Experimental

Catalysts and Apparatus.—The nickel-on-Celite and copper chromite catalyst were prepared according to the procedures of Adkins.[8] All hydrogenations were conducted in a rocker-type, high-pressure hydrogenation bomb assembly.

1,4,7-Heptanetriol.—1-Furylpropanol-3[9] (1009.6 g., 8 moles), 18 g. of freshly reduced nickel-on-Celite catalyst, 1.8 ml. of 90% formic acid and 570 ml. of water were combined in a 3-liter hydrogenation bomb. The initial hydrogen pressure was 200 atmospheres and approximately 16 moles of hydrogen was absorbed over a 6.5-hour period during which the temperature was gradually raised to a maximum of 210°. After removal of the catalyst by filtration and the water by distillation the residue was fractionally distilled. 1-Tetrahydrofurylpropanol-3, 540 g. (51.8%), n^{25}D 1.4557 was collected at 107–109° (14 mm.). The triol fraction boiled over a range of 149–155° (0.1 mm.), n^{25}D 1.4760, yield 461 g. (38.8%).

Redistillation gave an almost quantitative recovery of product b.p. 146° (0.1 mm.), n^{25}D 1.4773.[10]

Anal.[11] Calcd. for $C_7H_{16}O_3$: C, 56.7; H, 10.8; OH, 34.4. Found: C, 56.5; H, 10.8; OH, 34.8.

1,4,7-Octanetriol.—1-Furylbutanol-3, 70 g. (0.5 mole), was mixed with 6 g. of nickel-on-Celite catalyst, 0.6 ml. of 90% formic acid and 300 ml. of water in a 700-ml. hydrogenation bomb. The initial hydrogen pressure was 155 atmospheres and approximately 1.0 mole of hydrogen was absorbed in 3.5 hours during which the temperature had been gradually raised to a maximum of 198°. After removal of the catalyst and water the product mixture was fractionally distilled. The triol fraction was collected at 150–152° (0.17 mm.) and weighed 34.5 g. (42%), n^{25}D 1.4751. The redistilled product boiled at 148° (0.16 mm.), n^{25}D 1.4748.

Anal. Calcd. for $C_8H_{18}O_3$: C, 59.25; H, 11.2; OH, 31.5. Found: C, 59.3; H, 10.8; OH, 31.2.

1-Tetrahydrofuryl-3,6,9-nonanetriol.—The crude mixture of products obtained from the copper chromite-catalyzed hydrogenation of difurfuralacetone in alcohol was freed of catalyst and alcohol. This material, 440 g. (2.0 moles if assumed to be difurylpentanol) was mixed with 18.7 g. of nickel-on-Celite catalyst, 0.8 ml. of 90% formic acid and 590 ml. of water in a 3-liter hydrogenation bomb. Hydrogen absorption ceased after approximately 3 hours during which the temperature was gradually raised to 200°. Fractionation of the catalyst- and water-free residue gave the following products: (a) 1,5-ditetrahydrofurylpentanol-3, b.p. 144° (0.7 mm.), n^{25}D 1.4793; 167 g. (36.5%).

(b) 1-Tetrahydrofuryl-3,6,9-nonanetriol, b.p. 208–210° (0.12 mm.), n^{25}D 1.4907; 186 g. (38.6%); redistilled b.p. 189° (0.03 mm.), n^{25}D 1.4908.

Anal. Calcd. for $C_{13}H_{26}O_3$: C, 63.4; H, 10.63; OH, 20.7. Found: C, 63.1; H, 10.66; OH, 20.6.

(c) A residue, 102.4 g. (19.4%), containing 1,4,7,10,13-tridecane pentaol.

Purification of 1,4,7,10,13-Tridecanepentaol.—A composite sample, 145 g., of residues containing crude pentaol was dissolved in 290 ml. of boiling water, the solution treated with decolorizing carbon and filtered while hot. Removal of the water under reduced pressure left a light-colored residue weighing 141 g. This material was triturated with 200 ml. of boiling acetone, to extract dissolved triol, and left to stand overnight in contact with the acetone. The acetone was removed by decantation and the extraction was repeated with five additional 100-ml. portions of acetone. The residue from this treatment was then dissolved in 5 liters of boiling acetone. After the solution had cooled to room temperature it was placed in a refrigerator for 4 days during which the product slowly separated as a white solid. After removal by filtration and drying to constant weight *in vacuo* over calcium chloride, the white, granular product weighed 84 g. (58% of original crude). This product had no definite melting or freezing point. It liquefied fairly rapidly at 100° and on cooling to room temperature gradually solidified within 2–3 days; n^{60}D 1.4920, n^{25}D of the supercooled liquid, 1.5006.

