water and dried. After thorough drying the crude tryptamine melted at 106° and weighed 34 g. (71%). After recrystallization from Skelly B the melting point rose to 114°. A hydrochloride salt made from the crude base melted at 243–244° (lit.[3] 245°).

6-(p-Acetylaminobenzenesulfonamido)-hexylamine Hydrochloride. (a) **1-Cyano-5-(p-nitrobenzenesulfonamido)-pentane.**[14]—A solution of 9.8 g. (0.1 mole) of α-aminocapronitrile in 25 cc. of chloroform was added dropwise with stirring to a solution of 22.2 g. (0.1 mole) of p-nitrobenzenesulfonyl chloride in 100 cc. of chloroform. Thereafter a solution of 4.0 g. (0.1 mole) of sodium hydroxide in 25 cc. of water was added dropwise and the stirring continued for two hours. The chloroform layer was separated and washed with water and then distilled without drying. The residual solid was first recrystallized from aqueous dimethylformamide and further recrystallized from methanol. After thorough drying 19.4 g. (58.2%) of product melting at 85–87° was obtained.

Anal. Calcd. for $C_{12}H_{15}N_3O_4S$: C, 48.45; H, 5.09; N, 14.14. Found: C, 48.78; H, 5.16; N, 14.16.

(b) **1-Cyano-5-(p-acetylaminobenzenesulfonamido)-pentane.**—Fifteen and two-tenths grams (0.051-mole) of 1-cyano-5-(p-nitrobenzenesulfonamido)-pentane in 200 cc. of ethyl acetate containing 1 cc. of acetic anhydride was reduced in the presence of 1.5 g. of 5% palladium-on-charcoal. The crude product after removal of solvent was an oil and would not solidify after storage in the cold for three days.

(c) **6-(p-Acetylaminobenzenesulfonamido)-hexylamine Hydrochloride.**—Approximately 0.05 mole of the oily nitrile from experiment (b) was dissolved in 100 cc. of ethanol containing 5 g. of ammonia. Three grams of 5% rhodium-on-alumina was added and the mixture hydrogenated under 2 atmospheres pressure. Uptake was rapid and was completed in less than one hour. The solution was filtered from the catalyst and concentrated to dryness. The oily residue was treated with 0.075 mole of alcoholic hydrogen chloride and the resulting solution evaporated to dryness. The residual mass was recrystallized from absolute alcohol containing some hydrogen chloride. The salt obtained in 71.5% yield decomposed at 210–215°.

Anal. Calcd. for $C_{14}H_{23}N_3O_3S \cdot HCl$: C, 48.05; H, 6.91. Found: C, 47.43; H, 6.76.

NORTH CHICAGO, ILL.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

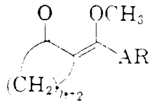
β-Diketones. I. Synthesis and Reactions of Some 2-Benzoylcyclanones[1]

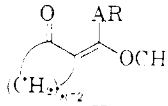
BY R. D. CAMPBELL AND H. M. GILOW[2]

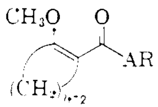
RECEIVED SEPTEMBER 26, 1959

2-(o-Chlorobenzoyl)-cyclohexanone (IV) reacted with diazomethane to form two isomeric methyl ethers, 2-(α-methoxy-o-chlorobenzal)-cyclohexanone (V) and 1-(o-chlorobenzoyl)-2-methoxycyclohexene (VI). The structures of the methyl ethers were identified by the reduction of the carbonyl group with sodium borohydride, followed by cleavage of the methyl ether and dehydration to form 1-(o-chlorobenzoyl)-cyclohexene and 2-(o-chlorobenzal)-cyclohexanone, respectively. In the process of studying the reaction of diazomethane, basic cleavage and enol content of some 1,3-diketones nine new 2-benzoylcyclanones were prepared.

Reactions with Diazomethane.—1,3-Diketones are known to react with diazomethane to form the methyl ether of the enol form.[3–6] If an unsymmetrical 1,3-diketone is treated with diazomethane, at least two different methyl ethers may be formed. For example, an aroylcyclanone may form three different methyl ethers (I, II, III) provided the ring is not too large.


