, V must in one case react with benzalacetophenone and in the other with benzalpinacolone. A comparison of the reaction of pinacolone with these two acceptors (Table I) shows that benzalpinacolone is the less reactive. Furthermore, in one reaction V must compete with pinacolone for the α,β-unsaturated ketone and in the other with acetophenone. The behavior of these two addenda with benzalpinacolone (Table I) shows clearly that pinacolone is the less reactive.

TABLE I

THE INFLUENCE OF STRUCTURE UPON THE REACTIVITY OF KETONES[a]

No.	Addendum	Acceptor	Yield, %[b] Di	Tri	Total[b] reaction, %
1	$C_6H_5COCH_3$	$C_6H_5CH{=}CHCOC_6H_5$	27[m]	56[m]	83
2	$C_6H_5COCH_2CH_3$	$C_6H_5CH{=}CHCOC_6H_5$	54[c]	27[d]	81
3	$C_6H_5COCH_2CH_2CH_3$	$C_6H_5CH{=}CHCOC_6H_5$	19[e]	58[f]	77
4	$C_6H_5COCH(CH_3)_2$	$C_6H_5CH{=}CHCOC_6H_5$	0	5[g]	5
5	$C_6H_5COCH(CH_3)_2$[h]	$C_6H_5CH{=}CHCOC_6H_5$	Trace[h]	30[h]	30
6	$(CH_2)_5CO$	$C_6H_5CH{=}CHCOC_6H_5$	..[i]	..[i]	90–100
7	$(CH_3)_3CCOCH_3$	$C_6H_5CH{=}CHCOC_6H_5$	0	69[j]	69
8	$C_6H_5COCH_3$	$C_6H_5CH{=}CHCOC(CH_3)_3$	39[k]	0	39
9	$(CH_3)_3CCOCH_3$	$C_6H_5CH{=}CHCOC(CH_3)_3$	0	0	0[l]
10	$C_6H_5COCH_3$	$C_4H_3OCH{=}CHCOC_6H_5$	25[m]	51[m]	76

[a] In every experiment except No. 5 the following procedure was used. A solution of 0.1 mole of each of the reactants in 250 ml. of anhydrous ether was prepared in a 500-ml., 3-necked flask fitted with a mercury-seal stirrer and protected by a calcium chloride tube. To this solution a solution of sodium ethoxide—prepared by dissolving 0.46 g. (0.02 mole) of sodium in 10 ml. of absolute ethanol—was added and stirring continued for twenty hours at room temperature (20–23°). At the end of this time 100 ml. of 2% hydrochloric acid was added. If a precipitate was present it was removed by filtration. The ether layer was dried over anhydrous magnesium sulfate and the solvent removed. The residue was allowed to stand until crystallization occurred and the solid removed at convenient times. In the cases indicated below the residue was distilled. The yields given in the table were calculated on the basis of the crude material which in some cases melted over a 5–6° range. The melting points given below are for the recrystallized material and are uncorrected unless otherwise indicated. All analyses are by the micro method and are the average of at least two determinations which checked with the theoretical within 0.2%.

[b] Calculated on the basis of the α,β-unsaturated ketone. The yields of dimolecular and trimolecular products are given under Di and Tri, respectively.

[c] 1-Methyl-2-phenyl-1,3-dibenzoylpropane,[4e] m. p. 102–103.5°.

[d] The product[4e] melted at 231–235°. No attempt was made to determine which of the possible isomers was formed but in view of what is known about the influence of substitution upon reactivity it seems likely that only the $—CH_2COC_6H_5$ group of the dimolecular compound would react to give the trimolecular compound.

[e] 1-Ethyl-2-phenyl-1,3-dibenzoylpropane, m. p. 91–92° (corr.) after recrystallization from alcohol. *Anal.* Calcd. for $C_{25}H_{24}O_2$: C, 84.32; H, 6.79. Found: C, 84.34; H, 6.83.

