heated by means of an oil-bath at 135°. The slurry of sodium acetone oxime was added in small portions over 1 hr. and the subsequent mixture stirred and heated for 24 hr. After cooling, the reaction mixture was filtered to remove the insoluble solids. The brown filtrate was distilled through a 42-cm. Vigreux column and the fraction boiling above 92° (20 mm.) collected. The lower boiling portion was distilled again and additional material boiling above 92° (20 mm.) collected. Approximately 40–50 g. was accumulated in this manner. Two more distillations gave 22–38 g. (29–51%), b.p. 40–45° (1.5 mm.), 98–99° (20 mm.), $n^{25}D$ 1.4259, of a colorless oil.

Anal. Calcd. for $C_9H_{19}NO_3$: C, 57.1; H, 10.1. Found: C, 56.5; H, 9.9.

The unchanged bromoacetal can be recovered from the lower boiling distillates with little trouble

A. The acid hydrolysis of acetone O-(2,2-(diethoxy)-ethyl)-oxime (VII) in the presence of an excess of acetone: In a solution of 35 ml. of acetone and 19 ml. of 1% hydrochloric acid were dissolved 2 g. (0.0212 mole) of acetone O-(2,2-(diethoxy)-ethyl)-oxime (VII). After refluxing for 1 hr., the solution was cooled in an ice-bath and then neutralized with anhydrous potassium carbonate to *p*H 7.5–8.5. The acetone was removed by evaporation *in vacuo* at temperatures not over 45°. The residue was chilled in an ice-bath and extracted with three to four portions of ether. Anhydrous sodium sulfate was used as a salting-out agent to ensure complete extraction. The ether extracts were dried with anhydrous sodium sulfate. After evaporation of the ether, 1.3–2.5 g. of a slightly yellow oil was obtained. This crude product decomposed even on vacuum distillation, and it was not possible to obtain pure material. However, the oil gave the typical tests expected for an aldehyde (Schiff and Tollens tests) and is probably crude **acetone O-formylmethyloxime** (VIII). Attempts to prepare several aldehyde derivatives were all unsuccessful. Treatment with dilute aqueous hydrochloric acid gave a white insoluble precipitate similar in its thermal properties to the polymeric material described in part B.

B. The acid hydrolysis of acetone O-(2,2-diethoxyethyl)-oxime with aqueous hydrochloric acid in the absence of acetone: When the acetal, acetone O-(2,2-(diethoxy)-ethyl)-oxime (VII), was hydrolyzed in 1:1 or 2:1 1% aqueous hydrochloric acid–95% ethanol in the absence of acetone by refluxing for 15–60 minutes, a cream colored to white gummy insoluble material was deposited. On drying over P_2O_5 *in vacuo*, it became more friable and amorphous. Two grams of the acetal gave about 0.55 g. of this material. The sample analyzed below melted over the range 90–190° dec. and gave positive Schiff and Tollens tests.

Anal. Calcd. for $C_2H_3NO(=NOCH_2CH=)$: C, 42.4; H, 5.3. Found: C, 42.9; H, 5.9.

This analysis suggests the material to be polymeric in nature and composed of the units $=NOCH_2CH=$ since the carbon and hydrogen content of possible monomeric products are much higher than that found for the material isolated.

Serine (IX).—The attempted synthesis of 3-aminoöxy-2-aminopropanoic acid *via* the Strecker reaction and the isolation of serine (IX): Material believed to be crude acetone O-formylmethyl-oxime (VIII) (4.1 g., 0.0356 mole) prepared as described above was added to 7.2 g. of 10% methanolic ammonia. To the resulting solution was added ammonium chloride (2.86 g., 0.534 mole) dissolved in 17 ml. of water. The mixture was heated at 80° for 4 hr. The dark red solution was cooled and then added to 50 ml. of concentrated hydrochloric acid (hood) and allowed to sit overnight. The next day, the solution was heated on the steam-bath for 3.5 hr.; additional acid (20 ml.) was added and heating continued for 6 hr. longer. The solution was then evaporated to dryness *in vacuo* and the residue redissolved in water and filtered to remove a black insoluble material. The clear brown colored filtrate was passed through an IRA-400 strongly basic anionic exchange resin to remove the anions from the solution. The resin was then eluted with 2 *N* hydrochloric acid to give an amino acid effluent which was identified by means of the ninhydrin test. The fractions containing the amino acid were evaporated to dryness and treated with silver carbonate (0.1068 equiv.) to remove chloride. After removing silver chloride, the filtrate was saturated with hydrogen sulfide and filtered again. The final solution was evaporated to dryness and 50 ml. of absolute alcohol added. The cloudy solution was placed in the refrigerator. The next day a slightly yellow crystalline material was removed and immediately recrystallized from water–isopropyl alcohol. A crystalline material, 0.46 g. (10.3% yield of serine), m.p. 175–275° dec., was thus obtained. The material was again recrystallized from water–isopropyl alcohol.

