The ester was treated with the methyl Grignard reagent to give the desired carbinol in 50% yield. Because of the low yields in the various stages of this synthesis, an alternative synthetic route was examined.

Cumene was treated with bromine in the presence of finely divided iron at −5° to 0°.[44] From 500 g. of the mixed monobromocumenes prepared in this manner, fractionation produced 29 g. of *o*-bromocumene, b.p. 71–72° (3 mm.), $n^{20}\mathrm{D}$ 1.5411.[45] This product was converted into the Grignard reagent and treated with acetone. A 60% yield of the carbinol was obtained (Table III). No depression in m.p. was observed in a comparison of the products from the three different routes.

***o*-*t*-Butylphenyldimethylcarbinol.**—Bromination of *p*-nitro-*t*-butylbenzene[14a] gave 45–62% yields of 2-bromo-4-nitro-*t*-butylbenzene, m.p. 93–94°.[46] This product was reduced catalytically (74% yield) to 2-bromo-4-amino-*t*-butylbenzene, b.p. 125° (1 mm.), $n^{20}\mathrm{D}$ 1.5828, which was deaminated with hypophosphorus acid to give *o*-bromo-*t*-butylbenzene, b.p. 93° (8 mm.), $n^{20}\mathrm{D}$ 1.5442.

The Grignard reagent from *o*-bromo-*t*-butylbenzene was treated with acetone. There was isolated from the reaction product *t*-butylbenzene, mesityl oxide and triacetone alcohol, m.p. 57–58°.[47]

The alcohol was finally synthesized by the following procedure. Under a nitrogen atmosphere 100 ml. of ether and 0.69 g. (0.10 g. at.) of lithium wire was placed in the usual Grignard-type apparatus and a solution of 11 g. (0.05 mole) of *o*-bromo-*t*-butylbenzene in 50 ml. of ether was added over a period of 1 hr. Reflux was maintained for 3 hr., until all the metal had gone into solution. The solution was cooled to −75° and a solution of 3.0 g. (0.05 mole) of acetone in 20 ml. of ether was added. The reaction mixture was permitted to warm to room temperature, hydrolyzed with ice and worked up in the usual manner. The product was distilled at 1 mm. until no more material distilled with a flask temperature of 100°. The residue in the flask was dissolved in pentane and cooled. A crop of white crystals was obtained, m.p. 123–128°. A second crop was obtained. The yield was 125 mg., 1.3% of theory. The product could be readily purified (m.p. 127.5–128.0°) by sublimation at 100° at 1 mm. A second preparation gave the product in a yield of 1.1%.

Conversion of Carbinols into Tertiary Chlorides.—In a small round bottom flask, 2–5 g. of the carbinol was placed and hydrogen chloride passed over the material until the mixture separated into two layers. The lower layer of aqueous hydrochloric acid was removed with a fine capillary, the chloride was treated with a crystal of calcium chloride, and dissolved hydrogen chloride removed by pumping for a few minutes. The product was utilized for the rate measurements without further purification. In the case of phenyldimethylcarbinyl chloride, which could be purified by distillation at low pressures, it was observed that identical rate constants were obtained with material distilled in this way as with the crude reaction product prior to distillation.

Kinetic Measurements.—Temperatures were controlled to ±0.02°. The solvent, 100 ml., was placed in a long necked flask and brought to reaction temperature. Approximately 1 ml. of the tertiary chloride was added, mixed thoroughly and 5-ml. aliquots removed at appropriate intervals of time. The aliquots are run into 100 ml. of cold (0°) dry acetone to stop the reaction and free hydrogen chloride titrated with 0.03 *N* sodium hydroxide using methyl red as the indicator. The reaction mixture was usually permitted to stand overnight (at least ten times the calculated half-life) to obtain the aliquot for the "infinity" titer. Some of the reactions were quite fast and considerable attention to detail was required to obtain reproducible results.

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[44] R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2876 (1949).

[45] Literature[44] value $n^{20}\mathrm{D}$ 1.54084.

[46] J. B. Shoesmith and A. Mackie, *J. Chem. Soc.*, 2334 (1928).

