the diallyl acetal-allyl ester formed and apparent decomposition and rearrangement of the diallyl acetal group occurred (*6, 9*). GLC analysis of the product showed one major peak (the diallyl acetal-allyl ester) and seven minor peaks, which were not identified.

The glycerol acetal was prepared directly from methyl azelaaldehydate (65% yield) as well as from the dimethyl acetal (100% yield). Although optimum conditions were not developed for the direct synthesis, glycerolysis of the dimethyl acetal appears to be much the preferred route. Glycerol acetals have been reported to exist largely in the dioxolane form (*3, 8*).

TRANSESTERIFICATION

Alcoholysis of the ester group was carried out in the presence of sodium methoxide. Heating at 100° C. up to 10 hours was required to obtain yields comparable with those from acetal reactions. For example, compound I (55.3 grams, 0.238 mole), *n*-butyl alcohol (400 ml.), and sodium methoxide (0.12 gram) were heated at 100° in a three-necked, round-bottomed flask fitted with a capillary inlet for nitrogen, a thermometer, and a distillation head. After 10 hours of heating with periodic removal of methanol, the catalyst was neutralized with glacial acetic acid. The product was dissolved in methylene chloride and washed with water until neutral to alkali-acid indicator paper. After drying over anhydrous sodium sulfate, the solvent was stripped off. The yield was 88%, based on GLC analysis. After distillation under reduced pressure, a 75% yield of butyl 9,9-dimethoxynonanoate was obtained; the purity was 99%+ by GLC analysis.

Other hydroxy compounds included 2-ethylhexyl and allyl alcohols, 2-methoxyethanol, ethylene glycol, and neopentyl glycol (Table I).

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Condensation of Cyclohexylacetone with Benzaldehyde, Nitrobenzaldehydes, and Chlorobenzaldehydes

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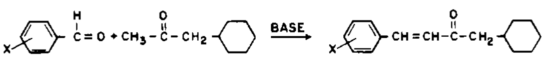
Cyclohexylacetone was condensed with benzaldehyde, *o*-, *m*-, *p*-nitrobenzaldehyde, and *o*-, *m*-, *p*-chlorobenzaldehyde under conditions which favor condensation at the methyl group of cyclohexylacetone. Straight-chain benzylidene ketones were obtained in 63 to 79% yields from all benzaldehydes except from *o*-nitro- and *o*-chlorobenzaldehyde.

AN UNSYMMETRICAL KETONE may undergo condensation at either of the two positions adjacent to the carbonyl group (*3*). To prepare new straight-chain benzylidene ketones from an unsymmetrical ketone, cyclohexylacetone, whose steric hindrance may favor condensation at the methyl group, was condensed with benzaldehyde, nitrobenzaldehydes, and chlorobenzaldehydes.



X = H, *o*-NO_2, *m*-NO_2, *p*-NO_2, *o*-Cl, *m*-Cl, *p*-Cl

The use of a base catalyst and a long reaction time were considered as factors which would favor the formation of straight-chain benzylidene ketone.

In a typical experiment, 14 ml. of cold aqueous sodium hydroxide (10%) was added to a benzaldehyde (0.05 mole) and excess cyclohexylacetone (0.071 mole) in 150 ml. of 95% ethanol. After the mixture stood for several days in the cold (2° C.), crystalline straight-chain benzylidene ketones, I-VI (Table I), precipitated. The attempted condensation of *o*-chlorobenzaldehyde with cyclohexylacetone gave only an oil.

The IR spectra of I-VI show the characteristic carbonyl (1700-1690 cm.$^{-1}$) and olefin (1670-1660 cm.$^{-1}$, 1625 cm.$^{-1}$

