

at 75°). Purified dioxane (25 ml.) was added to the product mixture. Flash distillation then gave a dioxane solution of the butenyl chlorides, which was fractionated as above.

Appropriate controls were run in order to establish the facts that the butenyl chlorides do not isomerize under the conditions of the distillation analysis and that  $\alpha$ -methylallyl chloride is optically stable under the same conditions.

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[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, FACULTY OF ENGINEERING, KYŌTO UNIVERSITY]

## Condensation of *t*-Butyl Esters with Organic Halides in the Presence of Alkali Amides

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The alkylation of *t*-butyl esters of acetic acid and its homologs with various organic mono- and dihalides has been effected with good yields by means of lithium or sodium amide in liquid ammonia. The resulting esters were hydrolyzed easily to give the corresponding free mono- and dibasic acids.

The possibility of direct alkylation of ethyl and *t*-butyl acetates was recently demonstrated by Hauser and Chambers<sup>1</sup> in the reaction with benzyl chloride and *n*-octyl bromide. This reaction constitutes a means of synthesizing higher esters and carboxylic acids along with the common malonic ester method. It was, however, unfortunate that few examples were published and the yields realized were not too good. Working independently on the same problem, the present authors have been able to gain fairly satisfactory yields in a number of the alkylations and the results have been summarized in Table I.

The reaction of *t*-butyl acetate and benzyl chloride was carried out under various conditions with lithium amide as a condensation agent in anhydrous ammonia and ether. Larger amount of ether decreased the yield, so that no condensation product could be isolated when the ammonia was completely substituted by ether prior to the addition of benzyl chloride to the suspension of the lithioacetate. When the volume ratio of ether to ammonia was less than 1:10, the treatment of equimolar mixture of *t*-butyl acetate and lithium amide with one mole of benzyl chloride gave a 31% yield of *t*-butyl hydrocinnamate, while the use of two equivalents each of lithium amide and ester increased the yield to 80% in contrast to the yield of 30% reported by Hauser and Chambers<sup>1</sup> in the benzylation of ethyl acetate by means of lithium amide.<sup>2</sup> Practically no *t*-butyl dibenzylacetate was isolated from the condensation mixture. Treatment of *t*-butyl acetate with two equivalents of benzyl chloride and sodium amide in place of the lithium compound resulted in the formation of *t*-butyl hydrocinnamate and *t*-butyl dibenzylacetate in yields of 19 and 61%, respectively, while attempted benzylation of *t*-butyl acetate by means of diethylaminomagnesium bromide<sup>3</sup> failed to give any desired product.

(1) C. R. Hauser and W. J. Chambers, *J. Org. Chem.*, **21**, 1524 (1956).

(2) Though the yield recorded by Hauser and Chambers is that of hydrocinnamic acid obtained on hydrolyzing the condensation product, the *t*-butyl hydrocinnamate is almost quantitatively hydrolyzed to the free acid so that these data are comparable with each other.

(3) K. Sisido, H. Nozaki and O. Kurihara, *THIS JOURNAL*, **74**, 6254 (1952).

The alkylation of *t*-butyl acetate could successfully be extended to some primary alkyl halides. Thus ethyl, isobutyl, isoamyl, *n*-octyl and allyl bromides gave fair to good yields of the corresponding higher esters. Though the action of isopropyl iodide did not give the condensation product, the reaction of *t*-butyl  $\alpha$ -bromoisobutyrate with *t*-butyl acetate gave a 71% yield of di-*t*-butyl  $\alpha,\alpha$ -dimethylsuccinate.

Benzylation of *t*-butyl ester of propionic, *n*-butyric and isovaleric acids gave the corresponding  $\alpha$ -alkylhydrocinnamates in 90, 92 and 74% yields, respectively.<sup>4</sup>

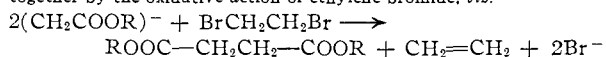
Table II summarizes the condensation of *t*-butyl acetate with some dihaloalkanes. In view of the experimental difficulties in isolating the di-*t*-butyl esters thus formed, the reaction products were hydrolyzed directly to free dibasic acids.

