Anal. Calcd. for $C_{23}H_{16}N_2O_2$: C, 78.4; H, 4.58. Found: C, 78.4; H, 4.44.

Reaction with phenylmagnesium bromide. A solution of 2.5 g. of III in 10 ml. of benzene was treated with 6 ml. of $2N$ ethereal phenylmagnesium bromide, giving a deep purple solution and a gummy black precipitate that dissolved when the mixture was kept overnight. Addition of dilute hydrochloric acid, etc. gave 2.9 g. of a pale tan oil that could not be obtained crystalline. This was treated with 10 ml. of 20% methanolic potassium hydroxide, rapid solution occurring, followed by separation of a colorless crystalline potassium salt. This salt was washed with methanol and then ether, then dissolved in water and acidified. The resulting *1,3-diphenyl-1-hydroxyindene-2-carboxylic acid* separated as an oil, which crystallized after it had been kept under ether-ligroin for several days. Recrystallization from dilute alcohol gave fine colorless needles, m.p. 163–164°. The compound gave a deep purple color with concd. sulfuric acid.

Anal. Calcd. for $C_{22}H_{16}O_3$: C, 80.5; H, 4.91. Found: C, 80.6; H, 4.92.

A solution of 0.5 g. of this acid in 5 ml. of acetic acid and 1 ml. of acetyl chloride was treated with 0.5 g. of zinc dust and boiled for 10 min. Water and ether were then added, and the ether solution was extracted with dilute sodium carbonate. This removed 50 mg. of *1,3-diphenylindene-2-carboxylic acid,* flat yellow needles from dilute acetic acid, m.p. 195–196° that gave no color with concd. sulfuric acid.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.6; H, 5.16. Found: C, 84.4; H, 5.16.

The same compound was synthesized by boiling 2 g. of 1,3-diphenylindene with 2 ml. of oxalyl chloride for 1 hr. The acidic product (500 mg.) from this reaction formed colorless needles, m.p. 173–181°, that gave a deep orange color with sulfuric acid; solution in dilute sodium carbonate and warming with 3 ml. of 3% hydrogen peroxide followed by reprecipitation and crystallization from dilute acetic acid gave yellow needles, m.p. 194–196° alone or mixed with the previously described acid; infrared spectra of the two samples were identical.

Acknowledgment. The author thanks Mrs. O. Hamerston for analytical data.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE VIRGINIA POLYTECHNIC INSTITUTE]

The Synthesis and Cyclization of Some 2'-Substituted 2-Benzylbenzophenones[1,2]

FRANK A. VINGIELLO, MARTIN O. L. SPANGLER, AND JAMES E. BONDURANT

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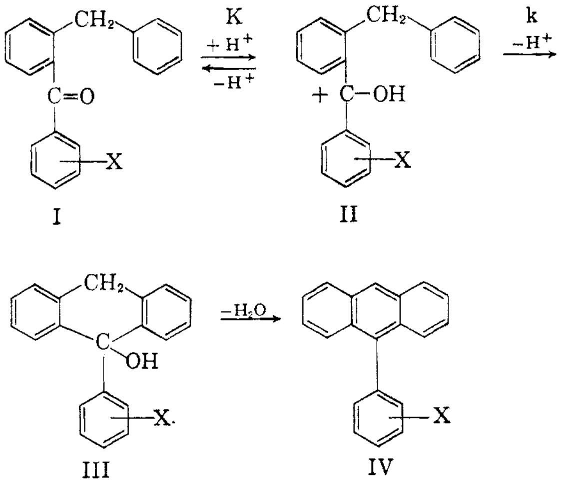
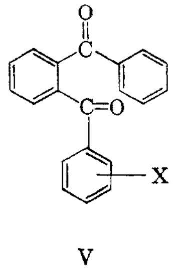
A series of new 2'-substituted 2-benzylbenzophenones has been prepared. These ketones have been cyclized to their corresponding 9-substituted phenylanthracenes. The rates of cyclization were measured and correlated with a mechanism proposed for aromatic cyclodehydration.

In 1940 Bradsher[3] introduced a new method of synthesis for the 9-alkyl- and 9-arylanthracenes. This method has been found to be of considerable value and to have a wide range of application.[4] Quite a few derivatives of 9-phenylanthracene have been prepared by this method in connection with rate studies.[5,6] Compounds of the type I were reported where X was in either the *para* or *meta* positions. The present investigation reports the synthesis of four new ketones of type I, in which X is an *ortho* substituent, and their subsequent cyclization to derivatives of 9-phenylanthracene.