A paper chromatogram using the phenol–water system with an authentic sample of serine showed the material to be predominantly serine with only a trace of some other material which also gave a ninhydrin test.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF CALIFORNIA

Substitution of Polynuclear Aromatic Compounds. I. The Friedel–Crafts Benzoylation of Naphthalene

BY FREDERICK R. JENSEN

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Excess benzoyl chloride added to the reaction mixture does not change the rate of the aluminum chloride-catalyzed benzoylation of toluene or *p*-xylene or the amount of *ortho* isomer (9.7%) formed in the reaction with toluene. In the reaction with naphthalene, the addition of excess benzoyl chloride to the reaction mixture causes a large decrease in the rate of reaction and an increase in the amount of β-ketone (less hindered) formed. It has been suggested previously that the change in isomer distribution in the reaction with naphthalene is due to the excess benzoyl chloride complexing with the attacking group to form a more bulky group. The results indicate that this postulate can be true only if the attacking groups are different in the reactions with toluene (and *p*-xylene) and naphthalene. It is shown that rearrangement is not responsible for the differences in isomer distribution.

Introduction

In 1886, Claus and Feist[1] reported that the α-ketone is exclusively formed in the Friedel–Crafts acetylation of naphthalene. Ten years later Rousset[2] reported that both the α- and β-isomers are formed. Since that time the isomer distribution in this reaction has been investigated by numerous workers, but many of the results are confusing and contradicting.[3] It is now recognized that the addition of a variety of substances, which complex strongly with aluminum chloride, to the reaction

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[1] A. Claus and P. Feist, *Ber.*, **19**, 2896 (1886).

[2] L. Rousset, *Bull. soc. chim.*, **15**, 58 (1896).

[3] An excellent review of the experimental work is given in the A.C.S. Monograph, C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1941, p. 271. Reviews are also given by G. Lock, *Monatsh.*, **74**, 77 (1943), and by H. F. Bassilios, S. M. Makar and A. Y. Salem, *Bull. soc. chim.*, 72 (1954).

mixture, or their use as solvent, results in a decrease of the amount of α-isomer formed.[4,5] Typical compounds that have been used are nitrobenzene and excess acid halide.

It was first suggested by Fieser[5] that these added substances complex strongly with the attacking species making a bulkier attacking group, and hence by a steric effect, more of the less hindered isomer (β-isomer) results. In the present work this hypothesis was tested by studying the effect of adding these substances on the absolute rates of reaction in hindered and non-hindered positions of naphthalene and benzene derivatives. If a steric effect is responsible for the differences, the rate of reaction should also be affected by the addition of these compounds. Also, the possibility that the differences result from rearrangement was investigated.

Benzoyl chloride was selected as the acid chloride since a convenient method is available for determining its concentration during the course of a Friedel–Crafts reaction.[6] Conditions were selected under which the reaction mixtures are homogeneous at all times. Benzoyl chloride was also selected as the added agent because its concentration is known to affect the isomer distribution in the reaction with naphthalene, it can be conveniently removed from the reaction mixture and in order to keep the system as simple as possible. If nitrobenzene were used, the situation might be greatly complicated since it is probably more basic than benzoyl chloride and would preferentially complex with the aluminum chloride. Under these conditions, the kinetics of the reaction would be much more complex.

Results and Discussion

Attempts to Rearrange α-Naphthyl Phenyl Ketone.—The solubilities of Friedel–Crafts complexes are greater in more polar solvents. Since less of the α-isomer is obtained in polar solvents, the differences in isomer distribution might be due to isomerization of the α-ketone under conditions where the product remains in solution.

It was found that α-naphthyl phenyl ketone does not isomerize under conditions more severe than usually used in this reaction. The experiments were carried out only under conditions where decomposition does not occur. α-Naphthyl phenyl ketone was recovered unchanged from a 0.6 *M* solution of its 1:1 complex with aluminum chloride in nitrobenzene (saturated with hydrogen chloride) at 35° after one week. Similarly no isomerization took place after heating the 1:1 complex (0.634 *M*) in ethylene chloride (saturated with hydrogen chloride and sealed in ampoules) at 50° for 30 days. The recovery from the nitrobenzene solutions was 96–98% and quantitative from the ethylene chloride solutions. The infrared spectra of the recovered and starting ketones were identical, and the isomerization was less than 2% (experimental error).