I


II


III

V (AR = o-ClC$_6$H$_4$–, n = 6) VI (AR = o-ClC$_6$H$_4$–, n = 6)

2-(o-Chlorobenzoyl)-cyclohexanone (IV) reacted with a methanol–ether solution of diazomethane to form 2-(α-methoxy-o-chlorobenzal)-cyclohexanone (V) and 1-(o-chlorobenzoyl)-2-methoxycyclohexene (VI) in a 74.1 and 25.9% yield, respectively. Whether V exists as a *cis* or *trans* form or a mixture of the two was not determined. However it seemed probable that the product obtained was the *cis* compound (corresponding to structure I). On the basis of spectral evidence to be discussed in a subsequent article, the enol exists as a *cis* chelate. Vigorous evolution of nitrogen was observed when the enol reacted with diazomethane in methanol–ether. When no methanol is present the reaction is slow. It has been suggested[7] that the methanol solvates the enol to break up the chelate ring, and permit reaction with the enolic hydrogen. It seems probable that the solvation and the reaction of the enol with diazomethane are faster by an order of magnitude or more than the tautomeric isomerization necessary to give the *trans* enol. Enol ether VI is a white solid which changes to a yellow oil on standing. Enol ether V is a yellow oil. When dissolved in methanol, both V and VI give a violet color with methanolic ferric chloride on standing. This is due to ether cleavage catalyzed by the reagent. Both ethers can be cleaved readily with dilute hydrochloric acid to form IV. The isolation of V and VI in 74.1 and 25.9% yield, respectively, does not necessarily indicate that the enols from which they must have been formed existed in the same ratio, since diazomethane may have reacted somewhat faster with one form than the other.[5] However, this does indicate that both enolic modifications of IV do exist, probably in roughly the ratio indicated.

The structure of methyl ether VI was established by the selective reduction of the carbonyl group to the hydroxyl group with sodium borohydride.[8]

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[1] Taken in part from the Ph.D. Thesis of H. M. Gilow, August. 1959.

[2] Ethyl Corporation Fellow, 1958–1959.

[3] B. Eistert, R. Weygand and E. Csendes, *Ber.*, **84**, 745 (1951).

[4] B. Eistert and W. Reiss, *ibid.*, **87**, 108 (1954).

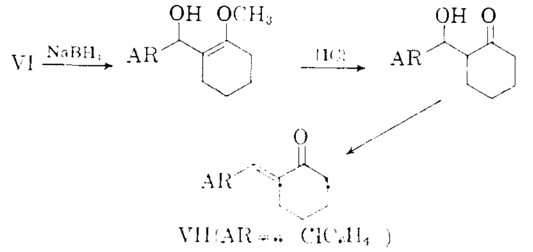
[5] B. Eistert and E. Merkel, *ibid.*, **86**, 895 (1953).

[6] B. Eistert, E. Merkel and W. Reiss, *ibid.*, **87**, 1513 (1954).

[7] B. Eistert, R. Arndt, L. Lowe and E. Ayca, *ibid.*, **84**, 156 (1951).

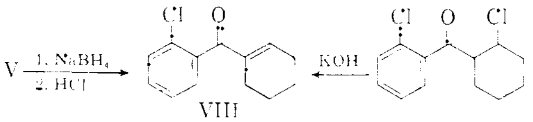
[8] S. W. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 122 (1949).

The ether linkage was then cleaved with acid followed by ketonization and dehydration of the intermediate alcohol to form 2-(*o*-chlorobenzal)-cyclohexanone (VII) in a 73.8% yield. Comparison with a known sample of VII prepared from the basic condensation of *o*-chlorobenzaldehyde and cyclohexanone[9] showed them to be identical.



VII (AR = *o*-ClC$_6$H$_4$)

Treatment of V in the same manner gave 1-(*o*-chlorobenzoyl)-cyclohexene (VIII). Comparison of the boiling point, ultraviolet and infrared spectra of VIII, which was also prepared by the condensation of *o*-chlorobenzoyl chloride and cyclohexene followed by dehydrochlorination,[10] showed the two samples to be the same.



VIII

In order to establish the path of this reaction more clearly, β-methoxy-*o*-chlorobenzalacetophenone (IX),[11] a stable enol methyl ether of known structure, was treated in the same manner as was V. Only benzal-*o*-chloroacetophenone (X) was isolated. For identification, X was also prepared from the basic condensation of benzaldehyde and *o*-chloroacetophenone. Comparison of the two samples of X and the dibromides indicated that the two samples were identical.

Similarly 2-benzoyltetralone (XI) and 2-benzoylindanone (XII) each readily react with a methanol–ether solution of diazomethane. In both cases only yellow oils could be isolated. Treatment of the oily products with sodium borohydride and then acid gave a 72.6% yield of 2-benzal-1-tetralone and a 59% yield of 2-benzal-1-indanone. This indicates that at least 72.6% of the methyl ether(s) from XI must have been 1-methoxy-2-benzoyl-3,4-dihydronaphthalene and at least 59% of the methyl ether(s) from XII must have been 2-benzoyl-3-methoxyindene.