While consistently higher yields of dibasic acids could be secured with tetra, hexa- and decamethylene bromides in the presence of lithium amide, ethylene chloride or bromide gave poor to fair yields of the normal condensation product, adipic acid. It should be noted that succinic acid has been isolated as a main product from the reaction using a higher mole ratio of ethylene bromide.<sup>5</sup>

Throughout these condensations of organic dihalides in the presence of lithium amide the sole isolable products were dibasic acids. Neither the  $\omega$ -haloacid, which should be formed when only one of the halogen atoms of the dihaloalkanes was substituted with the enolate anion, nor the cycloalkanecarboxylic acid, *i.e.*, the cyclic alkylation product of the acetate, could be isolated. Since the use of sodium or potassium amide as the condensation agent appeared to afford the dialkylation products as mentioned above, the reaction was repeated in the presence of sodium amide in order to examine the possible formation of cyclopropane-

(4) For the alkylation of tertiary esters of di-alkylacetic acids see C. R. Hauser and W. J. Chambers, *ibid.*, **73**, 3837 (1956).

(5) Though the origin of succinic acid is not certain, it is plausible that two moles of the lithium enolate of *t*-butyl acetate are coupled together by the oxidative action of ethylene bromide, *viz.*



This reaction may be analogous to the well-known formation of ethylene and bromide anion from ethylene bromide and magnesium.

TABLE I  
 ALKYLATION OF *t*-BUTYL ESTER WITH ORGANIC HALIDES<sup>a</sup>

Ester, <i>t</i> -butyl	Alkyl halides	Reacn. time, min.	Product	
			<i>t</i> -Butyl	Yield, % <sup>b</sup>
Acetate <sup>c</sup>	CH <sub>3</sub> CH <sub>2</sub> Br	100	<i>n</i> -Butyrate <sup>d</sup>	87
Acetate	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> Br <sup>e</sup>	180	(Isocaproic acid) <sup>f</sup>	(45)
Acetate	(CH <sub>3</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub> Br	140	Isoamylacetate <sup>g</sup>	47
Acetate	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> Br	75	Caprate <sup>h</sup>	70
Acetate	CH <sub>2</sub> =CHCH <sub>2</sub> Br	140	Allylacetate <sup>i</sup>	87
Acetate	BrC(CH <sub>3</sub> ) <sub>2</sub> COOC(CH <sub>3</sub> ) <sub>3</sub>	110	$\alpha,\alpha$ -Dimethylsuccinate, di. <sup>j</sup>	71
Acetate	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	160	Hydrocinnamate <sup>k</sup>	80
Propionate <sup>l</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	120	$\alpha$ -Methylhydrocinnamate <sup>m</sup>	90
<i>n</i> -Butyrate <sup>n</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	40	$\alpha$ -Ethylhydrocinnamate <sup>o</sup>	92
Isovalerate <sup>p</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	120	$\alpha$ -Isopropylhydrocinnamate <sup>q</sup>	74

<sup>a</sup> The reaction mixture was held at  $-40^{\circ}$  for the specified period of time after adding the organic halides. The halides were added as a solution in anhydrous ether (0.05 mole of halide in 20 ml. of ether) unless otherwise stated (see note *e*).

