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

β-Diketones. III.[1,2] The Effect of Ring Size and Conjugation on Tautomerism

BY R. D. CAMPBELL AND H. M. GILOW

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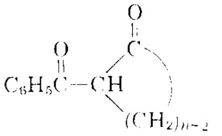
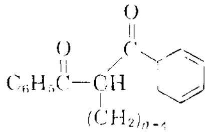
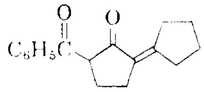
2-Benzoylcyclanones with five-, six- and seven-membered rings have been prepared. The corresponding benzoyl derivatives of indanone, tetralone and benzosuberone were also prepared. The infrared and ultraviolet spectra and the keto-enol equilibria are reported and discussed in terms of steric effects, coplanarity, ring size and bond angles, and conjugation.

It has been demonstrated[2] that the extent of enolization of various substituted benzoylcyclohexanones follows the Hammett correlation,[3] even with some *o*-substituents, and that electron-withdrawing groups and steric crowding both favored enolization. In the present study, a series of six compounds was prepared to test steric effects on the tautomerism. These were the benzoyl derivatives of cyclopentanone, cyclohexanone, cycloheptanone, indanone, tetralone and benzosuberone, with structures shown (I through VI, respectively).


I-III


IV-IV

These compounds were prepared by the method used previously,[2,4,5] *viz.*, treatment of the ketone with phenyl benzoate and sodamide. The yield of I was low due to self-condensation of cyclopentanone. Also formed was a 7% yield of 5-cyclopentylidene-2-benzoylcyclopentanone (VII).[4] The reported use of benzoyl chloride gives better yields.[6] In the other examples the yields are as good as, or better than, previously reported. The seven-membered ring compounds give poor yields. Other synthetic methods are presently under study. 1-(1-Cyclopentenyl)-pyrrolidine[7,8] was treated with benzoyl chloride to give I in 53% yield. In addition, 2,5-dibenzoylcyclopentanone (VIII) was formed. Comparable yields of substituted benzoylcyclopentanones are obtained by this method and will be reported in a subsequent article. This method has been used in the preparation of II,[7,9] but no percentage yield is reported.


VII

The extent of enolization of the benzoylcyclanones under study is expressed in precise measure by the equilibrium constant for the reaction: keto ⇄ enol. From the values listed in Table I one observes that: (a) the five-membered ring derivatives exhibit greatest tendency to enolize followed by the seven- and six-membered ring derivatives in decreasing order of enolizing tendency; (b) this pattern is found in both series, *viz.*, I–III and IV–VI; (c) the more conjugated series IV–VI shows a tenfold greater tendency to enolize than the less conjugated series I–III.

TABLE I

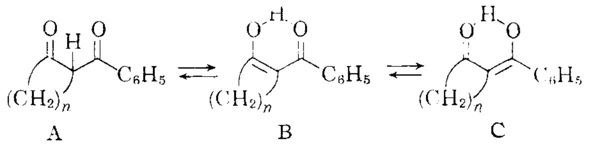
ENOL PERCENTAGE OF BENZOYLCYCLANONES

2-Benzoyl diketones	Enol, %[a]	K[b]	Ratio
Cyclopentanone (I)	39[c]	0.65	20
Cyclohexanone (II)	3	.034	1
Cycloheptanone (III)	9	.11	3
Indanone (IV)	78	3.5	100
Tetralone (V)	25	0.33	10
Benzosuberone (VI)	48	0.92	30

[a] In methanol by modified bromine-titration method. [b] K = [enol]/[ketone]. [c] For sample from pyrrolidene-enamine preparation, 40%, B. Eistert reports 45% (private communication).

An examination of the structure of the enol form is necessary before a rational analysis of structural factors is possible.

It can be seen that the enol can exist in two isomeric forms with structures B and C



Since the analysis for percentage enol does not distinguish between B and C, further evidence is required.