Enol Content.—The position of the keto–enol equilibrium was determined for all of the diketones studied. It was expected at first that conjugative and other electronic effects would be the principal influence in the tautomeric equilibrium. A comparison of enol content in the equilibrium of the various aroyl cyclanones shows the inductive and resonance effects of the substituents to be negligible. Electron donor substituents and electron-withdrawing substituents in the *p*-position of benzoylcyclohexanone do not cause a substantial change in enol content as compared with the unsubstituted diketone XXIV.

Introduction of an electronegative chlorine atom in the *m*-position increased the enolic content only slightly. Substitution in the *o*-position shifts the equilibrium considerably toward the enol form. The percentage of enol of the *o*-substituted products increases in the order: hydrogen < fluorine < methyl < chlorine < bromine. This is also the order of increasing size of the groups.[12] The difference in the percentage enol of the *o*-fluoro and *o*-methyl derivatives is not very great. If only the size of the group were a factor the difference would be expected to be greater. Thus the bulk steric effect seems to be important, but a dipolar interaction also seems to be operating.

The structural variations in the series including benzoylcyclohexanone (XXIV), benzoylcycloheptanone (XXVII), benzoyltetralone (XI) and benzoylindanone (XII) cause variation in the enol content. In the latter two instances, a much more conjugated system exists in the enol form than in the keto form. The substantially greater enol content found in XI and XII stresses the importance of the stabilizing effect of conjugation. A complex of other effects is expected to operate in the series. In the keto forms, the methylene carbon (C$_2$) is in the tetrahedral form with bond angles of 109°; in the enol form this carbon atom is trigonal with a bond angle of 120°. Bond distances between carbon atoms are generally expected to be slightly shorter in the enol due to higher bond orders. Structural strains which appear in this series would be expected to vary, both in bond angles and bond distances. A logical extension of this series to 2-benzoylcyclopentanone and 2-benzoylbenzosuberone is planned.

TABLE I

THE PERCENTAGE ENOL OF SOME 1,3-DIKETONES IN METHANOL

Compound	Enol, %
2-(*p*-Methoxybenzoyl)-cyclohexanone (XXIII)	2.6
2-Benzoylcyclohexanone (XXIV)	3.3
2-(2-Naphthoyl)-cyclohexanone (XXII)	3.3
2-(*p*-Fluorobenzoyl)-cyclohexanone (XXI)	4.2
2-(*p*-Methylbenzoyl)-cyclohexanone (XXV)	3.0
2-(*p*-Chlorobenzoyl)-cyclohexanone (XXVI)	4.1
2-(*m*-Chlorobenzoyl)-cyclohexanone (XX)	6.9
2-Benzoylcycloheptanone (XXVII)	9.6
2-(*o*-Fluorobenzoyl)-cyclohexanone (XXVIII)	48.7
2-(*o*-Methylbenzoyl)-cyclohexanone (XXIX)	50.0
2-(*o*-Chlorobenzoyl)-cyclohexanone (IV)	88.8
2-(*o*-Bromobenzoyl)-cyclohexanone (XXX)	92.9
2-Benzoyltetralone (XI)	24.9
2-Benzoylindanone (XII)	77.7

The structural factors which effect the tautomeric equilibrium may be summarized as follows: 1. The amount by which the conjugation is extended by enolization is related to enol stability. 2. Any structural feature which causes skewing and hinders coplanarity of the enol system or the conjugated system tends to decrease enol stability. 3. Skeletal strains which favor a bond angle at C$_2$ of 120°, or compressed C–C bond distance are

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[9] R. Baltzly, E. Lorz, P. B. Russell and F. M. Smith, THIS JOURNAL, **77**, 624 (1955).

[10] R. E. Christ and R. C. Fuson, *ibid.*, **59**, 895 (1937).

[11] C. L. Bickel, *ibid.*, **67**, 2204 (1945).

[12] W. M. Stanley and R. Adams, *ibid.*, **52**, 1200 (1930).