[47] E. E. Connolly, *ibid.*, 338 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Rates of Solvolysis of α- and β-Naphthyldimethyl- and -monomethylcarbinyl Chlorides. Steric and Electronic Effects of the Naphthalene System[1,2,3]

BY Y. OKAMOTO AND HERBERT C. BROWN

RECEIVED AUGUST 29, 1956

α- and β-naphthyldimethylcarbinyl chlorides and α- and β-naphthylmonomethylcarbinyl chlorides were synthesized and their rates of solvolysis in 80% and 90% aqueous acetone were determined. The rate of solvolysis of β-naphthyldimethylcarbinyl chloride in 90% acetone at 25° is faster than that of phenyldimethylcarbinyl chloride by a factor of 4.0. The increase is attributed to the greater capacity of the naphthyl system to accommodate an electron deficiency. The same effect is observed in β-naphthylmonomethylcarbinyl chloride which undergoes solvolysis in 80% acetone at a rate 9.0 times greater than that of the corresponding phenyl derivative. No significant difference in rates is observed in the solvolysis of α- and β-naphthyldimethylcarbinyl chlorides. It is concluded that steric inhibition of resonance due to the *peri* position must be reducing the expected greater capacity of the α-naphthyl system to stabilize the electron deficient transition state. In the case of the secondary derivatives, α- and β-naphthylmonomethylcarbinyl chlorides, the steric effect is less and the expected enhancement in rate of the α-naphthyl over the β-naphthyl derivative ($k^{\alpha}/k^{\beta} = 2.5$) is observed.

The substitution chemistry of the naphthalene system offers many points of both theoretical and practical interest.[4] Unfortunately, the available data are essentially qualitative in nature. In contrast to benzene derivatives no measurements are now available on the partial rate factors for electrophilic substitution in the naphthalene molecule.

In the previous paper[5] it was pointed out that the solvolysis data for *m*- and *p*-tolyldimethylcarbinyl chlorides agree with the empirical relationship previously proposed for the partial rate factors governing electrophilic substitution in the toluene system.[6] It appeared possible, therefore, to attain some quantitative information as to the relative reactivities of the α- and β-positions of naphthalene in electrophilic reactions by studying the solvolysis of α- and β-naphthyldimethylcar-

[1] Directive Effects in Aromatic Substitution. XI.

[2] Supported by the Petroleum Research Fund of the American Chemical Society.

[3] Based upon a thesis submitted by Y. Okamoto, in 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[4] L. F. Fieser, "Theory of the Structure and Reactions of Aromatic Compounds," Chapter 3 in "Organic Chemistry," Vol. I, edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943.

[5] H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, THIS JOURNAL, **79**, 1897 (1957).

[6] H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953); H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2300 (1955); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956).

Table I

Rate Constants and Derived Data for the Solvolysis of the Aryldimethylcarbinyl Chlorides in Aqueous Acetone[a]

Aryl group	Rate constants, k_1 (sec.$^{-1}$ × 10^5) 0° (80%)	0° (90%)	15° (90%)	25° (90%)	Rel. rate, 25°	$E_{act.}$	log A	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Phenyl		0.611		12.6	1.00				
α-Naphthyl	28.9	2.47	16.6	51.7	4.1	19.8	11.2	19.2	− 9.2
β-Naphthyl	33.1	2.51	16.5	50.6	4.0	19.5	11.0	19.0	−10.0

[a] 80 and 90% aqueous acetone by volume as indicated.

Table II

Rate Constants and Derived Data for the Solvolysis of the Arylmonomethylcarbinyl Chlorides in 80% Aqueous Acetone[a]

Aryl group	Rate constant, k_1 (sec.$^{-1}$ × 10^7) 25°	40°	50°	Rel. rate, 25°	E_{act}	log A	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Phenyl	5.86[b]			1.00				
α-Naphthyl	134	761	2310	23	21.7	11.1	21.3	−9.6
β-Naphthyl	52.5	319	981	9.0	22.3	11.1	21.8	−9.4

[a] By volume. [b] Extrapolated from rate constants in 50, 60 and 70% aqueous acetone.

binyl chlorides. Certain unexpected results led us to extend the study to the α- and β-naphthylmonomethylcarbinyl chlorides.

Results and Discussion

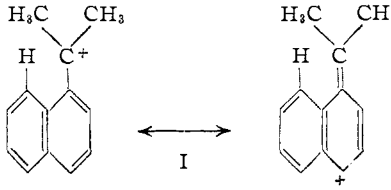
α- and β-naphthyldimethylcarbinols were prepared by the reaction of methylmagnesium iodide with α- and β-naphthylmethyl ketones. The tertiary alcohols were converted into the chlorides and the rates of hydrolysis run in both 80 and 90% aqueous acetone. The results are summarized in Table I along with rate constants for phenyldimethylcarbinyl chloride included for comparison.

