Metalation of Toluene. The Question of Kinetic *vs.* Thermodynamic Control

C. D. Broaddus

Contribution from the Procter and Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239. Received May 18, 1966

Abstract: Metalation of toluene by *n*-butylsodium has been shown to produce benzylsodium, as well as minor amounts of ring-substituted isomers, after short reaction periods. Studies on the stability of *p*-sodiotoluene to the reaction conditions indicate that rearrangement to benzylsodium is comparatively slow. Metalation of toluene by *n*-butylpotassium under the same reaction conditions gave exclusively benzylpotassium, as evidenced by carbonation. These results are compared to the metalation of α olefins, ethylbenzene, and cumene with alkylsodium and -potassium compounds.

Metalation of unsaturated hydrocarbons by alkylsodium and alkylpotassium compounds has received considerable study, resulting in a commonly accepted proton abstraction mechanism.[1] One of the more significant observations in metalation of both olefins and alkylbenzene systems is the fact that rather nonspecific reaction is observed. Ethyl- and isopropylbenzenes[1a-c] have been shown to produce both ring and side chain products upon carbonation of metalation mixtures, while both allylic and vinylic products have been identified from similar reactions[1e,2] with 1-olefins. These results contrast with the observations made during base-catalyzed exchange of hydrocarbons. With less basic reagents in solvating solvents, reaction is found to occur exclusively at resonance-stabilized positions.[3]

As concerns metalation of alkylbenzenes, two basic proposals have been offered for the various product distributions by anionic mechanisms. In work initiated in the mid-1950's, Bryce-Smith[1a] interpreted the product mixtures obtained on the basis of differences in thermodynamic acidities[4] of the various C–H bonds. At a later stage, Benkeser[5] demonstrated that ring-metalated derivatives can undergo rearrangement to the more stable α isomer, and suggested that kinetically controlled ring metalation followed by equilibration to the thermodynamically favored α isomer was an important factor in these processes. It was further shown[5] that metalation of ethylbenzene with alkylpotassium compounds gave less ring-substituted product than reaction with alkylsodium compounds under similar conditions, leading to the postulate that the equilibration step was much more rapid and complete in the potassium system.

Metalation of α olefins has been interpreted as initial competitive proton abstraction at vinylic and allylic positions, followed by comparatively slow rearrangement of the vinyl alkali metal compounds to the more stable resonance-stabilized allyl isomers.[1e] It was further proposed that in the initial step, alkylpotassium reagents favored metalation at the resonance-stabilized allyl position, relative to metalation with alkylsodium compounds.[1e]

In considering these various proposals, it was of interest to determine the importance of kinetic *vs.* thermodynamic factors in the metalation of toluene. While the earlier literature clearly demonstrates that ring-substituted toluene derivatives can undergo rearrangement to benzyl derivatives,[6] the extent to which this process operates during metalation of toluene is not clear. Thus, toluene has been reported to metalate predominantly at the benzyl position;[7] however, this observation can be accounted for by either kinetically controlled ring proton abstraction followed by the very rapid equilibration reactions,[8] or by simple initial metalation at the benzyl position to give the thermodynamically favored product. It was then the purpose of this study to attempt to distinguish between these two possibilities.

Results

Table I contains data obtained from the reaction of *p*-bromotoluene with sodium metal in octane diluent.

The acidic product was identified by its melting point[9] and by gas chromatographic (glpc) comparison of the corresponding methyl ester to an authentic sample.[10] It is noteworthy that this reaction results in high yields (entry 2) of acid product, so there can be little question that unobserved side reactions account for disappearance of the benzyl carbanionic species.[11]

Table II contains data obtained from the reaction of *p*-sodiotoluene with toluene. Experiments were conducted using 10 (entries 1 and 2) and 32 molar (entries

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[1] (a) D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954); (b) *ibid.*, 5983 (1963); (c) R. A. Benkeser, J. Hooz, T. V. Liston, and A. E. Trevillyan, *J. Am. Chem. Soc.*, **85**, 3984 (1963), and references therein; (d) R. A. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3234 (1964); (e) C. D. Broaddus, *ibid.*, **29**, 2689 (1964); (f) M. Schlosser, *Angew. Chem.*, **76**, 124 (1964); (g) for a different interpretation see A. A. Morton, C. E. Claff, and F. W. Collins, *J. Org. Chem.*, 20, 428 (1955).