These results were further checked by withdrawing samples from a reaction mixture at different lengths of time, using nitrobenzene as solvent. With initial naphthalene and benzoyl chloride–aluminum chloride complex concentrations 1.1 *M*, the product at 35° was 32 ± 1% β-ketone after 2 min., 16 min. and 46 hours with yields 71, 82 and 94%, respectively. These results indicate that isomerization is negligible during an actual reaction.

Isomerization of hindered aromatic ketones occurs if the ketones are melted with excess aluminum chloride and sodium chloride.[7]

Effect of Excess Benzoyl Chloride in the Reactions with Toluene, *p*-Xylene and Naphthalene.—The steric hindrance in the *ortho* position of toluene and the α-position of naphthalene are probably of the same order of magnitude. Any effects due to complexing of excess benzoyl chloride with the attacking group would be expected to appear in the reactions with either hydrocarbon provided the mechanisms of the reactions with the two hydrocarbons are the same. The formation of a bulkier complex would cause the rate of reaction to decrease in all positions but more in hindered positions. The effect was investigated first with toluene since it is a simpler compound than naphthalene.

In non-polar solvents, and for individual experiments, the Friedel–Crafts reaction follows second-order kinetics according to expression 1, where Ar–H may be one of a variety of benzene derivatives.

$$\text{rate} = k_2[\mathrm{C_6H_5COCl:AlCl_3}][\text{Ar–H}] \qquad (1)$$

However, the value of k_2 depends on the initial concentration of the complex.[8–12]

For the reaction with toluene and using ethylene chloride as solvent, second-order kinetics were obtained according to expression 1, with k_2 dependent on the initial concentration of the complex but independent of the toluene concentration.

When excess benzoyl chloride was added to the reaction mixture, the value of k_2 and the amount of *ortho* isomer[13] remained constant (Table I). These results clearly indicate that the excess benzoyl chloride does not combine to an appreciable extent with the attacking group to form a more bulky complex.

A more sensitive compound with which to study the effect is *p*-xylene, since all the positions are hindered. The value of k_2 obtained in the absence of excess benzoyl chloride was 2.05×10^{-3} l. mole^{-1} sec.$^{-1}$ and with excess benzoyl chloride concentra-

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[4] (a) M. Chopin, *Bull. Soc. Chim.*, **35**, 610 (1924); (b) G. Baddeley, *J. Chem. Soc.*, S-99 (1949). For other references see the review articles given in ref. 3.

[5] L. F. Fieser, "The Chemistry of Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, N. Y., 1936, p. 74.

[6] F. R. Jensen, Ph.D. Thesis, Purdue University, 1955.

[7] G. Baddeley and A. G. Pendleton, *J. Chem. Soc.*, 807 (1952).

[8] B. D. Steel, *ibid.*, 1470 (1903).

[9] S. C. J. Olivier, *Rec. trav. chim.*, **37**, 205 (1918).

[10] L. F. Martin, P. Pizzolate and L. S. McWaters, Jr., THIS JOURNAL, **57**, 2584 (1935).

[11] H. Ulich and P. V. Fragstein, *Ber.*, **72**, 620 (1939).

[12] Recently F. Smeets and J. Verhulst, *Bull. soc. chim. belg.*, **63**, 439 (1954), reported that *k* is essentially independent of the concentration of the complex at 35° when Ar–H is benzene (solvent). These results are not consistent with the results reported earlier by Olivier[9] for the same reaction at 30°, and although we have been able to reproduce Olivier's results, we have not been able to reproduce the results of Smeets and Verhulst. Smeets and Verhulst followed the reaction by titrating the evolved hydrogen chloride, while in Olivier's and in the present work, the reactions were followed by determining the rate of disappearance of benzoyl chloride.

[13] Unless otherwise indicated, the yields in all reactions were above 98%.