β-Naphthyldimethylcarbinyl chloride solvolyzes at a rate greater than that of the corresponding phenyl derivative by a factor of 4.0. This must mean that the β-naphthyl system is better able to stabilize an electron deficient center than the simple phenyl system. On this basis it can be predicted that the rate of electrophilic substitution in the *beta* position of naphthalene will be considerably greater than that of benzene.

m-Tolyldimethylcarbinyl chloride solvolyzes at a rate twice that of the phenyl derivative. It may therefore be estimated that if m_f represents the ratio of the rate for substitution in one of the *meta* positions of toluene as compared to one position in benzene, the relative rate of substitution in one of the *beta* positions of naphthalene will be m_f^2.

The available evidence is that the rate of substitution in the *alpha* position of naphthalene must be far greater than that of the *beta* position.[4] Consequently, the marked similarity in the rates of solvolysis of α- and β-naphthyldimethylcarbinyl chlorides is puzzling.

Baddeley and co-workers have shown in a number of instances that substituents which hinder the attainment of coplanarity in the carbonium ion greatly hinder the rates of solvolysis of aralkyl halides.[7] In the preceding paper it was shown that a similar effect was present in *o*-tolyldimethylcarbinyl chloride and the effect increased as the *o*-methyl group was replaced by ethyl and isopropyl groups.[5] A possible explanation for the behavior of α-naphthyldimethylcarbinyl chloride appeared to lie in a steric interaction of the *peri* position with the coplanar arrangement preferred by the incipient carbonium ion (I).

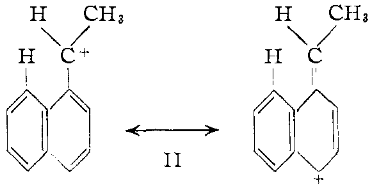

I

To test this interpretation we converted the α- and β-naphthylmethyl ketones to the carbinols (by reduction with sodium borohydride) and then into the corresponding chlorides with hydrogen chloride.

Rates of solvolysis were measured in 80% aqueous acetone. The results are summarized in Table II.

Here also the β-naphthyl derivative solvolyzed at a faster rate than the phenyl compound. The increase in the relative rate factor from 4.0 observed in the tertiary derivative (Table I) to 9.0 for the secondary compound presumably reflects the greater demand for electrons made by the secondary carbonium ion as compared to the more stable tertiary derivative.

As anticipated in these secondary derivatives with their lower steric requirements (II), the α-naphthyl compound undergoes solvolysis at a rate considerably greater than that of the β- (Table II).


II

This appears to be a general phenomenon. The available data indicate that the relative rates of solvolysis of α- and β-naphthyl derivatives, $ArCR_2Cl$, varies in a regular and consistent manner with the increasing steric requirements of the groups R (Table III).

It appears, therefore, that the present approach may serve as a satisfactory technique for obtaining a quantitative measure of the reactivity of the β-naphthyl position and similar unhindered positions. Extension of the technique to hindered

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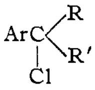
(7) G. Baddeley, J. Chadwick and H. T. Taylor, *J. Chem. Soc.*, 2405 (1954); 448 (1956).

TABLE III

RATIO OF SOLVOLYSIS RATES OF α- AND β-NAPHTHYL DERIVATIVES,



$ArC(R)(R')Cl$

Substituents R	R'	k_1 (α-naphthyl) / k_1 (β-naphthyl)
H	H	6.9[a]
H	Me	2.5[b]
Me	Me	1.0[c]
Ph	Ph	0.71[d]

[a] In mixed solvent (54.1% formic acid, 39.8% dioxane and 6.1% water) at 25°; H. Hannaert, Ph.D. Thesis, University of Brussels Library, 1954. [b] In 80% aqueous acetone at 25°; this study. [c] In 90% aqueous acetone at 25°; this study. [d] In 40% ethanol–60% diethyl ether at 0°; A. C. Nixon and G. E. K. Branch, THIS JOURNAL, **58**, 492 (1936).

positions in aromatic systems will require some method of eliminating the steric complication.

Experimental Part

Phenyldimethylcarbinyl Chloride.—α-Methylstyrene, b.p. 163–164° (742 mm.), was converted into the chloride by treatment with hydrogen chloride. The product distilled at 56–58° (1.5 mm.), n^{20}D 1.5210.