[2] A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, and R. L. Letsinger, *J. Am. Chem. Soc.*, 72, 3785 (1950).

[3] (a) A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 249 (1962), and later articles in this series; (b) A. J. Shatenshtein and E. A. Izraelevich, *Zh. Fiz. Khim.*, **32**, 2711 (1958), quoted in ref 3a; (c) S. Bank, C. A. Rowe, Jr., and A. Schriesheim, *J. Am. Chem. Soc.*, **85**, 2115 (1963); (d) D. J. Cram and R. T. Uyeda, *ibid.*, **86**, 5466 (1964); (e) D. H. Hunter and D. J. Cram, *ibid.*, **86**, 5478 (1964).

[4] The Brønsted catalysis law was invoked to relate reactivities to the thermodynamic acidities of the various positions.

[5] R. A. Benkeser, A. E. Trevillyan, and J. Hooz, *J. Am. Chem. Soc.*, **84**, 4971 (1962).

[6] W. E. Bachman and H. T. Clarke, *ibid.*, **49**, 2089 (1927); (b) H. Gilman and H. A. Pacevitz, *ibid.*, **62**, 673 (1940); (c) H. Gilman, H. A. Pacevitz, and O. Baine, *ibid.*, **62**, 1514 (1940).

[7] (a) P. Schorigin, *Ber.*, **41**, 2723 (1908); (b) A. A. Morton aud I. Hechenbleikner, *J. Am. Chem. Soc.*, **58**, 2599 (1936).

[8] This would be an analogous situation to that proposed for the metalation of ethylbenzene with alkylpotassium reagents.

[9] Crude acid melted 170–173°, recrystallized 178–179° (lit.[7] 178°).

[10] Acid purchased from Matheson Coleman and Bell and esterified with a catalytic amount of sulfuric acid in methanol.

[11] R. Asami, M. Levy, and M. Szwarc, *J. Chem. Soc.*, 361 (1962).

Table I. Stability of *p*-Sodiotoluene in Octane

	Mole of *p*-bromo-toluene	g-atom of sodium	Reaction time, hr	% yield	Carbonation product,[a] % *p*-Toluic acid	Phenyl-acetic acid
1	0.05	0.2	0.25	37	~100	0
2	0.05	0.2	18.5	95[b]	~100	0
3	0.05	0.2	68[c]		~100	0
4	0.05	0.2	92[c]		~100	0
5	0.05	0.2	240[c]		~100	0

[a] The carbonation product was esterified and analyzed by glpc. In all runs only methyl *p*-toluate was detected. [b] Run in triplicate. [c] These entries were obtained by removing portions of one reaction mixture after the time intervals indicated. Yield was not determined.

Table II. Stability of *p*-Sodiotoluene in Toluene

	Mole of *p*-sodio-toluene[a]	Moles of toluene[b]	Time, hr	Carbonation products,[c] % *p*-Toluic acid	Phenyl-acetic acid
1	0.05	0.5	1	~100	
2	0.05	0.5	18[d]	75	25
3	0.05	1.6	0.5[e]	>98	<2
	0.05	1.6	2	75	25
4	0.05	1.6	72	7	~93
5	0.05	1.6	69	4	96

[a] Based on the amount of *p*-bromotoluene used. [b] A constant volume of 200 ml was maintained by the use of octane diluent. [c] Carbonation was effected by pouring over solid carbon dioxide. Analyses were performed by glpc of the esterified product. [d] Under these conditions a 95% yield of crude acid product was obtained. [e] Approximately one-half of the reaction mixture was carbonated after 0.5 hr. The remaining mixture was stirred for an additional 1.5 hr before carbonation.

3 and 4) excesses of toluene for the time periods recorded.

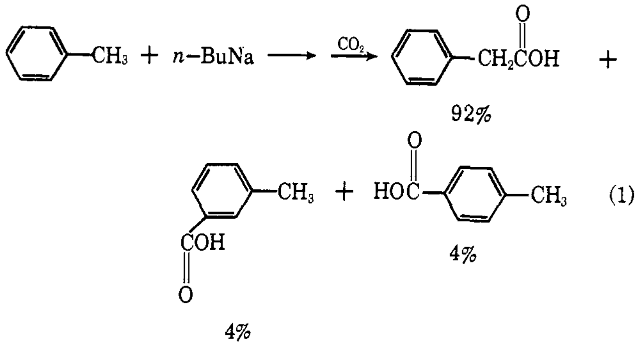
The acidic products were analyzed by glpc comparison of the corresponding methyl esters to authentic samples.[10] The analysis conditions were shown to distinguish *o*-, *m*-, and *p*-methyl toluates and methyl phenylacetate. It should be noted that no *o*- or *m*-methyl toluates were detected in these reaction mixtures.

