"stripped" with a mixture of hexane and acetone, followed by evaporation of the solvent to give a brown oil from which was isolated 1.7 g. (7%) of the rearranged alcohol, m.p. 62–63°, after two recrystallizations from petroleum ether. A mixed melting point with an authentic sample of the rearranged alcohol was the same.

When 10.0 g. (0.0393 mole) of independently synthesized alcohol Xd was treated with 4.68 g. (0.0393 mole) of phenyl isocyanate under similar conditions, there was obtained 13.4 g. (91%) of the urethan, m.p. 161–161.5° after recrystallization from carbon tetrachloride, reported m.p. 157°,[41b]

Anal. Calcd. for $C_{25}H_{27}NO_2$: C, 80.39; H, 7.29; N, 3.75. Found: C, 80.52; H, 7.41; N, 3.82.

When 5.95 g. (0.0234 mole) of independently synthesized alcohol XId was treated similarly with phenyl isocyanate (2.79 g., 0.0234 mole) and chromatographed there was obtained 2.4 g. (43%) of an olefin, b.p. 161–162° at 11 mm., $n^{25}D$ 1.5659, and 2.5 g. (42%) of recovered alcohol, m.p. 62–63°.

Independent Syntheses of Alcohols of Types X and XI (Scheme A).—**1-Phenyl-2,2-diethyl-1-butanol** (Xb) was prepared by adding 12 g. (0.059 mole) of triethylacetophenone (V) in 30 ml. of ether to a stirred suspension of 2.23 g. (0.06 mole) of lithium aluminum hydride in 30 ml. of ether. After 2 hours at room temperature, the reaction mixture was hydrolyzed with 10% sodium hydroxide to give 10.5 g. (87%) of the alcohol, b.p. 156° at 15 mm., $n^{25}D$ 1.5198.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.68; H, 10.90.

3-Ethyl-4-phenyl-3-hexanol (**XIb**) was synthesized from 20.0 g. (0.112 mole) of methyl α-phenylbutyrate (b.p. 113–114° at 17 mm., $n^{25}D$ 1.4951) and a benzene suspension (100 ml.) of ethylmagnesium bromide (prepared from 0.25 mole of ethyl bromide and magnesium in ether). After refluxing 24 hours, the reaction mixture was decomposed with ammonium chloride to give 16 g. (69%) of the alcohol, b.p. 137–138° at 16 mm., $n^{25}D$ 1.5096, d^{20}_4 0.937.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.49; H, 10.75. Found: C, 81.69; H, 10.69.

1-Phenylneophyl alcohol (**Xc**) was prepared from 8.70 g. (0.0388 mole) of dimethyldesoxybenzoin (VII, R = CH_3) and 1.47 g. (0.0388 mole) of lithium aluminum hydride in ether by the method described above; yield 6.8 g. (78%), b.p. 184° at 14 mm. (179° at 11.5 mm.), $n^{25}D$ 1.5735, reported b.p. 185–190° at 18 mm.[56]

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.17; H, 7.99.

2-Diphenylmethyl-2-propanol (**XIc**) was obtained by adding during 12 hours benzhydryl chloride (60.0 g., 0.296 mole) in 300 ml. of anhydrous ether to a stirred, refluxing suspension of 216 g. (8.9 g. atoms) of powdered magnesium in 400 ml. of ether,[57] followed (after cooling), by 17.2 g. (0.296 mole) of purified acetone. After 4 hours at room temperature, the mixture was poured onto ice and ammonium chloride to give (after dissolving the precipitated magnesium salts with cold 5% sulfuric acid) 30.6 g. (46%) of the alcohol, b.p. 151–152° at 5.5 mm. (168–169° at 11.5 mm.), $n^{25}D$ 1.5722.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.19; H, 8.14.

1,2-Diphenyl-2-ethyl-1-butanol (**Xd**) was synthesized from 15.0 g. (0.0595 mole) of diethyldesoxybenzoin (VII, R = C_2H_5) and 2.25 g. (0.0595 mole) of lithium aluminum hydride in ether by the method described above; yield 12.8 g. (85%), b.p. 197–197.5° at 12 mm., $n^{25}D$ 1.5686, reported b.p. 209° at 20 mm.[41b]

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 85.21; H, 8.69.

3-Diphenylmethyl-3-pentanol (**XId**) was prepared from 21.0 g. (0.0936 mole) of ethyl benzhydryl ketone (see above) and ethylmagnesium bromide (from 0.109 mole of ethyl bromide and magnesium) in 150 ml. of ether. After refluxing 24 hours, the mixture was hydrolyzed with saturated ammonium chloride solution to give 5.0 g. (21%) of the alcohol boiling at 161–162° at 5 mm. (181–182° at 12 mm.), m.p. 62.5–63.5° after recrystallization from petroleum ether.

