The shift reflects the change in aromatic character of the ring[33] and also the loss of the inductive and resonance effects of the 1-oxide function.[11]

3-Alkenyl-1-hydroxy-2-pyridones. The starting 1-oxides were dissolved in diglyme and rearranged in sealed tubes at 137°. The products were isolated and identified spectrally as before. The physical properties are given.

Nmr Analysis[26] of 3-Alkenyl-1-hydroxy-2-pyridones. *cis*- and *trans*-3-Crotyl-5-methyl-1-hydroxy-2-pyridones (XX): (CCl_4, TMS) 5-CH_3 2.09, singlet (relative area, 3.0); γ-CH_3 1.65, quartet (3.0); OH 12.4, broad singlet (1.1); CH_2 3.10, broad multiplet (2.0); CH=CH 5.43, broad multiplet (2.0); H_4 6.92, broad multiplet (1.0); H_6 7.33 ppm, broad multiplet (1.0).

3-Allyl-1-hydroxy-2-pyridone (XXI): (CCl_4, TMS) CH_2 3.23, doublet J = 6.7 cps (2.0); OH 13.5, broad singlet (0.8); CH_2= 5.05, multiplet (1.8); CH=, H_5 6.14, multiplet (2.0); $H_{4,6}$ 7.18 ppm, multiplet (1.9).

The position of the OH resonance was concentration dependent. Similar behavior has been noted for oximes.[34]

Note that the resonance due to the methylene group is upfield at 3.10 ppm for XX and at 3.23 ppm for XXI. It appears between 4.2 and 4.8 ppm in both the 1-oxides and the 1-alkenyloxy-2-pyridones. As can be seen, substitution of the methyl group in the 5 position results in the loss of the signal farthest upfield. Furthermore, the ring substituent has smeared the methylene signal in the alkene moiety.[23] Therefore, the allylic group is on the 3 position of the ring.

***cis*- and *trans*-3-Crotyl-5-methyl-1-hydroxy-2-pyridones (XX).** The solution of the 2-α-methylallyloxy-5-methylpyridine 1-oxide (IX, 0.1 g) was heated for 1 hr. After removal of the solvent and cooling, the product was isolated by suction filtration. Sublimation at 70° (0.01 mm) gave XX in 65% yield, mp 111–112° (softens 105°). Mass spectral analysis[17] using a direct inlet source showed the parent peak (22%) at *m/e* 179; ir (Nujol mull) broad OH and CH at 3.0–4.0 and carbonyl at 6.05 μ; uv_{max} (C_2H_5OH) 207, 234, and 303 mμ.

Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.05, 66.94; H, 7.43, 7.50; N, 7.77, 7.69.

3-Allyl-1-hydroxy-2-pyridone (XXI). The solvent was removed after heating a 0.2-g sample of 2-allyloxypyridine 1-oxide (I) for 3.5 hr. Partial separation to give 0.03 g (XXI) was achieved by column chromatography on silica gel using ethyl acetate as the eluent. Two sublimations at 60° (0.1 mm) gave the pure sample, mp 92–94°. Mass spectral analysis[17] using a direct inlet source showed the parent peak (10%) at *m/e* 151; ir (Nujol mull) broad OH and CH at 3.0–4.0 μ and carbonyl at 6.13 μ; uv_{max} (C_2H_5OH) 206, 231, and 304 mμ.

Crossover Experiment. Equimolar quantities (4×10^{-4} *M*) of 2-crotoxypyridine 1-oxide (II) and 2-allyloxy-5-methylpyridine 1-oxide (VII) were dissolved in 2 ml of diglyme and heated in a sealed tube at 83° for 24 hr when the reaction was complete. After concentration of the solution the components were partially resolved by using a 5-ft 20% DC 200 silicon oil column on Chromosorb W. Infrared analysis showed pure 1-allyloxy-2-pyridone (X) was present (20% by vpc).

Rate Determinations. Samples of 2-α-methylallyloxy-5-methylpyridine 1-oxide (VIII) were dissolved in diglyme and placed in sealed nmr tubes. The initial spectrum was taken on a Varian A-60 instrument before the tube was heated in a stirred oil bath at the appropriate temperature. The increase in the signal at 1.7 ppm due to the γ-methyl group was followed to infinite time by removing the tube at intervals and quenching the reaction by cooling in Dry Ice. The rate of 1-oxide disappearance was obtained by plotting log ($\text{integral}_\infty - \text{integral}_t$) *vs.* time. Excellent straight lines were obtained in this manner. This method assumes that the ratio of the individual rate constants remains constant throughout the reaction.[35] The composition was corrected for any signal due to the 1-crotoxy-5-methyl-2-pyridone (XVIII) by obtaining the ratio of it to 1-α-methylallyloxy-5-methyl-2-pyridone (XIX) using vpc analysis. The integral was then corrected and the percentages of XVIII, XIX, and XX obtained from the nmr integrations.