<sup>b</sup> The yields are based on the halides. The figure in parentheses is that of free acid obtained after hydrolysis. <sup>c</sup> *t*-Butyl acetate was prepared from acetic anhydride and *t*-butyl alcohol in the presence of a trace of acetyl bromide or hydrogen bromide (cf. K. Sisido and H. Nozaki, THIS JOURNAL, **70**, 3326 (1948)). <sup>d</sup> The product, b.p. 135–137.5° (760 mm.), *n*<sub>D</sub><sup>20</sup> 1.3939, proved to be analytically pure. Hydrolysis gave *n*-butyric acid in a 94% yield, b.p. 162–164° (760 mm.) (lit. 163.55 ± 0.01°, J. Timmermans, *Bull. soc. chim. Belg.*, **36**, 506 (1927)), whose anilide melted at 96° (lit. 93–94°; G. Natta, P. Pino and R. Ercoli, THIS JOURNAL, **74**, 4496 (1952)). <sup>e</sup> Neat halide was added. <sup>f</sup> The analytically pure *t*-butyl ester could not be obtained. The acid distilled at 194–197° (760 mm.) (lit. 199.2–199.7°; P. A. Levene and C. H. Allen, *J. Biol. Chem.*, **27**, 450 (1916)), *n*<sub>D</sub><sup>20</sup> 1.4124. The amide melted at 117.0–117.5° (lit. 120°; J. Seib, *Ber.*, **60**, 1397 (1927)), and gave correct analyses for carbon and hydrogen. <sup>g</sup> B.p. 81–84° (13 mm.). *Anal.* Calcd. for C<sub>11</sub>H<sub>20</sub>O<sub>2</sub>: C, 70.92; H, 13.02. Found: C, 70.69; H, 13.29. Hydrolysis gave isoamylacetic acid, b.p. 120° (24 mm.), 211–215° (760 mm.) (lit. 212–214°; H. Wieland, *Ber.*, **58**, 2015 (1925)), *n*<sub>D</sub><sup>20</sup> 1.4199 (lit. *n*<sub>D</sub><sup>20</sup> 1.4209; O. Wallach, *Ann.*, **408**, 190 (1915)), in a 92% yield, whose amide melted at 101.8–102.2° (lit. 102–103°; H. Wieland, *Ber.*, **58**, 2017 (1925)). <sup>h</sup> B.p. 123° (12 mm.), *n*<sub>D</sub><sup>20</sup> 1.4234. *Anal.* Calcd. for C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>: C, 73.63; H, 12.36. Found: C, 73.42; H, 12.53. Hydrolysis gave capric acid, b.p. 148–150° (13 mm.) (lit. 148–151° (11 mm.); J. Houben, *Ber.*, **35**, 3592 (1902)), m.p. 30.4–31.2° (lit. 31.5°; J. Houben, ref. above), in a 95% yield. <sup>i</sup> B.p. 68–69° (26 mm.), *n*<sub>D</sub><sup>20</sup> 1.4142. *Anal.* Calcd. for C<sub>9</sub>H<sub>16</sub>O<sub>2</sub>: C, 69.19; H, 10.32. Found: C, 69.32; H, 10.24. <sup>j</sup> B.p. 114–115° (14 mm.), *n*<sub>D</sub><sup>20</sup> 1.4191. *Anal.* Calcd. for C<sub>11</sub>H<sub>20</sub>O<sub>4</sub>: C, 65.08; H, 10.14. Found: C, 64.89; H, 10.33. Hydrolysis gave  $\alpha,\alpha$ -dimethylsuccinic acid, m.p. 134–135.5° (lit. 142°; F. Tiemann, *Ber.*, **30**, 260 (1897)), which gave correct analyses for carbon and hydrogen. <sup>k</sup> B.p. 119–121° (10 mm.) (lit. 144° (8 mm.)), C. R. Hauser, B. F. Hudson, B. Abramovitch and J. C. Shivers, "Organic Syntheses," Coll. Vol. 11, J. Wiley and Sons, Inc., New York, N. Y., 1955, p. 144), *n*<sub>D</sub><sup>20</sup> 1.4950 (lit. *n*<sub>D</sub><sup>20</sup> 1.4801; W. von Doering and R. H. Haines, THIS JOURNAL **76**, 485 (1954)). *Anal.* Calcd. for C<sub>9</sub>H<sub>16</sub>O<sub>4</sub>: C, 75.69; H, 8.80. Found: C, 75.42; H, 8.69. Hydrolysis gave hydrocinnamic acid, m.p. 48.5–49° (lit. 48.5–49°; see ref. 1), in a 97% yield. <sup>l</sup> *t*-Butyl propionate was prepared from *t*-butyl alcohol and propionyl chloride in the presence of dimethylaniline, see C. R. Hauser, *et al.*, note *k*. <sup>m</sup> B.p. 121–127° (11 mm.), *n*<sub>D</sub><sup>20</sup> 1.4730. *Anal.* Calcd. for C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>: C, 76.32; H, 9.15. Found: C, 76.45; H, 9.43. Hydrolysis gave  $\alpha$ -methylcinnamic acid, m.p. 37.5–38.5° (lit. 37.5°; C. Willgerodt and F. H. Merk, *J. prakt. Chem.*, [2] **80**, 198 (1909)), in a 93% yield. <sup>n</sup> *t*-Butyl *n*-butyrate used in this experiment was the alkylation product of *t*-butyl acetate with ethyl bromide. <sup>o</sup> B.p. 123.5–124° (10 mm.), *n*<sub>D</sub><sup>20</sup> 1.4750. *Anal.* Calcd. for C<sub>15</sub>H<sub>28</sub>O<sub>2</sub>: C, 76.88; H, 9.46. Found: C, 76.59; H, 9.53. Hydrolysis gave  $\alpha$ -ethylhydrocinnamic acid, b.p. 154° (9 mm.) (lit. 168.5–171° (14.5–15 mm.); E. Mohr, *J. prakt.*

