Vapor phase chromatography showed two peaks representing 27% and 73% of the product, respectively.

3-Chloro-1-butanol.—This material was prepared by lithium aluminum hydride reduction of 3-chlorobutyric acid as described by Searles, *et al.*,[3] b.p. 70–72.5°/17 mm., $n^{25}\mathrm{D}$ 1.4399. (Reported, b.p. 67–68°/15 mm.[4] and 74°/16 mm.;[3] $n^{25}\mathrm{D}$ 1.4446[4] and 1.4398[3]). Vapor phase chromatography showed only one peak with the same retention time as that of the large peak from the above mixture.

4-Chloro-2-butanol.—Lithium aluminum hydride reduction of 4-chloro-2-butanone gave this material, b.p. 68–70°/20 mm., $n^{25}\mathrm{D}$ 1.4395 (reported, b.p. 67°/20 mm.,[6] $n^{20}\mathrm{D}$ 1.4408[6] and 1.4440[3]). Gas chromatography showed a single peak with a retention time equal to that of the small peak from the cyclic sulfate product.

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[6] F. Sondheimer and R. B. Woodward, *J. Am. Chem. Soc.*, **75**, 5438 (1953).

Vinylogy in Alkylation of *t*-Butyl Esters

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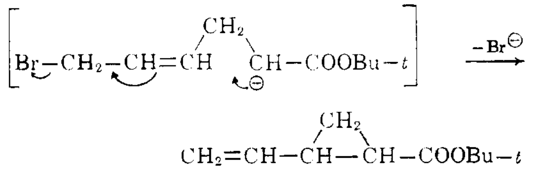
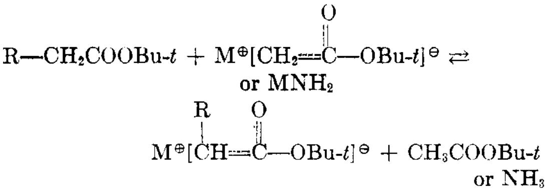
In an extention of studies on alkylation of *t*-butyl acetate with organic halides,[1] the reaction of 1,4-dibromo-*trans*-2-butene and *t*-butyl acetate has been investigated. When a mixture of *t*-butyl acetate with an equivalent amount of lithium amide suspended in liquid ammonia was treated with 1,4-dibromo-*trans*-2-butene dissolved in anhydrous tetrahydrofuran, a crystalline diester was obtained in 64–67% yields based on the bromide. The ester was found to be di-*t*-butyl *trans*-4-octene-1,8-dioate, as hydrolysis with ethanolic potassium hydroxide afforded *trans*-4-octene-1,8-dioic acid in an 88% yield and catalytic hydrogenation of the ester over Raney nickel gave crystalline di-*t*-butyl suberate, which was subsequently hydrolyzed to suberic acid.

The condensation of 1,4-dibromo-2-butene with sodiomalonate has already been described as resulting in the exclusive formation of 2-vinylcyclopropane 1,1-dicarboxylate.[2] An analogous reaction of *t*-butyl acetate according to equation 1 had been anticipated, but no cyclopropanecarboxylate could be isolated from the condensation product. A prerequisite to the cyclization should be the deprotonation of monoalkylated ester (equation 2).[3] As described previously,[1] the second alkylation of the *t*-butyl monoalkylacetates is scarcely perceptible with lithium amide, while dialkylated esters along with monoderivatives are produced in condensation by means of sodium or potassium amide. Accordingly the present reaction was repeatedly examined for possible formation of cyclized products in the presence of the latter amides, but the sole reaction product isolated in reduced yields was di-*t*-butyl *trans*-4-octenedioate, as before.


(1)



$$\mathrm{R{-}CH_2COOBu\text{-}}t + \underset{\text{or } \mathrm{MNH_2}}{\mathrm{M^{\oplus}[CH_2{=}\overset{\overset{O}{\|}}{C}{-}OBu\text{-}}t]^{\ominus}} \rightleftarrows \mathrm{M^{\oplus}[\overset{\overset{R}{|}}{C}H{=}\overset{\overset{O}{\|}}{C}{-}OBu\text{-}}t]^{\ominus} + \underset{\text{or } \mathrm{NH_3}}{\mathrm{CH_3COOBu\text{-}}t} \quad (2)$$