TABLE I

DATA SHOWING THAT ADDED BENZOYL CHLORIDE DOES NOT COMBINE WITH THE ATTACKING SPECIES TO FORM A BULKIER COMPLEX IN THE REACTION WITH TOLUENE

Solvent, CH_2ClCH_2Cl; temp., 25°; $[C_6H_5CH_3] = [C_6H_5COCl:AlCl_3] = 0.222$ *M*

$[C_6H_5COCl]$, *M*	% *ortho*	10^3k_2 (l. mole^{-1} sec.$^{-1}$)^a
0	9.4	1.12
0.050	9.7	1.08
.100	10.2	1.09
.222	9.5	1.11
.450	10.1	1.12
.827	9.4	
1.65	10.3	
3.31	9.0	

^{a} The average reproducibility of the rate constants was 3%.

tion 0.273 *M* the value of k_2 obtained was 2.16×10^{-3} l. mole^{-1} sec.$^{-1}$ (ethylene chloride as solvent, temp. 25°, and with initial concentrations of the complex and *p*-xylene 0.222 *M*). Since the addition of excess benzoyl chloride does not decrease the rate of reaction, the excess benzoyl chloride must complex with the attacking group in this reaction to a negligible extent.

It is known that excess benzoyl chloride affects the isomer distribution in the reaction with naphthalene.[4b] The effects of adding benzoyl chloride on the rate of reaction and isomer distribution were studied in detail.

Unexpectedly, the reaction with naphthalene

$$\text{rate} = k_3[C_6H_5COCl:AlCl_3]^2[C_{10}H_8] \qquad (2)$$

was found to follow third-order kinetics.[14] The value of k_3 is not entirely independent of the initial concentration of the complex. If excess benzoyl chloride is present, k_3 decreases markedly and the amount of the less hindered β-ketone[13] increases in the manner shown in Table II.

TABLE II

THE EFFECT OF ADDING EXCESS BENZOYL CHLORIDE ON THE ISOMER DISTRIBUTION AND THE RATE OF BENZOYLATION OF NAPHTHALENE

Solvent, CH_2ClCH_2Cl; temp., 25°; $[C_6H_5COCl:AlCl_3] = [C_{10}H_8] = 0.222$ *M*

$[C_6H_5COCl]$, *M*	% β-ketone	$10k_3{}^a$	$10^2k_\alpha{}^b$	$10^2k_\beta{}^c$
0	20	3.6	2.9	0.72
0.050	27	2.5	1.8	.67
.100	30	2.2	1.5	.66
.222	34	1.9	1.3	.65
.300	36	1.7	1.1	.61
.400	38	1.6	1.0	.61
.82	40			
1.65	43			
3.66	43			

^{a} l.^{2} mole^{-2} sec.$^{-1}$. ^{b} $k_\alpha = k_3 \times$ % α-ketone. ^{c} $k_\beta = k_3 \times$ % β-ketone.

The addition of a small amount of benzoyl chloride causes relatively large changes in the amount of β-ketone formed and the rate constant (k_3). This is probably the most striking feature of the results. With progressively larger amounts of benzoyl chloride, the changes become smaller until the values become essentially constant. The results indicate that k_3 does not vary in a simple fashion as the benzoyl chloride concentration is changed.

In the reaction with toluene the results were easily reproducible to within 3%. This is not the case with naphthalene, however, and the results are very sensitive to the presence of impurities. For example, with a standard solution of the complex, $C_6H_5COCl:AlCl_3$, in ethylene chloride which was slightly colored, the rate constant in the reaction with toluene was identical with that obtained previously, while the rate constant in the reaction with naphthalene was about 15% less than that obtained with colorless standard solutions. Any trace of impurity which complexes strongly with aluminum chloride would be expected to free benzoyl chloride from the complex, $C_6H_5COCl:AlCl_3$, and the effect would be the same as adding a very small amount of benzoyl chloride to the reaction mixture.

The rate constants for the reaction in the α-positions (k_α) and β-positions (k_β) are listed in Table II. According to the data k_α and k_β both decrease when excess benzoyl chloride is present. The decrease in k_β is small and was always observed in a number of experiments. Because the system is very sensitive to impurities, it is difficult to place absolute limits of error on these values.

The results with naphthalene are in accord with the postulate that the excess benzoyl chloride complexes with the attacking group but are not proof since there are several other reasonable explanations for the results. (Investigations are currently being carried out along several lines.) The results with toluene and *p*-xylene clearly indicate that the excess benzoyl chloride does not complex with the attacking group in these reactions. Therefore, *if the postulate is correct, the attacking groups must be different in the reactions with toluene (and p-xylene) and naphthalene.* There is no direct evidence indicating whether or not the attacking groups are the same; however, in the absence of any evidence, it would seem to be more reasonable to expect the attacking groups to be the same.

