The diethyl 3,4-dimethylmuconate isomers were isolated by gas chromatography and the structure was verified by infrared, nmr, and mass spectrometry.

Ethyl 5-Methyl-3,4-diaza-2,4-undecadienenoate (VII).—A solution of 22.8 g of ethyl diazoacetate (0.2 mole) in 20 ml of chloroform was added dropwise over 1.5 hr to a solution of 7.0 g of methyl *n*-hexyldiazirine (0.05 mole), 0.5 g of di-μ-chlorodi-π-allyldipalladium, and 10 ml of chloroform at 0–10°. After the evolution of nitrogen ceased, the orange solution was concentrated and analyzed by gas chromatography. The major peak was identified as diethyl fumarate, and the only other product was collected and identified as the title compound. The infrared spectrum (film) showed absorptions at 1755 (s), 1730 (s), 1640 (m), 1600 (w), 1375 (m), 1195 (s), 1040 (m), and 720 (w) cm^{-1}. The nmr spectrum showed signals at τ 8.65, 8.08, 5.66, and 2.63. The *n*-hexyl peaks in the nmr spectrum were complicated and not reported. The mass spectrum showed significant peaks at mass numbers of 183, 181, 169, and 153.

Reduction of Conjugated Double Bonds with Sodium Borohydride

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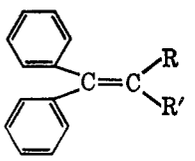
The use of sodium borohydride to effect the reduction of aldehydes and ketones is now a well-established and widely utilized procedure. More recently, its application in large excess to the preparation of alcohols from carboxylic acid esters has been reported.[1] The employment of sodium borohydride to reduce carbon–carbon double bonds, however, has not been widespread and there are but few references to such use. Shechter and co-workers[2] used this reagent to prepare a series of nitroalkanes starting with the corresponding α,β-unsaturated nitroalkenes; Le Moal and co-workers[3] employed potassium borohydride to reduce ethyl α-cyano-β-phenylcinnamate (Ia) to the appropriate hydrocinnamate; Adank and co-workers[4] converted a series of substituted 2,5-dioxo-5H-pyrrolo[2,1-*a*]-isoindoles to their dihydro derivatives using sodium borohydride; and, finally, Meschino and Bond[5] used the same reagent to reduce various ylidene cyanoacetates to their corresponding hydroxymethylpropionitriles, the carboethoxy group being attacked in addition to the double bond.



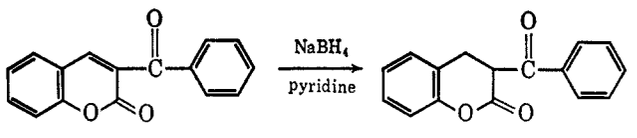
Ia, R = $COOC_2H_5$; R′ = CN
b, R = R′ = $COOC_2H_5$
c, R = R′ = CN

The application of sodium borohydride to the selective reduction of the ethylenic linkage of a number of simple organic compounds exhibiting α,β unsaturation is illustrated in Table I. These chemical reductions were carried out in a facile manner and within a short period of time. Equimolar quantities of the appropriate reactant and sodium borohydride in ethanol or 2-propanol were stirred for 3–4 hr in the cold and at room temperature, and the products were isolated by dilution of the reaction mixture with water, extraction of the aqueous mixture with ether or ethyl acetate, and distillation of the organic extracts. The yields of final material were generally good, although optimal conditions regarding temperature, reaction time, and solvent effects were not elucidated. The products thus prepared exhibited infrared spectra, refractive indices, and boiling points or melting points which were the same as those of materials obtained by independent means of synthesis. Physical properties are shown in Table II.

TABLE I
SODIUM BOROHYDRIDE REDUCTIONS

Reactant	Product	Yield, %
$CH_3CH{=}C(COOC_2H_5)_2$	$CH_3CH_2CH(COOC_2H_5)_2$	59
$(CH_3)_2C{=}C(COOC_2H_5)_2$	$(CH_3)_2CHCH(COOC_2H_5)_2$	74
$C_6H_5CH{=}C(COOC_2H_5)_2$	$C_6H_5CH_2CH(COOC_2H_5)_2$	69
$C_6H_5CH{=}C(CN)CONH_2$	$C_6H_5CH_2CH(CN)CONH_2$	81
$CH_2{=}C(COOC_2H_5)C_6H_5$	$CH_3CH(COOC_2H_5)C_6H_5$	80
$CH_2{=}CHCOOC_2H_5$	$CH_3CH_2COOC_2H_5$	25