Anal. Calcd. for $C_{13}H_{28}O_5$: C, 59.1; H, 10.67; OH, 32.2. Found: C, 59.0; H, 10.04; OH, 32.8.

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[8] H. Adkins, "Reactions of Hydrogen," The University of Wisconsin Press, Madison, Wisconsin, 1937.

[9] Prepared by $CuCr_2O_4$ catalyzed hydrogenation of furylacrolein in alcohol solution. *Cf.* H. E. Burdick and H. Adkins, This Journal, **56**, 438 (1934).

[10] J. Hammonet, *Ann. chim.*, **10**, 5 (1918), reports η^{18}D 1.4738 and η^{18}D 1.447 for the triacetate. H. Hinz, G. Meyer and G. Schücking, *Ber.*, **76**, 676 (1943), report η^{29}D 1.4725 for a triol obtained as a by-product from the hydrogenation of furylacrolein; triacetate η^{28}D 1.4440. 1,4,7-Heptanetriol triacetate prepared from 1-tetrahydrofurylpropanol-3 by treatment with Ac_2O according to procedure of Hinz, *et al.*, PB report 52009, p. 249 (*C. A.*, **41**, 5124 (1947)) and PB report 52020, p. 1050 (*C. A.*, **41**, 6559 (1947)) had b.p. 121° (0.02 mm.), η^{25}D 1.4400, and theoretical saponification equivalent. Methanolysis yielded the triol of η^{25}D 1.4772. The structure of the triol was confirmed by conversion to 1-tetrahydrofurylpropanol-3. This was accomplished by dehydration in toluene with *p*-toluenesulfonic acid as catalyst.

[11] All analyses are micro or semi-micro determinations by C. H. Van Etten and Mary B. Wiele of this Laboratory.

[Contribution from the Chemical Laboratories of the Virginia Polytechnic Institute]

The Synthesis and Cyclization of Some *o*-Benzylphenones[1,2]

By Frank A. Vingiello, James G. Van Oot and H. Hayden Hannabass

Received January 14, 1952

The synthesis of six new *o*-benzylphenones and six new anthracene derivatives has been accomplished. The rates of cyclization of the six new ketones have been measured and the data correlated with an electronic mechanism of aromatic cyclodehydration.

Bradsher and Vingiello[3] have postulated that the cyclization of *o*-benzylphenones proceeds through the following steps: (1) the reversible addition of a proton to the carbonyl oxygen; (2) reaction between the positive central carbon atom and the ortho position of the benzene ring into which cyclization is to occur; (3) elimination of a proton; and finally (4) transannular elimination of water. Vingiello and Van Oot[4] have recently presented data which substantiate Bradsher and Vingiello's conclusion that the rate of cyclization depends, among other things, on the electron density at the ortho position of the benzene ring into which cyclization occurs. We now have additional data to support the statement that a given substituent will change the cyclization rate in a given direction as regards

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[1] Presented before the Division of Organic Chemistry at the 121st Meeting of the American Chemical Society, Buffalo, N. Y., March, 1952.

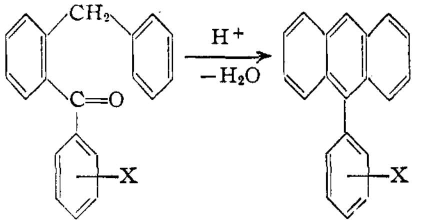
[2] This paper has been abstracted from the Doctorate thesis presented by James G. Van Oot to the Virginia Polytechnic Institute in December, 1950.

[3] C. K. Bradsher and F. A. Vingiello, This Journal, **71**, 1434 (1949).

[4] F. A. Vingiello and J. G. Van Oot, *ibid.*, **73**, 5070 (1951).

the first step and in the opposite direction as regards the second step. We also have data which we believe sheds light on the "anomalous" rate of cyclization of 4′-fluoro-2-benzylbenzophenone reported by Bradsher and Vingiello.[3]

The procedure used in our rate studies is the same as that used by the previous workers[3]; two of their rate measurements have been repeated in order to guarantee that our results should be strictly comparable to those already available.