The results indicate that there are differences in the details of the mechanisms of the reactions, but the differences could be at various stages in the reactions. Although the kinetic orders are different for the reactions with toluene and naphthalene, this does not necessarily imply that the attacking groups are different in the two reactions since the details of the reactions may differ after the attacking group and aromatic compound have come together to form the σ-complex. Also, there is evidence that the difference in the kinetic order may be due to the complexity of the kinetics.[14]

One possible explanation for the results is that the ability of various positions in polynuclear aromatic compounds to bear a positive charge varies greatly with the environment, and hence the rela-

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[14] The change in k_2 with concentration in the reaction with toluene in non-polar solvents can be rationalized on the basis that there are several terms in the rate expression, one of which is a third-order term, and that these reactions are subject to general acid catalysis by Lewis acids.[6] A possible explanation for the apparent difference in kinetic order obtained in the reactions with toluene and naphthalene is that the second-order terms predominate in the reaction with toluene and the third order term predominates in the reaction with naphthalene. The results of a detailed study of this and related reactions will be reported later.

tive reactivities of the various positions may not be a function of structure alone. In the present case this may be the result of a difference of stabilization of the σ-complexes in the α- and β-positions by the polar benzoyl chloride molecules. There are no data available which indicate whether the effects studied are unique to the Friedel–Crafts reaction or are general for electrophilic substitution of naphthalene.

Relationship between the Concentration of the Complex and the Isomer Distributions.—The problem is complicated by the finding that the isomer distributions in the reactions with both naphthalene and toluene depend on the initial concentration of the complex (Table III).[13] If the *naphthalene concentration is greater than the concentration of the complex*, the isomer distribution is independent of the naphthalene concentration (Tables III and V).

TABLE III

EFFECT OF THE CONCENTRATION OF THE COMPLEX ON THE ISOMER DISTRIBUTIONS IN THE REACTIONS WITH NAPHTHALENE AND TOLUENE

Solvent, CH_2ClCH_2Cl; temp., 25°; $[C_6H_5CH_3] = [C_{10}H_8] = 0.222$ *M*

[$C_6H_5COCl{:}AlCl_3$,] *M*	% β-Ketone	[$C_6H_5COCl{:}AlCl_3$], *M*	% *ortho*
0.0500	35	0.05	7
.100	32	.10	8.1
.222	20	.222	9.4
.400	10	.60	11.7
.500	10		
1.95	7		

Since the rate constants in the reactions with naphthalene and toluene depend on the initial concentration of the complex, it is not unexpected that the isomer distributions also depend on its concentration.

The data for naphthalene in Table III suggest one reason for the contradictory results obtained by previous workers. The isomer distribution will be appreciably different depending on whether the naphthalene is added to the complex or *vice versa*. Also, if the complex is added to the naphthalene, it is predicted that the isomer distribution will depend on the rate of addition.

It is hoped that a system can be found in which the above complication does not exist.

Investigation of the Possibility that the Varying Isomer Distribution May Be Due to Complex Formation between Naphthalene and Benzoyl Chloride.—One possible explanation for the results is that the excess benzoyl chloride forms a stable complex with naphthalene, and the reaction is forced to take place with this adduct. There is no report in the literature of complex formation between naphthalene and benzoyl chloride, but there is evidence which indicates that nitrobenzene, which causes a similar change of the isomer distribution, and naphthalene form an addition compound.[15]

The above explanation was tested in a simple fashion. If the proposed explanation is correct, the amount of β-ketone formed should depend on the relative concentrations of the excess benzoyl chloride and naphthalene. At high naphthalene concentrations and low benzoyl chloride concentrations, the isomer distribution should be essentially the same as in the absence of benzoyl chloride since the reaction would take place almost entirely with uncomplexed naphthalene. In testing this hypothesis it is necessary that the initial concentration of the complex, $C_6H_5COCl{:}AlCl_3$, is kept constant and that the same amount of complex reacts in each experiment. This was accomplished by using a low concentration of the benzoyl chloride–aluminum chloride addition compound and always having it as the limiting reagent.

The results are in Table IV and show that the explanation which was proposed above is incorrect. If a stable adduct is formed between the benzoyl chloride and naphthalene and if the formation of this adduct is responsible for the differences in the isomer distribution, then it should be possible to calculate maximum possible values for the amount of β-ketone formed at various benzoyl chloride concentrations. Typical calculations are given in the next paragraph.