In addition, 3-benzoylcoumarin (II) was converted to 3-benzoyl-3,4-dihydrocoumarin (III) by means of sodium borohydride in pyridine. The use of pyridine as a solvent to promote the preferential reduction of an ethylenic moiety over a ketone carbonyl group has been reported by Adank and co-workers.[4]



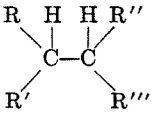
II III

The delocalization of the π-electrons of the ethylenic linkage, which occurs through conjugation of the carbon–carbon double bond with the ester, nitrile, phenyl, and/or amide groups present in the various reactants, results in the creation of an electrophilic center which is capable of being attacked by a nucleophile, in this case the borohydride anion. The failure[3] of diethyl diphenylmethylenemalonate (Ib) to undergo this type of reaction with potassium borohydride or other borohydrides is probably due to the lack of a relatively sufficiently strong and localized electro-

(1) M. S. Brown and H. Rapoport, *J. Org. Chem.*, **28**, 3261 (1963).
(2) H. Shechter, D. E. Ley, and E. B. Robertson, Jr., *J. Am. Chem. Soc.*, **78**, 4984 (1956).
(3) H. Le Moal, R. Carrie, and M. Bargain, *Compt. Rend.*, **251**, 2541 (1960).
(4) K. Adank, H. A. Pfenninger, W. G. Stoll, and M. Viscontini, *Helv. Chim. Acta*, **46**, 1030 (1963).
(5) J. A. Meschino and C. H. Bond, *J. Org. Chem.*, **28**, 3129 (1963).

TABLE II

PHYSICAL PROPERTIES OF PRODUCTS OBTAINED BY SODIUM BOROHYDRIDE REDUCTION



Compd	R	R′	R″	R‴	Method of prepn	Bp, °C (mm)	$n^{25}D$
I	C_2H_5	H	$COOC_2H_5$	$COOC_2H_5$	A[a]	93–94 (10)[b]	1.4155[c]
II	CH_3	CH_3	$COOC_2H_5$	$COOC_2H_5$	A	99–101 (11)[d]	1.4190[e]
III	C_6H_5	H	$COOC_2H_5$	$COOC_2H_5$	B[a]	170–173 (15)[f]	
IV	C_6H_5	H	$CONH_2$	CN	B	129–130[g,h]	
V	H	H	C_6H_5	$COOC_2H_5$	A	104–106 (10)[i]	1.4940[i]
VI	H	H	H	$COOC_2H_5$	A	96–98[j]	1.3805[j]

[a] See Experimental Section. [b] Lit.[15] bp 93–96° (10 mm). [c] D. E. Floyd and S. E. Miller [*J. Am. Chem. Soc.*, **69**, 2354 (1947)] reported $n^{25}D$ 1.4157. [d] Lit.[15] bp 103–107° (15 mm). [e] Lit.[16] $n^{22}D$ 1.4186. [f] I. Vogel [*J. Chem. Soc.*, 1013 (1928)] reported bp 163° (14 mm). [g] Melting point. [h] Lit.[18] mp 130°. [i] Lit.[19] bp 100.5° (8 mm), $n^{18}D$ 1.4943. [j] A. I. Vogel [*J. Chem. Soc.*, 624 (1948)] reported bp 98–99° (763 mm), $n^{20}D$ 1.38394.

philic center brought about by conjugation of the double bond with the β-phenyl groups. In contrast to this, diphenylmethylenemalononitrile[6] (Ic) and ethyl α-cyano-β-phenylcinnamate[3] (Ia) were reduced to their dihydro derivatives, a reaction which might be expected in view of the greater electron-withdrawing ability of the nitrile group as compared to the carboethoxy group. Likewise, whereas ethyl cinnamate was unaffected by sodium borohydride under the conditions of this reaction,[7] its structural isomer, ethyl atropate, was reduced in good yield to ethyl hydratropate. Finally, although cinnamonitrile was not reduced by sodium borohydride under the specified conditions, incorporation into the α position of a carbamoyl group, a relatively weak electron-withdrawing moiety, was nevertheless sufficient to allow the reduction of the resulting product, α-cyanocinnamamide, to take place.

Experimental Section

Melting points and boiling points are uncorrected.

