at 2 mm. and melted at 99–102°. The alcohol was not further purified but was characterized by the preparation of the following derivatives.

The phenylurethan was prepared by the reaction of the alcohol with phenyl isocyanate. The crude product (m.p. 141–144°) was recrystallized from benzene–petroleum ether (90–100°), m.p. 145–146°. An authentic sample of the phenylurethan of 3-hydroxynortricyclene was prepared according to the procedure of Roberts[2a] and co-workers, m.p. 146.5–147.5°. A mixture of the two samples melted at 145–146°.

The *p*-phenylazobenzoate was prepared by the reaction of the alcohol (0.2 g.) with *p*-phenylazobenzoyl chloride (0.4 g.) in pyridine. The crude product (0.6 g.) was dissolved in anhydrous ether and the solution was passed through a column of alumina. The ester was eluted by the ether very rapidly and was recovered by the evaporation of the ether solvent. The orange *p*-phenylazobenzoate obtained from the chromatogram melted at 115–117°. The product melted at 119.5–120.5° after recrystallization from aqueous ethanol and did not depress the melting point of an authentic sample obtained from 3-hydroxynortricyclene.[2a]

2-Phenyl-3-nitrobicyclo[2,2,1]heptene-5 (X) was prepared in 88% yield by allowing two moles of freshly distilled cyclopentadiene to react with ω-nitrostyrene for four hours at the reflux temperature of the mixture; b.p. 136–138° (1–2 mm.), $n^{20}\mathrm{D}$ 1.5641 (reported[6] b.p. 145° (1 mm.)).

2-Phenyl-3-amino[2,2,1]heptene-5 (XII).—The amine (b.p. 124–128° (7 mm.), $n^{25}\mathrm{D}$ 1.5694, 12 g., 40% yield) was obtained from X (36 g.) by reduction[7] with iron filings (35 g.) in hydrochloric acid (10 ml.). A sample boiling at 90° (1 mm.) had the following composition.

Anal. Calcd. for $C_{13}H_{15}N$: C, 84.28; H, 8.16. Found: C, 84.00; H, 8.18.

The benzenesulfonamide of XII was recrystallized from aqueous ethanol and melted at 165–166°.

Anal. Calcd. for $C_{19}H_{19}O_2SN$: C, 70.13; H, 5.89. Found: C, 70.13; H, 6.03.

2-Phenyl-3-aminobicyclo[2,2,1]heptane (XI). 1. From XII.—The reduction of 7.4 g. of XII was effected in 200 ml. of 95% ethanol using platinum oxide catalyst and hydrogen at atmospheric pressure. The saturated amine was distilled to give 6 g. (81%) of product as a colorless oil; b.p. 96–97° (1 mm.), $n^{30}\mathrm{D}$ 1.5560.

Anal. Calcd. for $C_{13}H_{17}N$: C, 83.37; H, 9.15. Found: C, 83.30; H, 9.24.

The benzenesulfonyl derivative of XI melted at 136–137.5° after two crystallizations from aqueous ethanol.

Anal. Calcd. for $C_{19}H_{21}O_2SN$: C, 69.69; H, 6.47. Found: C, 69.41; H, 6.60.

2. From X.—The catalytic hydrogenation of X (0.049 mole) to XI using Raney nickel catalyst (2 g.) in 95% ethanol solvent (120 ml.) was complete after three hours at 100–110°. The initial pressure was established by admitting carbon dioxide until the pressure was 500 p.s.i. and then hydrogen until the pressure was 2500 p.s.i. The amine was distilled at reduced pressure to yield 6.3 g. (69%) of product; b.p 138–142° (11–12 mm.), $n^{25}\mathrm{D}$ 1.5558. The identity of this amine to that prepared by the reduction of XII was established by a comparison of their benzenesulfonamide derivatives; m.p. and mixed m.p. 136–137.5°.

