(14.5 g., 0.59 mole), *t*-butyl perbenzoate (21.3 g., 0.11 mole) and 0.2 g. of cupric 3,3,5-trimethylhexanoate was heated (80°) under pressure with shaking for 24 hours. The reaction mixture was washed with 60 ml. of 10% sodium carbonate solution, water and dried over magnesium sulfate. The olefin was removed by distillation and the residue was molecularly distilled, b.p. 100° (block) (10 mm.), to yield 15 g. (71%) of mixed esters. An analysis of g.l.c. on a 5-ft. Craig succinate column at 150° showed two components with retention times of 7.0 and 12.5 min. The relative areas of the peaks were 6.1:1, respectively. The molecular distillate was fractionated through a 40-cm. spinning band column. A fraction, b.p. 124–126° (13 mm.), showed only one component, retention time 7.0 min. on g.l.c. analysis.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.80; H, 7.38. Found: C, 75.66; H, 7.38.

The ester (1.0 g., 0.0053 mole) was hydrogenated over platinum catalyst. The product was analyzed by g.l.c. One component, with a retention time of 13.8 min., was found with a 5-ft. 20 M Carbowax column at 140° and one component, with a retention time of 11.5 min., was found with a 10-ft. 6 M Carbowax column at 213°.

Authentic samples of the possible pentyl benzoates were prepared. The benzoate from 3-methyl-2-butanol showed identical g.l.c. behavior to that of the unknown. The infrared and n.m.r. spectra were also identical.

Copper Ion Catalyzed Reaction of Tetramethylethylene and *t*-Butyl Perbenzoate.—A mixture of tetramethylene[18] (35.0 g., 0.42 mole), *t*-butyl perbenzoate (15.5 g., 0.08 mole) and 2 ml. of a 0.1 *N* solution of cupric 3,3,5-trimethylhexanoate in benzene was heated (80°) under pressure with shaking for 24 hours. The reaction mixture was processed as before. Molecular distillation, b.p. 86–102° (block) (0.1 mm.), afforded 12.0 g. (78%); g.l.c. analysis on a 5-ft. 20 M Carbowax column at 135° showed two components with retention times of 6 and 24 min. The relative areas of the peaks were 2:98, respectively. The mixture was fractionated. A fraction, b.p. 108–112° (38 mm.), showed one peak on g.l.c. analysis, retention time 24 min.

Anal. Calcd. for $C_{13}H_{16}O_2$: C, 77.07; H, 8.09. Found: C, 76.47; H, 7.84.

The retention time of methyl benzoate on the 5-ft. 20 M Carbowax column was found to be 6 min. Addition of methyl benzoate to the molecular distillate increased the size of the 6-min. peak.

The fractionated ester obtained above (1.0 g., 0.0048 mole), was hydrogenated over a platinum catalyst. The hydrogenated material showed one component on a 5-ft. 20 M Carbowax column at 135° with a retention time of 16.5 min. Similarly, one component was found on a 5-ft. Craig succinate column at 160° with a retention time of 13.1 min. An authentic sample of 2,3-dimethyl-2-butyl benzoate had the same retention times on the two columns. A mixture of the known and unknown ester showed only one component on analysis on the Craig succinate column. The infrared spectra of the unknown and known were identical.

---

[17] Prepared according to the procedure of F. C. Whitmore *et al.*, *J. Am. Chem. Soc.*, **64**, 2970 (1942). The fraction used was 98% pure as shown by g.l.c. analysis.

[18] Prepared according to the procedure of G. B. Kistiakowsky *et al.*, *ibid.*, **58**, 141 (1936). The fraction used was 98% pure as shown by g.l.c.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

Factors Governing Orientation in Metalation Reactions. I. The Metalation of Ethylbenzene with Organosodium and Organopotassium Compounds