Materials.—Sodium borohydride was purchased from Metal Hydrides Inc. Diethyl ethylmalonate, diethyl benzylmalonate, and ethyl acrylate were commercial samples obtained from Matheson Coleman and Bell and ethyl propionate was similarly obtained from Trubek Chemical Co.

Method A.—To a cold (0–5°), stirred slurry of 0.05 mole of sodium borohydride in 20 ml of ethanol there was added over 20 min a solution of 0.05 mole of reactant in 20 ml of ethanol. The reaction mixture was stirred for 1 hr in the cold and for 2–3 hr at room temperature, during which time it either became very viscous or a precipitate appeared. The mixture was diluted with 400 ml of water, the resulting cloudy solution was thoroughly extracted with ether or ethyl acetate, and the combined organic extracts were dried over magnesium sulfate. After filtration and evaporation of the solvent, the residual material was distilled.

In the reduction of ethyl acrylate, the combined ether extracts were distilled through a 30-cm adiabatic column packed with glass helices.

Method B.—To a cold (0–5°), stirred solution of 0.05 mole of reactant in 50 ml of 2-propanol there was added at once 0.05 mole of sodium borohydride. The reaction mixture was stirred for 1 hr in the cold and for 2 hr at room temperature. It was then diluted with 400 ml of water, and work-up was performed as indicated in method A.

In the case of α-cyanocinnamamide, a precipitate was obtained upon dilution of the reaction mixture with water. This was filtered by suction and was recrystallized from water.

Diethyl Ethylidenemalonate.—This compound was prepared by the method of Goss and co-workers[8]: bp 109–113° (14 mm), $n^{26}D$ 1.4405 [lit.[9] bp 102–106° (10 mm), $n^{25}D$ 1.4394].

Diethyl Isopropylidenemalonate.—The procedure of Cope and Hancock[10] was used to prepare this ester: bp 115–118° (12 mm), $n^{25}D$ 1.4472 [lit.[10] bp 111–113° (9 mm), $n^{25}D$ 1.4478].

Diethyl Benzylidenemalonate.—This ester was prepared by the method of Allen and Spangler[11]: bp 184–186° (11 mm) [lit.[11] bp 140–142° (4 mm)].

α-Cyanocinnamamide.—A solution of 21.0 g (0.25 mole) of cyanoacetamide and 30.0 g (0.28 mole) of benzaldehyde in 250 ml of benzene containing 2 ml of piperidine was refluxed for 4 hr, during which time water was removed azeotropically by means of a Dean–Stark trap. Upon cooling, a heavy crop of crystals appeared. They were collected by suction filtration and were recrystallized twice from benzene: mp 120–122° (lit.[12] mp 123°).

Ethyl Atropate.—The method of Ames and Davey[13] was followed to obtain this ester: bp 115.5–117.5° (12 mm) [lit.[14] bp 114–116° (12 mm)].

Diethyl Isopropylmalonate.—Palladium-catalyzed hydrogenation of an ethanolic solution of diethyl isopropylidenemalonate at 35 psi provided this material in 90% yield: bp 102–104° (12 mm), $n^{26}D$ 1.4185 [lit. bp 103–107° (15 mm),[15] $n^{22}D$ 1.4186[16])].

α-Cyanohydrocinnamamide.—One gram of ethyl α-cyanohydrocinnamate[17] was warmed on a steam bath for 5 min with 5 ml of ammonium hydroxide. The clear solution which resulted was allowed to cool, and the crystals which deposited were recrystallized from water: mp 129° (lit.[18] mp 130°).

Ethyl Hydratropate.—A solution of ethyl atropate in acetic acid was hydrogenated at 35 psi using palladium on charcoal as a catalyst. Usual work-up procedure afforded ethyl hydratropate: bp 105–107° (10 mm), $n^{26}D$ 1.4919 [lit.[19] bp 100.5° (8 mm), $n^{18}D$ 1.4943].

3-Benzoylcoumarin.—A solution of 61.0 g (0.5 mole) of salicylaldehyde and 105.0 g (0.55 mole) of ethyl benzoylacetate in 200 ml of ethanol containing 1 ml of piperidine and 5 drops of acetic acid was refluxed for 2 hr. The material which crystallized upon cooling the reaction mixture was recrystallized once from ethanol–benzene: mp 134–135° (lit.[20] mp 135–136°).