It has been demonstrated[2] that 2-benzoyltetralone (V) and 2-benzoylindanone (IV) each react with diazomethane to give the methyl ether of enol B exclusively. The structure of the methyl ether was established by the sodium borohydride reduction method.[2] The result of the diazomethane reaction argues strongly[10] that the enol in these cases is predominately in the form B. Also, *o*-chlorobenzoylcyclohexanone reacts with diazomethane to give 26% of the methyl ether of enol B and 74% of the methyl ether of enol C.

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

[2] Previous papers, *J. Am. Chem. Soc.*, **82**, 2389, 5426 (1960).

[3] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186ff.

[4] C. R. Hauser, B. I. Ringler, F. W. Swamer and D. R. Thompson, *J. Am. Chem. Soc.*, **69**, 2649 (1947).

[5] C. R. Hauser, F. W. Swamer and B. I. Ringler, *ibid.*, **70**, 4023 (1948).

[6] B. O. Linn and C. R. Hauser, *ibid.*, **78**, 6066 (1956).

[7] G. Stork, R. Terrell and J. Szmuszkovicz, *ibid.*, **76**, 2029 (1954).

[8] E. D. Bergmann and R. Ikan, *ibid.*, **78**, 1482 (1956).

[9] U. S. Patent 2,773,099 to G. Stork; *C. A.*, **51**, 97030 (1957).

[10] The less acidic enol with the proton attached to the more basic (and more nucleophilic) oxygen atom is present in greater concentration. Diazomethane presumably reacts with the enol(s) to produce methanediazonium ion and the enolate anion. The anion then combines with the methanediazonium ion to give the enol ether. This combination occurs at the more nucleophilic (and more basic) oxygen of the anion.

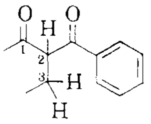
On the basis of these results, the benzoylcyclanones represent an exception to the generalization of Brown, Brewster and Schechter for such systems,[11,12] and are in contrast with observations on a large number of simpler systems.

The generalization[11,12] states that compounds containing double bonds exocyclic to a five-membered ring are more favored than the corresponding compounds containing a double bond exocyclic to a six-membered ring. Thus, it has been observed[13] that cyclohexanone with its exocyclic double bond contains a greater equilibrium enol content ($20 \times 10^{-3}\%$) than does cyclopentanone (enol: $4.8 \times 10^{-3}\%$). Similarly, the equilibrium enol content of 2-carbethoxycyclohexanone is 57% and for 2-carbethoxycyclopentanone it is 5%.[14]

The extensive work of Kon and Linstead[15] on the measurement of the *exo–endo* isomerization of a series of cycloalkylidene and cycloalkenyl acetic acids, esters and ketones provides data which are in accord with the proposed generalization. Only one previous exception to the generalization has been reported.[16] In the methylenecycloalkane–methylcycloalkene equilibrium in acetic acid, the percentage of *exo* isomer is larger (0.4%) in the six-membered ring than in the five-membered ring (0.1%).

The exceptional behavior of the benzoylcyclanones requires a rational explanation.

Several factors are expected to influence the effect of ring size upon the keto–enol equilibrium. Structural changes resulting from enolization[17] include: (a) a shortening hybridization of the C_1–C_2 bond; (b) an increase in the bond angle at C_2 due to the change from sp^3 to sp^2 type bonding; (c) a higher degree of coplanarity of the ring; (d) a higher degree of coplanarity of the tautomeric system.



The first three factors are involved in systems covered by the generalization of Brown, Brewster and Schechter, and the effects in ring planarity and conformation have been discussed elsewhere.[11,18] The fourth factor, *viz.*, coplanarity of the tautomerizing system, is of such importance that it can override those factors which control the behavior of simpler systems. Thus it appears that enol stability depends to a large extent upon the ability of C_1, C_2 and the benzoyl group to lie in the same plane.