Toluene was allowed to react with *n*-butylsodium[12] for short periods (30 min) and the mixture carbonated to provide an acidic product. Following esterification and removal of the low-boiling methyl valerate, an aromatic ester fraction was obtained which analyzed for 92% methyl phenylacetate, 4% methyl *m*-toluate, and 4% methyl *p*-toluate. Metalation and carbonation under the same conditions using *n*-butylpotassium[12] provided an aromatic acid product which was ~99% phenylacetic acid as evidenced by glpc analysis of the corresponding methyl ester. It is pertinent to note that approximately 10% of the crude acid product was valeric acid arising from carbonation of *n*-butylpotassium.[13]

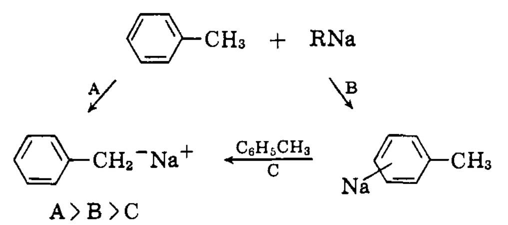
Discussion

The data summarized in Table I clearly demonstrate that *p*-sodiotoluene is stable in octane diluent for long periods of time at room temperature. This observation rules out the occurrence of intramolecular rearrangement of ring-substituted isomers[14] during metalation of toluene.

Since the feasibility of intramolecular rearrangement has been eliminated, kinetic *vs.* thermodynamic control during metalation of toluene would require rapid intermolecular equilibration. It is immediately obvious from Table II that, given sufficient time, *p*-sodiotoluene does undergo rearrangement to thermodynamically favored benzylsodium in the presence of toluene.[15,16] However, it appears equally clear that rearrangement is comparatively slow and cannot account for the high selectivity for metalation at the benzyl position. Thus, in metalation of toluene the aromatic product obtained following carbonation after 30 min contact with *n*-butylsodium was 92% phenylacetic acid from metalation at the benzyl position (reaction 1), while *p*-sodiotoluene after 30 min under the same reaction conditions gave >98% *p*-toluic acid (Table II, entry 3a), indicating little if any rearrangement after this time period. These results suggest that metalation of toluene with *n*-butylsodium can be outlined as in Scheme I. Initial proton abstraction from toluene is apparently competitive at ring (*meta* and *para*) positions and at the benzyl position, with reaction at the benzyl carbon being favored. This is followed by a comparatively slow conversion of the ring-substituted isomers to the thermodynamically favored benzylsodium.



Scheme I



It is of interst to consider the conversion of ring-substituted sodio derivatives to benzylsodium in greater

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[12] Prepared from *n*-butyl chloride and the appropriate metal as described in ref 1e.

[13] This observation leads to the conclusion that the metalating agent is *n*-butylpotassium, as assumed in this discussion, rather than its decomposition products [see R. A. Finnegan, *Trans. N. Y. Acad. Sci.*, [II] 27, 730 (1965)].

[14] Rearrangement of *o*- and *m*-sodio derivatives has not been excluded, but appears highly unlikely from these results with the *para* isomer.

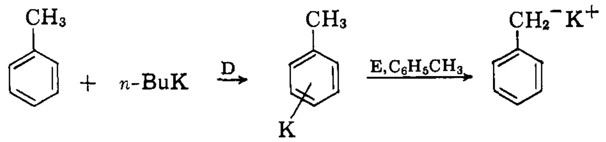
[15] In contrast to an earlier report,[1a] a preparation of *p*-sodiotoluene in benzene rearranged to benzylsodium to the extent of 23% after 1 week at room temperature. Thus, relative yields of 23% phenylacetic, 73% *p*-toluic, and 4% benzoic acids were obtained. See ref 1b for a discussion of this apparent discrepancy.