BY ROBERT A. BENKESER, ALVIN E. TREVILLYAN AND JOHN HOOZ

RECEIVED JULY 30, 1962

The metalation of ethylbenzene with *n*-amylsodium and *n*-amylpotassium has been studied in detail. The metalated products were carbonated, esterified with diazomethane, and the isomer ratios determined by vapor phase chromatography. The *n*-amylsodium and *n*-amylpotassium were prepared from *n*-amyl chloride as well as from di-*n*-amylmercury. It was found that the aromatic ring of ethylbenzene is metalated both *meta* and *para* in a kinetically controlled sequence by *both* metalating agents irregardless of their mode of preparation. The *meta* and *para* isomers are converted in time, and in the presence of excess ethylbenzene, to the more thermodynamically stable α-isomer. It has been shown that authentic specimens of *o*-, *m*- and *p*-ethylphenylsodium, prepared directly from pure samples of the aromatic halide, also convert to the α-isomer in the presence of ethylbenzene. The lower yield of metalation products obtained when *n*-amylpotassium is prepared from *n*-amyl chloride is caused by the incursion of side-reactions which involve the *n*-amyl chloride. Both 1-pentene and 2-phenylheptane were detected in such runs and together accounted for 55% of the *n*-amyl chloride. The 1-pentene is not formed in reactions in which the *n*-amylpotassium is prepared from di-*n*-amylmercury, indicating that it arises from a dehydrohalogenation of the *n*-amyl chloride rather than from thermal decomposition of *n*-amylpotassium.

Rather compelling evidence has been advanced in recent years that homogeneous metalation reactions involve a nucleophilic attack by the anionic species of the metalating agent on a hydrogen atom of the substrate undergoing metalation.[1]

Such a mechanistic picture generally predicts correctly the orientations observed when soluble metalating agents like organolithium reagents are employed. Thus, both anisole and benzotrifluoride are metalated by *n*-butyllithium in diethyl ether principally *ortho* to the substituent groups.[2,3] In such nucleophilic displacements, one would conclude that resonance effects of the substituent (*e.g.*, the methoxy group of anisole) would not be called into play; only the inductive effects of such groups should be important. Hence both the $-OCH_3$ group of anisole and the $-CF_3$ group of benzotrifluoride, by virtue of their -I inductive effect, should direct nucleophilic attack to the relatively acidic *ortho* hydrogens.

In contrast to the soluble organolithium reagents, organosodium and organopotassium compounds are generally rather insoluble in the solvents with which they do not react. Because of the insoluble nature of these materials, it does not follow *per se* that metalations involving these reagents will be governed by the same factors which control homogeneous metalations. This very reasonable premise has been asserted repeatedly by Professor A. A. Morton and his associates who pioneered in the field of organoalkali metalations.[4]

---

[1] G. E. Hall, R. Piccolini and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 4540 (1955).

[2] H. Gilman and R. L. Bebb *ibid.*, **61**, 109 (1939).

[3] J. D. Roberts and D. Y. Curtin, *ibid.*, **68**, 1658 (1946).

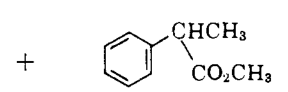
[4] See for example, A. A. Morton, *Chem. Revs.*, **35**, 1 (1944); A. A. Morton, *J. Am. Chem. Soc.*, **69**, 969 (1947); A. A. Morton, C. E. Claff, Jr., and F. W. Collins, *J. Org. Chem.*, **20**, 428 (1955).

In most of this early work,[4] the insoluble nature of the organosodium and potassium compounds was emphasized and deemed most important. Some of the discrepancies which seemed to exist in orienting effects, for example, were attributed to the heterogeneity of these metalations. In one instance[5] it was argued that different modes of preparing the organosodium and potassium compounds can cause differences in their orienting effects because of the surface changes resulting from their different modes of preparation.[6] On the other hand, recent work by Bryce-Smith and co-workers[7] has emphasized the similarities which exist between homogeneous and heterogeneous metalations. The latter experimenter explained his results in the same terms which were used for the homogeneous reactions, *i.e.*, nucleophilic attack on hydrogens made acidic by the -I inductive effect of substituent groups.[1]

In an attempt to decipher the apparent differences which exist between homogeneous and heterogeneous metalations, as well as to resolve the conflicting views which have been expressed in their regard, our laboratory has undertaken a systematic and thorough study of metalations involving organosodium and organopotassium compounds.

The first hydrocarbon chosen for study was ethylbenzene. Both Shorigin[8] and Morton[9] had reported that metalation of ethylbenzene produced the α-isomer. In the former case, ethylsodium prepared from diethylmercury was employed as the metalating agent, while, in the latter, *n*-amylsodium was used, but this time it was prepared from *n*-amyl chloride. The yields in both cases were low and the material balance poor.

We have studied the metalation of ethylbenzene, with both *n*-amylsodium and *n*-amylpotassium prepared from *n*-amyl chloride and from di-*n*-amylmercury. The results are listed in Table I. The isomer distributions were determined by carbonating the intermediates to carboxylic acids. The latter were esterified with diazomethane and the products analyzed by vapor phase chromatography. In order to establish that the analytical procedure was reliable, a synthetic mixture of *m*- and *p*-ethylbenzoic acids and 2-phenylpropionic acid was prepared. This mixture was subjected to treatment with diazomethane and the resulting esters were analyzed by vapor phase chromatography. The results indicated the method was reliable to ±0.5%.