2-Phenyl-3-dimethylaminobicyclo[2,2,1]heptane.—The methylation of XII (12 g.) was effected using formaldehyde and formic acid according to the general procedure described by Clarke.[8] The tertiary amine (9.5 g.) was obtained as a colorless oil; b.p. 107–113° (3–4 mm.), $n^{29}\mathrm{D}$ 1.5398. Redistillation of this amine through a six-inch Vigreux column gave 8.0 g. (57%) of product boiling at 120–124° (3–4 mm.), $n^{25}\mathrm{D}$ 1.5412–1.5427.

For analytical analysis a sample of the amine was converted into its picrate. The picrate was crystallized from 95% ethanol and melted at 159–162°, with softening at 150°.

Anal. Calcd. for $C_{21}H_{24}N_4O_7$: C, 56.75; H, 5.44. Found: C, 56.86; H, 5.68.

The Hoffman Degradation of 2-Phenyl-3-dimethylamino-[2,2,1]heptane.—The Hoffmann methylation and degradation was carried out in the usual way, and two products were obtained: (1) trimethylamine (identified as its picrate) and (2) a neutral substance, presumably 2-phenylbicyclo[2,2,1]heptene-2, which decomposed upon attempted distillation at atmosphereic pressure.

Attempts to hydrolyze X by the addition of an aqueous solution of its sodium salt to cold dilute sulfuric acid resulted in an oil, b.p. 130–149° (10–11 mm.), which failed to react with sodium bisulfite and which did not form a phenylhydrazone. The product appeared to be principally unchanged X; whether an inversion in configuration of the nitro group occurred was not established.

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(6) C. F. H. Allen, A. Bell and J. W. Gates, *J. Org. Chem.*, **8**, 373 (1948).

(7) *Cf.* K. Johnson and Ed. F. Degering, THIS JOURNAL, **61**, 3194 (1939), for a more complete description of the method.

(8) H. T. Clark, H. B. Gillespie and S. Z. Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

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

The Synthesis and Cyclization of Some 2-(Substituted Benzyl)-benzophenones[1,2]

BY FRANK A. VINGIELLO AND JAMES G. VAN OOT[3]

It has been shown that one of the important factors concerning the rate of cyclization of 2-benzylbenzophenones is the electron density at the ortho position of the benzene ring into which cyclization occurs.

The mechanism of the cyclization of *o*-benzylbenzophenones is pictured by Bradsher and Vingiello[4] as proceeding 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) shedding of a proton; and finally (4) transannullar elimination of water. In conclusion these authors stated that the rate of cyclization, for similar experimental conditions, depends on several factors, one of these being the electron density at the ortho position of the benzene ring into which cyclization takes place. We now have experimental evidence to substantiate this statement since we have synthesized and measured the rates of cyclization of several 2-benzylbenzophenones substituted in the benzyl ring. The syntheses and cyclizations are shown below.

The procedure used in our rate studies is the same as that used by Bradsher and Vingiello[4]; and indeed, we repeated two of their rate measure-

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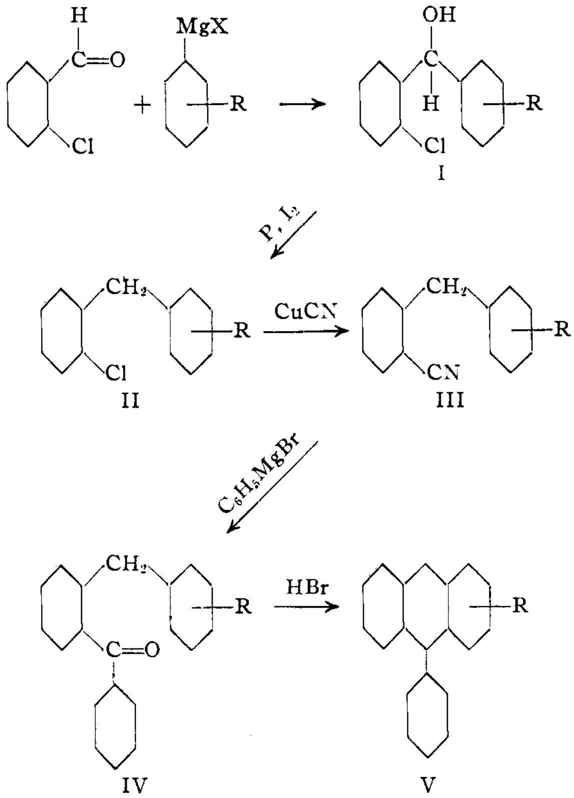
(1) Presented before the Division of Organic Chemistry at the 119th Meeting of the American Chemical Society, Boston, Massachusetts, April, 1951.