[16] As seen in Table II, complete rearrangement was not attained; however, ~95% of the organometallic was present as benzylsodium after ~70 hr.

detail. As noted in Table II neither *meta* nor *ortho* isomers were detected during this rearrangement[17] process although the analytical technique (glpc) easily distinguished the various isomers. A direct conversion is then indicated rather than a series of equilibration reactions, suggesting that *p*-sodiotoluene is even more selective in metalation of toluene at the benzyl position than is *n*-butylsodium. Since *p*-sodiotoluene is less basic than *n*-butylsodium, greater selectivity for reaction at the thermodynamically favored position is not surprising.[18,19]

Extension of this line of reasoning to metalation reactions involving organopotassium compounds does not appear to be supported by the observations. Since the carbon–metal bond in organopotassium reagents is more ionic[20] and these compounds have been shown[21] to be more reactive than the corresponding organosodium reagents, it might be expected that sp^2 C–H positions would be favored during metalation. In the present case, however, metalation of toluene with *n*-butylpotassium under the same conditions as used in the *n*-butylsodium reaction gave phenylacetic acid upon carbonation with no evidence for the formation of ring-substituted isomers. It could be argued that this metalation reaction represents a case in which the kinetically favored ring isomers rearrange so rapidly that they cannot be detected in the reaction mixture; however, the foregoing demonstration that a sequence of this nature is not the controlling factor during metalation with *n*-butylsodium makes such a proposal appear unlikely. Moreover, at these short reaction times carbonation provides valeric acid, as well as the toluene derivative, requiring that metalation by the ring potassio derivatives be more rapid than metalation by *n*-butylpotassium for such a scheme to be operative, *i.e.*, E > D in Scheme II.

Scheme II



It therefore seems more reasonable to propose that in comparison of alkylsodium and alkylpotassium reagents the potassium compound favors initial metalation at the resonance-stabilized position relative to the organosodium reagent.[22] This then suggests that resonance factors become more important as the ionic character of the organometallic is increased.

A similar scheme was proposed earlier in the 1-olefin system, which contains vinylic and allylic positions comparable to the ring and benzylic positions of alkylbenzenes, and it appears that many of the observations concerning alkylaromatic metalations are rational on the same basis. In fact the over-all agreement with the experimental data, which is discussed below, lends perhaps the strongest support to the proposals outlined in this paper.

In agreement with the proposal that metalation reactions generally involve relatively rapid initial steps followed by slower rearrangement processes, Benkeser, *et al.*,[1c] have made the following observations on the metalation of ethylbenzene. Using alkylsodium reagents, a high degree of ring metalation (82% relative yield) was realized at short reaction time (3 hr). Moreover, it was shown that longer reaction periods (20 hr) gave a lower relative yield (33%) of ring-substituted product. Finally, it was demonstrated that ring-substituted sodio compounds, prepared by an alternate route, underwent conversion to the resonance-stabilized isomer (~90% conversion after 20 hr) in the presence of excess ethylbenzene. These studies show that a kinetically favored process, producing intermediates which undergo rearrangement to a more stable product, is operative, as was concluded by these authors. These data do not, however, relate the comparative rates of the initial metalation reaction to the subsequent rearrangement process, and it appears both likely and reasonable[23] that an initial metalation reaction is followed by a comparatively slow isomerization to the more stable species. Thus, after a 3-hr reaction period, ~32% actual yield of product was reported and after 20 hr, ~43% was obtained. This can be interpreted as meaning that the metalation reaction was ~75% complete after 3 hr, while the rearrangement process required 20 hr to go to 90% completeness. At the very least, these data are compatible with the above proposal relating the relative rates of metalation to rearrangement.

In the same paper metalation of ethylbenzene with *n*-amylpotassium was reported. With this reagent only minor amounts of ring-substituted products were realized at the shortest reaction time employed (~7% after 0.5 hr). While the rearrangement may be more rapid in this system than in the organosodium case, it is doubtful that rearrangement becomes more rapid than the initial metalation reaction.[23] This suggests that the use of organopotassium metalating agents favored initial reaction at the resonance-stabilized position relative to organosodium compounds in this system also.[1e]

Metalation of cumene has also received recent attention.[1b,c] The over-all results can be briefly described

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[17] This result contrasts with those of Benkeser[1c] on rearrangements in the ethylbenzene and cumene systems.

[18] W. H. Puterbaugh and C. R. Hauser, *J. Am. Chem. Soc.*, **85**, 2467 (1963), have reported similar observations in comparison of the metalation of benzyldimethylamine with phenylsodium and *n*-butylsodium; *i.e.*, phenylsodium gave more selective reaction at the benzyl position.