[f] The trimolecular compound was very insoluble in ordinary solvents. Recrystallized from acetophenone it melted at 219.3–219.6° (corr.). *Anal.* Calcd. for $C_{40}H_{36}O_3$: C, 85.06; H, 6.43. Found: C, 85.06; H, 6.43.

[g] Recrystallized from acetophenone, m. p. 308.2–308.7° (corr.). *Anal.* Calcd. for $C_{40}H_{36}O_3$: C, 85.06; H, 6.43. Found: C, 84.85; H, 6.45. Distillation of the filtrate gave 19.1 g. (92%) of unreacted benzalacetophenone.

[h] Due to the unreactivity of isobutyrophenone as shown in Experiment 4, this reaction was catalyzed by a solution of 2.3 g. (0.1 mole) of sodium in 20 ml. of absolute ethanol. The major portion of the product was 8.7 g. of material which did not melt below 250° and which by two recrystallizations from acetophenone was divided into two parts, A and B. Product A melted at 304–310° (corr.) and showed no depression of the melting point when mixed with the product from Experiment 4. Product B did not melt below 360° and was apparently a tetramolecular compound, although it was too insoluble for a molecular weight determination. *Anal.* Calcd. for $C_{55}H_{48}O_4$: C, 85.45; H, 6.26. Found: C, 85.74; H, 6.13. The original reaction mixture also gave 0.5 g. of material (C) melting (after one recrystallization from alcohol) at 139.6–139.9° (corr.). The melting point would indicate that this was a dimolecular product but the analyses indicated that it was either a different compound or was quite impure. The quantity was insufficient for a detailed examination. *Anal.* Calcd. for $C_{25}H_{24}O_2$: C, 84.82; H, 6.79. Found: C, 87.92; H, 7.19.

[i] The product weighed 28.2 g., corresponding to 90% of the dimolecular or 110% of the trimolecular compound. The first solid fraction (A) melted at 96–101°, the next at 135–140° and the next at 125–130°. The reported melting points[5k] for the dimolecular and trimolecular compounds are 149 and 168°, respectively. Fraction A gave, after two recrystallizations from alcohol, a small amount of the trimolecular compound, m. p. 163.5–165°. No other pure product could be isolated. In view of the possibility for the formation of isomers no prolonged effort was made to separate the mixture into its components.

[j] Recrystallization from butyl alcohol and acetophenone gave a product which melted at 244.6–246° (corr.). *Anal.* Calcd. for $C_{36}H_{36}O_3$: C, 83.67; H, 7.03. Found: C, 83.70; H, 7.04.

[k] Two recrystallizations from ligroin did not raise the melting point of the original material (53–57°) but recrystallization from alcohol gave pure 2-phenyl-1-benzoyl-3-pivalylpropane, m. p. 59–59.5°. *Anal.* Calcd. for $C_{21}H_{24}O_2$: C, 81.77; H, 7.85. Found: C, 81.77; H, 7.81.

[l] Crystallization and distillation gave 15.8 g. (84%) of unchanged benzalpinacolone.

[m] These compounds have been prepared previously.[4c,g]

Therefore, comparing the reaction of pinacolone and benzalacetophenone with the reaction of acetophenone and benzalpinacolone, in the latter case V would be expected to form less trimolecular compound because the acceptor is less reactive and because V must compete for the acceptor with a stronger addendum. A combination of these two factors is probably responsible for the results obtained.

When the dimolecular product from these condensations is not symmetrical, the possibilities of isomerism in the trimolecular product formed from it become extremely complex.[6] In some cases the trimolecular compounds did not melt sharply even when analytically pure, indicating that they were a mixture of isomers. For the purpose of this work, however, it did not seem advisable to examine the isomerism of the products.

Summary

The reactions of simple ketones in the Michael condensation with α,β-unsaturated ketones have been investigated with a view to determining the influence of the structure of the ketone upon its reactivity. The conclusions drawn from the nature and amount of the reaction products are similar to those based on a previous study of addenda possessing two labilizing groups—that is, an increase in substitution about an active methylene group greatly lowers its reactivity and the influence of a methyl group is less than that of the ethyl group.