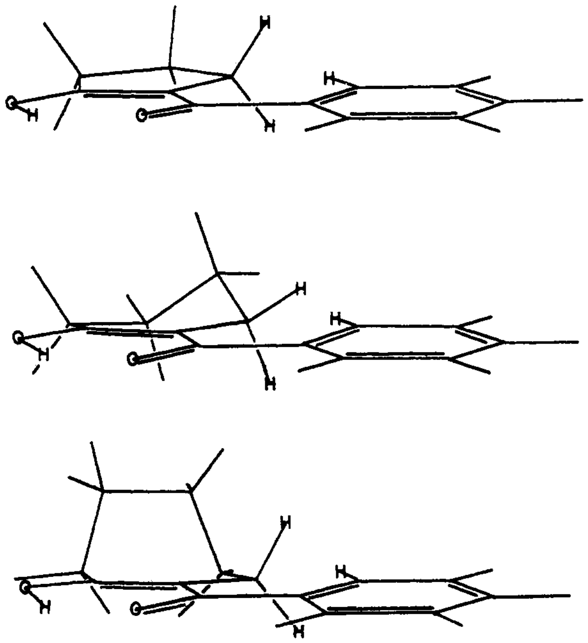


Fig. 1.—Enol forms of I, II and III.

The influence of ring size upon the coplanarity of the tautomeric system in the benzoylcyclanones is expected to operate in the form of steric crowding between the hydrogen atoms on C_3 and the *ortho* hydrogen atom on the benzene ring. The skew of the C–H bonds at C_3 depends upon ring conformation and ring puckering. The enol forms of I, II and III are shown in perspective in Fig. 1.[19] The structures are drawn in the conformation with the tautomerizing system coplanar with the benzoyl group, and with the alicyclic ring in the conformation most favorable to coplanarity.

In the five-membered ring derivative the C_3-hydrogen atoms are held by rigid conformation in position to cause minimum interference with the *ortho* hydrogen atom of the coplanar benzene ring. The carbon atom (C_3) is also drawn away from the benzene ring by the bond angle distortion (contraction) in the five-membered ring.

In the six-membered ring one C_3-hydrogen atom is almost in the plane of conjugation in the most favorable "chair" conformation. The C_3-hydrogen atom crowds the *ortho* hydrogen atom of the benzene ring, hindering coplanarity. Other conformations (chair and boat) are less favorable to coplanarity.

In the seven-membered ring derivative, several conformations are possible. In the most favorable conformation, the C_3-hydrogen atoms are in essentially the same position relative to the *ortho* hydrogen atom of the benzene ring that exists in the five-membered ring derivative. Conformations less favorable to coplanarity are possible in the seven-membered ring case.

Thus, it is apparent that the steric crowding interference of hydrogen atoms in the coplanar conformation is maximum in the case of the six-membered ring derivative, minimum in the five-

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(11) H. C. Brown, J. H. Brewster and H. Schechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).

(12) H. C. Brown, *J. Org. Chem.*, **22**, 439 (1957).

(13) G. Schwarzenbach and C. Wittmer, *Helv. Chim. Acta*, **30**, 656, 669 (1949).

(14) G. Schwarzenbach, M. Zimmerman and V. Prelog, *ibid.*, **34**, 1954 (1951); see also W. Dieckmann, *Ber.*, **55**, 2470 (1922).

(15) (a) A. H. Dickins, W. E. Hugh and G. A. R. Kon, *J. Chem. Soc.*, 572 (1929); (b) A. H. Dickins, W. E. Hugh and G. A. R. Kon, *ibid.*, 1630 (1928); (c) R. P. Linstead, *ibid.*, 1603 (1930), see also *Ann. Rep. Chem. Soc.*, **28**, 109 (1931); (d) R. P. Linstead and C. J. May, *J. Chem. Soc.*, 2565 (2929).

(16) A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell and Z. Jecura, *J. Am. Chem. Soc.*, **82**, 1750 (1960).

(17) The first structural change will be less if enol C predominates. The other changes will be the same for either enol.

(18) H. C. Brown, *J. Chem. Soc.*, 1248 (1956).