TABLE IV

EFFECT ON THE ISOMER DISTRIBUTION OF CHANGING THE CONCENTRATION OF EXCESS BENZOYL CHLORIDE AT VARIOUS NAPHTHALENE CONCENTRATIONS

Solvent, CH_2ClCH_2Cl; temp., 25°; $[C_6H_5COCl{:}AlCl_3] = 0.224$ *M;* the yields were greater than 95% in all reactions

[$C_{10}H_8$], *M*	[C_6H_5COCl], *M*	% β-ketone
0.224	0	20
.224	0.10	29
.224	.40	38
.224	1.20	43
.450	0	20
.450	0.10	28
.450	.40	38
.450	1.20	40
1.35	0	20
1.35	0.1	24
1.35	.4	36
1.35	1.20	39

From the data in Table II and under the hypotheses assumed above, it is seen that if all the naphthalene is complexed with benzoyl chloride, the maximum amount of β-ketone formed is 43%, and if *none* is complexed, the amount of β-ketone formed is 20%. In the experiments (Table IV) in which the initial naphthalene concentration was 1.35 *M*, the concentration of the naphthalene was always greater than 1.12 *M*. For benzoyl chloride concentrations of 0.1 and 0.4 *M*, the amounts of free naphthalene (uncomplexed with benzoyl chloride) would be more than 1.02 and 0.72 *M*, respectively, at all times during the reactions. Then assuming that the reaction with the naphthalene–benzoyl chloride complex is one-half that with the free naphthalene (*from the data in Table II it is seen to be less than one-half*), it is calculated that less than 21 and 24% of the β-ketone would be formed at benzoyl chloride concentrations 0.1 and 0.4 *M*, respectively. Since the amounts of β-ketone formed exceed these values, the postulate must be invalid.

The yields in the reactions with high naphthalene concentrations were 95–96%. The excess naph-

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(15) G. Briegleb and J. Kambeitz, *Z. physik. Chem.*, **B25**, 253 (1934).

TABLE V

DATA SHOWING THE RELATIONSHIP BETWEEN THE RELATIVE BENZOYL CHLORIDE AND NAPHTHALENE CONCENTRATIONS AND THE ISOMER DISTRIBUTION AT HIGH CONCENTRATIONS OF THE COMPLEX

Solvent, CH_2ClCH_2Cl; temp., 25°

$[C_6H_5COCl:\text{-}AlCl_3]$, *M*	$[C_{10}H_8]$, *M*	$[C_6H_5COCl]$, *M*	% β-ketone
1.95	0.100	0	6.7
1.95	.100	0.05	6.8
1.95	.100	.10	6.8
1.95	.100	.40	(9.8)
1.95	.250	0	6.6
1.95	.250	0.05	6.9
1.95	.250	.10	7.7
1.95	.250	.40	10.3
1.95	.60	0	9.8
1.95	.60	0.10	10.6
1.95	.60	.40	11.2
1.95	.60	.80	13.8
1.70	1.03	0	10.6
1.70	1.03	0.09	12.3
1.70	1.03	.35	14.8
1.70	1.03	1.40	21.3

thalene was removed from the ketone by steam distillation, and some of the ketone was lost in this operation.

The first attempts to detect a relationship between the relative benzoyl chloride and naphthalene concentrations and the isomer distribution were carried out at high concentrations of the complex, $C_6H_5COCl:AlCl_3$. These experiments failed because the isomer distribution depends on the amount of complex, $C_6H_5COCl:AlCl_3$, reacted. The results[13] are shown in Table V and are interesting because at high concentrations of the complex, $C_6H_5COCl:AlCl_3$, the amount of β-isomer formed is relatively insensitive to the benzoyl chloride concentration. This suggests a relationship exists between the relative benzoyl chloride and complex concentrations and the isomer distribution; however, this would be very difficult to establish in the present system because the isomer distribution depends on the initial concentration of the complex.

Experimental

Purification of Starting Materials. Benzoyl Chloride.—Aluminum chloride (3 mole %) was dissolved in the benzoyl chloride, and toluene (2 mole %) was added. After allowing the reaction mixture to stand 6 hr., the unreacted benzoyl chloride was distilled off at 0.5 mm. It was next fractionated three times through a 30 stage Odershaw perforated plate column at 6 mm. The center three-fourths was retained in each fractionation.

Aluminum Chloride.—The aluminum chloride (Baker Chemical Company) was purified by subliming three times down a straight Pyrex tube (with constrictions) which contained a small amount of nitrogen gas (50 mm.). In the first sublimation, the aluminum chloride was sublimed through a section of granular aluminum metal, which was supported with plugs of glass wool. After the final sublimation and before sealing the tube off, aluminum chloride was sublimed back down the tube until the remaining material formed a loose plug.

In order to remove the aluminum chloride from the tube, the tube is scratched and then the scratch touched with a hot rod in such a manner that the tube cracks but does not open. The tube may then be weighed, the tube tapped slightly to open, and after removing the aluminum chloride, the empty tube weighed. Using these techniques, it is possible to prepare very pure samples of aluminum chloride and weigh and transfer them without bringing them into contact with air. Only samples of aluminum chloride which were entirely colorless and crystalline were used in the experiments.