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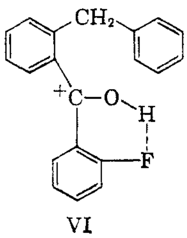

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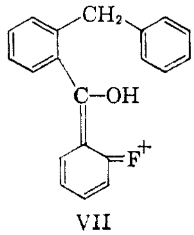

VII

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(1) Presented before the Chemistry Section at the Southeastern Regional Meeting of the American Chemical Society, Durham, N. C., Nov. 1957.

(2) This paper has been abstracted in part from the Masters thesis of Mr. James Bondurant presented to the Virginia Polytechnic Institute in 1955 and in part from the Doctorate thesis of Mr. M. O. L. Spangler presented to the Virginia Polytechnic Institute in 1958.

(3) C. K. Bradsher, *J. Am. Chem. Soc.*, **62**, 486 (1940).

(4) C. K. Bradsher, *Chem. Rev.*, **38**, 447 (1946).

(5) C. K. Bradsher and F. A. Vingiello, *J. Am. Chem. Soc.*, **71**, 1434 (1949).

(6) F. A. Vingiello, J. G. Van Oot, and H. H. Hannabass, *J. Am. Chem. Soc.*, **74**, 4546 (1952).

TABLE I

RATES OF CYCLIZATION OF SOME 2-BENZYLBENZOPHENONES (I) AT 150°

X	$k_1 \times 10^{-2}$ (Hr.$^{-1}$)	X	$k_1 \times 10^{-2}$ (Hr.$^{-1}$)
2-F	38.6	2-CH_3	9.5[a]
2-Cl	6.9	3-CF_3	31.7
2-Br	3.3	H	55

[a] This value is very crude because of partial decomposition of the product.

TABLE II

NEW KETONES (I)

X	Yield, %	B.P.	Mm.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-F	55	194	1.8	82.74	83.06	5.21	5.21
2-Cl	59	207	0.5	78.30	78.69	4.93	4.92
2-Br	60	215	2	68.39	68.85	4.30	4.46
2-CH_3	73	215	5	88.08	88.08	6.33	6.32

TABLE III

NEW DIKETONES (V)

X	Yield, %	M.P.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-F	62[a]	116.7–117	78.94	79.40	4.30	4.55
2-Cl	100	87.5–88	74.88	74.94	4.08	4.10
2-Br	77	93.2–94	65.77	65.75	3.59	3.72
2-CH_3	64[a]	76–77	83.98	84.10	5.37	5.54

[a] Sodium dichromate and sulfuric acid in glacial acetic acid was used to effect oxidation of these ketones.

TABLE IV

NEW ANTHRACENES[a] (IV)

X	Yield,[b] %	M.P.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
2-F	94	143–144	88.21	88.24	4.81	5.05
2-Cl	52	139.5–140	83.18	83.22	4.54	4.58
2-Br	21	139–139.5	72.08	72.42	3.92	4.08
2-CH_3[c]	10	125–126	93.98	93.52	6.02	6.36

[a] The ultraviolet absorption spectra of the anthracenes were taken with a Beckman spectrophotometer (model DU, 1-cm. silica cell) using 95% ethanol as the solvent. The maxima for all four anthracene derivatives appear at the same wave lengths. The log e values are listed after each wave length value in the same order as the compounds appear in Table IV: λ 255 mμ (5.03, 5.06, 5.08, 5.04); λ 317 mμ (3.14, 3.24, 3.19, 3.18); λ 331 mμ (3.52, 3.57, 3.55, 3.54); λ 347 mμ (3.82, 3.86, 3.86, 4.84); λ 366 mμ (4.01, 4.04, 4.04, 4.03); λ 386 mμ (3.97, 4.01, 4.02, 4.00). [b] These are the maximum yields obtained by the use of the sealed tube technique at 150°. [c] First prepared by E. C. Kramer, M.S. thesis, Virginia Polytechnic Institute, Blacksburg, Va., 1954.

The three halogen substituted ketones (I, X = 2—F, 2-Cl, 2-Br) were prepared by the addition of the appropriately substituted benzoyl chloride to the cadmium chloride reagent[7] of 2-bromodiphenylmethane. The methyl substituted ketone was prepared by the action of the Grignard reagent of 2-bromotoluene on 2-benzylbenzonitrile followed by subsequent hydrolysis of the resulting ketimine. The boiling points, analytical data, and yields of the new ketones are recorded in Table II. These ketones were further identified[8] by oxidation to the corresponding diketones (V) by means of chromium trioxide in acetic acid. These diketones were also used to identify the oily residues (starting ketones) obtained when cyclizations failed. Oxidation of the residue to the diketone indicated the presence of unreacted monoketone in the residue. The melting points, analytical data and yields of the new diketones are recorded in Table III.