Table I. Benzylidene Ketones

No.	X	Molecular Formula	Yield, %	M.P., ° C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % Found
I	H	$C_{16}H_{20}O$[a]	79	41 –41.5	84.21	84.30	8.77	8.79	. . .	. . .	. . .	. . .
II	*p*-NO_2	$C_{16}H_{19}NO_3$[b]	79	92 –93	70.33	70.65	6.96	7.00	5.13	5.50	. . .	. . .
III	*m*-NO_2	$C_{16}H_{19}NO_3$[c]	75	97 –97.5	70.33	70.34	6.96	7.11	5.13	5.10	. . .	. . .
IV	*o*-NO_2	$C_{16}H_{19}NO_3$[d]	10	45.5–46	70.33	70.11	6.96	6.99	5.13	5.02	. . .	. . .
V	*p*-Cl	$C_{16}H_{19}OCl$[e]	63	57 –58	73.14	73.37	7.24	7.32	. . .	. . .	13.52	13.50
VI	*m*-Cl	$C_{16}H_{19}OCl$[f]	72	45 –45.5	73.14	73.14	7.24	7.13	. . .	. . .	13.52	13.30

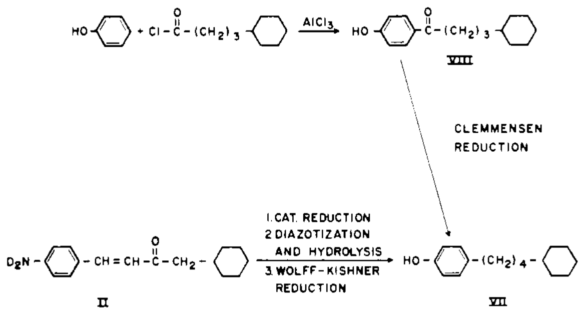
[a] Semicarbazone, m.p., 164–165° C. [b] Semicarbazone, m.p. 187–188° C. [c] 2,4-Dinitrophenylhydrazone, m.p. 258° C. [d] Semicarbazone, m.p. 183° C. [e] Semicarbazone, m.p. 183–184° C. [f] 2,4-Dinitrophenylhydrazone, m.p 245° C.

for II) but no hydroxyl and methyl bands (*1*). The NMR spectra have: phenyl proton resonance centered about 1.8 to 3.0τ depending on the substitution; a quartet, owing to olefinic protons centered about 2.6τ; a distorted α-methylene proton doublet at 7.3τ; and a broad signal (unresolved structure) centered at 8.4τ, owing to cyclohexyl protons. These NMR data are consistent with the structure of the expected straight-chain benzylidene products.

A partial structure proof of 4-(4′-nitrophenyl)-1-cyclohexyl-3-buten-2-one, II, was obtained by converting it to 1-(4′-hydroxyphenyl)-4-cyclohexylbutane, VII. The nitrogen group and the double bond were hydrogenated at room temperature over a platinum catalyst. The crude aniline obtained was converted to its diazonium sulfate and hydrolyzed to give 4-(4′-hydroxyphenyl)-1-cyclohexylbutan-2-one, m.p. 111-112° C. Finally, the carbonyl group was reduced in diethylene glycol by the Wolff-Kishner method to give VII, m.p. 67–68° C. The IR spectrum of VII has 3350, 1200, and 822 cm.$^{-1}$ bands. Calculated for $C_{16}H_{24}O$: C, 82.76; H, 10.34. Found: C, 82.51; H, 10.54. *p*-Nitrobenzoate of VII, m.p. 97–98° C.

1-(4′-Hydroxyphenyl)-4-cyclohexylbutane, VII, was also prepared by an alternate route. Using a modified Friedel-Crafts reaction (*2*), phenol (1.59 moles) in nitrobenzene (300 ml.) was added to anhydrous aluminum chloride (3.19 moles) in 800 ml. of nitrobenzene. Then γ-cyclohexylbutyryl chloride (1.39 moles) was added gradually (1 hour) to the cooled (10° C.) mixture. After stirring for 24 hours at room temperature, the mixture was hydrolyzed. The white crystalline product was washed with pentane and water. Recrystallization from hot acetic acid gave 1-(4′-hydroxyphenyl)-4-cyclohexylbutan-1-one, VIII, m.p. 153–154° C. (91%). The IR spectrum of VIII has 3350, 1670, 1200, and 825 cm.$^{-1}$ bands. Calculated for $C_{16}H_{22}O_2$: C, 78.05; H, 8.94. Found: C, 77.81; H, 8.80. Semicarbazone of VIII, m.p. 184–185° C.

The alkali-soluble VIII was reduced by the Clemmensen method in acetic acid–toluene solution to give VII (72%). From its melting point, mixed melting point, and IR spectrum, it is identical to VII prepared from II.



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