Naphthalene.—The naphthalene was purified by distillation and then six recrystallizations from ethanol.

Ketone Standard Samples.—The standard samples were prepared by treating the corresponding methylbenzoyl chloride or naphthoyl chloride with benzene using aluminum chloride as the catalyst. The compounds were purified by recrystallization from ethanol. The *o*-tolyl phenyl ketone was recrystallized at low temperature, since it melts below room temperature.

The solid ketones had the following melting points (cor.): α-naphthyl phenyl ketone, m.p. 75.4–75.9° (lit.[5] m.p. 75.5°); β-naphthyl phenyl ketone, m.p. 82.0–82.3° (lit.[5] m.p. 82.0°) and *p*-methylbenzophenone, m.p. 55.8–56.6°. The infrared spectrum of the liquid *o*-methylbenzophenone was identical with that of the pure isomer.[16]

Ethylene Chloride.—Commercial ethylene chloride was shaken with portions of technical grade fuming sulfuric acid until darkening no longer occurred. The chloride was washed with water and allowed to stand over NaOH pellets for several days. Finally, it was fractionated twice from CaH_2 through a 44″ vacuum jacketed column (i.d. 24 mm.), which was packed with $^3/_{16}$″ diam. glass helices. The material boiled at a constant temperature (b.p. 83.3° (752 mm.) uncor.). The reflux ratio was greater than 25:1. Some of the material was heated over the CaH_2 at total reflux for 4 days. No detectable temperature drop occurred, which indicates CaH_2 does not dehydrohalogenate ethylene chloride under these conditions.

Infrared Analysis.—The isomer distributions were determined by infrared analysis using a Baird Associates double beam recording spectrophotometer. The analyses were carried out using 0.1 mm. matched NaCl cells and CS_2 as solvent. For each separate series of experiments, fresh solutions of the standard samples were prepared and new plots of log I_0/I *vs.* concentration were made over the concentration range encountered in the experiments (total concentration, about 0.25 g. ketones/5 ml. CS_2 solution).

In the reaction with toluene, only the *ortho* and *para* isomers were determined. The *meta* isomer, which is characterized by a peak at 8.3 μ,[16] was present to the extent of 1–2% in all experiments. Over a period of three months and for a large number of experiments, 4 out of 5 values from different reactions (same conditions but different standard solutions) checked to within 1%.

Compound	Peak (μ)
p-Tolyl phenyl ketone	12.8[16]
o-Tolyl phenyl ketone	13.2[16]
α-Naphthyl phenyl ketone	8.0, 12.9
β-Naphthyl phenyl ketone	13.3

In order to isolate the reaction product when ethylene chloride was used as solvent, the reaction mixture (usually 5-ml. sample) was shaken with 20 times its volume of water, and then this mixture was extracted three times with chloroform. The solvents were removed under reduced pressure and the residue was refluxed for 1 hr. with 20 ml. 1 *M* NaOH solution. If a large excess of naphthalene was present, it was removed at this stage by steam distillation.

The solution, after cooling, was extracted three times with distilled methylene chloride. The samples were placed in weighing bottles and the methylene chloride was removed under reduced pressure in a vacuum desiccator. The bottles were brought to constant weight at 4 mm. In blank runs using 0.25-g. samples of the purified ketones, the ketones were recovered in each case to within 1 mg.

In the experiments using nitrobenzene as solvent, the reactions were carried out on a much larger scale. The product was isolated using a very simple procedure. The reaction mixture was washed with water in order to remove the aluminum chloride. Without drying the solution, the water, benzoyl chloride, nitrobenzene and traces of benzoic acid and benzoic anhydride were removed at atmospheric pressure by distillation through a 20″ heated Vigreux column. The residue was distilled at reduced pressure and a fraction, b.p. 216–218° (10 mm.), was collected.

Techniques.—The techniques used to prepare, store and

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(16) H. L. Young, Ph.D. Thesis, Purdue University, 1956.

transfer the materials under entirely anhydrous conditions were developed previously,[6] with some improvements, and will be described elsewhere.[14,17]

Rate Measurements.—Standard solutions of the complex, $C_6H_5COCl:AlCl_3$, were prepared by adding aluminum chloride to a mixture of benzoyl chloride in ethylene chloride, and this mixture was stirred (using a magnetic stirrer) until the aluminum chloride dissolved. Data are reported only for experiments in which colorless standard solutions were used and which remained colorless for at least 4–5 days. Portions of this solution were diluted as necessary with ethylene chloride, and the reactions were started by adding the hydrocarbon to the diluted solution. The reaction mixtures for toluene and *p*-xylene were colorless. Upon addition of naphthalene to the diluted standard solution, the mixture turned orange and gradually darkened upon standing. The standard solutions and reaction mixtures were protected at all times by a blanket of dry nitrogen gas. The reaction vessels were placed in a stirred water-bath which was controlled to ±0.01°.