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.99; H, 8.72. Found: C, 84.95; H, 8.52.

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DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF REED COLLEGE, UNIVERSITY OF WASHINGTON AND UNIVERSITY OF CALIFORNIA]

The α-Hydrogen Reactivity of Thiolesters[1,2]

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RECEIVED DECEMBER 13, 1954

Ethyl thiolacetate has been found to undergo Claisen condensation with isopropylmagnesium bromide to give 60–70% yields of ethyl acetothiolacetate and the relative rate of reaction of benzaldehyde with ethyl dithiolmalonate in the Knoevenagel condensation has been found to be about four times the rate for the corresponding reaction with ethyl malonate. These observations are indicative of an increase in the acidity of the hydrogen alpha to a carbethoxy group upon replacement of oxygen by sulfur to give a thiolester. Isopropylmagnesium bromide reacts with *t*-butyl thiolacetate to give a relatively stable Grignard of the thiolester, $BrMgCH_2COSC(CH_3)_3$. This reagent reacted with cyclohexanone in a Reformatsky-type reaction to give 65% of *t*-butyl 1-hydroxycyclohexylthiolacetate which was desulfurated with Raney nickel to give 80% of 2-(1-hydroxycyclohexyl)-ethanol.

Although there have been some indications of differences in the behavior of esters and thiolesters[4–8] the chemical and physical properties of thiolesters have not been investigated extensively. The discovery of coenzyme A and its importance in acylation and other metabolic processes[9,10] and the finding that acyl derivations of coenzyme A are thiolesters[11] has created additional interest in the chemistry of these esters.[12–14]

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(2) We wish to acknowledge the support of a part of this work by a grant from the H. V. Tartar Fund of the Department of Chemistry, University of Washington.

(3) Department of Chemistry, Reed College, Portland 2, Oregon.

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Since coenzyme A is involved in enzymatic acylation processes, several studies have been made of the chemical reactivity of thiolacetates as acylating agents.[12-14] In addition to its function as an acylation catalyst, coenzyme A is involved in the methylene activation of acetate for acetoacetate[15] and citrate[16] formation and for other synthetic and degradative processes.[10,17] However, until Wessely and Lynen found the pK_a value for S-acetoacetyl-N-acetylthioethanolamine[18] to be 8.5 compared to 10.7 for ethyl acetoacetate, there had been no definite evidence concerning the effect of the thiolester group on an adjacent methylene.

There was an indication in the work of Baker and Reid[6] of some difference in the behavior of ethyl acetate and ethyl thiolacetate in the Claisen condensation. Equal molar quantities of ethyl acetate and ethyl thiolacetate with sodium gave, in a low yield, a product which was found to be 98% ethyl acetothiolacetate and 2% ethyl acetoacetate. Furthermore, ethyl acetothiolacetate was found to be 31% enolic by Meyer's bromine titration method as compared to 7% for ethyl acetoacetate.

In the present work a study was made of a variety of reagents and conditions for the Claisen condensation of ethyl thiolacetate. The yields were poor and the purity of the product was unsatisfactory until isopropylmagnesium bromide was used as the condensing reagent. Claisen condensation occurred to give 60–70% yields of ethyl acetothiolacetate. Ethyl acetate with isopropylmagnesium chloride has been reported[19] to give the ketol of methyl isopropyl ketone. This reaction was repeated with isopropylmagnesium bromide and there was no indication of any acetoacetate formation as indicated by testing the distillate from an acidified reaction product with 2,4-dinitrophenylhydrazine reagent. Thus there is a rather clear qualitative difference in the behavior of ethyl acetate and ethyl thiolacetate with the isopropyl Grignard reagent.

Since Shivers, Hudson and Hauser[20] had found that *t*-butyl acetate is sufficiently hindered to give a Claisen condensation with isopropylmagnesium bromide, it was expected that *t*-butyl thiolacetate would likewise give a Claisen product with this reagent. The reaction of *t*-butyl thiolacetate and isopropylmagnesium bromide proceeded as expected, but was much slower than for the ethyl ester and gave a 30% yield of *t*-butyl acetothiolacetate with a 60% recovery of unchanged thiolester after 24 hours at room temperature. This suggested that the Grignard of the thiolester was stable enough to undergo a Reformatsky-type[21] reaction as indicated (equations 1 and 2).

$$(CH_3)_2CHMgBr + CH_3COSC(CH_3)_3 \longrightarrow BrMgCH_2COSC(CH_3)_3 + C_3H_8 \quad (1)$$

$$BrMgCH_2COSC(CH_3)_3 + RCOR \longrightarrow \underset{\displaystyle OH \quad CH_2COSC(CH_3)_3}{\overset{\displaystyle R}{R-C}} \quad (2)$$