(19) The projections are tracings from photographs of Büchi models (W. Büchi Glasapparatefabrik Flawil, Switzerland).

TABLE II

2-BENZOYLCYCLANONES

Compound	M.p., °C.[a] Keto	M.p., °C.[a] Enol	Yield, %	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
I	...[b,c]		25	$C_{12}H_{12}O_2$				
			53[d]		76.6	77.0	6.43	6.09
II	88–89	42–44	79	$C_{13}H_{14}O_2$	75.2	76.10	6.54	6.89
III	55–56	64–65[e]	35	$C_{14}H_{16}O_2$	77.7	77.8	7.41	7.35
IV		72–73.5[e]	83	$C_{16}H_{12}O_2$	81.4	81.2	5.12	4.91
V		98.5–99[e]	69	$C_{17}H_{14}O_2$	81.2	80.9	5.64	5.64
VI[f]	116–117	88.5–89	30	$C_{18}H_{16}O_2$	81.6	81.8	6.06	6.03
VII		101–102	7	$C_{17}H_{18}O_2$	80.3	80.4	7.13	7.75
VIII		121–122		$C_{17}H_{16}O_2$	78.1	78.3	5.52	5.74
IX[g]		225–228	83	$C_{24}H_{22}O_4Cu$	65.8	65.4	5.06	5.10

[a] All melting points uncorrected. [b] B.p. 114–117° (1 mm.), 150–153° (4 mm.). E. Bauer, *Ann. chim. phys.*, [9] 1, 393 (1914), reports 41–42°. [c] Reported by P. J. Hamrick, C. F. Hauser and C. R. Hauser, *J. Org. Chem.*, **24**, 583 (1959). [d] Method of Stork[7]; b.p. 132–134° (2 mm.). [e] Isolated by the copper chelate method. [b] Copper chelate, m.p. 227–230°. [g] Copper chelate of I.

membered ring derivative, and intermediate in the seven-membered ring derivative.

The ultraviolet spectra provide evidence for the importance of coplanarity and conjugation in these systems. The spectra exhibit the same pattern of absorption behavior with tautomerism that was observed before.[2] The pure enols are characterized by the more intense long-wave-length band. These are the cinnamoyl and benzoyl chromophores, respectively. In the series IV, V and VI, the order of intensity of the 2500 Å. band is 10:8:6. The same decreasing order is seen in the 4500 Å. region. This order of intensity has been discussed elsewhere,[20,21] and related to decreasing coplanarity of the chromophere with increasing size of the ring.

The effect of ring size upon the coplanarity of the ring carbonyl and the aromatic nucleus has been reported[21,21] for the series: indanone, tetralone, benzosuberone. The extent of skew is calculated as 22° for the six-membered ring and 39° for the seven-membered ring.[20] The eight-membered ring was not substantially different from the seven-membered ring. The value of 17° for the skew of the five-membered ring is not enough to give substantial inhibition of resonance interaction.[21] It has been suggested[22] on the basis of spectral data and solvolysis rates of various benzyl chlorides (*via* S_N1 carbonium ion) that the seven-membered ring is skewed "normally," *viz.*, to the same extent that the open chain analogs are skewed, and that the five- and six-membered rings are "abnormally" coplanar by comparison.

TABLE III

INFRARED SPECTRAL DATA

Compound	Ring size	C=O Unconj.	C=O Conj.	Enol[a]
I	5	1743m[b]	1690s	1640–1510
II	6	1724s	1683s	1603–1589w
III	7	1720w[c]	1688w[c]	1620–1520s
IV	5			1640–1500s
V	6			1610–1480s
VI	7			1620–1500s
VII	5		1665m	1635-1515s

[a] No band appears in the 3100-3500 cm.$^{-1}$ region. [b] Numbers are in cm.$^{-1}$; letter indicates strong (s), medium (m) or weak (w) bands. [c] These bands appear only on standing several days.