(1)

It will be noted from Table I that the use of amylsodium generally resulted in higher yields of carboxylic acids then did amylpotassium. The principal difficulty with the potassium runs was the incursion of two side reactions which led to 1-pentene and 2-phenylheptane. Both of these materials were identified in one of the amylpotassium metalations (entry 5, Table I), and together accounted for almost 55% of the *n*-amyl chloride. The origin of the 2-phenylheptane was not investigated, but it presumably arises from a Wurtz-type coupling between *n*-amyl chloride and the α-potassium derivative of ethylbenzene.[10]

TABLE I

METALATION OF ETHYLBENZENE WITH *n* AMYLSODIUM AND *n*-AMYLPOTASSIUM

	Metalating agent	Method[a] of prepn.	Reaction time, hr.	Yield, %, of methyl esters[b]	Product composition, %[c] Alpha[d]	*Meta*[d]	*Para*[d]
1	*n*-AmNa	I	20	46(43)	68(60)	19(26)	13(15)
2	*n*-AmNa	II	20	48(36)	68(69)	21(20)	12(12)
3	*n*-AmNa	I	3	32	18	52	30
4	*n*-AmK	I	20	31(27)	100(100)	..	..
5	*n*-AmK	I[e]	20	31	100	..	..
6	*n*-AmK	I	3	12	100	..	..
7	*n*-AmK	I	0.5	10	93	6	1
8	*n*-AmK	II	20	51[f]	100	..	..

[a] Method I employed *n*-AmCl + metal; method II employed Am_2Hg + metal. [b] The values in parentheses represent duplicate runs; yields are based on weight of starting *n*-AmCl or *n*-Am_2Hg. [c] It is perhaps significant that no *o*-isomer was detected in any of these runs. [d] The *alpha*, *meta* and *para* refer to the methyl esters obtained after carbonation and treatment with diazomethane; see eq. 1 in text. [e] This run was essentially the same as run 4 except that the *n*-AmK was prepared in heptane instead of ethylbenzene. In addition to the 31% of methyl esters obtained, there was also isolated 1-pentene (13%), *n*-pentane (36%) and 2-phenylheptane (42%), giving an over-all material balance of 86%. [f] The volatiles from this run were trapped and analyzed. No 1-pentene could be detected, only *n*-pentane.

The 1-pentene (13%), along with *n*-pentane (36%), were collected in a Dry Ice trap during the first twelve hours of the amylpotassium reaction (entry 5, Table I). Both of these materials could be identified by their infrared absorption as well as their retention time by vapor phase chromatography. It is significant that the 1-pentene could not be detected in the run in which the *n*-amylpotassium was prepared from di-*n*-amylmercury (entry 8, Table I). This clearly indicates that the olefin was arising from a dehydrohalogenation of the *n*-amyl chloride and not from thermal decomposition of *n*-amylpotassium itself. Further

$$n\ C_5H_{11}Cl \xrightarrow{n\text{-}C_5H_{11}K} C_5H_{12}\uparrow + C_5H_{10}\uparrow\ KCl$$

evidence that such a reaction is occurring can be obtained from the amount of *n*-pentane collected (36%). This was somewhat greater than the yield of methyl esters realized (31%), indicating that the amylpotassium was extracting protons from some other molecule in addition to ethylbenzene. By taking the by-products into account in this reaction, an over-all 86% material balance could be obtained.

---

(5) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1636 (1958).

(6) This explanation was offered to account for the puzzling discrepancies reported for the metalation of cumene. Three different laboratories had reported different results in the metalation of this hydrocarbon. This case will be taken up in detail in the next paper in this series.

(7) D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954); D. Bryce-Smith, V. Gold and D. P. N. Satchell, *ibid.*, 2743 (1954).

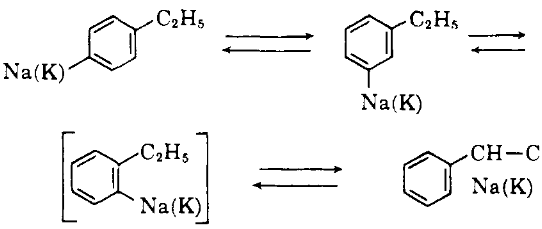
(8) P. Shorigin, *Ber.*, **41**, 2723 (1908).