In the analytical procedure, the reactions were quenched by shaking with ice-water. The organic compounds were extracted with chloroform and 80% pyridine–water mixture was added to the combined extracts. After allowing to stand, a large amount of ethanol was added, and the benzoic acid and pyridine hydrochloride were titrated with standard base. The procedure was developed previously[6] and the details will be reported elsewhere.[17]

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[17] Forthcoming papers by H. C. Brown and F. R. Jensen.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

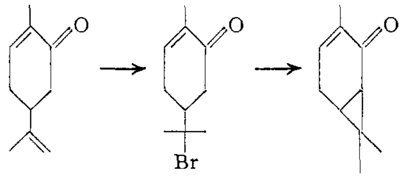
Mechanism of the Carvone Hydrobromide → Eucarvone Transformation

BY EUGENE E. VAN TAMELEN, JOHN MCNARY AND FRANK A. LORNITZO

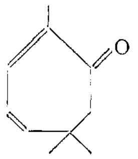
RECEIVED SEPTEMBER 24, 1956

A detailed mechanism for reactions of the carvone hydrobromide → eucarvone type is supported by various pieces of evidence, including the isolation of bicyclo[4.1.0]-3-hepten-2-one intermediates.

In 1894, Baeyer[1] described the properties of the elimination product, later called eucarvone, which results when carvone hydrobromide is treated with alkali. Following the establishment of the correct structure (I) for carvone, Baeyer proposed,[2] by analogy with the dihydrocarvone hydrobromide → carone transformation, that eucarvone possessed the structure III ("carenone"). It remained, however, for Wallach[3] to gather evidence which led to assignment of the correct structure (IV).

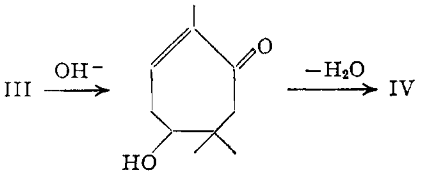


I II III

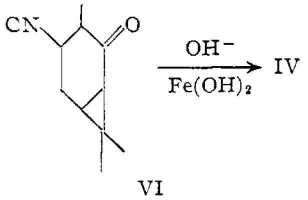


IV

It is natural that detection of this novel change would engender speculation on the nature of the reaction course. Wallach[3] suggested that carvone hydrobromide (II) does in fact ring-close to carenone, but that the primary product is unstable under the conditions of the reaction, suffering ring opening by base to the α,β-unsaturated-δ-hydroxyketone V, which dehydrates to IV. Clarke and Lapworth[4] prepared cyanocarone (VI) and showed that it was converted, on treatment with alkali in the presence of ferrous hydroxide, to eucarvone.



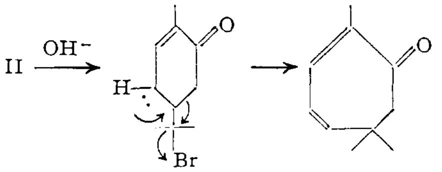
V



VI

The reasonable assumption was made that the reagent pair effected initial elimination to carenone, which subsequently rearranged to eucarvone; this behavior was construed as support for the Wallach mechanism, in particular the instability of carenone.

These suggestions for the course of the reaction, although reasonable, are not proved by the experimental findings described. The results of Clarke and Lapworth strongly suggest that carenone does readily ring-expand in a basic medium, but they do not *necessitate* its intermediation in the carvone hydrobromide → eucarvone change. By applying simple electronic principles, one can write a *concerted, elimination–rearrangement process* (1) which does not require III and therefore contrasts with the Wallach mechanism or any other ring closure operation. Since there is no appreciable amount



(1)

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[1] A. Baeyer, *Ber.*, **27**, 810 (1894).

[2] A. Baeyer, *ibid.*, **31**, 2067 (1898).

[3] O. Wallach, *Ann.*, **305**, 242, 274 (1899); **339**, 94 (1905).

[4] R. W. L. Clarke and A. Lapworth, *J. Chem. Soc.*, **97**, 15 (1910).