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[34] G. C. Kleinspehn, J. A. Jung, and S. A. Studniarz, *J. Org. Chem.*, **32**, 460 (1967).

[35] J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chapter 3; F. Daniels and R. A. Alberty, "Physical Chemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 12.

Factors Governing Orientation in Metalation Reactions. IV. The Role of Alkoxide in Metalation Reactions Involving Organosodium Compounds

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Abstract: The metalation of *t*-butylbenzene with *n*-amylsodium, both in the presence and absence of sodium *t*-butoxide, was studied. The yield of the alkoxide metalation was much higher than the yield without alkoxide. A variable which affects isomer distribution, both in the presence or absence of alkoxide, is the amount of dimetalation which occurs, since the latter takes place principally at the expense of the *meta* isomer. In the presence of alkoxide, the *meta* isomer, which initially forms rapidly (presumably because of favorable statistics, *i.e.*, two *meta*, one *para* position), equilibrates with excess *t*-butylbenzene *via* a transmetalation and ultimately is converted to the more thermodynamically favored *para* isomer. Pure *m*-*t*-butylphenylsodium in the presence of sodium *t*-butoxide and excess *t*-butylbenzene was isomerized 70–80% to the *para* isomer. Under comparable conditions, pure *p*-*t*-butylphenylsodium was isomerized only about 2% to the *meta* isomer. A study of the supernatant layers which arise from centrifuging *n*-amylsodium and *n*-amylsodium–sodium alkoxide combinations in nonane was carried out. Evidence was obtained that the sodium *t*-butoxide tends to disperse or peptize the *n*-amylsodium aggregates.

In his pioneering work on organosodium chemistry, Professor A. A. Morton and his collaborators demonstrated that metal alkoxides[1] exert a profound effect on certain reactions involving organosodium compounds. Thus, the rate of Wurtz coupling reactions between organosodium compounds and alkyl halides is accelerated by a variety of alkoxides,[2] and the catalytic activity of

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[1] A. A. Morton, C. E. Claff, Jr., and F. W. Collins, *J. Org. Chem.*, **20**, 428 (1955).

[2] A. A. Morton and A. E. Brachman, *J. Am. Chem. Soc.*, **73**, 4363 (1951).

allylsodium in the polymerization of butadiene is altered as well.[3]

It was also reported that the yields of metalation products and the amount of *meta* isomer is greatly increased when *t*-butylbenzene is metalated by *n*-amylsodium in the presence of certain alkoxides.[1] The suggestion was made that, in the latter reaction, the alkoxides facilitate the dissociation of the R^-Na^+ ion pairs into radicals which initiate the reaction. In a later[4] and more detailed explanation of this alkoxide effect, it was stated that the amount of *p*-*t*-butylphenylsodium diminishes with time, both in the presence and absence of alkoxides. This was said to be the result of a secondary metalation of unchanged *t*-butylbenzene by the initially formed *p*-*t*-butylphenylsodium. Obviously the results could be explained if the secondary metalation occurred preferentially in the *meta* position.

In recent years, the importance[5] of "alkoxide effects" and of heterogeneity[6] has been questioned in connection with metalation reactions involving organoalkali compounds.[7] Such conclusions seemed eminently reasonable since a number of earlier experimental observations in this field, originally attributed to heterogeneity, were shown to be caused by other phenomena.[8]

We have carefully reexamined the metalation of *t*-butylbenzene by *n*-amylsodium both in the presence and absence of sodium *t*-butoxide. While our results are in agreement with earlier observations[1] that such alkoxides increase the yield of metalation products, they are at sharp variance with the previous reports[1,4] of the effects of these alkoxides on isomer distribution.

When 0.1 mol of *t*-butylbenzene was treated with *n*-amylsodium (from 0.2 mol of *n*-amyl chloride) in nonane for 20 hr, only a 15–20% yield of metalation product resulted as adjudged by the methyl esters obtained after carbonation and treatment with diazomethane. The isomer distribution varied with time as shown in Table I. Initially, almost a 50:50 *meta*:*para* isomer distribution was obtained, but, with time, the *meta* isomer diminished (not the *para* as was claimed[4]). At the same time, dimetalation was occurring, obviously at the expense of the *meta* isomer.[9]

Table I. Variation of Isomer Distribution when *t*-Butylbenzene is Metalated with *n*-Amylsodium

Time, hr	*meta*, %	*para*, %	Di.[a] %
0.25	49	51	0
5	31	51	18
20	31	50	18

[a] The purity of the dimethyl 5-*t*-butylisophthalate is yet to be established. It may be contaminated with small amounts of another isomer.