(9) A. A. Morton and E. L. Little, *J. Am. Chem. Soc.*, **71**, 487 (1949).

(10) See A. A. Morton and F. Fallwell, Jr., *ibid.*, **60**, 1429 (1938), where such coupling reactions have been studied.

It becomes apparent from Table I (entries 5 and 8) that most of these side reactions can be avoided by preparing the amylpotassium from diamylmercury. As would be predicted, the yield of methyl esters is increased 20% by so doing.

By comparing entries 1 and 2 and 4 and 8 in Table I it is apparent that the isomer distributions were unaffected by the two different modes of preparing the metalating agents. It is also apparent from entries 1 and 3 that initially metalation with *n*-amylsodium has occurred in the *m*- and *p*- positions of the phenyl ring, but that, with time, these two isomers disappear in favor of the more thermodynamically stable α-isomer. The same phenomenon is apparently occurring with the potassium compounds, but conversion to the α-isomer is so rapid and complete here that the ring isomers can be detected only at the very early stages of the reaction (see entry 7, Table I). Clearly the data of Table I point to a kinetically controlled ring attack followed by a conversion of the ring isomers to the more thermodynamically stable α-isomer. It should be noted that no *o*-isomer was detected in any of the runs listed in Table I, despite the fact that the analytical method employed was sensitive enough to detect a minimum of 0.5% of this material. Hence it cannot be concluded with certainty that the *o*-isomer takes part in the series of equilibria shown in eq. 2.



(2)

In order to obtain corroborating evidence for the equilibria depicted in 2, authentic samples of *o*-, *m*- and *p*-ethylphenylsodium were prepared in ethylbenzene. This was accomplished by treating carefully purified samples of *o*-, *m*- and *p*-chloroethylbenzenes with sodium metal in a solvent of ethylbenzene. Table II lists the results of these experiments. Of particular interest is entry 1 in this table since all four isomeric acids were detected in this run. There can be little doubt that initially the metal was present on the aromatic ring at the site of the halogen. Entry 4, Table II, shows that when no ethylbenzene was present, only the *para* acid was obtained when *p*-chloroethylbenzene was used as the starting halide. The data of Table II thus clearly support the equilibria depicted in eq. 2.

Conclusions.—It must be concluded that ethylbenzene undergoes ring substitution by the metal atom in a kinetically controlled sequence. The *meta* and *para* (and perhaps *ortho*) substituted ethylphenylsodium and potassium compounds revert to the more thermodynamically stable α-isomer in the presence of excess ethylbenzene. Most likely the α-isomer derives stability from its ionic nature and the resonance stabilization afforded to the benzylic carbanion.

TABLE II

REACTION OF CHLOROETHYLBENZENE WITH SODIUM IN ETHYLBENZENE FOLLOWED BY CARBONATION

	Chloroethylbenzene	Reacn. time, hr.	Yield,[a] %	Product composition, %			
				Alpha	*Ortho*	*Meta*	*Para*
1	*o*-$ClC_6H_4C_2H_5$	20	18	77	4	13	6
2	*m*-$ClC_6H_4C_2H_5$	20	45(34)	87(86)	..	9(9)	4(5)
3	*p*-$ClC_6H_4C_2H_5$	20	48(60)	88(62)	..	7(6)	6(32)
4	*p*-$ClC_6H_4C_2H_5$	1	75	...	..	...	100[b]

[a] The values in parentheses represent duplicate runs; yields are based on weight of starting chloroethylbenzene. [b] This reaction was carried out in *n*-decane; no ethylbenzene was present.

It is obvious from this work that different modes of preparing the alkylsodium and potassium compounds *do not necessarily ensure* differences in orienting effects.[5] It is of interest that ethylpotassium, prepared from ethyllithium and sodium–potassium alloy, metalates ethylbenzene 50% *alpha*, 30% *meta* and 20% *para*.[7] This metalating combination will be dealt with in a future publication in this series.

