pound in certain respects. Thus, for example, 2,6-dibromophenol had two bands (in μ) at 13.2(strong) and 13.0-(medium), both assignable to C–H out-of-plane deformations.[27] These two bands were absent from the spectrum of the deuterated product and their complete absence was taken to indicate that the deuterium exchange had essentially gone to completion. The best grades available of other materials were used.

Kinetic Method.—In a typical kinetic run 40 ml. of an aqueous solution containing $NaNO_2$, $NaNO_3$ and the dibromohydroxy acid was brought to 30.0 ± 0.1° and then 10 ml. of aqueous perchloric acid of appropriate strength, which had also been previously brought to the same temperature, was added. The time of addition of perchloric acid was taken as zero time. About 3 ml. of this reaction solution, which contained 4×10^{-5} *M* dibromohydroxy-acid, 0.40 *M* $NaNO_2$ and 0.40 *M* $NaNO_3$, was transferred to a thermostated spectrophotometric cell immediately after mixing. The cells were maintained at 30.0 ± 0.1°. The wave length 425 mμ was monitored for the appearance of 2,6-dibromo-4-nitrosophenol. It was confirmed that Beer's law was obeyed in buffered solutions and that no other materials present in the reaction solution absorbed at 425 mμ. The *p*H was measured at the end of the reaction; Beckman *p*H meter model GS was used for most of the measurements. It was found in preliminary experiments that the absorbancy at infinite time (A_∞) of a reaction solution containing $4 \times 10^{-5}M$ dibromohydroxy acid was the same as that of a $4 \times 10^{-5}M$ solution of 2,6-dibromo-4-nitrosophenol at identical *p*H, showing that the conversion of the acid to the nitroso compound was quantitative. When 2,6-dibromophenol or its 4-deuterated form was the substrate, the conversion to the nitroso compound was about 90%. Therefore, for nitrosodeprotonation, A_∞ used was that from a parallel run on the dibromohydroxy acid under identical conditions. The rate constants reported for nitrosodeprotonation are, therefore, obtained from a study of the first 40–50% of the reaction.

The equilibrium constants of the various related systems were determined by methods described in the section entitled Results.

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[27] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 65.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, N. J.]

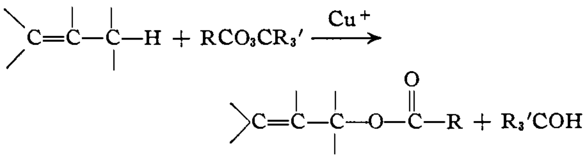
A Study of the Copper Ion Catalyzed Reactions of *t*-Alkyl Peresters with Several Olefins

BY DOROTHY Z. DENNEY, ARTHUR APPELBAUM AND DONALD B. DENNEY

RECEIVED JUNE 29, 1962

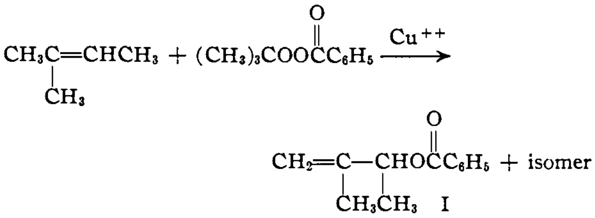
Optically active Δ^1-*p*-menthene was allowed to react with *t*-butyl peracetate in the presence of copper ion to give a mixture of menthenyl acetates. Saponification and chromic acid oxidation afforded a mixture of ketones from which the optically inactive semicarbazone and 2,4-dinitrophenylhydrazone of 2-methyl-5-isopropylcyclohex-2-eneone were obtained. Tetramethylethylene reacted with *t*-butyl perbenzoate in the presence of copper ion to give 2,3-dimethylbut-1-ene-3-yl benzoate. Trimethylethylene yielded a mixture of benzoates. The major components, *ca.* 87%, was shown to be 2-methylbut-1-ene-3-yl benzoate.