Table II. Variation of Isomer Distribution when *t*-Butylbenzene is Metalated with *n*-Amylsodium in Nonane Containing Sodium *t*-Butoxide

Time, hr	*meta*, %	*para*, %	Di, %
0.25	58	42	Trace
5	49	43	8
20	47	45	8
25[a]	32[a]	64[a]	5[a]

[a] At the end of 20 hr, an additional 0.2 mol of *t*-butylbenzene was added, and the reaction was allowed to proceed for an additional 5 hr. The final entry shows the isomer distribution at the end of this time.

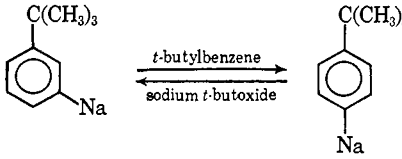
In Table II are listed the results of an identical metalation, except that the reaction was carried out in the presence of 0.08 mol of externally prepared sodium *t*-butoxide. Several points of comparison are noteworthy. (1) The yield of the alkoxide metalation (Table II) was 70% in contrast to 17% in the absence of alkoxide (Table I). (2) The yield of *meta* isomer starts out only 9% higher in the alkoxide run, but diminishes more slowly with time because of the slower formation of dimetalation products. Clearly, one variable which affects isomer distribution, either in the presence or absence of alkoxide, is the amount of dimetalation which occurs.

Table III vividly illustrates another variable affecting isomer distribution in the presence of alkoxides—the concentration of the *t*-butylbenzene relative to the *n*-amylsodium. When *t*-butylbenzene is in large excess, *para* substitution predominates and not *meta* (Table III). This is illustrated in another way by the last entry in Table II. After 20 hr, the addition of more *t*-butylbenzene caused a shift of the *meta* to *para* isomer.

Table III. Variation of Isomer Distribution when Excess *t*-Butylbenzene is Metalated with *n*-Amylsodium in Nonane Containing Sodium *t*-Butoxide

Time, hr	*meta*, %	*para*, %	Di, %
0.25	33	67	...
5	31	69	...
20	26	74	...

The reason for the preponderance of *para* isomer in the presence of excess *t*-butylbenzene (Table III) was traced to a rather rapid equilibration which occurs between the *meta* and *para* isomers in the presence of alkoxides.



When pure *m*-*t*-butylphenylsodium in nonane was added to *t*-butylbenzene, only about 5% transmetalation occurred to form *para* isomer, even after reaction times of up to 3 days. By contrast, in the presence of sodium *t*-butoxide, 75–80% of the *meta* isomer isomerized to *para* in the same time period. Under comparable conditions, pure *p*-*t*-butylphenylsodium was isomerized to *meta* only about 2% in the presence or absence of sodium *t*-butoxide.[10]

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(3) A. A. Morton, *Ind. Eng. Chem.*, 42, 1488 (1950).

(4) A. A. Morton, "Solid Organoalkali Metal Reagents," Gordon and Breach Science Publishers, Inc., New York, N. Y., 1964, pp 42–43.

(5) D. Bryce-Smith, *J. Chem. Soc.*, 1079 (1954).

(6) D. Bryce-Smith, *ibid.*, 5983 (1963).

(7) See A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1636 (1958), for a partial rebuttal.

(8) R. A. Benkeser and J. L. Bach, *J. Am. Chem. Soc.*, **86**, 890 (1964), and earlier papers in this series. See also D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956), and previous papers in this very excellent series.

(9) It would seem very reasonable that *m*-*t*-butylphenylsodium should metalate more readily than the *para* isomer. See A. A. Morton and C. E. Claff, Jr., *J. Org. Chem.*, **21**, 736 (1956), for substantiation of this premise.

(10) A finding at extreme variance with published results. See ref 4, p 42.

It is also significant that the mode of preparing[7] the samples of *m*- and *p*-*t*-butylphenylsodium did not affect their tendency to rearrange. When the sodium compounds were prepared from either bis(*p*-*t*-butylphenyl)mercury or bis(*m*-*t*-butylphenyl)mercury rather than from the corresponding aryl halides, comparable results were obtained.

It is now eminently clear that once again a kinetic *vs.* a thermodynamic effect is in operation.[11] In the presence of alkoxides, the *meta* isomer, which initially forms rapidly (probably because of favorable statistics: 2-*meta;* 1-*para* position), equilibrates with excess *t*-butylbenzene by a transmetalation process and ultimately is converted to the more thermodynamically favored *para* isomer. In the absence of alkoxides, the *meta* isomer slowly diminishes with time because of its conversion to dimetalated materials by unreacted *n*-amylsodium in the system.