*Chem.*, [2], **71**, 333 (1905)), in a 92% yield, whose amide melted at 114–114.5° (lit. 117–118°; F. F. Blicke and A. P. Cantolella, THIS JOURNAL, **60**, 2926 (1938)) and gave correct analyses for carbon and hydrogen. <sup>p</sup> *t*-Butyl isovalerate was prepared from *t*-butyl alcohol, isovaleryl chloride and potassium; see C. R. Hauser and W. J. Chambers, THIS JOURNAL, **78**, 3827 (1956). <sup>q</sup> B.p. 139–142° (14 mm.), *n*<sub>D</sub><sup>20</sup> 1.4764. *Anal.* Calcd. for C<sub>16</sub>H<sub>24</sub>O<sub>2</sub>: C, 77.37; H, 9.74. Found: C, 77.43; H, 9.56. Hydrolysis gave  $\alpha$ -isopropylhydrocinnamic acid, b.p. 158° (9 mm.) (lit. 305–308°; M. M. Guerbet, *Compt. rend.*, **146**, 1407 (1908)), in a 93% yield, whose amide melted at 93.5–93.8° (lit. 94–95°; M. M. Guerbet, ref. above).

 TABLE II  
 DIBASIC ACIDS FROM *t*-BUTYL ACETATE  
 AND DIHALOALKANES<sup>a</sup>

Halide <sup>b</sup>	Alkali amide	Mole ratio of reactants, ester:halide	Product <sup>c</sup>	
			Acid	Yield, %
ClCH <sub>2</sub> CH <sub>2</sub> Cl	LiNH <sub>2</sub>	1:0.5	Adipic <sup>d</sup>	6
BrCH <sub>2</sub> CH <sub>2</sub> Br	LiNH <sub>2</sub>	1:0.25	Adipic	33
BrCH <sub>2</sub> CH <sub>2</sub> Br	LiNH <sub>2</sub>	1:0.5	Succinic <sup>e</sup>	41 <sup>f</sup>
BrCH <sub>2</sub> CH <sub>2</sub> Br	NaNH <sub>2</sub>	1:0.25	None <sup>g</sup>	
BrCH <sub>2</sub> CH <sub>2</sub> Br	NaNH <sub>2</sub>	1:0.5	None	
Br(CH <sub>2</sub> ) <sub>4</sub> Br <sup>h</sup>	LiNH <sub>2</sub>	1:0.25	Suberic <sup>i</sup>	68
Br(CH <sub>2</sub> ) <sub>4</sub> Br	LiNH <sub>2</sub>	1:0.5	Suberic	71
Br(CH <sub>2</sub> ) <sub>4</sub> Br	NaNH <sub>2</sub>	1:0.25	Suberic	ca. 100
Br(CH <sub>2</sub> ) <sub>4</sub> Br	NaNH <sub>2</sub>	1:0.5	Suberic	44
Br(CH <sub>2</sub> ) <sub>6</sub> Br <sup>j</sup>	LiNH <sub>2</sub>	1:0.25	Sebacic <sup>k</sup>	ca. 100
Br(CH <sub>2</sub> ) <sub>6</sub> Br	LiNH <sub>2</sub>	1:0.5	Sebacic	79
Br(CH <sub>2</sub> ) <sub>10</sub> Br <sup>l</sup>	LiNH <sub>2</sub>	1:0.25	Tetradecane- 1,14-dioic acid <sup>m</sup>	98
Br(CH <sub>2</sub> ) <sub>10</sub> Br	LiNH <sub>2</sub>	1:0.5	Tetradecane- 1,14-dioic acid	73