[19] A rationale for reaction at nonstabilized sp^2 C–H positions has been offered [C. D. Broaddus, T. J. Logan, and T. J. Flautt, *J. Org. Chem.*, **28**, 1174 (1963)], based on the extent of bond breaking in the transition state. Thus, following the Hammond postulate [G. S. Hammond, *J. Am. Chem. Soc.*, 77, 334 (1955)], it can be proposed that more basic reagents result in transition states more nearly resembling the ground-state molecule. Since resonance factors should operate less effectively as the ground state is approached, the extent of s character of the C–H bond would become more important in determining the kinetic acidity and therefore the initial site of metalation. Thus, reaction of alkylbenzenes at ring positions, having high s character relative to the benzyl positions, would be favored with saturated alkylsodium compounds compared to reaction with less basic unsaturated organosodium reagents.

[20] E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p 65.

[21] H. Gilman and J. W. Morton, Jr. [*Org. Reactions*, **8**, 283 (1954)], report that in comparative metalations of dibenzofuran using ethyllithium, ethylsodium, and ethylpotassium the extent of metalation increases by factors of 1, 46, and 139 in the order given when the reactions are interrupted after 2.5 hr.

[22] See also A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1636 (1958).

[23] Greater reactivity of a saturated metalating agent, as compared to an sp^2 anionic species, would be expected. See R. Waack and P. West, *J. Am. Chem. Soc.*, **86**, 4494 (1964), for kinetic data supporting this order in metalation of triphenylmethane with organolithium compounds. This paper also discloses inordinately rapid reactions of resonance-stabilized organolithium species. See also ref 1e.

as follows. Alkylsodium reagents gave almost exclusively ring-metalated products in relatively high yields after a 20-hr reaction period. At longer reaction times, decomposition of the organosodium product through formation of unstable α-cumylsodium resulted.[1c,24] From the yield data it appears that the initial metalation reaction, to produce ring-substituted isomers, is complete after the 20-hr interval and is followed by slower rearrangement reactions. With alkylpotassium compounds, formation of the resonance-stabilized species is favored. At the shortest time employed (3 hr) a 42% relative yield of this benzylic material was obtained, while at longer times, rearrangement of the ring isomers to the more stable isomer resulted. Again a rationale based on a relatively rapid metalation rection which favors initial attack at the resonance-stabilized position, relative to organosodium reactions, followed by a slower rearrangement is reasonable.

If it can be accepted that metalation reactions involve competitive reactions at nonstabilized sp^2 C–H positions and at resonance stabilized positions, as the data apparently require, then the over-all trends in metalation of toluene, ethylbenzene, and cumene fit the general concepts derived from kinetic hydrocarbon acidity studies.[25] Thus, Streitwieser[26] has shown that the relative rates of exchange of these compounds at the α position decrease in the order, toluene (1.00), ethylbenzene (0.116), and cumene (0.0079). This rate retardation has been attributed to the inductive effect of the attached methyl groups which would be expected to exert only comparatively small effects into the ring.[27] Therefore, in a competitive situation a greater extent of reaction would be expected at ring positions as the number of methyl groups at the α position is increased.

That this type explanation is consistent with the reported results can be seen more clearly by briefly considering metalation of these compounds with organosodium and organopotassium compounds separately. With alkylsodium compounds, initial metalation of toluene gives high relative yields of benzylsodium; with ethylbenzene, reaction at ring positions is favored, although it appears that metalation at the α position competes effectively;[1c] and finally, cumene gives almost exclusively ring-metalated products.[1c] These results agree with the expectations based on competitive metalations. In the case of organopotassium reagents, toluene apparently gives exclusive α metalation, reaction of ethylbenzene gives high relative yields of α-metalated products at very short reaction times,[1c] and metalation of cumene is apparently competitive at the two types of reaction sites.[1c] It can be seen that the same general trend is observed in the two systems; however, the use of the more ionic organopotassium reagent results in more extensive reaction at the resonance-stabilized position, relative to organosodium, in all cases.

While metalation reactions can be explained using the same general concepts as those employed for base-catalyzed exchange reactions, it is immediately apparent, as was pointed out by Benkeser, that the kinetically favored position of metalation is *not* controlled by the thermodynamic acidity of the hydrocarbon.