That the conversion of the *m*-sodio to the *p*-sodio isomer was occurring by a transmetalation process involving unchanged *t*-butylbenzene, was clearly indicated by the fact that this transformation did not occur at any appreciable rates in the *absence* of *t*-butylbenzene. This was true even in the presence of sodium *t*-butoxide.

We next turned our attention to the problem of *why* sodium *t*-butoxide activates *n*-amylsodium. Dramatic differences were revealed when we compared the supernatant liquid which resulted from centrifuging suspensions of *n*-amylsodium in nonane with the supernatants obtained from suspensions of *n*-amylsodium in nonane containing sodium *t*-butoxide. The former were colorless and contained no detectable amounts of *n*-amylsodium. The latter were deep brown in color and contained small, but definite quantities of *both* *n*-amylsodium and sodium *t*-butoxide (in the ratio of about 1 to 5). Treatment of these clear, colored layers with trimethylchlorosilane resulted in the formation of *both* *n*-amyltrimethylsilane and *t*-butoxytrimethylsilane. When *t*-butylbenzene was added to these colored hydrocarbon layers, "homogeneous" metalations occurred as adjudged by peaks in the gas chromatogram corresponding in retention times to the *m*- and *p*-*t*-butylmethyl benzoates and the *t*-butylphenyltrimethylsilanes.

Discussion

n-Amylsodium probably exists as a highly associated species,[12] and, as such might be expected to be very insoluble in hydrocarbon solvents particularly in view of its ionic nature. The metalation of *t*-butylbenzene with *n*-amylsodium in the absence of alkoxides would seem to be a heterogeneous process occurring almost entirely on the surface of the *n*-amylsodium aggregates. As these rather coarse aggregate particles become coated by the metalation products (themselves rather insoluble), the rate of the metalation gradually slows down and finally stops. This would explain why *n*-amylsodium, suspended in nonane, metalates *t*-butylbenzene in such low yield and why rather considerable amounts of unreacted *n*-amylsodium remain after the metalation has stopped.

Seemingly, the sodium *t*-butoxide has a dispersing or peptizing action on the *n*-amylsodium aggregates causing them to disintegrate into much finer particles. The extent of this disintegration is so complete in the case of *some* of the particles that they form essentially a "homogeneous" solution resulting in the clear, colored supernatant layers we observed. Actual complex formation between the two species might occur during this process or simply a physical adsorption of the sodium *t*-butoxide on the surface of the *n*-amylsodium. Whatever the mechanism, the result is a breakdown in the particle size of the *n*-amylsodium and a considerable increase in its surface area and reactivity. What may be related phenomena have been reported for other systems, particularly those involving RLi compounds and amines.[13]

It is not certain whether the clear, highly colored hydrocarbon layers obtained by centrifuging contain monomeric or dimeric *n*-amylsodium complexed with sodium *t*-butoxide or not. What is eminently clear is that the particles in these layers are considerably smaller than the gross particle size which exists when *n*-amylsodium or sodium *t*-butoxide are prepared separately in nonane. While we have demonstrated that "homogeneous" metalations can occur in these clear brown layers, it must be borne in mind that the concentration of *n*-amylsodium in these layers is extremely small. We are inclined to believe that, even in the presence of alkoxides, under normal metalation conditions, the *bulk* of the reaction may still be heterogeneous, occurring on the surface of the finely dispersed *n*-amylsodium particles.

Experimental Section

Glassware was dried at 120° and flushed with nitrogen before being used in organosodium reactions. Reactions involving the organosodium compounds were run in a Morton flask fitted with a high-speed stirring apparatus. The latter can be purchased from LaPine Scientific Co. under the name "Stir-O-Vac."

***m*- and *p*-Bromo-*t*-butylbenzenes.** Pure *m*-bromo-*t*-butylbenzene was prepared by the following reaction sequence.[14] Acetanilide and *t*-butyl chloride in the presence of aluminum chloride produced *p*-*t*-butylacetanilide, mp 169–170° (lit.[15] 170–171°). Treatment of the latter with bromine and iron filings in an adaptation of the method[16] to make 2-bromo-4-isopropylacetanilide produced 2-bromo-4-*t*-butylacetanilide, mp 155–157° (lit.[17] 156–157°). Hydrolysis and deamination of this compound gave *m*-bromo-*t*-butylbenzene free of *ortho* and *para* isomers (vpc analysis), bp 100° (10 mm) (lit.[18] 103–106° (17 mm)); $n^{20}\mathrm{D}$ 1.5350 (lit.[19] $n^{20}\mathrm{D}$ 1.5356).

p-Bromo-*t*-butylbenzene was obtained by reaction of bromobenzene and *t*-butyl chloride in the presence of ferric chloride. The product (85% pure as adjudged by vpc) boiled at 231°; $n^{20}\mathrm{D}$ 1.5238 (lit.[20] bp 227°; $n^{20}\mathrm{D}$ 1.5268).[21]