TABLE II

2-BENZOYLCYCLANONES

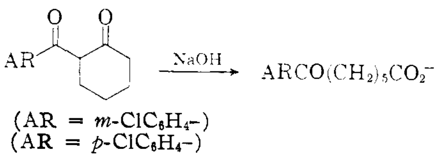
Compound	M.p., °C.[a] Keto	M.p., °C.[a] Enol	Yield, % Method A	Yield, % Method B	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
XXVI	91.5–92			50.7	$C_{13}H_{13}O_2Cl$	65.97	65.80	5.54	5.54
XX	65.5–66	44.5–45.5	67.9		$C_{13}H_{13}O_2Cl$	65.97	65.77	5.54	5.41
IV		64–65	72.4	69.2	$C_{13}H_{13}O_2Cl$	65.97	66.08	5.54	5.48
XXII	98–99.5	73.5–75	58	56.5	$C_{17}H_{16}O_2$	80.92	80.54	6.39	6.14
XXI	77–78.5	56–57	41.5		$C_{13}H_{13}O_2F$	70.89	70.49	5.95	5.94
XXVIII		51–52	52.5		$C_{13}H_{13}O_2F$	70.89	70.50	5.95	5.72
XXX		63–63.5	55.5		$C_{13}H_{13}O_2Br$	55.53	55.65	4.66	4.51
XXV	102.5–103			54.8	$C_{14}H_{16}O_2$	77.74	77.97	7.41	7.25
XXIX		64–65		48	$C_{14}H_{16}O_2$	77.74	77.97	7.41	7.60
XXVII		64–65[b]	34.7		$C_{14}H_{16}O_2$	77.74	77.77	7.41	7.35

[a] All melting points are uncorrected. [b] Hamrick, *et al.*,[13] report a melting point of 55–56°.

expected to favor enol stability; this effect is small. 4. Ring size is important only as it operates through the factors listed above. The six-membered ring tends to pucker, skewing attached groups; the five-membered ring is essentially planar. The seven-membered ring is rather more flexible with respect to bond angle, bond distance and rotational conformation.

Alkaline Cleavage.—Earlier workers[13–16] have observed the ring opening of acylcyclanones. It was found that introduction of a 2-methyl group caused the base to attack the side chain carbonyl to a larger extent than the ring carbonyl. This is attributed to the greater shielding effect at the ring carbonyl than at the side chain carbonyl by the 2-methyl group.[13] This shielding effect may also be operating in the case of the *o*-substituted 2-benzoylcyclohexanones preventing cleavage under the experimental conditions used. The *o*-substituted 2-benzoylcyclohexanones, which were found to be highly enolized in methanol, may also exist predominantly as the enol or the enolate ion inhibiting the cleavage.

2-(*o*-Methylbenzoyl)-cyclohexanone (XXIX) and IV when treated with a methanol–water solution of sodium hydroxide did not undergo ring cleavage to form the expected ε-aroylcaproic acid. Even under fairly vigorous conditions only starting material could be isolated in both cases. On the other hand, 2-(*p*-chlorobenzoyl)-cyclohexanone (XXVI) and the enol form of 2-(*m*-chlorobenzoyl)-cyclohexanone (XX) readily underwent ring cleavage when treated with base to form the corresponding ε-aroylcaproic acid.



XIX (AR = *m*-ClC_6H_4–)
XX (AR = *p*-ClC_6H_4–)

Synthesis of Diketones.—In connection with the diazomethane and alkaline cleavage reactions, and also the investigation of the enol content of some 1,3-diketones, a number of new 1,3-diketones were prepared. Cyclohexanone, tetralone and indanone have been benzoylated with equal molar quantities of a phenyl benzoate and the cyclic ketone in the presence of two moles of sodamide.[14,17,18] This reaction has been extended to benzoylation with certain substituted phenyl benzoates and the benzoylation of cycloheptanone.

In Table II are summarized the yields and other data for the benzoylations. The yields of the diketones range from 72.4 to 34.7%. Addition of two moles of cyclohexanone, instead of one, had little effect on the yield. The diketones were isolated by two different methods. Separation of the diketones as the copper chelate (method A) afforded a purer product and, in the two cases in which both methods were used, a slightly higher yield. In method B, in which the reaction mixture was acidified and extracted with ether to obtain the diketone, some difficulty was encountered in trying to free the diketones of phenol.

The enol forms of 2-(*p*-fluorobenzoyl)-cyclohexanone (XXI), 2-(*m*-chlorobenzyl)-cyclohexanone (XX) and 2-(2-naphthoyl)-cyclohexanone (XXII) were isolated by the decomposition of the copper chelate in a mixture of dilute hydrochloric acid and ether. Evaporation of the ether after washing with water left an oil which was quickly taken up in methanol and cooled to obtain the enol form of the 1,3-diketone. If a methanolic solution of the enol form was allowed to stand in solution for two days and then cooled, the diketo form was isolated. In all three cases the enol forms melted at a lower temperature than the corresponding diketo forms. The enol forms also gave an immediate color with ferric chloride when dissolved in methanol. The diketo forms did not give an immediate color under these conditions, but a violet color did develop on standing.