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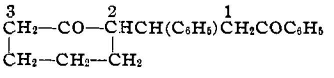
[6] For example, the dimolecular compound (VI) from cyclohexanone and benzalacetophenone may react through the active groups 1, 2 or 3. Reaction at carbon 2 is unlikely because it is so highly substituted. However, reaction at carbons 1 and 3 would give trimolecular products capable of existing in eight and five inactive modifications, respectively.



$$\begin{array}{l}\overset{3}{C}H_2-CO-\overset{2}{C}HCH(C_6H_5)\overset{1}{C}H_2COC_6H_5\\ |\qquad\qquad\quad |\\ CH_2-CH_2-CH_2\end{array}$$

VI

[CONTRIBUTION FROM THE CITY COLLEGE OF NEW YORK]

The Ultraviolet Absorption Spectra of α- and β-Phenylglucosides

BY DAVID LEWIS

The ultraviolet absorption spectrum of a glycoside is determined by the aglycone residue, since the cyclic sugar group is non-absorbing,[1] or transparent, to the usual limit of investigation, λ = 2200 Å. The purely aliphatic glycosides, such as α-methyl glucoside,[2] β-methyl glucoside,[1] and α-methyl mannoside,[2] show no selective absorption as far as 2300 Å. Aglycones containing a chromophore confer selective absorption on a glycoside. Ramart-Lucas and Rabaté,[1] on the basis of an examination of a series of β-glucosides, have recently shown that such spectra can be classified according to the manner in which the transparent glucosido group is linked to the aglucone. If attached through an aliphatic carbon the positions of the absorption bands nearest the visible are the same for the glucoside and the aglucone, *e. g.*, β-phenylethylglucoside and phenylethyl alcohol. If linked to an aromatic nucleus the bands of the glucoside are displaced to shorter wave lengths and have a smaller intensity as compared to the aglucone, *e. g.*, β-phenylglucoside and phenol. The results reported in this paper show the effect of the configuration of the glucoside link upon this shift.

Experimental

The absorption spectra were obtained with a Hilger rotating sector photometer in conjunction with a Hilger E316 quartz spectrograph. The source of illumination was a condensed spark between iron electrodes. Cells were 1 and 2 cm. The glucosides were examined in water solution of concentration 1.2×10^{-3} *M* and 1.6×10^{-3} *M*. The molecular extinction coefficients were calculated from the equation, $\epsilon = 1/cd \log I_0/I$ where c is concentration in moles per liter, d is cell length in cm., and $\log I_0/I$ was read on the sector. The results are plotted with $\log \epsilon$ as ordinates and frequencies as abscissas. Each curve represents about one hundred points.

The glucosides were prepared by deacetylation[3] of the corresponding acetyl glucosides prepared according to Helferich and Schmitz-Hillebrecht.[4] They were recrystallized alternately from water and hydrous ethyl acetate until constant melting point, specific rotation and absorption spectrum were obtained. The constants, after drying at 100°, were: α-phenylglucoside, m. p. 172–172.5° (corr.), $[\alpha]^{30}_D$ +181°; β + phenylglucoside, m. p. 175° (corr.), $[\alpha]^{28}_D$ −72.0°.

Discussion of Results

The curves for the two glucosides are practically identical. Except around the high frequency minimum the differences are within 4 frequency units (10 Å). The curve for β-phenyl-

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[1] Ramart-Lucas and Rabaté, *Compt. rend.*, **196**, 1493 (1933).

[2] Harris, Hirst and Wood, *J. Chem. Soc.*, 2108 (1932).

[3] Zemplén and Pacsu, *Ber.*, **62B**, 1613 (1929).

[4] Helferich and Schmitz-Hillebrecht, *ibid.*, **66B**, 378 (1933).