***p*-Chloro-*t*-butylbenzene.** Prepared by the reaction of chlorobenzene and *t*-butyl chloride in the presence of ferric chloride.[14,22] The product contained about 2% of the *meta* isomer as adjudged

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(11) (a) R. A. Benkeser, A. E. Trevillyan, and J. Hooz, *J. Am. Chem. Soc.*, 84, 4971 (1962); (b) R. A. Benkeser, J. Hooz, T. V. Liston, and A. E. Trevillyan, *ibid.*, 85, 3984 (1963); See also C. D. Broaddus, *ibid.*, 88, 4174 (1966), and previous papers for very cogent experiments bearing on this concept.

(12) See ref 4, pp 5–6.

(13) T. L. Brown, *et al.*, *J. Am. Chem. Soc.*, 84, 1371 (1962); 86, 2135 (1964); *J. Organometal. Chem.* (Amsterdam), 3, 1 (1965); J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, 85, 2171 (1963); see also H. E. Zaugg and A. D. Schaefer, *ibid.*, 87, 1857 (1965).

(14) See T. V. Liston, Ph.D. Thesis, Purdue University, 1960, for experimental details.

(15) M. S. Carpenter, W. M. Easter, and T. F. Wood, *J. Org. Chem.*, **16**, 608 (1951).

(16) E. C. Sterling and M. T. Bogert, *ibid.*, 4, 20 (1939).

(17) E. Berliner and M. M. Chen, *J. Am. Chem. Soc.*, 80, 343 (1958).

(18) C. S. Marvel, R. E. Allen, and C. G. Overberger, *ibid.*, 68, 1088 (1946).

(19) H. C. Brown, *et al.*, *ibid.*, **79**, 1897 (1957).

(20) M. E. Boedtker, *Bull. Soc. Chim. France*, (3), **35**, 829 (1906).

(21) D. I. Legge, *J. Am. Chem. Soc.*, **69**, 2086 (1947).

(22) M. Lerer and C. Fabre, *Bull. Soc. Chim. France*, 198 (1956).

by vpc analysis and boiled at 211–213°; $n^{20}D$ 1.5099 (lit.[14] bp 211°; $n^{20}D$ 1.5104).

Bis(*m*- and *p*-*t*-butylphenyl)mercurys. Both compounds were prepared in essential accordance with the method described for diphenylmercury.[23] The bis(*m*-*t*-butylphenyl)mercury (8 g, 8% yield) was obtained after recrystallizing the crude product from hot benzene. It melted at 134–135°.

Anal. Calcd for $C_{20}H_{26}Hg$: C, 51.44; H, 5.57; mol wt, 466. Found: C, 51.88; H, 5.87; mol wt, 448.

The nmr spectrum of the *meta* compound showed a singlet at 1.33 ppm (aliphatic H's) and a multiplet at 7.28 ppm (aromatic H's).

The bis(*p*-*t*-butylphenyl)mercury was prepared similarly and 40 g (19%) of material was obtained melting at 188–190° after two recrystallizations (benzene) and one sublimation.

Anal. Calcd for $C_{20}H_{26}Hg$: C, 51.44; H, 5.57; mol wt, 466. Found: C, 50.97; H, 5.28; mol wt, 427.

The nmr spectrum of the *para* compound showed a singlet at 1.28 ppm (methyl H's) and a quartet at 7.38 ppm (aromatic H's).

***n*-Amylsodium** was prepared by the dropwise addition of *n*-amyl chloride (21.3 g, 0.2 mol) in 25 ml of nonane (Phillip's Petroleum, 99 mol % pure) to a sodium dispersion (10.6 g, 0.46 g-atom) covered with 75 ml of nonane over a 1.5-hr period to 0 to −10°. The mixture was stirred for an additional hour to ensure complete reaction.

Metalation of *t*-Butylbenzene with *n*-Amylsodium. a. General Procedure. To a nonane suspension (100 ml) of *n*-amylsodium (*vide supra*) maintained at 0 to −10° was added 13.4 g (0.1 mol) of *t*-butylbenzene (Phillip's Petroleum 99 mol % pure) in 100 ml of nonane. The mixture was allowed to warm to room temperature and was then stirred for 20 hr. It was carbonated by pouring onto a Dry Ice–ether slurry. After the mixture had warmed to room temperature, a small piece of Dry Ice was added to produce a carbon dioxide atmosphere and then water was added to destroy excess sodium. The organic layer was separated and washed twice with water. The washings were combined with the original aqueous layer, and the latter was now extracted three times with ether. After the aqueous layer was acidified with concentrated HCl, it was extracted five times with ether. The combined ethereal extracts were treated with diazomethane[24] and dried over Drierite. After filtration, the solvent was removed (1-ft Vigreux column) and the crude methyl ester solution which remained was analyzed without further purification. The 17% yield[25] of esters was comprised of 30% methyl *m*-*t*-butylbenzoate, 51% methyl *p*-*t*-butylbenzoate, and 19% dimethyl *t*-butylbenzenedicarboxylate based on vpc analysis.[26]