Experimental

1-(*o*-Chlorobenzoyl)-2-methoxycyclohexene (VI) and 2-(α-Methoxy-*o*-chlorobenzal)-cyclohexanone (V).—To an excess of diazomethane in 200 ml. of anhydrous ether was added 10 g. of 2-(*o*-chlorobenzoyl)-cyclohexanone (IV) and 20 ml. of anhydrous methanol. The solution was kept in an ice-bath in the dark overnight. Evaporation of the solvent left an oil which was diluted with 10 ml. of methanol. This solution was placed in a Dry-Ice–acetone-bath. Upon scratching the sides of the container, 2.59 g. of 1-(*o*-chlorobenzoyl)-2-methoxycyclohexene (VI), which melted at 74–75.5°, was obtained. Enol ether VI was crystallized from

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(13) P. J. Hamrick, C. F. Hauser and C. R. Hauser, *J. Org. Chem.*, **24**, 583 (1959).

(14) C. R. Hauser, F. W. Swamer and B. I. Ringler, THIS JOURNAL, **70**, 4023 (1948).

(15) E. Bauer, *Ann. chim. phys.*, [9] **1**, 393 (1914).

(16) M. G. Leser, *Compt. rend.*, **141**, 1032 (1905).

(17) C. R. Hauser, B. I. Ringler, F. W. Swamer and W. F. Thompson, THIS JOURNAL, **69**, 2649 (1947).

(18) B. Abramovitch and C. R. Hauser, *ibid.*, **64**, 2271 (1942).

Skellysolve B to give white crystals which melted at 76–76.5°.

Anal. Calcd. for $C_{14}H_{15}O_2Cl$: C, 67.06; H, 6.03; CH_3O, 12.32. Found: C, 66.93; H, 5.98; CH_3O, 12.39.

Evaporation of the solvent left 7.4 g. of a yellow oily ether, 2-(α-methoxy-*o*-chlorobenzal)-cyclohexanone (V), which boils at 148–150° (0.7 mm.) and 164–166° (3 mm.), $n^{28}D$ 1.6788. Methyl ether VI accounted for 25.9% of the product and V for 74.1%. The over-all yield was 94.5%.

Anal. Calcd. for $C_{14}H_{15}O_2Cl$: C, 67.06; H, 6.03; CH_3O, 12.32. Found: C, 67.56; H, 5.94; CH_3O, 11.99.

2-(*o*-Chlorobenzoyl)-cyclohexanone when dissolved in methanol for one day and then treated with ethereal diazomethane gave approximately the same ratio of isomeric ethers.

Cleavage of V and VI.—A solution of 1 g. of VI, 20 ml. ethanol, 2 ml. of dilute hydrochloric acid and 2 ml. of water was allowed to stand for one hour at room temperature. Upon cooling, 0.85 g. (89.5%) of IV (m.p. 63.5–64.5°, mixed melting point with an authentic sample showed no depression) was isolated.

Treatment of 0.5 g. of V, 10 ml. of methanol and 2 ml. of dilute hydrochloric acid in the same manner gave 0.3 g. (71.8%) of IV which melted at 64.65°. Mixed melting point with an authentic sample showed no depression.

Reduction of V and VI with Sodium Borohydride.—A solution of 1 g. of sodium borohydride in 10 ml. of methanol was added to 2 g. of VI which was dissolved in 5 ml. of methanol. After standing at room temperature for two hours the solution was acidified with dilute hydrochloric acid and placed on a steam-bath for 10 minutes and made basic again with dilute sodium hydroxide. The solution was extracted with ether. After evaporation of the ether an oil remained from which 1.3 g. (73.8%) of 2-(*o*-chlorobenzal)-cyclohexanone (VII) was obtained after dilution with methanol and cooling; VII when crystallized from hexane melts at 69.5–70.5°. The 2,4-dinitrophenylhydrazone of VII melted at 162–163°. The ultraviolet spectrum showed one maximum at 278 mμ and the infrared spectrum showed bands at 1681 and 1610 cm.$^{-1}$.

A solution of 5 g. of V and 10 ml. of methanol was treated with 2.5 g. of sodium borohydride in 5 ml. of methanol in the same manner as was VI. A yellow oil (3.5 g., 73.9%) with a boiling point of 144–146° (3 mm.), $n^{28}D$ 1.5699, was isolated. Attempts to prepare the semicarbazone, oxime and 2,4-dinitrophenylhydrazone were unsuccessful. The ultraviolet spectrum shows one maximum at 240 mμ and the infrared spectrum shows bands at 1655 and 1640 cm.$^{-1}$.