<sup>a</sup> The reaction mixture was held at  $-40^{\circ}$  for 180 min. after adding the dihalides. <sup>b</sup> While a solution of 0.05 mole of dihalides of C<sub>4</sub>, C<sub>6</sub> and C<sub>10</sub> in 10 ml. of anhydrous ether (or 0.025 mole in 5 ml., as specified in column 3) was added to the suspension of lithioacetate, the ethylene dihalides were used without diluting. <sup>c</sup> The condensation products were hydrolyzed without any purification to give the free dibasic acids, whose yields are based on the dihalides with exception of the case of succinic acid. All of these acids thus obtained, *i.e.*, succinic acid through tetradecane-1,14-dioic acid, gave correct analyses of carbon and hydrogen. <sup>d</sup> M.p. and mixed m.p. 150.0–150.5° (lit. 151–152°; B. A. Ellis, "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1943, p. 18). <sup>e</sup> M.p. and mixed m.p. 181–182°, after several recrystallizations from concentrated nitric acid (lit. 185°; O. Davidoff, *Ber.*, **19**, 407 (1896)). <sup>f</sup> The yield is that of the crude product melting at 143–153°, which is apparently a mixture of succinic and adipic acids, and is based on *t*-butyl acetate. The exact analysis of this mixture was not done. <sup>g</sup> No acidic product other than acetic acid. <sup>h</sup> Tetramethylene bromide was prepared according to the method of C. L. Wilson (*J. Chem. Soc.*, **48** (1945)), b.p. 194.5–196.5°, *n*<sub>D</sub><sup>20</sup> 1.5188. <sup>i</sup> M.p. 138.0–139.5° (lit. 144°; E. E. Blaise and A. Köhler, *Bull. soc. chim. France*, [4] **5**, 689 (1909)). <sup>j</sup> Hexamethylene bromide was prepared from diethyl adipate through reduction with sodium and alcohol (R. H. Manske, THIS JOURNAL, **53**, 1104 (1931); "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1948, p. 154) and the subsequent bromination (E. P. Taylor, *J. Chem. Soc.*, 2068 (1958)); b.p. 130–134° (31 mm.) (lit. 108–112° (8 mm.)); W. L. McEwen, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p. 227); *n*<sub>D</sub><sup>20</sup> 1.5055 (lit. *n*<sub>D</sub><sup>20</sup> 1.5037; W. E. Vaughan, F. F. Rust and T. W. Evans, *J. Org. Chem.*, **7**, 482 (1942)). <sup>k</sup> M.p. 131.0–132.0° (lit. 134.5°; G. L. Voerman, *Rec. trav. chim.*, **28**, 265 (1904)). <sup>l</sup> Decamethylene bromide was prepared from diethyl sebacate in the same way as hexamethylene bromide, b.p. 125–129° (4 mm.) (lit. 166–168° at 10 mm.); E. P. Taylor (see note *j*); *n*<sub>D</sub><sup>20</sup> 1.4917 (lit. *n*<sub>D</sub><sup>20</sup> 1.4927; G. C. H. Stone, THIS JOURNAL, **58**, 488 (1936)). <sup>m</sup> M.p. 124.5–125.0° (lit. 125.8°; P. Chuit, *Helv. Chim. Acta*, **9**, 265 (1926)).

and cyclopentanecarboxylic acids from ethylene and tetramethylene bromides, respectively. The hydrolysis of the ester resulting from ethylene bromide was effected by means of an aqueous solution of potassium hydroxide in order to avoid the cleavage of the cyclopropane ring which might have been formed, while a mixture of dioxane and concentrated hydrochloric acid was used for hydrolyzing the ester from tetramethylene bromide. Although suberic acid was obtained with an excellent yield in the latter reaction, the ethylene bromide failed to afford any acidic product other than acetic acid by means of this amide.

It seems safe to conclude from these results that the direct alkylation of *t*-butyl acetate is of value as an alternate of malonic ester synthesis for preparing mono- and dibasic carboxylic acids.

### Experimental<sup>6</sup>

**Alkylation.**—To a suspension of 0.1 mole of lithium amide in 200 ml. of liquid ammonia 0.1 mole of *t*-butyl ester was added rapidly with continuous stirring at  $-40^{\circ}$ . Since the use of anhydrous ether as a solvent of the ester lowered the yields of alkylated products, no solvent other than ammonia was used at this stage of the reaction. After 15–40 minutes stirring at  $-40^{\circ}$  0.05 mole of organic halide (neat) or its solution in 20 ml. of anhydrous ether was added during 3–30 minutes. The stirring was continued for an additional 40–

(6) All temperatures are uncorrected. Analyses by Miss Kenko Ogawa.