I II

TABLE I

RATES OF CYCLIZATION OF SOME *o*-BENZYLPHENONES (I)

X	*K*, (hr.$^{-1}$) × 10^{-2}
4′-CH_3	4.2*[a]
4′-Br	4.2*
4′-Cl	4.1*
4′-F	2.8*
4′-CF_3	9.3
H	4.4*
3′-CH_3	4.4
3′-Br	5.0
3′-Cl	5.3
3′-F	5.3
3′-CF_3	6.4

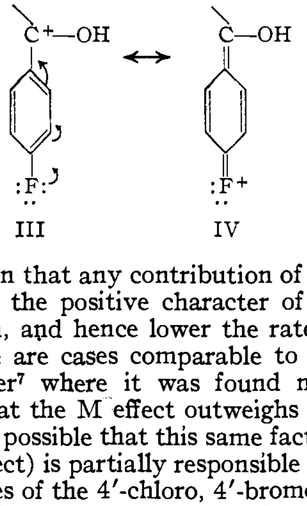
[a] Values taken from Bradsher and Vingiello's work[3] are indicated with an asterisk.

One of the outstanding features of this series of rate constants is that there is very little numerical difference in the rate constants when substituents with such widely differing electronic effects as the trifluoromethyl group and the methyl group are present. These groups, located in the ring into which cyclization takes place [*e.g.*, compounds 2-(3′-trifluoromethyl)-benzophenone and 2-(3′-methylbenzyl)-benzophenone] cause a tremendous retarding and accelerating effect, respectively.[4] This fact corroborates the statement of Bradsher and Vingiello[3] that there are involved in the cyclization of *o*-benzylphenones two steps of opposing electrical requirements.

There is, however, a general trend in the reaction rates of the ketones studied in the present work which shows that perhaps the second step in the reaction is slightly more susceptible to the effects of the substituents than the first step is. As we change from the unsubstituted ketone to the ketones containing the halogens in the 3′-position, we find a slight increase in the rate. This can be interpreted as being caused by the −I nature of the substituent. With the 3′-trifluoromethyl group, there is a stronger −I effect, and correspondingly a slight increase in the over-all rate of cyclization. When this trend was noted, it was predicted that the 4′-trifluoromethyl group, which exerts not only a strong −I effect but also a strong −T effect,[5] would cause a larger jump in the rate of cyclization; this prediction was borne out by experiment. It is also to be noted that the rates for ketones in which a +T effect can operate are lower than for ketones in which a +T effect cannot operate.

When the work which preceded the present investigation was done the significance of the lower rate shown by the 4′-fluoro ketone was not clear.[3] The results of the present work show that fluorine in the 3′-position actually increases the rate of cyclization slightly. Since the tautomeric effect does not operate significantly from the 3′-position, it follows that the presence of the tautomeric effect operating from the 4′-position would seem to be the cause of the lower rate.

Step two might be considered a nucleophilic attack by the carbon atom at the ortho position of the ring into which cyclization occurs on the carbonium ion, and hence the +E effect of the fluorine would not be called into play since it would not aid the reaction. The +M effect would serve to impede this step.[6] The +M effect of the fluorine atom is larger than that of the other halogens in a neutral molecule. Moreover, in the present case, we find that there is a full positive charge on the carbonium ion, and the +M effect is undoubtedly considerably greater here than in the neutral molecule. This would result in a relatively significant contribution of the form on the right below (IV) to the carbonium ion



III IV

It can be seen that any contribution of such a form would lower the positive character of the central carbon atom, and hence lower the rate of cyclization. There are cases comparable to this quoted by Alexander[7] where it was found necessary to postulate that the M effect outweighs the I effect.

It may be possible that this same factor (increase in the M effect) is partially responsible for the similarity in rates of the 4′-chloro, 4′-bromo, 4′-methyl and unsubstituted benzophenones, by acting in the halogenated compounds to nullify the large −I effect.

Since the M effect of the methyl group is of hyperconjugative origin, its magnitude is quite small by comparison to that of the halogens. This fact, and the fact that the +E effect is not called into play in the second step of the reaction, may be the reasons why no difference is noted in the rates of cyclization of the 3′- and 4′-methyl ketones.

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(5) J. D. Roberts, R. L. Webb and E. A. McElhill, THIS JOURNAL, **72**, 408 (1950).

(6) E. A. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., Second Edition, 1949.

(7) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 89 and 238.

Acknowledgment.—This work was made possible by a grant from the Research Corporation of New York to the senior author who gratefully acknowledges this aid.

Experimental

The procedure for cyclization, the cyclizing medium and the apparatus used in the rate studies were the same as were used by Bradsher and Vingiello[3] except that a thermostatically controlled oil-bath was used as the constant temperature unit.