2-(*o*-Chlorobenzal)-cyclohexanone (VII).—A solution of 4 g. of potassium hydroxide in 10 ml. of methanol was added to a solution of 5 g. of *o*-chlorobenzaldehyde and 30 ml. of cyclohexanone. This solution was cooled to room temperature and allowed to stand for 5 minutes after which 10 ml. of dilute hydrochloric acid was added. The low boiling liquids were removed by heating the solution on a steam-bath under reduced pressure. Upon distillation of the remaining oil, two fractions were obtained: one with b.p. 110–114° (3 mm.) and the other b.p. 158–160° (3 mm.). The higher boiling fraction was dissolved in hexane and boiled to form 2.6 g. (33%) of VII melting at 69–70° (Baltzly, *et al.*,[9] reported b.p. 110–120° (10 mm.) and m.p. 70–71° for VII). Further crystallization from hexane gave pale yellow crystals which melted at 69.5–70.5°. A mixed melting point with the product obtained from the sodium borohydride reduction of ether VI showed no depression. The 2,4-dinitrophenylhydrazone of VII melted at 161–162°. The ultraviolet and infrared spectra were identical with the product obtained from the sodium borohydride reduction of VI.

1-(*o*-Chlorobenzoyl)-cyclohexene (VIII).—The method used to prepare VIII was the same as reported by Christ and Fuson.[10] A 31.1% yield (34 g.) of VIII was obtained; b.p. 144–146° (3 mm.), $n^{27}D$ 1.560. The ultraviolet and infrared spectra were identical with the product obtained from the sodium borohydride reduction of VI.

Reduction of β-Methoxy-*o*-chlorobenzalacetophenone (IX) with Sodium Borohydride.—A solution of 3 g. of sodium borohydride in 20 ml. of methanol was added to 5 g. of IX dissolved in 50 ml. of methanol. The exothermic reaction was cooled in an ice-bath when necessary and then allowed to stand at room temperature for 3 hours. The solution was acidified with dilute hydrochloric acid and allowed to stand on a steam-bath for 10 minutes and then made basic again with a sodium hydroxide solution. The solution was extracted with ether. After evaporation of the ether 3.68 g. (83%) of a yellow oil remained boiling at 190–192° (3 mm.). The ultraviolet spectrum showed a maximum at 303 mμ and the infrared spectrum showed bands at 1640 and 1600 cm.$^{-1}$.

To a stirred solution of 2.6 g. of benzal-*o*-chloroacetophenone (X) in 20 ml. of chloroform was slowly added 1.8 g. of bromine in 20 ml. of chloroform. After the addition was complete stirring was continued for 0.5 hour. The chloroform was then evaporated and the residual oil taken up in methanol and cooled to give 3.9 g. (86.7%) of the white dibromide of X which melted at 92.5–93.5°.

Anal. Calcd. for $C_{15}H_{11}OClBr_2$: C, 44.75; H, 2.76. Found: C, 44.95; H, 2.73.

Benzal-*o*-chloroacetophenone (X).—To a solution of 21 g. (0.136 mole) of *o*-chloroacetophenone, and 14.4 g. (0.136 mole) of benzaldehyde was added 3 g. of potassium hydroxide dissolved in 50 ml. of methanol. This solution was stirred for one hour and extracted with ether. After distillation of the ether 25.3 g. (77.3%) of a yellow oil boiling at 184–186° (3 mm.) remained. The ultraviolet and infrared spectra were identical with the product obtained from the sodium borohydride reduction of IX.

Addition of bromine to X in the same manner as just described gave an 82% yield of the dibromide of X which melted at 91.5–92.5°. A mixed melting point with the above dibromide showed no depression. The infrared spectra of the two dibromides were superimposable.

Treatment of 2-Benzoyltetralone (XI) and 2-Benzoylindanone (XII) with Diazomethane.—Five grams of XI and 6.7 g. of XII were treated with diazomethane as was previously described in the reaction of IV with diazomethane. Evaporation of the solvent left 4.8 g. (90.6%) and 6.3 g. (89%), respectively, of a yellow oil from which no crystals were obtained. In both cases the oil did not form a copper chelate but both did give a color with ferric chloride after standing in methanolic ferric chloride for 0.5 hour. The crude oil from XI contained 12.29% methoxyl; calcd. 12.40%.

Cleavage of the corresponding crude methyl ethers with dilute hydrochloric acid, as was described for the cleavage of V and VI, gave an 85.5% yield of XI and an 83.6% yield of XII.