Experimental

Preparation of Pure *o*-, *m*, and *p*-Chloroethylbenzenes.—*o*-Chloroethylbenzene was prepared from *o*-ethylaniline by a Sandmeyer reaction; b.p. 177° (751 mm.), $n^{20}D$ 1.5219 (lit. b.p. 178.4°, $n^{20}D$ 1.52175).[11] This material was free of *m*- and *p*-isomers as determined by V.P.C. (column "R," 150°, 15 p.s.i.).

m-Chloroethylbenzene was prepared by adding chlorine to acetophenone containing a large excess of anhydrous aluminum chloride.[12] The product boiled at 99–100° (9 mm.). The literature b.p. is 80° (2.5 mm.). This material was reduced[13] by classic Clemmensen reduction conditions to a material which boiled at 179–181°. This was shown by vapor phase chromatography to contain 95% *m*-chloroethylbenzene and 5% *o*-chloroethylbenzene (Perkin-Elmer Fractometer, flame ionization detector, 150-ft. capillary column containing a polyglycol liquid phase, 150°, 15 p.s.i.). Fractionation of this material in a Podbielniak Mini-cal high temperature distillation assembly gave pure *m*-chloroethylbenzene (analysis by V.P.C. as described above) boiling at 181.8° (751 mm.), $n^{20}D$ 1.5175 (literature[11] b.p. 183.7°, $n^{20}D$ 1.51949).

p-Chloroethylbenzene was prepared by treating chlorobenzene with acetic anhydride and aluminum chloride, followed by a Clemmensen reduction of the resulting *p*-chloroacetophenone. The crude *p*-chloroethylbenzene thus produced was fractionated in a Podbielniak Mini-cal high temperature distillation apparatus. It boiled at 183.5° (751 mm.), $n^{20}D$ 1.5177, and was shown by V.P.C. to be free of both the *o*- and *m*-isomers. The literature[11] boiling point is 184.4°, $n^{20}D$ 1.51751.

Preparation of Authentic Samples of Methyl Esters of *o*-, *m*- and *p*-Ethylbenzoic Acids.—Methyl *o*-ethylbenzoate was obtained as a mixture of the *o*- and *p*-esters by the following sequence. Bromination of ethylbenzene at 0° in the presence of iron powder gave a mixture of *o*-bromoethylbenzene (10%) and *p*-bromoethylbenzene (90%) boiling at 202–203°. The isomer ratio was determined by means of a Perkin-Elmer Fractometer (model 154C, 2-meter column "R," 180°, 15 p.s.i.). When this mixture was cooled to −58° and filtered rapidly on a cold Buchner funnel, a mixture of 70% *p*-bromoethylbenzene and 30% *o*-bromoethylbenzene was obtained (V.P.C. analysis under conditions listed above). This mixture of bromides was converted *via* magnesium in ether to their Grignard reagents and then carbonated with Dry Ice. A mixture of *o*- and *p*-ethylbenzoic acids was obtained melting at 80–90° (pure *ortho* acid[14] melts at 68° and pure *para*[15] at 110–111°). Conversion of this mixture to the methyl esters *via* diazomethane in ether gave a mixture which contained 30% methyl *o*-

---

(11) R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2875 (1949).

(12) D. E. Pearson and H. W. Pope, *J. Org. Chem.*, **21**, 381 (1956).

(13) N. J. Leonard and S. N. Boyd, *ibid.*, **11**, 405 (1946).

(14) Th. Zinke and C. Frölich, *Ber.*, **20**, 2056 (1887).

(15) R. Fittig and J. König, *Ann.*, **144**, 290 (1867).

ethylbenzoate and 70% methyl *p*-ethylbenzoate (Perkin–Elmer Vapor Fractometer, model 154C, 2-meter column "R," 150° 15 p.s.i.).

Methyl *m*-ethylbenzoate was obtained pure by treatment of *m*-ethylbenzoic acid[16] with diazomethane in ether. *m*-Ethylbenzoic acid was obtained by carbonating the Grignard reagent obtained from *m*-bromoethylbenzene.

Methyl *p*-ethylbenzoate was obtained in exactly the same manner as described for the *m*-isomer.

Methyl 2-Phenylpropionate[17] and Methyl 3-Phenylpropionate.[18]—Both of these esters were prepared by treating the corresponding acids with diazomethane. Their physical constants agreed with those in the literature.

Analytical Method.—An authentic mixture of known acids was prepared with the following composition

Acid	Wt. %
p-Ethylbenzoic	10.5
m-Ethylbenzoic	33.5
2-Phenylpropionic	56.0

The acid mixture was dissolved in ether, and then added to an excess of diazomethane also dissolved in ether. The work-up procedure was identical to that employed for the analysis of the acid mixtures obtained from metalation. The methyl esters thus obtained were analyzed with a Perkin–Elmer model 154C Vapor Fractometer equipped with a 2-meter column "R" at 150°, 15 p.s.i. The following results were obtained.