α-Dialkylation of ester by means of lithium amide was observed in the benzylation of *t*-butyl crotonate. When a mixture of *t*-butyl crotonate and lithium amide suspended in liquid ammonia was treated with an equivalent amount of benzyl chloride and the condensation products were hydrolyzed by boiling hydrochloric acid dissolved in dioxane, two crystalline acids melting at 101–102° and 98.5–99.5°, respectively, were isolated. Analyses of the higher melting acid agreed with a monobenzylated crotonic acid, while the lower melting acid with a dibenzylated product. Infrared spectrum of the dibenzylated acid indicated the presence of a vinyl group and a carbonyl group which is *not* in conjugation with the ethylene bond. The assigned structure of 2,2-dibenzyl-3-butenoic acid was confirmed by NMR spectrum as described in the Experimental.[4] Infrared spectrum of the monobenzylated crotonic acid revealed the presence of a carboxyl group in conjugation with an ethylene bond, but comparison with authentic 5-phenyl-2-pentenoic acid[5] exhibited remarkable differences and a mixed melting point showed depression. Evidence supporting the structure of 2-benzyl-2-butenoic acid was again obtained by means of NMR spectrum. These benzylated crotonic acids were always accompanied by a considerable amount of insoluble polymeric products, which were not investigated. The yields and relative ratio of mono- and dibenzylated products were variable. In most favorable conditions 2-benzyl-2-butenoic acid was obtained in a 31% yield, while 2,2-dibenzyl-3-butenoic acid in a 36% yield.

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[1] K. Sisido, Y. Kazama, H. Kodama, and H. Nozaki, *J. Am. Chem. Soc.*, **81**, 5817 (1959).

[2] (a) R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 3610 (1952); (b) S. F. Birch, R. A. Dean, and N. J. Hunter, *J. Org. Chem.*, **23**, 1390 (1958); (c) J. Nickl, *Chem. Ber.*, **91**, 553 (1958).

[3] For a recent publication on related problems see (a) W. R. Dunnavant and C. R. Hauser, *J. Org. Chem.*, **25**, 1693 (1960). (b) O. Mårtensson and E. Nilson, *Acta Chem. Scand.*, **15**, 1026 (1961).

[4] The signal of benzyl methylene protons of 2,2-dibenzyl-3-butenoic acid was observed as a quartet of typical AB coupling pattern. This is a token indicating that two protons of the methylene group are non-equivalent possibly because of the hindered free rotation of benzyl groups.

[5] H. Staudinger and H. Schneider, *Ber.*, **56**, 699 (1923).

Condensation of *t*-butyl crotonate with *n*-butyl bromide in the presence of lithium amide afforded similarly a nearly equimolar mixture of mono- and dibutylated crotonates. Fractional saponification of this mixture gave 2-*n*-butyl-2-butenoic acid in a 15% over-all yield, besides *t*-butyl 2,2-di-*n*-butyl-3-butenoate which was recovered unchanged in a 28% yield, both based on *n*-butyl bromide. This difference in the hydrolysis rates would be ascribed to the increased steric hindrance of the ester group in the latter dialkylated product. The γ-alkylated products could not be identified throughout these alkylations of the crotonate. Analogous α-alkylations of crotonic acid[6] and of alkylidenemalonates[7] have been mentioned.[8]

Experimental[9]

Di-*t*-butyl *trans*-4-Octene-1,8-dioate.—To a lithium amide suspension prepared from 1.3 g. (0.19 g.-atom) of metallic lithium in 300 ml. of liquid ammonia and cooled at −40°, 21 g. (0.18 mole) of *t*-butyl acetate was added with continuous stirring. After an additional 15 min. a solution of 16 g. (0.075 mole) of 1,4-dibromo-*trans*-2-butene[10] in 30 ml. of anhydrous tetrahydrofuran was added dropwise, and the whole mixture was stirred at −40° for 3 hr. The mixture was treated in the usual way[1] and extracted with ether. Evaporation residue (14.2 g. or 67%) solidified and melted at 54–56°. Recrystallizations from petroleum ether (b.p. 30–60°) afforded an analytical sample, m.p. 56–57°.

Anal. Calcd. for $C_{16}H_{28}O_4$: C, 67.57; H, 9.93. Found: C, 67.88; H, 10.01.

Infrared absorptions (Nujol mull): 1720 cm.$^{-1}$ (nonconjugated ester), 970 cm.$^{-1}$ (*trans*-ethylenic hydrogen).

***trans*-4-Octene-1,8-dioic Acid.**—Hydrolysis of 10 g. of the di-*t*-butyl ester by refluxing for 3 hr. with 20 g. of potassium hydroxide in 60 ml. of aqueous ethanol afforded 5.3 g. (88%) of the dibasic acid melting at 171–174°. Single recrystallization from a mixture of petroleum ether (b.p. 30–60°) and ethanol gave a pure sample, m.p. 175–176°.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.77; H, 7.08.