Summary. The products obtained from metalation of toluene with alkylsodium reagents have been shown to be determined predominantly by the initial position of metalation rather than by a kinetically controlled process followed by equilibration reactions. Since alkylpotassium compounds give exclusively the thermodynamically favored product (benzylpotassium) at short reaction times, it is proposed that this process is also controlled by the initial position of metalation. It is also proposed that an increase in the electropositive character of the metal used in the metalating agent favors initial reaction at a resonance-stabilized sp^3 position relative to a nonstabilized sp^2 position, and this proposal is discussed in view of the results obtained with α olefins, toluene, ethylbenzene, and cumene.

Experimental Section

Materials. *p*-Bromotoluene was purchased from Matheson Coleman and Bell and used as received. Toluene was obtained from Baker and Adamson and used as received. *n*-Butyl chloride was purchased from Matheson Coleman and Bell and distilled before use. Methyl *p*-toluate, methyl *m*-toluate, methyl *o*-toluate, and methyl phenylacetate were purchased as the acids from Matheson Coleman and Bell and esterified with methanol using a catalytic amount of sulfuric acid.

Reaction of *p*-Bromotoluene with Sodium Metal. A typical experiment from which the data contained in Table I were obtained will be described. To 200 ml of octane contained in a three-necked flask equipped with high-speed stirrer[28] was added sodium metal (4.6 g, 0.2 g-atom). The mixture was heated above the melting point of sodium and the metal dispersed by rapid stirring. After cooling to 0 to −10°, *p*-bromotoluene (8.5 g, 0.049 mole) was added dropwise. Stirring was continued for 1 hr at 0° and the reaction mixture than allowed to warm to room temperature. After standing overnight, the mixture was carbonated by pouring over excess solid carbon dioxide. The acidic product (6.3 g, 95%) was worked up as usual. The crude acid product melted at 170–173°. The reported melting point for *p*-toluic acid is 179–180°. Esterification by refluxing in methanol with a catalytic amount of sulfuric acid provided an ester which was identical with methyl *p*-toluate by glpc and infrared analyses. This material was at least 98% pure by glpc analysis. The yields and nature of the product upon carbonation at various time intervals are recorded in Table I.

Reaction of *p*-Sodiotoluene with Toluene. These reactions were conducted both by the addition of toluene to a preformed mixture of *p*-sodiotoluene in octane and by the formation of *p*-sodiotoluene in neat toluene. To obtain entries 1 and 2 of Table II, toluene (46 g, 0.5 mole) was added to a preformed mixture of *p*-sodiotoluene which was prepared as described above. The reaction mixture was then stirred for the specified length of time and carbonated by pouring over excess solid carbon dioxide. Work-up and esterification was followed by glpc comparison to authentic samples of methyl *o*-toluate, methyl *p*-toluate, methyl *m*-toluate, and methyl phenylacetate to obtain the compositions of acid products recorded in Table II.

Metalation of Toluene with *n*-Butylsodium. These metalations were conducted by formation of the metalating agent in toluene. A sodium (4.6 g, 0.2 g-atom) dispersion was prepared in 200 ml of toluene. To this mixture was added *n*-butyl chloride (9.2 g, 0.1 mole) dropwise at 0°. After addition was complete (required *ca.* 20 min), the mixture was stirred for 30 min. The usual carbonation procedure provided 5.7 g of acid product. Analysis of the methyl esters by glpc showed the aromatic products to be 92% methyl phenylacetate, 4% methyl *p*-toluate, and 4% methyl *m*-toluate.

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[24] Some disparity in ref 1b and 1c exists on the occurrence of rearrangement, although it appears clear that the initial metalation sequence occurs prior to any rearrangement process in both systems. The fact that rearrangement occurs in one case[1c] and is not reported in the other[1b] may be due to inclusion of lithium in the reaction system[1b] (see ref 15).

[25] A. Streitwieser, Jr., R. A. Caldwell, R. G. Lawler, and G. R. Ziegler, *J. Am. Chem. Soc.*, **87**, 5399 (1965), and references therein.

[26] A. Streitwieser, Jr., and D. E. Van Sickle, *ibid.*, **84**, 249 (1962).

[27] A. I. Shatenshtein [*Tetrahedron*, **18**, 95 (1962)] has related the partial rate factor for exchange at the *ortho* position of substituted benzenes to Taft's σ constants.

[28] The apparatus used is described in "Sodium Dispersions," U. S. Industrial Chemical Co., New York, N. Y., p 18.