Kochi[1] has very lucidly summarized existing knowledge on the copper salt catalyzed reactions of peroxides. Of particular interest is the reaction of *t*-alkyl peresters with olefins in the presence of copper ions. This is a typical allylic substitution process which leads to introduction of an ester function α to the double bond. Considerable confusion has arisen because of the reports that this substitution occurs without double bond isomerization.[2,3] Recently Kochi[4] has shown that *cis*-2-butene, *trans*-2-butene and 1-butene react with *t*-alkyl peresters in in the presence of copper ions to give the same mixture of butenyl benzoates.[5] Although there is no question about the intervention of an intermediate which allows equilibration over the allylic positions in the butene reactions, a general demonstration that this is the case in olefins more highly substituted about the double bond has not been provided. It was the purpose of this work to investigate such systems.



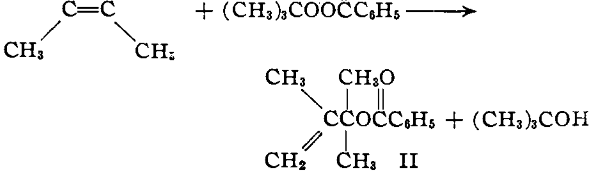
Results and Discussion

Trimethylethylene was allowed to react with *t*-butyl perbenzoate in the presence of cupric ion. A two-component mixture of methylbutenyl benzoates was obtained in 70% yield. The major component of the mixture was separated by careful fractionation. Hydrogenation afforded 2-methyl-3-benzoyloxybutane. Thus the major product of the reaction was 2-methyl-3-benzoyloxy-1-butene (I). Similarly, tetramethylene gave a 78% yield of 2,3-dimethyl-3-benzoyloxy-1-butene (II) contaminated with 3% methyl benzoate.



$$\mathrm{CH_3\underset{CH_3}{C}{=}CHCH_3 + (CH_3)_3COO\overset{O}{\overset{\|}{C}}C_6H_5 \xrightarrow{Cu^{++}} CH_2{=}\underset{CH_3}{C}{-}\underset{CH_3}{C}HO\overset{O}{\overset{\|}{C}}C_6H_5 + isomer}$$

I



II

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[1] J. K. Kochi, *Tetrahedron*, **18**, 483 (1961).

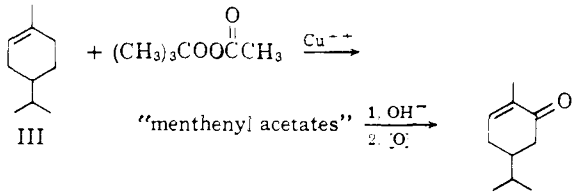
[2] (a) M. S. Kharasch and G. Sosnovsky, *J. Am. Chem. Soc.*, **80**, 756 (1958); (b) M. S. Kharasch, G. Sosnovsky and N. C. Yang, *ibid.*, **81**, 5819 (1959).

[3] D. B. Denney, D. Z. Denney and G. Feig, *Tetrahedron Letters*, **No. 15**, 19 (1959).

[4] J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 774 (1962).

[5] Substantially the same results have been obtained in this Laboratory by D. Z. D.

Optically active Δ^1-*p*-menthene (III), prepared by selective hydrogenation of limonene, was allowed to react with *t*-butyl peracetate in the presence of copper ions. A mixture of menthenyl acetates was obtained. No attempt was made to separate this mixture but instead it was saponified and oxidized. Treatment of the ketonic fraction obtained with semicarbazide and 2,4-dinitrophenylhydrazine afforded the optically *inactive* derivatives of 2-methyl-5-isopropylcyclohex-2-eneone (IV). It is possible that a small excess of one of the optical isomers of IV would not be detected because of the use of solid derivatives which could lead to fractionation during their formation. It seems most reasonable though to conclude that the copper ion catalyzed reaction yields racemic IV.