Suberic Acid.—A solution of 5.7 g. of di-*t*-butyl *trans*-4-octene-1,8-dioate in 50 ml. of anhydrous ethanol was shaken with 1.0 g. of Raney nickel (W-5 grade)[11] in an atmosphere of hydrogen at room temperature. After 1 equivalent of hydrogen was absorbed, the catalyst was filtered and the solution was concentrated to afford colorless crystals (5.1 g. or 89%) of **di-*t*-butyl suberate**, m.p. 30–31°.

Anal. Calcd. for $C_{16}H_{30}O_4$: C, 67.09; H, 10.56. Found: C, 67.01; H, 10.44.

Hydrolysis with hydrochloric acid in dioxane[1] gave a nearly quantitative yield of suberic acid, m.p. and mixed m.p. 139–140°.

Condensation of *t*-Butyl Crotonate with Benzyl Chloride.—The reaction was repeatedly examined over ten times, but the yields of products were variable due to the tendency of the olefinic esters to polymerize into a resinous product. In one experiment a lithium amide suspension prepared from 1.1 g. (0.16 g.-atom) of lithium and 300 ml. of liquid ammonia was treated with 21 g. (0.15 mole) of *t*-butyl crotonate.[12] After stirring for 4 hr. at −50°, a solution of 19 g. (0.15 mole) of benzyl chloride in 50 ml. of anhydrous ether was added and the stirring was continued for an additional 8 hr. at −50°. The condensation product was hydrolyzed directly by heating with a mixture of 40 ml. of hydrochloric acid and 32 ml. of dioxane and the resulting acid was recrystallized from ligroin (b.p. 60–80°) to afford 7.2 g. (36% based on benzyl chloride) of **2,2-dibenzyl-3-butenoic acid**, m.p. 98.5–99.5°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.33; H, 6.80.

The infrared absorptions (potassium bromide tablet); 1724 cm.$^{-1}$ (nonconjugated carboxylic acid), 995 and 920 cm.$^{-1}$ (a vinyl group). The NMR spectrum, run on a 5 *M* carbon tetrachloride solution at 56.4 Mc. with water as an external reference, showed peaks: a singlet at δ −2.36, weight 10, assigned to protons of two phenyl groups; a sextet centering at δ −1.25 (X) and two quartets centering at values of δ −0.46 (B) and −0.36 (A), respectively, each weight 1, assigned to three protons of a vinyl group[13]; a quartet at δ +1.70, weight 4, assigned to protons of methylene group which showed a typical AB coupling pattern with J_{AB} 13.6 c.p.s. and δ_{AB} 8.5 c.p.s. All observations support the structure given.

In another run the reaction was carried out as above with 0.7 g. (0.1 g.-atom) of lithium, 300 ml. of liquid ammonia, 14.2 g. (0.1 mole) of *t*-butyl crotonate, and 12.7 g. (0.1 mole) of benzyl chloride. The halide was added immediately after the addition of the ester. Upon distillation of the condensation products a fraction boiling at 112–135°/4 mm. was obtained and was hydrolyzed by heating with a mixture of hydrochloric acid and dioxane. Fractional recrystallizations of the acidic materials from aqueous ethanol afforded 5.5 g. (31%) of **2-benzyl-2-butenoic acid**, m.p. 96–99°. Recrystallizations from ligroin (b.p. 60–80°) yielded a sample, m.p. 101–102°,[14] which gave correct analyses for carbon and hydrogen. The infrared spectrum (Nujol mull) showed 1665 and 1630 cm.$^{-1}$ (α,β-unsaturated carboxylic acid).

The NMR spectrum, run on 4 *M* carbon tetrachloride solution at 56.4 Mc. with water as an external reference, showed absorptions: a quartet centering at δ −2.31, weight 1, assigned to an olefinic proton adjacent to terminal methyl group; a singlet at δ −2.30, weight 5, assigned to protons of phenyl group; a singlet at δ +1.18, weight 2, assigned to protons of a benzylmethylene group; a doublet centering at δ +2.91, weight 3, assigned to terminal methyl group which is coupled with the olefinic proton with *J* 7.2 c.p.s. These findings support the structure of 2-benzyl-2-butenoic acid. 2,2-Dibenzyl-3-butenoic acid could not be isolated in this run.