Cyclizations of the ketones (I) were carried out in sealed tubes in a Carius furnace. This technique was first employed in reactions of this type by Vingiello and Borkovec[9] to synthesize 9- and 10-aryl-1,2-benzanthracenes. The melting points, analytical data, and yields of these new compounds are recorded in Table IV. The absorption maxima in the ultraviolet region are recorded after Table IV. In each case the maxima are almost identical with those of 9-phenylanthracene[10] itself as is to be

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[7] J. Cason, *J. Am. Chem. Soc.*, **68**, 2080 (1946).

[8] F. A. Vingiello and J. G. Van Oot, *J. Am. Chem. Soc.*, **73**, 5070 (1951).

[9] F. A. Vingiello, A. Borkovec, and J. Shulman, *J. Am. Chem. Soc.*, **77**, 2320 (1955).

[10] E. Clar and D. G. Steward, *J. Am. Chem. Soc.*, **74**, 6235 (1952).

expected, as the phenyl group is not coplanar with the anthracene group.[11] This would prevent resonance interactions between the anthracene moiety and the substituted phenyl ring.

The rates of aromatic cyclodehydration were measured using essentially the method described previously[5,6] except that the reactions were run in Carius tubes at 150°.

Bradsher and Vingiello[5] and Vingiello and Van Oot[3] have shown that the electronic effects of *meta* and *para* substituents on the rate generally cancel one another giving only small variations in the rate with changes in the electronic character of the substituents. This provided the basis for the postulate that there are two rate-controlling steps: (1) the reversible addition of a proton to the carbonyl oxygen ($I \rightleftarrows II$) and (2) the attack of the positive central carbon atom on the *ortho* position of the ring into which cyclization occurs ($II \rightarrow III$). A substituent which decreases the electron density at the carbonyl carbon atom would enhance the electrophilic attack by that atom ($II \rightarrow III$) and increase the rate of cyclization. However, the same effect would decrease the electron density on the carbonyl oxygen and thereby decrease its attraction for the proton. This would shift the equilibrium $I \rightleftarrows II$ to the left, retarding the rate of cyclization.[12]

Analogous *ortho* compounds show comparatively large variations in rates of cyclization; all cyclize more slowly than 2-benzylbenzophenone. As might have been expected, the variations appear to be due to the increasing steric requirements of the substituents in the order $Br > Cl > F$. A steric factor had been postulated by previous workers.[5] In contrast to electronic effects, the steric effect inhibits the attack of the electropositive carbon atom on the benzene ring into which cyclization is to occur, while it probably has a negligible effect on the tendency of a proton to add to the carbonyl oxygen. Because of this lack of selfcompensation, the steric retardation of this reaction is more readily observed than electronic effects.

Again it was noted that the fluoro ketone, I, where $X = 2\text{-F}$, cyclized at a lower rate than the unsubstituted ketone, I, where $X = H$. As the fluorine atom could presumably exert its strong $+M$ effect from the *ortho* position as well as from the *para* position and as it was previously suggested[6] that the lower rate of cyclization of the *para* fluoro ketone, I, where $X = 4\text{-F}$, as compared with the unsubstituted ketone was due to this $+M$ effect in the ionic intermediate II, we now would like to suggest that the reduced rate of cyclization of the fluoro ketone, I, where $X = 2\text{-F}$, as compared with the unsubstituted ketone is due to the strong $+M$ effect of the fluorine atom in the ionic intermediate VII where $X = 2\text{-F}$.

We are aware of the possibility that the ionic intermediate II where $X = 2\text{-F}$ may form a six membered ring involving hydrogen bonding (VI). This would tend to shift the equilibrium $I \rightleftarrows II$ to the right. Although we have no data which would identify this hydrogen-bonded structure we did reduce the ketone, I, where $X = 2\text{-F}$ to the corresponding secondary alcohol, 2′-fluoro 2-benzylbenzhydrol.[13] The infrared spectrum of this compound,[14] a smear sample, showed a strong and broad absorption band in the region of 3.0 μ and a weaker absorption at 2.83 μ. The former is due to the fundamental O—H stretching vibration in an intermolecular hydrogen bonded functional group rather than an intramolecular hydrogen bonded functional group. The latter is probably the normal wave length position for nonhydrogen bonded OH functional groups. These observations were confirmed by further study in carbon tetrachloride solvent. In this nonpolar solvent, the intermolecular hydrogen bonds were broken and the near infrared spectrum showed the first overtone absorption band at 1.416 μ. If intramolecular hydrogen bonding were present, one would have observed the first overtone at approximately 1.50 μ, as this type of bond is independent of the concentration.