Methyl ester	Wt. %	Retention time, min.
p-Ethylbenzoate	10.9	62
m-Ethylbenzoate	33.0	58
2-Phenylpropionate	56.0	37

The retention time of methyl *o*-ethylbenzoate was determined as 41 min. and methyl 3-phenylpropionate as 56 min. under identical analytical conditions to those listed above.

Di-*n*-amylmercury.—Mercuric chloride (54.2 g., 0.20 mole) was added in three portions to a stirred solution of the *n*-amyl Grignard reagent, prepared by the addition of *n*-amyl bromide (100 g., 0.60 mole) in 100 ml. of anhydrous ether to magnesium turnings (19.0 g., 0.8 g. atom) in 400 ml. of ether. (The Grignard solution had been filtered free of magnesium before use.)

The resulting solution was refluxed for 90 hr. and was then hydrolyzed by the dropwise addition of saturated ammonium chloride solution. The precipitate was removed by filtration and the filtrate dried over Drierite. Solvent was removed under vacuum and the residue was distilled yielding 60.0 g. (87%) of di-*n*-amylmercury boiling at 83–85° (0.2 mm.), n^{20}D 1.5010 (lit.[19] b.p. 106° (0.5 mm.), n^{20}D 1.4998).

Metal Dispersions.—In a typical preparation, sodium metal (11.0 g., 0.48 g. atom) was placed in a dry 500-ml. Morton-type flask along with 100 ml. of dry decane (heptane was used in the case of potassium) under an atmosphere of dry nitrogen. The flask was wrapped with glass wool and then heated until the sodium was molten. The heating mantle was replaced by a metal pail loosely packed with glass wool and the contents of the flask were stirred at high speed (10,000–12,000 r.p.m.) for 1 minute. It was then allowed to cool slowly. The solvent was removed by forcing it though a gas dispersion tube with a pressure of nitrogen gas. Dry ethylbenzene (20 ml.) was added as a wash and was removed in the same manner, followed by the addition of another 100 ml. of dry ethylbenzene. The latter mixture was used for the metalations.

Metalation of Ethylbenzene with *n*-Amylsodium (Method I).—*n*-Amylsodium was prepared by the dropwise addition of *n*-amyl chloride (16.0 g., 0.15 mole) in 30 ml. of dry ethylbenzene to a sodium dispersion (11.0 g., 0.48 g. atom) covered by 100 ml. of dry ethylbenzene. High speed stirring (10,000–12,000 r.p.m.) at −10° under an atmosphere of dry nitrogen was employed during the addition and was continued at −10° for 1 hr. and at room temperature for 20 hr.

Carbonation was effected by pouring the mixture onto a Dry Ice–ether slurry. After it was allowed to warm to room temperature, the excess metal was decomposed by the addition of 80% aqueous *t*-butyl alcohol. Water was added until two clear layers resulted. The layers were separated and the water layer was washed twice with ether. The aqueous layer was then acidified with dilute hydrochloric acid and saturated with sodium chloride. The organic acids were extracted approximately seven times with 50-ml. portions of ether. The combined extracts were dried over Drierite and the dried filtered solution concentrated by the removal of some of the solvent. This solution was cautiously added to an excess of diazomethane in ether prepared according to the method of DeBoer.[20] The excess diazomethane was decomposed by the dropwise addition of 85% formic acid. The resulting solution was extracted successively with 20 ml. of water, 20 ml. of saturated sodium bicarbonate solution and twice more with 20 ml. of water. It was dried over Drierite, filtered, and the solvent removed under vacuum in a Rinco rotary evaporator. The esters remaining were then analyzed by vapor phase chromatography.

Metalation of Ethylbenzene by *n*-Amylsodium (Method II).—*n*-Amylsodium was prepared by the addition of di-*n*-amylmercury (20.6 g., 0.06 mole) in 20 ml. of ethylbenzene to a sodium dispersion (5.3 g., 0.22 g. atom) covered by 45 ml. of ethylbenzene at room temperature. High speed stirring and an atmosphere of dry nitrogen was maintained throughout the addition and entire course of the reaction. The carbonation, work-up and method of analysis was identical to that described above under method I.