α-Naphthyldimethylcarbinyl Chloride.—α-Acetonaphthone, b.p. 158–160° (4 mm.), was treated with methylmagnesium iodide and the crude carbinol was recrystallized from hexane. The product, m.p. 86–87°, was obtained in 57.5% yield.[8] The carbinol was converted into the tertiary chloride by treatment in methylene chloride solution with hydrogen chloride at 0°. The solution was dried, the methylene chloride removed under reduced pressure and the product used directly in the rate measurements.

β-Naphthyldimethylcarbinyl Chloride.—The reaction of methylmagnesium iodide with β-acetonaphthone, m.p. 53–54°, yielded β-naphthyldimethylcarbinol, m.p. 63–64.5°, in 71% yield.

Anal. Calcd. for $C_{13}H_{14}O$: C, 83.8; H, 7.58. Found: C, 83.8; H, 7.73.

The carbinol was transformed into the chloride as described above for the *alpha* isomer. The chloride, recrystallized from ligroin, decomposed at 70°.

Phenylmethylcarbinyl Chloride.—Acetophenone, b.p. 203° (750 mm.), was converted into α-phenylethyl alcohol, b.p. 77–78° (8 mm.), n^{20}D 1.5274, in 95% yield by reduction with sodium borohydride. The alcohol was treated with dry hydrogen chloride to form the chloride, b.p. 63–64° (3 mm.), n^{20}D 1.5269.

α-Naphthylmethylcarbinyl Chloride.—α-Acetonaphthone was converted into the carbinol,[9] m.p. 62–64°, in 72% yield by reduction with sodium borohydride. It was treated with hydrogen chloride to form the chloride, b.p. 125–126° (2 mm.), in a yield of 75%.

β-Naphthylmethylcarbinyl Chloride.—β-Acetonaphthone was reduced to the carbinol,[10] m.p. 76–77°, in 82% yield. The carbinol was transformed into the chloride, m.p. 68–69°,[11] in 61% yield.

Kinetic Measurements.—The procedure utilized for the determination of the rate constants was similar to that previously described, with one exception. It proved convenient to utilize as indicator a solution of three parts of brom cresol green and 2 parts of methyl red in ethanol solution. The solvents used were prepared by mixing appropriate volumes of acetone and water, *i.e.*, 80% aqueous acetone is prepared by mixing 2 parts by volume of water with 8 parts by volume of acetone.

A typical kinetic run for the solvolysis of α-naphthyldimethylcarbinyl chloride is reported in Table IV.

TABLE IV

RATE DATA FOR THE SOLVOLYSIS OF 2-CHLORO-2-(α-NAPHTHYL)-PROPANE IN 90% AQUEOUS ACETONE SOLUTION AT 25°

Time, min.	x, ml.	$a - x$, ml.	k_1, hr.$^{-1}$
0	0.793	2.877	
6	1.295	2.375	1.91
12	1.690	1.980	1.87
23	2.270	1.400	1.88
30	2.510	1.160	1.82
37	2.743	0.927	1.84
47	2.983	.687	1.83
57	3.170	.500	1.84
72	3.350	.320	1.83
85	3.450	.220	1.82
∞	3.670		
		Average	1.85[a]

[a] A duplicate study of this compound at 25° yielded k_1 1.87 hr.$^{-1}$.

The rate of solvolysis of α-phenylethyl chloride in 80% aqueous acetone was desired for comparison. Since the reaction in this solvent is very slow, the rate was measured at 25° in 50% (k_1 0.130, 0.133 hr.$^{-1}$), 60% (k_1 0.0311 hr.$^{-1}$) and 70% (k_1 0.00599, 0.00608 hr.$^{-1}$) aqueous acetone. The logarithm of these rate constants was plotted against the quantity $(D-1)/(2D+1)$.[12] The resulting linear relationship was extrapolated to give a value of k_1 0.00211 hr.$^{-1}$ (5.86×10^{-7} sec.$^{-1}$). The rate constants are summarized in Tables I and II.

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[8] F. W. Kay and A. Morton, *J. Chem. Soc.*, **105**, 1565 (1914), report m.p. 86°.

[9] R. H. Pickard and J. Kenyon, *ibid.*, **105**, 115 (1914), report m.p. 66°.

[10] T. A. Collyer and J. Kenyon, *ibid.*, 676 (1940), report m.p. 71–72°.

[11] J. W. Cook and C. L. Hewett, *ibid.*, 1098 (1933), report 67–68°.

[12] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 419.