Reduction of the Crude Enol Ethers of XI and XII with Sodium Borohydride.—Each of the crude enol ethers of XI and XII was treated with sodium borohydride in the same manner as was described for IV. After the solution was made basic with dilute sodium hydroxide, enough water was added so that the total volume was approximately 75 ml. Filtration of the mixtures, after standing in the refrigerator overnight, gave 0.41 and 0.38 g. of crude products, respectively. Crystallization of the crude products from methanol gave 0.32 g. (72.6%) of 2-benzal-1-tetralone which melted at 104–105°, and 0.26 g. (59%) of 2-benzal-1-indanone which melted at 107–108°. Comparison with authentic samples of 2-benzal-1-tetralone and 2-benzal-1-indanone indicated that the samples were identical. Along with the 2-benzal-1-tetralone obtained, a small amount of oil was also obtained which had bands at 1650, 1378, 1284, 1178 and 1093 cm.$^{-1}$ in the infrared region which were different from the bands observed with 2-benzal-1-tetralone. No evidence of any other product was obtained in the case of 2-benzal-1-indanone.

Alkaline Cleavage (Retro-Claisen) on Aroylcyclohexanones IV, XX, XXVI and XXIX.—A solution of 0.1 g. of XXVI, 10 ml. of methanol and 2 ml. of 6 *M* sodium hydroxide was heated on a steam-bath for 2 minutes. The solution was acidified and upon cooling 0.08 g. (74%) of ε-(*p*-chlorobenzoyl)-caproic acid, which melted at 129–131°, was obtained.[19]

Treatment of 1.5 g. of XX (enol form) in the same manner gave 0.46 g. of an acid, m.p. 93–95°.

Treatment of IV and XXIX in the same manner, except that the basic solution was refluxed for 0.5 hour, gave only an 80 and 96% yield, respectively, of starting material. No acid could be isolated.

Quantitative Enol Determination of Some 1,3-Diketones.—Approximately 0.2 g. of the diketone was dissolved in 50 ml. of anhydrous methanol and allowed to stand in the dark for 24 hours at room temperature. After this time the

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(19) S. Skraup and S. Guggenheimer, *Ber.*, **58**, 2499 (1925).

procedure of Smith and Shriner[20] was followed with the results given in Table I.

2-Aroylcyclanones.—To an ether solution of 12.8 g. of sodamide (0.33 mole) was added 16.2 g. (0.165 mole) of cyclohexanone. After 5 minutes an ether solution of the desired phenyl ester (0.165 mole) was added over a period of 10 minutes and refluxed for 1.5 hours. In the case of the *p*-chloro-, *p*-fluoro-, *p*-methylbenzoates and phenyl-2-naphthoate the portions were cut in half because of the decreased solubility of the phenyl ester in ether. The reaction was then cooled in an ice-bath and carefully poured onto 300 g. of crushed ice. (There was very little danger of fire when pouring the reaction mixture onto the ice; however, rinsing the flask with water does on occasion break into flames. A good hood should be used with a fire extinguisher nearby.) Methods A and B were used to isolate the diketones.

Method A.—The ice-cold solution was immediately acidified with dilute hydrochloric acid and extracted twice with ether. The ether extracts were washed with two portions of 10% sodium bicarbonate and one portion of water. An excess of aqueous copper acetate and the extracts were vigorously shaken and allowed to stand overnight. The copper chelate was filtered and dried. Decomposition of the chelate was best carried out by shaking a mixture of ether, dilute hydrochloric acid and the copper chelate in a separatory funnel. After the copper chelate had completely dissolved the ether solution was washed with water and distilled. A small amount of methanol was added to the residue and cooled to obtain the crystalline diketone.

Method B.—The cold solution was extracted with ether, from which a small amount of the diketone was obtained after evaporation of the ether. The aqueous solution was acidified with dilute hydrochloric acid and extracted with ether. The ether was thoroughly washed with sodium bicarbonate and water and distilled to leave an oil from which more of the diketone was obtained after dilution with methanol. Some of the properties of the diketones prepared are listed in Table II.

Isolation of Keto and Enol Forms of 2-(2-Naphthoyl)-cyclo-hexanone (XXII), 2-(*m*-Chlorobenzoyl)-cyclohexanone (XX) and 2-(*p*-Fluorobenzoyl)-cyclohexanone (XXI).—Some white crystals of XXII were dissolved in ether and thoroughly shaken with a saturated solution of copper acetate at various intervals for 0.5 day. As much of the aqueous solution was separated as possible. The precipitate suspended in the ether was washed with water, filtered and dried. The chelate was then suspended in ether and thoroughly shaken with dilute hydrochloric acid. After all of the chelate had gone into solution the ether was washed with water and distilled. The remaining oil was diluted with methanol. Cooling of the methanolic solution formed white needles and white diamond-shaped crystals, which melted at 99–100°, together with yellow crystals which melted at 73.5–75°.