Metalation of Ethylbenzene by *n*-Amylpotassium in *n*-Heptane. Isolation of 1-Pentene and 2-Phenylheptane.—*n*-Amylpotassium was prepared by the slow, dropwise addition of *n*-amyl chloride (16.0 g., 0.15 mole) in 20 ml. of *n*-heptane to potassium sand (13.0 g., 0.33 g. atom) covered by 80 ml. of *n*-heptane with high speed stirring (10,500 r.p.m.) at −10° under a nitrogen atmosphere. After 90 minutes at −10°, 125 ml. of ethylbenzene was added. The temperature was maintained at −10° for an additional 30 min. The reaction vessel was then allowed to warm to room temperature and high speed stirring was continued for 20 hr. Volatile products which formed during this time were swept by nitrogen into two receivers, connected in series, and cooled by a Dry Ice–acetone-bath. Pentane and 1-pentene (trace amounts of 2-pentene could also be detected) were identified by infrared and V.P.C. analysis (Perkin–Elmer model 154C Vapor Fractometer, 2-meter adiponitrile column, 30°, 3 p.s.i. He). Aliquots collected in this manner were analyzed at various time intervals up to 12 hr., at which time the evolution of the pentane and pentenes had ceased. A total of 1.37 g. of 1-pentene (13%) and 3.99 g. of *n*-pentane (36%) was collected.

After 20 hr. the mixture was carbonated and worked up in the same manner as described above. The aqueous layer, after subsequent esterification with diazomethane, yielded 7.6 g. (31%) of methyl ester which by V.P.C. was shown to be 100% α-ester (entry 5, Table I). The organic layer was fractionated (Todd column) and 5.4 g. (42%) of 2-phenylheptane boiling 140–143° at 10 mm. (n^{21}D 1.4869) was obtained. The literature[21] b.p. is 228–231° (n^{20}D 1.4857). This material had a superimposable infrared spectrum and identical V.P.C. retention time (Perkin–Elmer model 154C Vapor Fractometer, 2-meter column "R", 196°, 20 p.s.i. He) with an authentic sample.[22] The material balance was thus 86%.

Metalation of Ethylbenzene with *n*-Amylpotassium. Method II.—The proportion of reagents and general procedure was identical to that described above for metalation with *n*-amylsodium under the heading of method II.

Reaction of Chloroethylbenzenes with Sodium in Ethylbenzene.—The reaction of each of the chloroethylbenzenes with sodium was carried out in a similar fashion. The following procedure for the reaction of *p*-chloroethylbenzene with sodium can be taken as typical of all.

---

(16) A. Voswinkel, *Ber.*, **21**, 2831 (1888).

(17) K. Neure, *Ann.*, **250**, 152 (1889).

(18) E. Erlenmeyer, *ibid.*, **137**, 334 (1866).

(19) W. J. Jones, D. P. Evans, T. Gulwell and D. C. Griffiths, *J. Chem. Soc.*, 40 (1935).

(20) Th. J. DeBoer and H. J. Backer, *Rec. trav. chim.*, **73**, 229 (1954).

(21) A. Dobrjanski and Aliew, *Neftyanoe Khozyaistvo*, **9**, 229 (1925); *Chem. Zentr.*, **97**, II, 676 (1926).

(22) Prepared by treating 2-heptanone with the phenyl Grignard reagent. The 2-phenyl-2-heptanol thus formed was dehydrated with $KHSO_4$. The resulting olefin was then hydrogenated over Raney nickel.

p-Ethylphenylsodium was prepared by the slow dropwise addition of pure *p*-chloroethylbenzene (10.0 g., 0.071 mole) in 20 ml. of dry ethylbenzene to a sodium dispersion (3.5 g., 0.15 g. atom) covered by 75 ml. of ethylbenzene at 10° with high speed stirring under an atmosphere of dry nitrogen. High speed stirring was continued for 1 hour at 10° and for 20 hr. at room temperature. The carbonation, work-up esterification with diazomethane and analysis were all identical to the methods described previously.

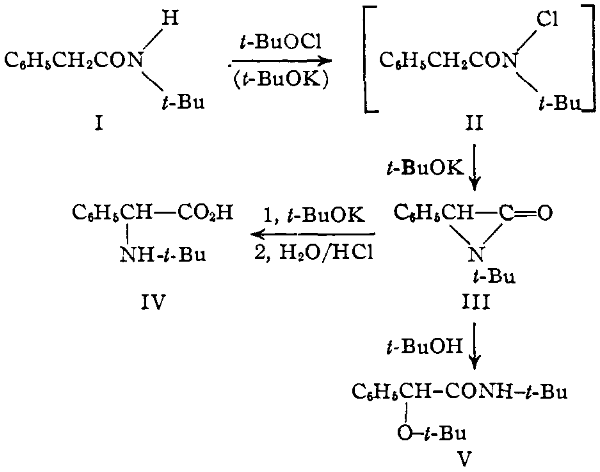
Acknowledgment.—The authors are grateful for financial assistance from the Petroleum Research Fund which made this work possible.