3-Benzoyl-3,4-dihydrocoumarin.—A stirred solution of 12.5 g (0.05 mole) of 3-benzoylcoumarin in 75 ml of pyridine was treated with 1.89 g (0.05 mole) of sodium borohydride. The solution quickly warmed to 50°, at which point it was cooled

(6) E. Campaigne and W. L. Roelofs, *J. Org. Chem.*, **30**, 396 (1965).

(7) The use of a large excess of sodium borohydride in refluxing methanol has converted ethyl cinnamate in small yield to ethyl hydrocinnamate; see ref 1.

(8) F. R. Goss, C. K. Ingold, and J. F. Thorpe, *J. Chem. Soc.*, **123**, 3353 (1923).

(9) W. S. Fones, *Org. Syn.*, **32**, 54 (1952).

(10) A. C. Cope and E. M. Hancock, *J. Am. Chem. Soc.*, **60**, 2644 (1938).

(11) C. F. H. Allen and F. W. Spangler, *Org. Syn.*, **25**, 42 (1945).

(12) J. N. E. Day and J. F. Thorpe, *J. Chem. Soc.*, **117**, 1465 (1920).

(13) G. R. Ames and W. Davey, *ibid.*, 1794 (1958).

(14) H. Schinz and M. Hinder, *Helv. Chim. Acta*, **30**, 1349 (1947).

(15) F. W. Swamer and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 1352 (1950).

(16) H. Adkins and H. R. Billica, *ibid.*, **70**, 695 (1948).

(17) P. E. Gagnon, R. Gaudry, and F. E. King, *J. Chem. Soc.*, 13 (1944).

(18) J. C. Hessler, *Am. Chem. J.*, **22**, 169 (1899).

(19) H. Olsson, *Z. Physik. Chem.*, **125**, 247 (1927).

(20) O. Widman, *Ber.*, **51**, 533 (1918).

in an ice bath. After 30 min the reaction mixture was poured onto 600 ml of cold 2 *N* hydrochloric acid. An oil appeared which solidified after a few minutes. The solid material was collected on a filter and was recrystallized from ethanol to yield 10.0 g (79%) of white needles, mp 100–101°.

Anal. Calcd for $C_{16}H_{12}O_3$: C, 76.18; H, 4.80. Found: C, 76.44; H, 5.07.

Material having the same melting point and exhibiting a superimposable infrared spectrum was obtained by the hydrogenation of an acetic acid solution of 3-benzoylcoumarin at 35 psi, using platinum oxide as catalyst.

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Some Reactions of Cyclobutylcarbinyl Radical Intermediates

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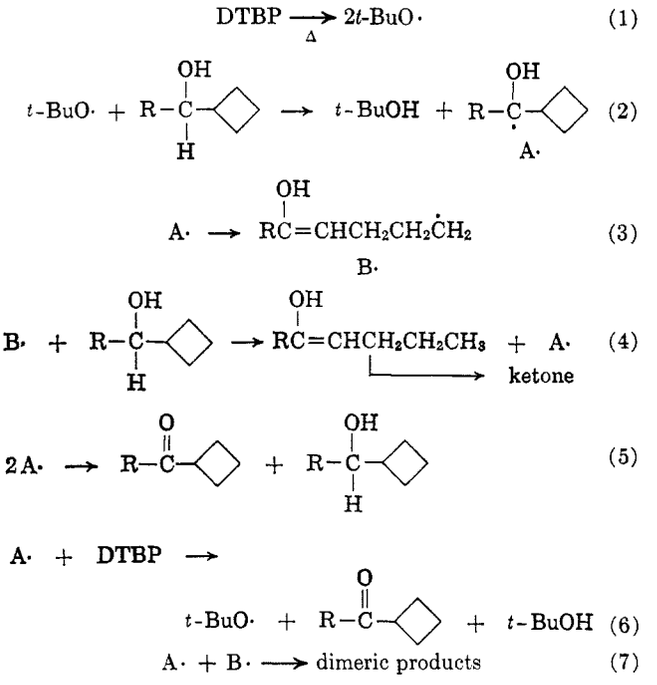
Ring-opening rearrangement reactions of cyclobutylcarbinyl free radicals have been reported to result from the peroxide-induced addition of certain polyhaloalkanes to β-pinene.[2] The quantities of rearranged product obtained, as in the case of addition reactions to certain vinylcyclopropanes,[3] are known to be a function of radical lifetime.[4] Few other examples of cyclobutylcarbinyl radical ring-opening reactions are reported.