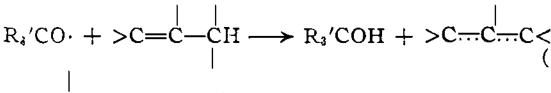


III

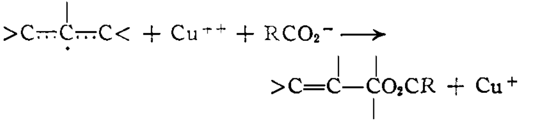
IV

Kochi[1,6] has suggested the following general mechanism for these reactions. The results of this study are in accord with this mechanism. It is quite clear that intermediates have been formed, in all three cases, which allow equilibration over the allylic positions. Thus, it has been demonstrated that double bond isomerization takes place with substances having increasing substitution about the double bond.[7] It should be noted that the products obtained from the reactions of trimethylethylene and tetramethylethylene were not obtained in quantitative yields. It is possible that minor amounts of other allylic benzoates were formed but were decomposed or lost in isolation.

$$\mathrm{RCO_3CR_3' + Cu^+ \longrightarrow RCO_2^- + Cu^{++} + R_3'CO} \quad (1)$$



$$\mathrm{R_3'CO\cdot + {>}C{=}\overset{|}{C}{-}\underset{|}{\overset{|}{C}}H \longrightarrow R_3'COH + {>}C\overset{\cdots}{-}\overset{|}{C}\overset{\cdots}{-}C{<}} \quad (2)$$



$$\mathrm{{>}C\overset{\cdots}{-}\underset{\cdot}{\overset{|}{C}}\overset{\cdots}{-}C{<} + Cu^{++} + RCO_2^- \longrightarrow {>}C{=}\overset{|}{C}{-}\underset{|}{\overset{|}{C}}O_2CR + Cu^+} \quad (3)$$

The isomers formed from these reactions are of particular interest. They are undoubtedly the thermodynamically least stable[8] of the possible pair in either case. Similar results were obtained with the butene reactions.[4] These findings have a bearing on the nature of step 3. The results are most adequately explained if, during the electron transfer process, an electron-deficient species is generated which combines with the carboxylate ion to yield the product. Whether a free carbonium ion is formed is not known. This may depend on the system studied. The suggestion[4] that stabilization of the transition state occurs by π-bond formation between copper ion and the forming double bond is not in disagreement with the results of this study.

Acknowledgment.—Research supported in part by the U. S. Army Research Office, Durham, N. C. The n.m.r. spectra were obtained on an instrument purchased in part with funds supplied by the National Science Foundation.

Experimental[9]

Δ^1-*p*-Menthene (III).—*d*-Limonene (86 g., 0.5 mole, $\alpha^{25}\mathrm{D}$ +98.75° neat) in 85 ml. of ethanol containing 0.2 g. of platinum oxide was hydrogenated until 0.5 mole of hydrogen was absorbed. Water (85 ml.) was added and the mixture was extracted with three 200-ml. portions of pentane. The pentane solution was dried over magnesium sulfate and distilled. There was obtained 70.0 g. (100%) of Δ^1-*p*-menthene, b.p. 56° (9 mm.), $\alpha^{25}\mathrm{D}$ + 89.54° (neat) (lit.[10,11] 174–175° (760 mm.) and $\alpha^{25}\mathrm{D}$ +96°). Gas liquid chromatographic (g.l.c.) analysis on a 10 ft. 6 M Carbowax column indicated that this material contained about 5% limonene.

Reaction of *d*-Δ^1*p*-Menthene with *t*-Butyl Peracetate.—To a stirred mixture of Δ^1-*p*-menthene (60.0 g., 0.435 mole) and cupric 3,3,5-trimethylhexanoate (0.2 g.) was added 35.2 g. of a 75% solution of *t*-butyl peracetate in benzene. The reaction was complete after 3 hours at 80°. The reaction mixture was washed with 10% sodium bicarbonate solution, water and then dried with magnesium sulfate. The material was fractionated to yield nine fractions, the last four of which had similar infrared spectra. They had an ester carbonyl absorption at 1725 cm.$^{-1}$ and a trisubstituted double bond absorption at 805 cm.$^{-1}$. The combined weight of these fractions was 25.6 g. (65.4%). A major fraction (11 g.), b.p. 96–101° (9 mm.), was used for further reactions.