TABLE IV

ULTRAVIOLET SPECTRAL DATA

Compound	Ring size	Tautomer Equilibrium	Tautomer Enol	Tautomer Keto
I	5	2470[a](6.8)[b]		
		3220 (5.6)		
II	6	2450 (7.72)	2450 (3.82)	2450 (9.74)
		3140 (4.46)	3140 (10.1)	
III	7	2460 (9.0)	2450 (3.3)	
		3100 (5.4)	3100 (12.2)	
				Monoketones[c]
IV	5	2480 (10.8)	2480 (10.5)	2390 (12.7)[c]
				2440 (10.6)
		3510 (19.7)	3510 (19.7)	2810 (2.6)
				2910 (2.5)
V	6	2510 (10.9)	2460 (8.2)	2430 (11.5)[c]
		3060 (4.5)	3060 (6.0)	2860 (1.5)
		3590 (12.2)	3590 (17.6)	2960 (1.4)
VI	7	2490 (8.2)	2370 (6.2)	2400 (9.00)[c]
		3360 (14.6)	2550 (5.9)	2810 (1.2)
			3360 (16.9)	

[a] Wave length of maximum (Å.). [b] Extinction coefficient × 10^{-3}. [c] Data for indanone, tetralone and benzosuberone from ref. 7.

The infrared data show the expected[2] behavior. The ring carbonyl stretching frequency decreases with increasing ring size[23]; the carbonyl bands are absent and the broad enol band[2,23] is present for the enol forms; no hydroxyl absorption appears in any of the spectra, indicating strong hydrogen chelation even in the five-membered ring.[24] The band at 1665 cm.$^{-1}$ for VII suggests that this strongly enolic compound is chelated weakly so that the carbonyl band still appears. The possibility that this band is due to the *exo* double bond must not be excluded. Further study of this series is now underway.

Experimental

2-Benzoylcyclanones (I-VII).—The phenyl benzoate-sodamide procedure[2,4] was used with results listed in Table II. The copper chelate isolation method (method A)[2] was

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(20) G. D. Heddon and W. G. Brown, *J. Am. Chem. Soc.*, **75**, 3744 (1953).

(21) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

(22) G. Baddeley, J. Chadwick and S. B. Rawlinson, *Nature*, **164**, 833 (1949).

(23) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 142–143.

(24) Compare the chelating effect in nitroketones; R. D. Campbell and F. J. Schultz, *J. Org. Chem.*, **25**, 1877 (1960).

used for compounds III, IV and V. Method B[2] was used in the other cases. In the isolation of I, when methanol was added to the extract residue, 1.5 g. (7.1%) of yellow needles formed, identified as VII. The filtrate yielded no other crystalline product. Distillation gave fractions boiling in the ranges: 95° (35 mm.) (phenol) about 10 g.; 80–110° (1 mm.) (mostly phenyl benzoate), about 15 g.; 110–150° (1 mm.). The last fraction was redistilled to give I.

The pyrrolidine-enamine procedure of Stork[7] was employed. Cyclopentanone pyrrolidine-enamine (0.2 mole, 27.4 g.) in dioxane was treated with benzoyl chloride (0.1 mole). The mixture was stirred at room temperature and then at reflux. The product of this reaction was hydrolyzed and the organic portion distilled as above to give 10.0 g. (53%) of I. The copper chelate IX formed in 83% yield and melted at 225–228°.

The residue from the distillation on crystallization from methanol gave yellow needles, VIII, m.p. 121–122°. Analytical data are listed in Table I.

Percentage Enol Determination.—The method of Smith and Shriner[25] was used with the reported[2] modification for equilibriation in absolute methanol.

Measurement of Spectra.—The ultraviolet spectra were determined using a Cary recording spectrophotometer, model 11. Procedure used was according to the manufacturer's instructions. Matched quartz cells were used. The spectrophotometer was housed in a constant temperature room at 28°. The concentration employed was 10^{-4} molar in all cases. The solutions were freshly prepared and, for equilibrium data, were stored in the dark. Data obtained are listed in Table IV.