Condensation of *t*-Butyl Crotonate with *n*-Butyl Bromide.—To a suspension of lithium amide prepared from 0.7 g. (0.1 g.-atom) of lithium and 300 ml. of liquid ammonia, 14.2 g. (0.1 mole) of *t*-butyl crotonate was added at −40°. After 1 hr. stirring, 13.7 g. (0.1 mole) of *n*-butyl bromide was added and the stirring was continued at the same temperature for 10 hr. Upon distillation of the reaction product 8.2 g. of an oil boiling at 75–90°/3 mm. was obtained. Microanalyses for carbon and hydrogen on this product gave values in agreement with those calculated for a nearly

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[6] A. J. Birch, *J. Chem. Soc.*, 1551 (1950).

[7] A. C. Cope, H. C. Holmes, and H. O. House, *Org. Reactions*, **9**, 114 (1957).

[8] For condensation of *t*-butyl crotonate with acetophenone, which occurs at γ-carbon of the ester, see C. R. Hauser and W. H. Puterbaugh, *J. Am. Chem. Soc.*, **75**, 1068 (1953).

[9] All temperatures are uncorrected. Microanalyses were performed by Miss Kenko Ogawa.

[10] E. H. Farmer, C. D. Lawrence, and J. F. Thorp, *J. Chem. Soc.*, 729 (1928).

[11] H. R. Billica and H. Adkins, *Org. Syn.*, Coll. Vol. III, 176 (1955).

[12] R. H. Baker and F. G. Bordwell, *Org. Syn.*, Coll. Vol. III, 141 (1955).

[13] For examples of such an unusual splitting of vinyl protons forming an ABX system into fourteen lines with a sextet in the X proton region, see E. Wenkert and P. Beak, *J. Am. Chem. Soc.*, **83**, 998 (1961) and also J. D. Roberts, "An Introduction to the Analysis of Spin-Spin Splitting in High-Resolution Nuclear Magnetic Resonance Spectra," W. A. Benjamin, Inc., New York, N. Y., 1961, p. 83. Quartets of A and B protons are normal and splittings are about 11 and 1.4 c.p.s. for B proton, and about 17 and 1.4 c.p.s. for A proton.

[14] Lit., m.p. 99° [F. Fichter and E. Alber, *J. prakt. Chem.* [2], **74**, 335 (1906)].

equimolar mixture of mono- and dibutylated *t*-butyl crotonates.

Hydrolysis of 7.5 g. of this oil by refluxing with a solution of 10 g. of potassium hydroxide in 40 ml. of aqueous ethanol from 6 hr. afforded 2.0 g. (15% based on *n*-butyl bromide) of crystalline acid melting at 22–24°. Single recrystallization from petroleum ether (b.p. 30–60°) afforded an analytical sample of **2-*n*-butyl-2-butenoic acid,**[15] m.p. 24.5–25.5°, which gave correct analyses for carbon and hydrogen. The infrared spectrum (neat liquid) showed absorptions at 1680 and 1640 cm.$^{-1}$ (α,β-unsaturated carboxylic acid). No vinyl absorptions were observed.

Catalytic hydrogenation of 0.71 g. of 2-*n*-butyl-2-butenoic acid was carried out at room temperature in 50 ml. of ethanol and in the presence of 0.5 g. of Raney nickel (W-5 grade).[11] The resulting **2-butylbutyric acid** distilled at 88–95° (bath temperature)/1 mm., and had n^{15}D 1.4280. Chlorination with thionyl chloride, followed by treatment with aqueous ammonia, afforded **2-*n*-butylbutyramide,** m.p. 100–101° (lit.,[16] 101–102°), after recrystallizations from water. The amide gave correct analyses for carbon and hydrogen.

Upon distillation of the neutral portion of the hydrolysis products under reduced pressure 3.3 g. (28% based on *n*-butyl bromide) of ***t*-butyl 2,2-di-*n*-butyl-3-butenoate,** b.p. 90–91°/2.5 mm., n^{16}D 1.4385, was obtained.

Anal. Calcd. for $C_{16}H_{30}O_2$: C, 75.53; H, 11.89. Found: C, 75.32; H, 11.87.

The infrared spectrum (neat liquid) showed absorptions at 1720 cm.$^{-1}$ (nonconjugated ester) and at 1000 and 910 cm.$^{-1}$ (a vinyl group).

Acknowledgment.—The authors are indebted to Mr. N. Hayakawa, Japan Atomic Energy Institute, for NMR measurements. His assistance is gratefully acknowledged.

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[15] R. Adams and L. J. Roll, *J. Am. Chem. Soc.*, **53**, 3469 (1931). These authors recorded the acid as an oil.