3′-Bromo-2-benzylbenzophenone (I, X = 3′-Br).—A Grignard reagent was prepared from 2.4 g. (0.1 mole) of magnesium, a crystal of iodine and 24.7 g. (0.1 mole) of *o*-bromodiphenylmethane in 150 ml. of anhydrous ether. The reaction mixture was stirred and heated under reflux for 4 hr. The Grignard reagent was siphoned with nitrogen pressure into a separatory funnel and added dropwise, with stirring, to 25 g. (0.09 mole) of *m*-bromobenzoyl bromide in 400 ml. of anhydrous benzene The benzene solution was maintained at 40–50° during this addition. The mixture was heated under reflux for two hours allowing the ether to distil off and then decomposed with ice and cold HCl. The benzene layer was separated and the aqueous layer was extracted with fresh benzene. The combined benzene layers were washed with water, then with 10% NaOH, and finally with water. The benzene solution was dried over calcium sulfate, concentrated and fractionated. The material distilling at 220–221° (3 mm.) weighed 15.4 g. (46%).

3′-Trifluoromethyl-2-benzylbenzophenone (I, X = 3′-CF_3).—A Grignard reagent was prepared in ether from 38.3 g. (0.17 mole) of *m*-bromobenzotrifluoride and 4.1 g. (0.17 mole) of magnesium. The reaction started within two minutes, and required only half an hour of heating under reflux before all the magnesium had disappeared. A solution of 11 g. (0.057 mole) of *o*-cyanodiphenylmethane in benzene was added rather rapidly and the ether allowed to distil off. The benzene solution was heated under reflux with stirring for 15 hr. The solution turned dark red soon after the addition of the nitrile and remained that way overnight, with no sign of a precipitate. The solution was then cooled and decomposed with the theoretical amount of cold 20% ammonium chloride solution. The benzene solution was poured off, and the residue extracted twice with fresh benzene, and the combined benzene solutions heated under reflux with stirring, in contact with 200 ml. of 2 *N* HCl for 22 hr. The benzene layer was then separated, washed with 10% NaOH, then with 2 *N* HCl, finally twice with water and dried over $CaSO_4$, concentrated and fractionated. The material distilling at 195–197° (3 mm.) weighed 18.7 g. (96.5%).

The remaining new ketones were prepared in a similar way and are recorded in Table II together with further details.

9-(3-Methylphenyl)-anthracene (II, X = 3′-CH_3).—Considerable difficulty was experienced in the cyclization of 3′-methyl-2-benzylbenzophenone in order to obtain a crystalline product. Several attempts to crystallize the oil obtained from the usual cyclization procedure were unsuccessful. The use of phosphoric acid in acetic acid gave no crystalline product. Chromatography on alumina using hexane gave a colorless fluorescent oil from which no crystalline material could be obtained. The successful attempt is described now. Two grams of the ketone was heated in 125 ml. of the standard cyclizing acid for 49 hr. On cooling this solution slowly a heavy black oil separated. This oil was thick enough to filter off; it was washed once with water, dissolved in ethanol, and the solution treated with charcoal. The yellow solution was concentrated, and then cooled in a Dry Ice–acetone-bath. This treatment precipitated a tan material which, when it warmed up to room temperature, was quite gummy. The mother liquor from this treatment, standing at room temperature overnight deposited amber crystals. Using these as seed, no subsequent difficulty was encountered in getting the anthracene to crystallize directly from the cyclizing mixture. Recrystallized four times from a mixture of formic acid and ethanol, the anthracene melted at 97–98.5°.

The remaining new anthracenes were prepared in the usual way (by heating them under reflux with standard cyclizing acid) and are recorded in Table III together with further details.

Table II

New Ketones (I)

X	Yield, %	B.p., °C.	Mm.	Analyses, %[8] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
3′-CH_3	68	205–206	3	88.08	87.98	6.33	6.46
3′-Br	46	220–221	3	68.39	67.98	4.32	4.42
3′-Cl	59	222–224	5	78.30	78.50	4.93	5.09
3′-F	36	174–176	1	82.74	82.78	5.21	5.53*
3′-CF_3	97	195–198	3	74.11	74.16	4.44	4.63
4′-CF_3	61	169–170	0.9	74.11	74.20	4.44	4.52

Table III

New Anthracenes (II)

X	Yield, %	M.p., °C.[9]	Analyses, %[8] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
3′-CH_3	67	97 – 98.5	93.99	93.84	6.01	6.10
3′-Br	92	135 –137	72.08	72.37	3.93	3.96
3′-Cl	74	133 –134	83.19	83.36	4.53	4.72
3′-F	60	143.5–144.5	88.21	88.22	4.81	4.78*
3′-CF_3	67	116 –117	78.18	78.45	4.07	4.08
4′-CF_3	61	205 –206	78.18	78.50	4.07	4.13

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(8) All the analyses were carried out by the Micro-Tech Laboratories, Skokie, Illinois, except the ones marked with an asterisk which were done by the Oakwold Laboratories, Alexandria, Virginia.

(9) All melting points are corrected.