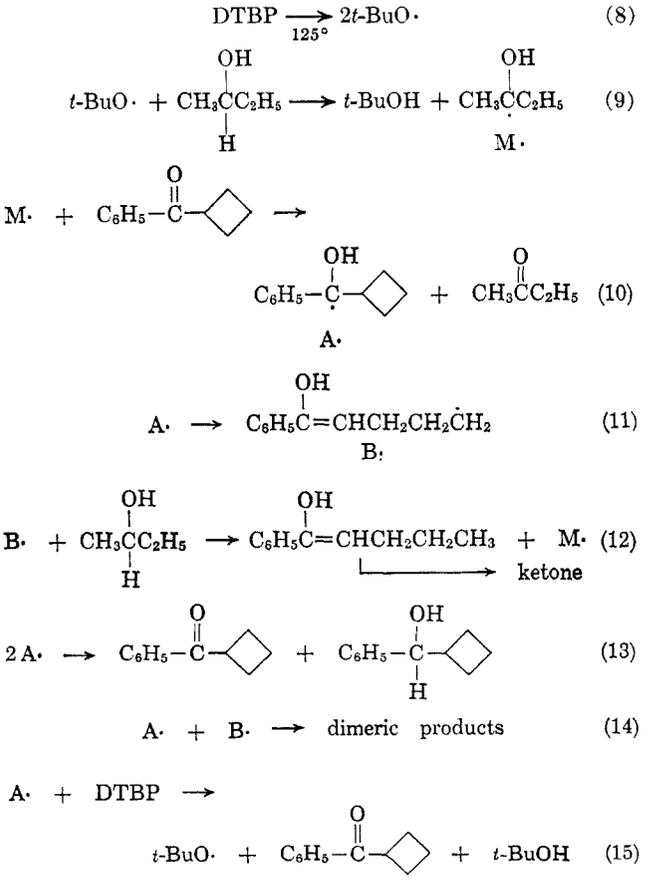
We wish to report a unique ring-opening rearrangement reaction of (α-hydroxy)cyclobutylcarbinyl free radicals. As in the case of (α-hydroxy)cyclopropylcarbinyl free radicals,[5,6] the major reaction product is a straight-chain aromatic ketone. Specifically, we have found treatment of cyclobutylphenylcarbinol with di-*t*-butyl peroxide (DTBP) at 125° to give valerophenone as a major product. Similarly, treatment of cyclobutylmethylcarbinol with DTBP at 125° gives good yields of 2-hexanone. The results of typical experiments are given in Table I.

Of interest is the fact that 2-hexanone predominates over cyclobutyl methyl ketone by a factor of about 8:1 when DTBP is decomposed in cyclobutylmethylcarbinol, whereas cyclobutyl phenyl ketone predominates over valerophenone by 2.7:1 when DTBP is decomposed in cyclobutylphenylcarbinol, a fact indicative of the increased resonance stability imparted to the cyclobutylcarbinyl free radical by the adjacent phenyl group. Details of further experiments on resonance and polar factors influencing cycloalkylcarbinyl radical stability will be reported shortly.[6]

A mechanism for the reaction of DTBP with cyclobutylmethyl- and cyclobutylphenylcarbinol may be as follows (1–7).



Cyclobutyl phenyl ketone, when treated with 2-butanol and DTBP, also yields valerophenone. Presumably a reaction intermediate similar to A· precedes the rearrangement reaction, although such an intermediate may not be totally necessary. The results of a typical experiment are given in Table II. A reasonable mechanism for the reaction may be as follows (8–15).



(1) Financial support from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

(2) (a) D. M. Oldroyd, G. S. Fisher, and L. A. Goldblatt, *J. Am. Chem. Soc.*, **72**, 2407 (1950); (b) G. Dupont, R. Dulou, and G. Clement, *Compt. Rend.*, **236**, 2512 (1953); (c) G. Dupont, R. Dulou, and G. Clement, *Bull. Soc. Chim. France*, 1056, 1115 (1950); (d) G. Dupont, R. Dulou, and G. Clement, *ibid.*, 257 (1951); (e) L. A. Goldblatt and D. M. Oldroyd, U. S. Patent 2,533,240 (1950); *Chem. Abstr.*, **45**, 2262 (1951).

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(4) F. G. Bordwell and W. A. Hewett, *J. Am. Chem. Soc.*, **79**, 3493 (1957).

(5) D. C. Neckers, *Tetrahedron Letters*, 1889 (1965).

(6) D. C. Neckers, J. Hardy, and A. P. Schaap, in preparation.