b. Isomer Distribution with Time. *t*-Butylbenzene (13.4 g, 0.1 mol) was metalated with a 200-ml nonane suspension of *n*-amylsodium (*vide supra*). Aliquots (25 ml) were removed at 15-min, 5-hr, and 20-hr intervals, carbonated, esterified, and analyzed by vpc in the usual way.[27] The results are in Table I.

c. In the Presence of Sodium *t*-Butoxide. The same conditions were employed as described under general procedure a above, except that 7.7 g (0.08 mol) of sodium *t*-butoxide[28] was also present during the 20-hr reaction. Analysis of the methyl esters in the usual fashion indicated a yield of 70%, comprised of 51% methyl *m*-*t*-butylbenzoate, 41% methyl *p*-*t*-butylbenzoate, and 8% dimethyl *t*-butylbenzenedicarboxylate.

d. In the Presence of Sodium *t*-Butoxide and with Additional *t*-Butylbenzene Added after 20 Hr. Another reaction identical with c above was run and 25-ml aliquots were removed at 15-min, 5-hr, and 20-hr intervals. These were esterified and analyzed in the usual fashion. After the last aliquot was removed, additional *t*-butylbenzene (26.8 g, 0.2 mol) was added and the entire reaction mixture carbonated after 25 hr. The results appear in Table II.

e. In the Presence of Sodium *t*-Butoxide and with Excess *t*-Butylbenzene. The same reaction as described in c was repeated except that a large excess (40.2 g, 0.3 mol) of *t*-butylbenzene was used. Aliquots were withdrawn in the usual way. The results are given in Table III.

Attempted Isomerization of *p*-*t*-Butylphenylsodium in the Presence of *t*-Butylbenzene. a. Method I. To 3.45 g (0.15 g-atom) of sodium sand in 15 ml of nonane was added 7.6 g (0.045 mol) of *p*-chloro-*t*-butylbenzene in 10 ml of nonane over a 0.5-hr period. After about 0.5 ml of the halide solution had been added, a mildly exothermic reaction commenced. The mixture was maintained at 30° by means of a cooling bath during the addition of the remaining *p*-chloro-*t*-butylbenzene. One hour after the addition was completed, 12 g (0.09 mol) of *t*-butylbenzene in 85 ml of nonane was added. After 1 day, the mixture was carbonated and esterified in the usual way. A 62% yield of methyl *t*-butylbenzoates was obtained comprised of 2% *meta* isomer and 98% *para*.

In a similar experiment, the mixture was carbonated after a 2-week reaction period. The yield of esters was only 28% comprised of 2% *meta* and 98% *para* isomers.

b. Method II. To a flask heated to 50° and containing 3.45 g (0.15 g-atom) of sodium sand in 100 ml of nonane was added 11.7 g (0.025 mol) of bis(*p*-*t*-butylphenyl)mercury in several portions over 0.5 hr. The mercurial was added at such a rate that the temperature of the flask was maintained at 50° by the heat of the reaction. One hour after the *p*-*t*-butylphenylsodium was prepared, 13.4 g (0.10 mol) of *t*-butylbenzene was added to the flask. After 1 week the mixture was carbonated, worked up, and esterified in the usual manner. A 52% yield of methyl *t*-butylbenzoates was obtained comprised of 2% *meta* and 98% *para* isomer.

c. Method I in Conjunction with Sodium *t*-Butoxide. *p*-*t*-Butylphenylsodium was prepared from *p*-chloro-*t*-butylbenzene essentially as described above for method I using 0.3 g-atom of sodium sand and 0.1 mol of the chloro compound. One hour after the halide addition was completed, 1.48 g (0.02 mol) of *t*-butyl alcohol[29] and 13.4 g (0.1 mol) of *t*-butylbenzene were added. After 1 day the mixture was carbonated and esterified in the usual way. A 76% yield of esters was obtained containing 3% *meta* and 97% *para* isomers.

Another reaction which proceeded 3 days gave a 66% yield of esters which contained 2% *meta* and 98% *para* isomers.