(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) E. I. du Pont de Nemours and Company, Wilmington, Delaware.

(4) C. K. Bradsher and F. A. Vingiello, THIS JOURNAL, **71**, 1434 (1949).



ments in order to guarantee that our results should be strictly comparable to those already available.

TABLE I

RATES OF CYCLIZATION AT 117.5° OF SOME 2-BENZYLBENZOPHENONES SUBSTITUTED IN THE BENZYL RING

Compound IV	K, (hr.$^{-1}$) × 10^{-2}
R = H	4.4
R = 2'-CH_3	15.4
R = 3'-CH_3	200.
R = 4'-CH_3	13.8
R = 3'-CF_3	Does not cyclize in 10 days
R = 4'-F	Does not cyclize in 3 days

TABLE II

R	Yield, %	M.p., °C.[7]	B.p., °C.	Mm.	Analyses, %[5] Calcd. C	Calcd. H	Found C	Found H
2'-CH_3	67	113.5–114.5	179–184	5	72.25	5.63	72.84	5.73
3'-CH_3	76	56.5–57.5	161–163	2	72.25	5.63	72.36	5.76
3'-CF_3	93		174–176	6	58.65	3.52	58.20	3.59
4'-F	72		175–178	7	65.97	4.26	66.00	4.18

In general, it appears that the variations in rates of cyclization may be adequately interpreted in terms of the known electronic effects of the substituents if one keeps in mind that the reaction involves an electrophilic substitution on the aromatic ring.[5]

In order to prove that the 3'-CF_3 and the 4'-F compounds (liquids) did not cyclize, the liquids recovered from the attempted cyclizations were oxidized to their corresponding diketones (solids) in almost quantitative yield.

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[6,7]

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[4] except that a thermostatically controlled oil-bath was used as the constant temperature unit.

2-Chloro-4'-methyldiphenylcarbinol (I, R = 4'-CH_3).—A Grignard reagent was prepared from 6 g. (0.25 mole) of magnesium and 42.7 g. (0.25 mole) of *p*-bromotoluene in 600 ml. of dry ether. The yield was considerably improved when the flask was baked out before the reaction using a free flame with a stream of dry nitrogen passing through the system, and the amount of coupling was reduced by using the dilute solution above. After the heat of reaction had subsided, the Grignard solution was heated under reflux for one hour, then cooled to room temperature. A solution of 28 g. (0.2 mole) of *o*-chlorobenzaldehyde in 300 ml. of dry ether was added rather rapidly, thus maintaining a vigorous rate of refluxing. The mixture was then heated under reflux for 16 hours, and cooled in an ice-bath, and decomposed to the equivalence point with ice-cold 20% ammonium chloride solution. The ether solution was poured off, the residue extracted once with fresh ether, and the combined ether solutions concentrated, and the residue fractionated. After a forerun of 8 g. which consisted mostly of solid coupling product, the colorless viscous oil boiling at 173–175° (6 mm.)[8] weighed 29.8 g. (64%).

The other carbinols were prepared in a similar way.

2-Chloro-4'-methyldiphenylmethane (II, R = 4'-CH_3).—A slurry of 6.4 g. (0.16 mole) of red phosphorus, 6.4 g. of iodine and 29.8 g. (0.13 mole) of 2-chloro-4'-methyldiphenylcarbinol in 300 ml. of glacial acetic acid was heated under reflux, with stirring, for 36 hours. The cooled mixture was filtered, the flask and filter rinsed with fresh acid, the solution diluted with 800 ml. of water, and the acid neutralized with solid sodium carbonate. The solution was extracted with ether, and the ether solution washed twice with 10% sodium hydroxide, twice with water, and finally dried over "Drierite." The ether was removed by distillation, and the residue fractionated, the colorless liquid distilling at 146–147° (6 mm.) weighed 16.4 g. (59%).