It is interesting to note that for the ketone I, where $X = 3\text{-CF}_3$, and I, where $X = H$, the relative rates measured at 150° in this study are inverted from the relative rates previously measured[5,6] at 118°.

EXPERIMENTAL[15,16]

o-Bromodiphenylmethane.[17] *o*-Bromobenzohydrol was prepared by the action of the Grignard reagent from 207 g (1.32 moles) of bromobenzene and 32.1 g. (1.32 moles) of magnesium turnings on 122 g. (0.66 mole) of *o*-bromo-

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[11] R. N. Jones, *J. Am. Chem. Soc.*, **67**, 2127 (1945).

[12] The experimentally determined rate (k_1) is equal to the product of the equilibrium constant K for the reaction $I \rightleftarrows II$ multiplied by the specific rate constant k for the reaction $II \rightarrow III$.

[13] Sodium borohydride was used to reduce 2′-fluoro 2-benzylbenzophenone to 2′-fluoro 2-benzylbenzhydrol in 67% yield. The hydrol distilled at 188° (0.06 mm.). *Anal.* Calcd. for $C_{20}H_{17}FO$: C, 82.17; H, 5.86. Found: C, 82.45; H, 6.01. This hydrol was converted to 9-(2-fluorophenyl)-9,10-dihydroanthracene in 65% yield (m.p. 91–91.5°, from 95% ethanol) using a mixture of acetic anhydride and trifluoroacetic acid. *Anal.* Calcd. for $C_{20}H_{15}F$: C, 87.56; H, 5.51. Found: C, 87.33; H, 5.81.

[14] We are indebted to Mr. M. V. Otis, Research Laboratories, Tennessee Eastman Co., Kingsport, Tenn., for the infrared data and its interpretation.

[15] All melting points are corrected.

[16] All analyses were carried out by Geller Microanalytical Laboratories, Bardonia, N. Y.

[17] This compound had previously been prepared by reduction of the keto group of *o*-bromobenzophenone. The carbinol group of *o*-bromobenzohydrol is more readily reduced. [E. Bergmann, *J. Org. Chem.*, **4**, 1 (1939); F. A. Vingiello, Ph.D. dissertation, Duke Univ. (1947) p. 68.] The present method is similar to that used by Bradsher[3] for the preparation of *o*-chlorodiphenylmethane.

benzaldehyde.[18] The crude product was reduced with 25 g. of red phosphorus and 25 g. of iodine in 1200 ml. of glacial acetic acid and 120 ml. of water. The mixture was stirred and heated under reflux for 31 hr. Then the phosphorus was filtered, the mixture cooled, and the acid neutralized with a saturated solution of sodium carbonate. The resulting material was extracted thrice with isopropyl ether, the combined extracts washed with water, twice with 10% sodium hydroxide, and twice again with water, dried over calcium chloride, concentrated, and distilled at 1 mm. The fraction distilling at 119–122° (lit.,[19] b.p. 179–183° (21.5 mm.)) weighed 105 g. (65% based on aldehyde).

2'-Chloro-2-benzylbenzophenone.[20] A Grignard reagent was prepared from 54.5 g. (0.22 mole) of *o*-bromodiphenylmethane and 5.35 g. (0.22 mole) of magnesium in 250 ml. of anhydrous ether. The reaction was initiated by means of a few drops of methyl iodide. After all the solution had been added, reflux was continued until most of the magnesium had dissolved (about 1 hr.). The solution was cooled to room temperature and 40.4 g. (0.22 mole) of anhydrous cadmium chloride was added in one portion. The mixture was then heated under reflux for 40 min. after which the ether was allowed to distil from the mixture as 150 ml. of anhydrous benzene was added to replace it. The mixture was cooled and 34.4 g. (0.22 mole) of *o*-chlorobenzoyl chloride in 150 ml. of anhydrous benzene was added slowly enough to give moderate boiling of the benzene. The mixture was heated under reflux for 1.5 hr, the mixture cooled, poured on an ice–hydrochloric acid mixture, and left overnight. The layers were separated, the aqueous layer extracted thrice with fresh ether, the combined extracts washed with 10% sodium hydroxide and twice with water, dried over calcium chloride, concentrated, and fractionated at 1 mm. The fraction distilling at 201–204° weighed 40 g. (59%). On redistillation an analytical sample was taken at 207° at 0.5 mm.