Attempted Isomerization of *m*-*t*-Butylphenylsodium in the Presence of *t*-Butylbenzene. a. Method III. One milliliter of a solution of *m*-bromo-*t*-butylbenzene (21.3 g, 0.10 mol) and nonane (25 ml) were added to a sodium sand (5.75 g, 0.25 g-atom) which was maintained at 60–80°. When the reaction started as adjudged by the darkening of the mixture and a rise in temperature, the *m*-bromo-*t*-butylbenzene solution was added dropwise over 1 hr while the interior temperature of the flask was kept around 50°. One hour after the *m*-*t*-butylphenylsodium had been prepared, 13.4 g (0.10 mol) of *t*-butylbenzene was added to the reaction. After 1 day, the mixture was carbonated, worked up, and esterified in the previously described manner. A 58% yield of product was obtained containing 99% methyl *m*-*t*-butylbenzoate and 1% methyl *p*-*t*-butylbenzoate.

In an additional run, *m*-*t*-butylphenylsodium was prepared from 6.9 g (0.30 g-atom) of sodium sand covered with 75 ml of decane and 21.3 g (0.10 mol) of *m*-bromo-*t*-butylbenzene in 25 ml of decane. One hour after the *p*-*t*-butylphenylsodium had been prepared, 13.4 g (0.10 mol) of *t*-butylbenzene was added to the reaction. After 3 days, carbonation was effected followed by the usual workup and esterification. A solution of 97% methyl *m*-*t*-butylbenzoate and 3% methyl *p*-*t*-butylbenzoate was obtained in a 71% yield.

b. Method III in Conjunction with Sodium *t*-Butoxide. *m*-*t*-Butylphenylsodium was prepared essentially as described under method III above. To the organometallic was added 1.48 g (0.02 mol) of *t*-butyl alcohol and 13.4 g (0.1 mol) of *t*-butylbenzene. After 1 day, the mixture was carbonated and esterified. A yield of 76% of product was obtained containing 24% methyl *m*-*t*-butylbenzoate and 76% methyl *p*-*t*-butylbenzoate.

In a second experiment, externally prepared sodium *t*-butoxide (1.9 g, 0.02 mol) and 13.4 g (0.1 mol) of *t*-butylbenzene was added to the *m*-*t*-butylphenylsodium prepared as described above. After 3 days, there was obtained a 77% yield of esters comprised of 20% methyl *m*-*t*-butylbenzoate and 80% methyl *p*-*t*-butylbenzoate.

c. Method IV in Conjunction with Sodium *t*-Butoxide. *m*-*t*-Butylphenylsodium was prepared from 7 g (0.015 mol) of bis(*m*-*t*-

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[23] H. O. Calvery, "Organic Syntheses," Coll. Vol. I, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p 228.

[24] J. A. Moore and D. E. Reed, *Org. Syn.*, 41, 16 (1961).

[25] Based on 0.1 mol of *t*-butylbenzene. 2-Methylnaphthalene was used as an internal standard and appropriate corrections made for differences in thermal conductivities.

[26] An F&M Model 720 gas chromatogram fitted with a Ucon Polar column was used. The oven temperature was 180°, the detector and injector temperatures were 300°, and the helium flow was 40 cc/min.

[27] In a separate experiment, it was shown that the aliquot method of analyzing these heterogeneous mixtures gave a representative sample of the material in the reaction.

[28] H. Feuer, J. W. Shepherd, and C. Savides, *J. Am. Chem. Soc.*, 78, 4364 (1956).

[29] Thereby forming sodium *t*-butoxide *in situ*. It was shown in several experiments that sodium *t*-butoxide has the same effect in these systems whether prepared *in situ* or externally and then added.

butylphenyl)mercury and 3.45 g (0.015 g-atom) of sodium sand covered with 75 ml of nonane. After the mixture was stirred for 1 hr to ensure complete reaction, 6.7 g (0.05 mol) of *t*-butylbenzene containing 0.44 g (0.006 mol) of *t*-butyl alcohol was added to the flask. The reaction was carbonated, worked up, and esterified after 1 day to give a 10% yield of product which was composed of 34% methyl *m*-*t*-butylbenzoate and 66% methyl *p*-*t*-butylbenzoate.

Attempted Isomerization of *m*-*t*-Butylphenylsodium in the Presence of Sodium *t*-Butoxide but in the Absence of *t*-Butylbenzene. Essentially, method III was used as described above to prepare *m*-*t*-butylphenylsodium. To the nonane solution of this reagent was added 1.9 g (0.02 mol) of sodium *t*-butoxide but no *t*-butylbenzene. After 1 day, the mixture was carbonated and esterified. There was obtained a 76% yield of methyl *t*-butylbenzoates composed of 97% *meta* and 3% *para* isomer.