COMMUNICATIONS TO THE EDITOR

REACTIONS OF AMINES. X. 1-*t*-BUTYL-3-PHENYLAZIRIDINONE[1,2]

Sir:

In an earlier communication[1] we reported presumptive evidence for the existence of an α-lactam intermediate (III) (or some closely related substance (*vide infra*)) in the base-catalyzed rearrangement of N-chloro-N-*t*-butylphenylacetamide (I) to derivatives of phenylglycine (V). The present communication describes the isolation and characterization of this intermediate, which is believed to be the first authentic α-lactam to be so isolated and characterized.



In the earlier experiments potassium *t*-butoxide was employed as the base and benzene–*t*-butyl alcohol solution as solvent. Many subsequent experiments by several workers in this Laboratory yielded mixtures of what appeared to be 1-*t*-butyl-3-phenylaziridinone (III) and α-*t*-butoxy-N-*t*-butylphenylacetamide (V), but all attempts to separate the components either failed or resulted in the destruction of III. However, examination of the results of these and other experiments carried out on mixtures of III and V, as well as of II, III, and V, suggested that the successful isolation of III would require substantial completion of step II → III and minimization of step III → V. Accordingly, the base-solvent system was changed to potassium *t*-butoxide–toluene to reduce the concentration of *t*-butyl alcohol, and the quantities of reactants were adjusted so that the principal contaminant at the end of the reaction was unreacted (or regenerated) I, which was separated easily from III by virtue of the former's lower solubility in pentane.

In a typical experiment a solution of 3.4 g. of potassium *t*-butoxide in 250 ml. of toluene was added slowly with stirring over a period of 1 hr. to a solution of 5.7 g. of I and 3.3 g. of *t*-butyl hypochlorite in 120 ml. of toluene held at 5 ± 5°.[3] The toluene was evaporated under vacuum at 0 ± 5°, and the residue was extracted with pentane. After 24 hr. in the freezer, the precipitated I was filtered off and the filtrate was concentrated to a small volume, yielding 1.75 g. (31%) of III, m.p. 29–31°. Samples III were recrystallized from pentane for analysis, m.p. 32–33° (Kofler) (Found for $C_{12}H_{15}NO$: C, 75.97; H, 8.02; N, 7.28; mol. wt., (thermistor method), 185, 186). The infrared spectrum showed a very strong $\nu(C{=}O)$ band at 1844 (CH_3CN), 1847 ($CHCl_3$), 1849 (CCl_4) or 1848 (Nujol mull) cm.$^{-1}$. Freshly recrystallized samples showed no significant absorption in the 1600–1800 cm.$^{-1}$ range, nor in the 3100–3500 cm.$^{-1}$ range.[4] In the n.m.r. spectrum[5] (CCl_4) of III peaks corresponding to the nine CH_3 protons appeared at 8.67 τ, the five aromatic ring protons at 2.63 τ, and the single proton of the α-lactam ring at 6.22 τ.

The purified α-lactam III appeared to be a moderately stable but reactive substance, which could be kept (dry) in the solid state for several months in the freezer or several days at room temperature without serious decomposition. It reacted with *t*-butyl alcohol in 2 hr. at room temperature to give V[1] as the sole product, and with a saturated solution of potassium *t*-butoxide in *t*-butyl alcohol with subsequent hydrolysis by aqueous hydrochloric acid to give IV[1] as the sole product.

The physical data, together with the two modes of ring cleavage, are compatible with the α-lactam structure assigned to III and are most easily rationalized in terms of that structure.[1] However,

---

[1] Paper IX, *J. Am. Chem. Soc.*, **83**, 4469 (1961).

[2] This work was supported in part by grant G-21405 of the National Science Foundation.

[3] Fortuitously, for this specific series of experiments the theoretical quantities (*assuming* 100% purity for reagents) were also the optimum quantities. In other experiments and with derivatives of III it has been found necessary to adjust either the amount of a given sample of base or of *t*-butyl hypochlorite for optimum yield and separation. For some analogs of III optimum quantities of reagents have yet to be found.

[4] Attempts to prepare KBr pellets under ordinary conditions led to destruction of the compound. However, by minimizing both the time and final pressure of the pressing operation, a moderately satisfactory KBr-pellet spectrum has been obtained for the *p*-chloroderivative of III (James Fuerholzer, unpublished results).

[5] The author is indebted to Dr. James P. Collman for the determination of the n.m.r. spectrum.