Anal. Calcd. for $C_{14}H_{13}Cl$: C, 77.59; H, 6.05. Found: C, 77.85; H, 6.01.

The other diphenylmethanes were prepared in a similar way.

2-Cyano-4'-methyldiphenylmethane (III, R = 4'-CH_3).—A mixture of 25.5 g. (0.12 mole) of 2-chloro-4'-methyldiphenylmethane, 13 g. of cuprous cyanide, a small crystal of anhydrous cupric sulfate in about 25 ml. of dry pyridine, was heated in a metal-bath maintained at 250° for 32 hours, with an air-cooled condenser to allow the slow evaporation of the pyridine. The reaction mixture was then cooled and

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(5) It might be thought that since the 4'-methyl compound has two ortho positions into which cyclization could take place, it would cyclize faster than the 2'-methyl compound which has only one such ortho position. An examination of the results shows that the 2'-methyl compound cyclizes slightly faster. With the present information, it is only possible that there is some preferred orientation in the molecule in the case of the 2'-methyl compound.

(6) 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, Va.

(7) All melting points are corrected.

(8) W. O. Cohen, *Rec. trav. chim.*, **38**, 117 (1919), prepared this carbinol by reducing the corresponding ketone with aluminum amalgam, and gave a melting point of 67°. The attempt made here to crystallize the oil was unsuccessful.

TABLE III

NEW *o*-CHLORODIPHENYLMETHANES

R	Yield, %	B.p., °C.	Mm.	Analyses, %			
				Calcd.		Found	
				C	H	C	H
2′-CH_3	77	159–159.5	9	77.59	6.05	77.87	6.13
3′-CH_3	78	151–153	8	77.59	6.05	77.80	6.10
4′-CH_3	59	146–147	6	77.59	6.05	77.85	6.01
3′-CF_3	80	134–135	4	62.12	3.72	62.00	3.82
4′-F	66	149–154	11	70.75	4.57	70.75	4.55

subjected to a crude distillation in a von Braun flask (4 mm.). The distillate was poured into about 150 ml. of 1:1 ammonium hydroxide, stirred well and extracted with ether. The combined ether extracts were washed twice with 2 *N* hydrochloric acid, then with water, and finally dried over "Drierite." The ether was distilled off, leaving a clear mobile liquid which was fractionated. The portion distilling at 165–171° (4.5 mm.) weighed 14.7 g. (60%).

The other nitriles were prepared in a similar way.

TABLE IV

NEW *o*-BENZYLBENZONITRILES

R	Yield, %	B.p., °C.	Mm.	Analyses, %[4]			
				Calcd.		Found	
				C	H	C	H
2′-CH_3	77	174–175	6	86.91	6.32	86.86	6.42
3′-CH_3	67	167–169	5	86.91	6.32	87.05	6.72
4′-CH_3	60	165–171	5	86.91	6.32	87.20	6.28*
3′-CF_3	79	135.5–136	1	68.96	3.86	69.08	3.98
4′-F	62	171–173	8	79.60	4.77	80.00	4.73

2-(4′-Methylbenzyl)-benzophenone (IV, R = 4′-CH_3).—A Grignard reagent was prepared from 23.6 g. (0.15 mole) of bromobenzene and 3.6 g. (0.15 mole) of magnesium in about 100 ml. of dry ether. Most of the ether was distilled off, and to the cooled solution was added 10.6 g. (0.05 mole) of 2-cyano-4′-methyldiphenylmethane in 100 ml. of dry benzene. The mixture was heated under reflux with stirring for about 18 hours. It was then cooled and decomposed with the equivalent amount of cold 20% ammonium chloride solution. The benzene solution was poured off and the residue extracted with fresh benzene. The combined benzene solutions were heated with about 250 ml. of 2 *N* hydrochloric acid under reflux, with stirring, for 17 hours. The benzene layer was separated, washed with 10% sodium hydroxide, then with water, and finally dried over calcium chloride. The benzene was removed at atmospheric pressure, and the residue fractionated. The portion distilling at 194–196° (1 mm.) weighed 13.6 g. (95%).

The other benzophenones were prepared in a similar way.