[16] H. S. Raper, *J. Chem. Soc.*, **91**, 1831 (1907).

Improved Production of Phenylchlorocarbene

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McElvain[1] and Breslow[2] generated phenylchlorocarbene by the action of potassium *t*-butoxide on benzal chloride; the carbene, in each case, was trapped *via* addition to ketene acetals. We have prepared adducts I, III, IV, VII, VIII, IX, and X in a similar manner (see Table I). The preparation of II, IV, VI, VIII, and X required the prior synthesis of *p*-methylbenzal chloride, a white, crystalline solid (m.p. 50–51°, from methanol) obtainable through reaction of phosphorus pentachloride and *p*-tolualdehyde.

Production of 1-chloro-1-phenylcyclopropanes by the butoxide α-elimination method is limited. The reaction does not proceed well at temperatures much below 70°, thus precluding the use of butenes as acceptors under simple reaction conditions. Indeed, the attempted synthesis of IX *via* the butoxide method at 0° failed. In no case does the yield exceed 40%, adducts III and IV were obtained in highly impure form, while adduct II could not be prepared in sufficient yield to permit separation from concomitant impurities.[3] In all cases, considerable quantities of quite high-boiling and presumably polymeric materials were formed.

These difficulties may be obviated if methyllithium is employed rather than the butoxide.[5] Adducts II, V, VI, and X were produced in this manner. The methyllithium benzal chloride reaction may be carried out at 0° and gives little polymer, no impurities boiling in the same range as the desired product and higher yields. For example, X was obtained in only 17% yield by the butoxide reaction, but in 42% yield by the methyllithium route. Adduct II, which could not be obtained by the butoxide method, resulted in 21% yield by the methyllithium method. The butene adducts V and VI were also preparable by this method only.

Structures of adducts V, VI, IX, and X are in accord with NMR data. In all pairs the methyl analog exhibits a signal in the region 7.69–7.82 τ, whereas the remainder of the spectrum is identical in shape to that of the unsubstituted adduct.

All adducts possessed an infrared absorption in the region 1030–1000 cm.$^{-1}$. In accord with the literature, the band nearest 1021 cm.$^{-1}$ was considered as characteristic of the cyclopropane ring.[6]

Experimental

Olefins.—1-Hexene and isobutylene were Phillips Petroleum C.p. Tetramethylethylene was prepared by the method of Whitmore.[7] *trans*-Hexene-3 was prepared by the method of Pomeranz.[8] Methylenecyclohexane was prepared by pyrolysis of cyclohexylmethyl acetate at 500° on a glass-packed column.

Benzal chloride was Matheson technical grade, purified by distillation over a tantalum spiral column at 103°/28 mm.

***p*-Methylbenzalchloride.**—An 85-g. sample of phosphorus pentachloride was placed in a two-neck 500-ml. flask, fitted with a dropping funnel and mechanical stirrer. The temperature was kept at 25° by means of a water bath. A 50-g. sample of *p*-tolualdehyde was added dropwise, with stirring over 1 hr. Stirring was continued for 6 hr., care being taken to exclude direct light. The reaction mixture was

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[1] S. M. McElvain and P. L. Weyna, *J. Am. Chem. Soc.*, **81**, 2586 (1959).

[2] R. Breslow, R. Haynie, and J. Mirra, *ibid.*, **81**, 247 (1959).

[3] These impurities absorb at 1700–1680 cm.$^{-1}$ in the infrared. Though there is evidence that butoxide can cause elimination in ketene acetal adducts,[1,4] we have treated V for eighteen hours with butoxide in refluxing hexene-1 without effecting any noticeable change. In addition, a prepared mixture of several adducts was not affected by methyllithium at 0°. We conclude that the impurities result from an alternate consumption of benzal chlorides when these are reacted with butoxide in the presence of a poor acceptor olefin. No such impurities were formed when the olefin was a better acceptor or when methyllithium was employed.

[4] K. B. Wiberg, R. K. Barnes, and J. Albin, *J. Am. Chem. Soc.*, **79**, 4994 (1957).

[5] G. L. Closs and L. E. Closs, *ibid.*, **82**, 5723 (1960).

[6] L. J. Bellamy, "Infrared Spectra of Complex Molecules," J. Wiley and Sons, Inc., New York, 1960, pp. 29f.

[7] F. C. Whitmore and L. Black, *J. Am. Chem. Soc.*, **64**, 1619 (1942).

[8] P. Pomeranz, A. Fookson, T. W. Mears, S. Rothberg, and F. L. Howard, *J. Res. Natl. Bur. Std.*, **52**, 59 (1954).