Saponification of Menthenyl Acetates.—The fraction obtained above (9.8 g.) was boiled for 2 hours with a mixture of methanol (50 ml.) and water (30 ml.) containing potassium hydroxide (3.0 g.). The reaction mixture was extracted with four 75-ml. portions of pentane. The combined pentane extracts were washed with water, dried with magnesium sulfate and distilled to afford 6.0 g. (78%) of material, b.p. 95–100° (8 mm.); reported[12] for Δ^1-*p*-menthene-6-ol, 112° (14 mm.). The infrared spectrum had hydroxyl band at 3450 cm.$^{-1}$ and a trisubstituted olefinic absorption at 805 cm.$^{-1}$.

Oxidation of Menthenols.—To a stirred mixture of the alcohol (4.0 g., 0.026 mole), potassium dichromate (15.0 g., 0.051 mole) and 100 ml. of water was added concentrated sulfuric acid (15 g.) at such a rate that the temperature was maintained between 28 and 30°. The mixture was stirred for 12 hours and then extracted with three 75-ml. portions of ether. The ether extracts were washed with 5% sodium bicarbonate solution, water and dried over magnesium sulfate. The ether was removed to give 4.0 g. of product. A portion of this material was converted to the 2,4-dinitrophenylhydrazone which was recrystallized from ethanol-ethyl acetate; m.p. 191–192° (lit.[13] 193°), $[\alpha]^{25}\mathrm{D}$ 0.0° (*c* 0.426, chloroform). The semicarbazone was prepared and recrystallized from ethanol–water; m.p. 174–175° (lit.[13] 174°); $[\alpha]^{26}\mathrm{D}$ 0.0° (*c* 0.011, ethanol), $[\alpha]^{24.5}\mathrm{D}$ 0.0° (*c* 0.011, pyridine). The literature values for the specific rotation of the semicarbazone show considerable differences depending on the solvent, $[\alpha]^{20}\mathrm{D}$ −71.4° and −72.1° in chloroform[14], $[\alpha]^{20}\mathrm{D}$ −112°[14] and $[\alpha]^{22}\mathrm{D}$ + 115°[12] in methanol and $[\alpha]^{20}\mathrm{D}$, +89.54°[16] in pyridine.

Copper Ion Catalyzed Reaction of Trimethylethylene and *t*-Butyl Perbenzoate.—A mixture of trimethylethylene[17]

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[6] This mechanism was first proposed to the present authors in 1959 by Prof. C. Walling.

[7] The report of ref. 3 that propenylbenzene gives only cinnamyl benzoate with *t*-butyl perbenzoate in the presence of copper ion is in error. Other products besides esters are formed from this reaction. These may result from radical addition reactions. Work in this Laboratory on the allylbenzene–propenylbenzene systems has ceased.

[8] P. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 753 (1956).

[9] Analyses by G. Robertson, Florham, Park, N. J.

[10] O. Wallach, *Ann.*, **381**, 58 (1911).

[11] H. Pines and H. E. Eschinazi, *J. Am. Chem. Soc.*, **78**, 1178 (1956).

[12] W. Treibs and H. Bast, *Ann.*, **561**, 165 (1949).

[13] G. Dupont, R. Dulou and N. Defay, *Bull. soc. chim. France*, **16**, 310 (1949).

[14] H. G. Smith, P. G. Carter and J. Read, *J. Chem. Soc.*, **125**, 930 (1924).

[15] O. Wallach and E. Beschke, *Ann.*, **336**, 35 (1904).

[16] J. Simonsen and M. Rau, *J. Chem. Soc.*, 876 (1922).

(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.

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(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]

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(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).