TABLE V

NEW *o*-BENZYLBENZOPHENONES

R	Yield, %	M.p., °C.[7]	B.p., °C.	Mm.	Analyses, %[4]			
					Calcd.		Found	
					C	H	C	H
2′-CH_3	84	85–86	228–230	5	88.08	6.33	88.48	6.31
3′-CH_3	86		193–196	1	88.08	6.33	87.98	6.47
4′-CH_3	95		194–196	1	88.08	6.33	88.42	6.36
3′-CF_3	84		185–186.5	1	74.11	4.44	73.74	4.55
4′-F	89		193–195	2	82.74	5.21	83.07	5.14

3-Methyl-10-phenylanthracene (V, R = 3-CH_3).—A solution of 0.5 g. of 2-(4′-methylbenzyl)-benzophenone in 20 ml. of stock acid mixture[9] was heated under reflux for 15 hours. The solution was cooled yielding 0.41 g. of white crystals (88%). Recrystallized from ethanol the crystals melted at 117–118°.

The other anthracenes were prepared in a similar way.

TABLE VI

NEW HYDROCARBONS

R	Yield, %	M.p. °C[7]	Analyses, %[5]			
			Calcd.		Found	
			C	H	C	H
1-CH_3	90	104–104.5	93.99	6.01	93.70	6.14
3-CH_3	88	117–118	93.99	6.01	93.86	6.05

3-Trifluoromethyl-2′-benzoylbenzophenone. A. From **2-(3′-Trifluoromethylbenzyl)-benzophenone.**—This ketone (0.415 g.) was added to 10 ml. of glacial acetic acid and 0.5 g. of sodium dichromate. The mixture was warmed to effect solution, and then cooled. Then 1 ml. of concd. sulfuric acid was added. When the exothermic reaction subsided, the mixture was heated under reflux for about 10 minutes, with occasional shaking. The mixture was then cooled and poured onto about 50 g. of ice in 100 ml. of water, and allowed to stand for about 15 minutes. The gummy precipitate was collected, washed with water, and recrystallized from 50% ethanol; 0.35 g. of crystalline material was formed and, on concentrating the mother liquor, another 0.06 g. of crystals was obtained: total yield 0.41 g. (94%) of white needles, m.p. 107.5–108°.

Anal. Calcd. for $C_{21}H_{13}O_2F_3$: C, 71.19; H, 3.70. Found: C, 71.20; H, 3.77.

(B) From **2-(3′-Trifluoromethylbenzyl)-benzophenone after the Attempted Cyclization.**—Two grams of this ketone was heated under reflux in 80 ml. of stock acid mixture for 246 hours, then cooled and poured into 200 ml. of water, and the acid neutralized with 30% sodium hydroxide. The organic matter was extracted with ether, clarified with a minimum of charcoal, dried over calcium chloride, and the solution concentrated. The residual oil was oxidized by the same procedure as that described above, 0.97 g. of oil giving a total of 0.87 g. of the diketone (87%). This material gave no depression in melting point when mixed with the authentic sample prepared above.

4-Fluoro-2′-benzoylbenzophenone. A. From **2-(4′-Fluorobenzyl)-benzophenone.**—This ketone (0.88 g.) was oxidized as previously described to give 0.87 g. (95%) of white crystalline material melting at 99–100°.[10]

Anal. Calcd. for $C_{20}H_{30}O_2F$: C, 78.94; H, 4.30. Found: C, 79.26; H, 4.36.

(B) From **2-(4′-Fluorobenzyl)-benzophenone after the Attempted Cyclization.**—This ketone was heated under reflux in the stock acid solution for 72 hours and worked up and oxidized as described previously yielding 95% of the corresponding diketone, shown to be identical to the above by mixed m.p.

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[9] A stock acid mixture was prepared by adding 700 ml. of redistilled glacial acetic acid to a mixture of 166.4 ml. of 48% hydrobromic acid and 43.6 ml. of distilled water. This is the same solution that Bradsher and Vingiello[3] used.

[10] This compound was first prepared by Mr. R. A. Kasey, Jr., M.S. Thesis, Virginia Polytechnic Institute, 1950.