180 minutes and then ammonium chloride was added. Ammonia was evaporated by external heating, while 50 ml. of wet ether was added slowly. The reaction mixture was treated with 50 ml. of water, extracted with ether, the combined ethereal solutions were washed with water and dried over anhydrous sodium sulfate. Upon removing the solvent, followed by fractional distillation of the residue in the presence of magnesium oxide, the alkylated product could be isolated. The details of each experiment were summarized in Tables I and II. When the isolation of the *t*-butyl ester was accompanied with difficulties, the evaporation residue of the ethereal extracts was directly subjected to hydrolysis.

**Hydrolysis of the *t*-Butyl Ester.**—A mixture of 0.02 mole of the alkylation products, 6 ml. of dioxane and 10 ml. of concentrated hydrochloric acid was refluxed for 2–5 hours. After cooling to room temperature the mixture was extracted several times with ether, the combined ethereal solutions were washed with a small amount of water and then thoroughly extracted with 10% aqueous sodium hydroxide solution or saturated sodium bicarbonate solution. The combined alkaline solutions were washed with ether and acidified with concentrated hydrochloric acid. The carboxylic acid which separated was taken up in ether or collected through filtration and purified through distillation or by recrystallizations. Yields were almost quantitative in each case.

The condensation product obtained from ethylene bromide in the presence of sodium amide was hydrolyzed by heating with 50% excess of 50% aqueous potassium hydroxide solution. The reaction mixture was washed with ether and acidified with concentrated hydrochloric acid. The solution was extracted with ether, but failed to afford any acidic product. Though the non-saponifiable portion was examined to recover the condensation product, if any, no appreciable amount of neutral ester could be isolated.

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[CONTRIBUTION FROM THE INSTITUTE OF ORGANIC CHEMISTRY, THE UNIVERSITY OF CHICAGO]

## Reactions of *t*-Butyl Peresters. I. The Reaction of Peresters with Olefins<sup>1</sup>

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*t*-Butyl peresters react smoothly with olefins in the presence of copper or cobalt salt catalysts to form allylic esters in moderate to good yields. With terminal olefins, such as 1-octene, 1-hexene or allylbenzene, the only products isolated are the allylic esters with a terminal double bond. When the reaction of cyclohexene, *t*-butyl perbenzoate and cuprous bromide is carried out in an aliphatic acid as the solvent, the aliphatic ester of cyclohexenol instead of the benzoate is obtained. The scope and limitation of this reaction are discussed.

Tertiary alkyl peresters were first prepared by Milas and Surgenor.<sup>4</sup> However, the chemistry of these substances, except for several kinetic studies, has received little attention. Blomquist<sup>5</sup> and his associates studied the decomposition of *t*-butyl perbenzoate in great detail. They found that *t*-butyl perbenzoate decomposes about as rapidly at  $115^{\circ}$  as benzoyl peroxide does at  $80^{\circ}$ . In most aromatic solvents the rate of decomposition is of first order; in aliphatic solvents the situation is more complex, and it appears that an induced chain reaction (involving free radicals derived from solvent) takes place in addition to the unimolecular cleavage of the perester. More recently, Bartlett and Hiatt<sup>6</sup> examined the decomposition of various

*t*-butyl peresters in chlorobenzene. They found that most of the peresters examined give a mixture of products with carbon dioxide as the major constituent. In view of these findings, it is not surprising that in a variety of substrates the decomposition of *t*-butyl perbenzoate gives a complex mixture of products; and that few useful preparative results have been obtained from such reactions.

In a previous communication<sup>7</sup> it was shown that the addition of catalytic amounts of copper or cobalt salts to the reactions of perester and olefins has a decisive effect on the composition of the end-products. Thus, *t*-butyl perbenzoate reacts with ethylenic compounds to give esters of benzoic acid. These reactions are stereospecific, namely, the benzoyloxy group enters the position alpha to the double bond, and there is no rearrangement of the ethylenic system. The present paper contains experimental details which amplify the original observations.

The possibility of utilizing *t*-butyl peresters as synthetic reagents was first noted when *t*-butyl

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(2) Deceased.

(3) To whom inquiries of this publication may be sent.

(4) N. A. Milas and D. M. Surgenor, *THIS JOURNAL*, **68**, 642 (1946).

(5) A. T. Blomquist, A. F. Ferris and I. A. Berstein, *ibid.*, **73**, 3408, 3421, 5546 (1951).

(6) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

(7) M. S. Kharasch and G. Sosnovsky, *ibid.*, **80**, 756 (1958).