The infrared spectra were measured using a Perkin-Elmer model 21 double-beam recording spectrophotometer, with a sodium chloride prism. The control settings were maintained constant at: resolution, 926; response 1; gain, 5; speed, 4; suppression, 4. The concentration used was 10 mg./ml. Matched 1-mm. cells were used in standard double beam operation. Data obtained are listed in Table III.

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(25) 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.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TENNESSEE, KNOXVILLE, TENN.]

Competitive Catalytic Hydrogenation of Benzene, Toluene and the Polymethylbenzenes on Platinum

BY CHARLES P. RADER AND HILTON A. SMITH

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The competitive catalytic hydrogenation of benzene, toluene and all of the possible polymethylbenzenes has been studied on a platinum catalyst. The relative ease of adsorption of each of these hydrocarbons on the active catalyst surface has been measured by a method based on Langmuir kinetics. It has been found that the relative ease of adsorption does not necessarily parallel the relative rates of reduction of the individual hydrocarbons. The ease of adsorption decreases with increasing nuclear substitution except in the case of hexamethylbenzene which is slightly more strongly adsorbed than pentamethylbenzene. For a given isomeric set of polymethylbenzenes, the ease of adsorption always decreases with increasing symmetry of substitution. It is suggested that the relative ease of adsorption may result from the relative amount of steric strain arising from the flatwise adsorption of the nucleus on the active surface.

Introduction

The ease with which the benzene nucleus is reduced on a platinum surface is known to be a function of the amount and symmetry of nuclear substitution. On Adams platinum catalyst the rate of hydrogenation decreases with increasing nuclear substitution and increases with symmetry of substitution. Much of this work has been previously summarized.[1]

Smith and Pennekamp[2] hydrogenated benzene, toluene and all of the polymethylbenzenes over Adams platinum in glacial acetic acid at room temperature and hydrogen pressures of 1–4 atmospheres. They found that the reduction rate was zero order in the concentration of hydrogen acceptor and first order in hydrogen pressure under conditions where diffusion processes did not affect the velocity of the reaction. The rate constants for the reduction of these hydrocarbons clearly reveal a decrease in the rate of hydrogenation as nuclear substitution is increased, and within any group of isomers, an increase in rate as the symmetry of substitution increases. These effects upon the reduction rate have also been observed in the hydrogenations on platinum of the methyl and polymethylbenzoic acids,[3] the methoxybenzenes[4] and the hydroxybenzenes.[5]

It has been suggested that the relative reduction rate depends upon the steric interference caused by the methyl substituents preventing ready attack of the hydrogen on the benzene nucleus[6] or by steric interference by the methyl groups with activated adsorption of the benzene ring on the active catalyst surface.[1] This latter type of hindrance should be reflected in the relative ease of adsorption of various methylbenzenes on the active portion of the catalyst surface. As the steric hindrance is increased the ease of adsorption should decrease. Thus, a measurement of the relative ease of adsorption of benzene and its methyl substituted derivatives should enable one to examine the relation between steric influence on adsorption and reduction rate.

The basic purpose of this research was, then, to measure the relative ease of adsorption of benzene, toluene and the polymethylbenzenes on the active platinum surface and to compare the relative ease of adsorption with the relative reduction rates

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(1) H. A. Smith in P. H. Emmett, "Catalysis," Vol. V, Reinhold Publishing Corp., New York, N. Y., 1957, p. 175.

(2) H. A. Smith and E. F. H. Pennekamp, *J. Am. Chem. Soc.*, **67**, 279 (1945).

(3) H. A. Smith and J. A. Stanfield, *ibid.*, **71**, 81 (1949).

(4) H. A. Smith and R. G. Thompson, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1957, p. 727.

(5) H. A. Smith and B. L. Stump, *J. Am. Chem. Soc.*, **83**, 2739 (1961).

(6) H. A. Smith, D. M. Alderman and F. W. Nadig, *ibid.*, **67**, 272 (1945).