Metalation of Toluene with *n*-Butylpotassium. Molten potassium metal (3.9 g, 0.1 g-atom) was subjected to high-speed stirring in 150 ml of octane for 3 min. To the cooled mixture was added *n*-butyl chloride (4.6 g, 0.05 mole) in 25 ml of octane, dropwise, over a 15-min interval. The temperature was maintained between −10 and −5° and the reaction mixture allowed to stir for 30 min after completion of addition while warming to room temperature. Toluene (46 g, 0.5 mole) was added rapidly and stirring was continued for 30 min. Carbonation was effected by pouring over a large excess of solid carbon dioxide. All operations were conducted under an argon atmosphere. The usual work-up[1e] provided a crude acid product (2.65 g) which was esterified using methanol and a catalytic amount of sulfuric acid. Analysis by glpc gave two peaks with relative areas of 11.5 and 88.5. These two peaks accounted for a minumum of 99% of the total area recorded on the chromatogram. The minor component had a retention time identical with that of methyl valerate and a sample of this compound, collected by glpc, had an infrared spectrum superimposable on that obtained from an authentic sample of methyl valerate. The major peak was identical with methyl phenylacetate by glpc.

The Problem of Metal Atom Participation in Electrophilic Substitution Reactions of the Iron Group Metallocenes

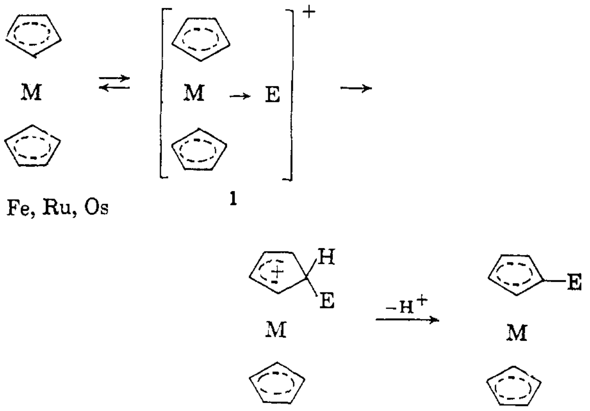
M. Rosenblum and F. W. Abbate[1]

Contribution from the Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154. *Received March 30, 1966*

Abstract: In order to examine the question of metal atom participation in the electrophilic substitution reactions of ferrocene, intramolecular ring acylation by the epimeric pair of acids **13** and **14**, which are constrained by their stereochemistry to either exo- or endocyclic electrophilic attack, has been studied. The synthesis and proof of structure of these acids are described. Each of these acids cyclized in the presence of trifluoroacetic acid to a homocyclic ketone, the rate of cyclization of the *exo* acid being somewhat more rapid than that of the *endo* acid. These results demonstrate that the metal atom is not an essential participant in the acylation of ferrocene, and suggest furthermore that it does not provide any particular energetic advantage in these processes.

Participation by the nonbonding metal 3d-orbital electrons in the reactions of the iron group metallocenes has been a subject of continued interest since the major outlines of the chemistry and electronic structure of these substances became apparent. Aside from oxidation of the metallocenes in which one or more of these electrons are undoubtedly involved, the metal atom has been suggested as the site of protonation[2] and of hydrogen bonding,[3] and has been invoked as a neighboring group in internal electron-transfer reactions of α-metallocenyl carbonium ions[4] and in solvolyses of α-metallocenylcarbinyl acetates.[3b,5] The latter attribution has recently been questioned by Ware and Traylor.[6]

Recently we suggested that the metal atom might play a critical role in electrophilic substitution reactions of the metallocenes by functioning as the primary site of electrophilic attack.[7] Ring substitution was proposed to occur through rate-limiting rearrangement of this cation **1** to a σ complex **2** followed by the loss of a proton.



M = Fe, Ru, Os

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2

Although many features of this mechanism seemed attractive, the evidence supporting it was indirect and largely inferential. Moreover, certain other observations[8] appeared to be at variance with it, and, accordingly, a more rigorous examination of these proposals was undertaken. The present paper provides some preliminary results of this investigation.

Results

Since an essential aspect of the proposed mechanism is the endocyclic mode by which ring substitution is assumed to take place, we chose to examine the intramolecular acylation reactions of an epimeric pair of ferrocenecarboxylic acids which would be constrained by their stereochemistry to either exocyclic or endocyclic electrophilic attack.

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(1) Taken in part from a dissertation submitted by F. W. Abbate in partial fulfillment of the requirements for the Ph.D. degree.

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