The other haloketones were prepared in a similar manner.

2'-Chloro-2-benzoylbenzophenone.[21] To a mixture of 1.95 g. (0.006 mole) of 2'-chloro-2-benzylbenzophenone in 8 ml. of glacial acetic acid was added 1.98 g. (0.02 mole) of chromium trioxide in 6.5 ml. of glacial acetic acid and 4 ml. of water. The mixture was heated under reflux with stirring for 48 hr. The hot mixture was poured on 70 g. of ice. A white gum separated which crystallized on standing overnight. This was filtered, washed with water, and air dried. The 2.07 g. melted at 78–83°. Crystallization from methanol gave a m.p. of 87.5–88°.

2'-Bromo-2-benzoylbenzophenone was prepared in a similar manner.

9-(2-Bromophenyl)anthracene. A mixture of 1.47 g. of 2'-bromo-2-benzylbenzophenone, 30 ml. of 48% hydrobromic acid and 60 ml. of glacial acetic acid was heated in a sealed tube in a Carius furnace at 150° for 7 hr. A sticky semisolid separated which was filtered without suction, washed twice with water, and removed from the paper with acetone. The acetone was removed on a steam bath and the residue crystallized from methanol using activated charcoal. Almost white, very small rosettes separated, m.p. 136–137°, 29 g. (21%).

When yields were high the product of cyclization would crystallize in the tube as it cooled. This only needed to be filtered, washed, and weighed. Rates calculated from weights measured in either case were the same for the same compound. Rate calculations were made using at least three and usually four different time intervals. The intervals used were 3 hr., 7 hr., 12 hr., and 29 hr. For the less active ketones the 3 hr. interval gave only an oil from which no crystalline product could be obtained. When this occurred the oil could be oxidized to the corresponding diketone (V) except in the case of the methyl analog (I, X = 2-CH_3). The identity of these products was checked by means of mixed melting points with authentic samples.

BLACKSBURG, VA.

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(18) R. Adams and E. H. Vollweiler, *J. Am. Chem. Soc.*, **40**, 1737 (1918).

(19) C. K. Bradsher and F. A. Vingiello, *J. Org. Chem.*, **13**, 786 (1948).

(20) This procedure is similar to that developed by Cason[7] for the aliphatic halides and acid halides which are more active than the analogous aromatic halides.

(21) The procedure of Vingiello and Van Oot[6] using sodium dichromate and sulfuric acid on our new ketones often gave dark products which were purified with some difficulty. Yields were also lower than reported in the *para*-substituted compounds.

[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Syntheses of Four Spiro Hydrocarbons

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Synthetic routes to four spiro hydrocarbons are described.

As a portion of a continuing study[3] of hydrocarbon structure and physical properties, spiro[4.5]decane, spiro[5.5]undecane, spiro[5.6]dodecane, and 7-hexadecylspiro[4.5]decane were prepared. The first three of these compounds have been reported previously.[4–9] However, because many of the properties reported were seriously

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(1) American Petroleum Institute Fellow, 1956–58. Esso Research and Development Company Fellow, 1958–59.

(2) Taken in part from the dissertation submitted by P. A. Naro in partial fulfillment of the requirements for the Ph.D. degree at The Pennsylvania State University.

(3) For the previous paper in this series see S. G. Clark II, and J. A. Dixon, *J. Org. Chem.*, **23**, 1628 (1958).

(4) N. D. Zelinsky and N. I. Schuikin, *Ber.*, **62**, 2180 (1929).

(5) R. Ya. Levina, V. R. Skvarchenko, and O. Yw. Okhlobystin, *Zhur. Obshcheĭ Khim.*, **25**, 1466 (1955); *Chem. Abstr.*, **50**, 4797a (1956).

(6) G. A. Laber, *Ann.*, **588**, 79 (1954).

(7) M. Mousseron, R. Jacquier, and H. Christol, *Bull. soc. chim. France*, 346 (1957).

(8) R. Mayer, G. Wenschuh, and W. Topfelman, *Chem. Ber.*, **91**, 1616 (1958).