Examination of Supernatant Layers. a. *n*-Amylsodium in Nonane. *n*-Amylsodium was prepared from a 10.6-g (0.46 g-atom) sample of sodium sand in 175 ml of nonane and 21.3 g (0.20 mol) of *n*-amyl chloride in 25 ml of nonane. One hour after the *n*-amylsodium had been prepared, the *n*-amylsodium suspension was pipetted[30] into a centrifuge bottle and then centrifuged for 0.5 hr at 2500 rpm. A clear water white supernatant layer resulted. A 30-cc aliquot of this supernatant was removed with a hypodermic syringe and treated with 5 cc of trimethylchlorosilane. After 2 hr the resulting solution was analyzed by vpc.[31] Within the accuracy of the analytical method, it was shown that *n*-amylsodium was not present in the supernatant as adjudged by the absence of a peak corresponding in retention time to *n*-amyltrimethylsilane.[32]

b. *n*-Amylsodium–Sodium *t*-Butoxide in Nonane. *n*-Amylsodium was prepared in nonane exactly as described in a above. Sodium *t*-butoxide was prepared *in situ* by the addition of 5.92 g (0.08 mol) of *t*-butyl alcohol to the flask. The mixture was pipetted after 1 hr to a centrifuge bottle and centrifuged for 0.5 hr at 2500 rpm; a clear brown supernatant resulted. A 30-cc aliquot of the supernatant layer was treated with 5 cc of trimethylchlorosilane.[33] Analysis of this solution by vpc showed that the supernatant contained *n*-amylsodium and sodium *t*-butoxide as adjudged by the identification of *t*-butoxytrimethylsilane[34] and *n*-amyltrimethylsilane in the gas chromatogram by comparing the retention times with authentic samples.

A second 30-cc sample of the brown hydrocarbon layer was added to 10 ml of *t*-butylbenzene and after 6 hr trimethylchlorosilane was added to the solution. Vpc analysis showed that *t*-butylphenyltrimethylsilane (35% *meta* and 65% *para*) had formed as determined by comparing the gas chromatographic retention times with authentic samples.

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(30) All transfer operations were carried out in glassware which had been dried at 120° and flushed with nitrogen.

(31) Silicone oil column at 100°. Helium flow of 40 cc/min.

(32) F. C. Whitmore, *et al.*, *J. Am. Chem. Soc.*, 68, 475 (1946).

(33) The *n*-amylsodium was also characterized by carbonation and conversion to methyl caproate in the usual manner.

(34) W. Gerrard and K. D. Kilburn, *J. Chem. Soc.*, 1536 (1956).

Carbon Monoxide Reactions. IV. The Mechanism of Cyclohexane Chlorocarbonylation

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Abstract: The free-radical reaction of cyclohexane with carbon monoxide and carbon tetrachloride produces cyclohexanecarboxylic acid chloride and chloroform. The chlorination of cyclohexane by carbon tetrachloride is a competing process leading to chlorocyclohexane and chloroform. A quantitative relationship between these two processes and reaction variables such as CO pressure and CCl_4 concentration has been established and may be used to calculate the selectivity for the formation of acid chloride [RCOCl/(RCOCl + RCl)] under different reaction conditions. The relative concentration of cyclohexane–carbon tetrachloride exerts an unusual influence on both the reaction rate and conversion levels. This influence has been attributed to an autoinhibition of both chlorination and chlorocarbonylation by the acid chloride product. A competition between radical attack on cyclohexane and attack on acid chloride has been postulated wherein attack on acid chloride leads to stable free radicals incapable of propagating the reaction chain.

Paraffins are converted to acid chlorides by means of a free-radical "chlorocarbonylation" reaction with carbon tetrachloride and carbon monoxide utilizing either peroxide[1] or γ radiation[2] to initiate the radical chain. These reactions have been conducted in chrome–vanadium steel Aminco pressure reactors equipped with glass insert liners. Marked inhibition of both the chlorocarbonylation and the chlorination (in the absence of CO) of cyclohexane[1] was observed when traces of metal in combination with a small quantity of acid chloride contaminated the peroxide-initiated reactions. This difficulty, which was lessened by the use of glass liners, could be circumvented by using γ radiation from a cobalt-60 source instead of peroxide, and was subsequently attributed to a metal–acid chloride catalyzed destruction of the peroxide initiator.

The γ-initiated reaction was used successfully for the synthesis of a variety of primary and secondary acid chlorides, and product distributions were correlated with reaction conditions (temperature, CO pressure) and hydrocarbon structures. However, some inexplicable observations, such as the inability to prepare difunctional acid chlorides, as well as unusual decreases in rate, which limited the extent of conversion of reagents to products, prompted this more detailed examination of the influence of reaction variables.

Results and Discussion

Chlorocarbonylation of paraffins with carbon tetrachloride and carbon monoxide would be expected to

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(1) W. A. Thaler, *J. Am. Chem. Soc.*, 88, 4278 (1966).

(2) W. A. Thaler, *ibid.*, 89, 1902 (1967).