The yellow enol form when dissolved in methanol for one day and then cooled yielded the white crystalline keto form which melts at 98–99°. The enol form shows a maximum at 324 mμ in the ultraviolet and a broad band at 1600 cm.$^{-1}$ in the infrared region. The keto form shows a maximum at 250 mμ in the ultraviolet and sharp bands at 1714 and 1680 cm.$^{-1}$ in the infrared region. Upon addition of an alcoholic solution of ferric chloride to a methanolic solution of the yellow enol form an immediate deep violet color is formed while the addition of ferric chloride to a methanolic solution of the white keto form forms a violet color only on standing.

Diketones XXI and XX were isolated from the reaction mixture as the copper chelates. The enol form was isolated on decomposition of the chelate. The enol form XXI is a white solid which melts at 56–57°. It shows an intense maximum at 315 mμ in the ultraviolet region and a broad band at 1490–1600 cm.$^{-1}$ in the infrared. The enol form of XX is a yellow solid which melts at 44.5–45.5°. It also shows an intense maximum at 312 mμ in the ultraviolet and a broad band at 1590 cm.$^{-1}$ in the infrared. Both enols give an immediate color with ferric chloride. If the enol forms were dissolved in methanol and allowed to stand for two days, the keto forms were isolated upon cooling the solution. The keto form of XX melts at 65.5–66° and shows one maximum at 245 mμ in the ultraviolet region. The keto form of XXI melts at 56–57°, shows a maximum at 248 mμ in the ultraviolet region and shows bands at 1721 and 1684 cm.$^{-1}$ in the infrared region. Both keto forms form a violet color with ferric chloride on standing in a methanolic solution.

Acknowledgment.—The infrared spectraphotometer used in this study was purchased by the assistance of a National Science Foundation Grant.

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[20] W. T. Smith, Jr., and R. L. Shriner, "The Examination of New Organic Compounds," John Wiley and Sons. Inc., New York, N. Y., 1956, p. 101.

COMMUNICATIONS TO THE EDITOR

CONFORMATIONAL ANALYSIS. X. THE ENERGY OF THE BOAT FORM OF THE CYCLOHEXANE RING[1,2]

Sir:

The theoretical possibility of a cyclohexane ring existing in a boat form was recognized long ago by Sachse.[3] Recently actual compounds have been shown to exist in this form preferentially,[4,5] and they do so in each case only because of their unusual environments.

Theoretical calculations have been made of the difference in energy (actually enthalpy) between the chair and boat forms of a single simple isolated cyclohexane ring.[6–8] We wish now to report an experimental measurement of this quantity.

The compounds chosen for study were the *cis* and *trans* isomers of 1,3-di-*t*-butylcyclohexane (I). The *cis* isomer can exist comfortably in the chair form with both groups equatorial, but the *trans* isomer can exist in the chair form only if one of the *t*-butyl groups occupies an axial position. Scale models indicate a tremendous distortion with such an arrangement, which would lead to molecules of very high energy.[9] The *trans* molecules might lower their energy by going into the boat

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[1] This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of the fund.

[2] Paper IX, N. L. Allinger and V. Zalkow, *J. Org. Chem.*, **25**, in press (1960).

[3] H. Sachse, *Ber.*, **23**, 1363 (1890).

[4] Various fused systems, such as camphor, in which the cyclohexane ring is necessarily in a boat form are, of course, well known.

[5] (a) D. H. R. Barton, D. A. Lewis and J. F. McGhie, *J. Chem. Soc.*, 2907 (1957); (b) R. E. Lyle, *J. Org. Chem.*, **22**, 1280 (1957); (c) M. V. George and G. F. Wright, THIS JOURNAL, **80**, 1200 (1958); (d) C. Djerassi, N. Finch and R. Mauli, *ibid.*, **81**, 4997 (1959).

[6] P. Hazebroek and L. J. Oosterhoff, *Discussions Faraday Soc.*, **10**, 87 (1951).

[7] N. L. Allinger, THIS JOURNAL, **81**, 5727 (1959).

[8] K. E. Howlett, *J. Chem. Soc.*, 4353 (1957).

[9] S. Winstein and N. J. Holness, THIS JOURNAL, **77**, 5562 (1955).