With cyclohexanone there was obtained a 65% yield of *t*-butyl 1-hydroxycyclohexylthiolacetate which was identified by hydrolysis to 1-hydroxycyclohexaneacetic acid. Treatment of the hydroxythiolester with Raney nickel gave an 80% yield of 2-(1-hydroxycyclohexyl)-ethanol. Thus, these reactions constitute a convenient process for the conversion of a ketone to a 1,3-glycol as indicated (equation 3).

$$R_2C{=}O \longrightarrow \underset{\displaystyle R_2C-CH_2COSC(CH_3)_3}{\overset{\displaystyle O-H}{|}} \longrightarrow \underset{\displaystyle R_2C-CH_2CH_2OH}{\overset{\displaystyle O-H}{|}} \quad (3)$$

The Claisen condensation of ethyl thiolacetate would seem to indicate rather clearly that the thiolester has a greater α-hydrogen acidity than an ester.[22] In order to obtain more specific evidence concerning the degree of activation of the α-hydrogen by the thiolester group, the method devised by Pratt and Werble[23] for the comparison of the activity of active methylene compounds was applied to ethyl dithiolmalonate. The rate of reaction of benzaldehyde in a Knoevenagel reaction with ethyl dithiolmalonate was determined and compared with the same reaction rate for ethyl malonate. With a catalyst concentration of one-half that used for the ethyl malonate–benzaldehyde reaction, the thiol ester gave a reaction rate "constant," calculated from the slope of a log *c vs. t* plot (Fig. 1), of 20.8×10^{-3} l. $\times$ mole^{-1} $\times$ min.$^{-1}$ as compared to 9.96×10^{-3} for ethyl malonate. Thus the relative reaction rate was about 4:1. If, as has been postulated,[23] the over-all rate for the Knoevenagel reaction is controlled by the rate of removal of the proton from the active methylene compound by the piperidine catalyst this is further evidence for the activating effect of the thiolester group on an adjacent α-hydrogen.

This difference in the α-hydrogen acidity of esters and thiolesters may be interpreted as another indication of the relative weakness of the overlapping of the C(2p) and S(3p) orbitals in the carbon–sulfur double bond, $\underset{\displaystyle +}{\overset{\displaystyle |}{C}}-S-R$, when compared with $\underset{\displaystyle +}{\overset{\displaystyle |}{C}}-O-R$. The contribution of (a) to the ester resonance

$$\underset{\displaystyle RCH_2C=O-R'}{\overset{\displaystyle O^-}{|}} \qquad \underset{\displaystyle RCH_2C=S-R'}{\overset{\displaystyle O^-}{|}}$$
(a) (b)

decreases the acidity of the α-hydrogen, relative to the acidity of a ketone, by a cross-conjugation effect on the ester–anion equilibrium.[24a] If the rela-

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(22) Ethyl phenylacetate, whose enolate ion is stabilized by resonance interaction with the aromatic system, gives 93% of the Claisen product with isopropylmagnesium bromide; J. B. Conant and A. H. Blatt, THIS JOURNAL, **51**, 1227 (1929).
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tive contribution of (b) to the stability of the thiolester is less than (a), then the α-hydrogen of the thiolester should be intermediate in acidity between an ester and a ketone. This difference in the resonance energy of the two types of esters also would explain the difference in enol content of ethyl acetoacetate (7%) and ethyl acetothiolacetate (31%)[6,24b] and the pK_a value for S-acetoacetyl-N-acetylthioethanolamine[18]; although in this last case it is apparent that some additional factor may be operating to increase the stability of the anion since the pK_a value reported, 8.50, is very close to that of acetylacetone, 8.24.[25] Other evidence for the weakness of $-\overset{|}{\underset{+}{C}}=S-R$ compared to $-\overset{|}{\underset{+}{C}}=O-R$ has been found in the σ-constants for *m*-CH_3S and *p*-CH_3S as determined from the rate of saponification of the substituted ethyl benzoates.[26] The difference between σ_{para} and σ_{meta} is 0.42 for CH_3O and 0.17 for CH_3S; furthermore, there is no difference in the acidity of the *p*-CH_3S and *m*-CH_3S phenols while there is a considerable difference between the *p*-CH_3O and *m*-CH_3O phenols, with the *p*-CH_3O showing an acid-weakening resonance effect.[27]

Experimental[28]

Claisen Condensations with Isopropylmagnesium Bromide. Ethyl Thiolacetate.—The Grignard reagent prepared from 5.0 g. (0.21 mole) of magnesium and 21.0 g. (0.17 mole) of isopropyl bromide in 40 ml. of ether was cooled in Dry Ice and *n*-butyl carbitol to −20° and 20.0 g. (0.19 mole) of ethyl thiolacetate was added slowly at this temperature. After the addition was complete the mixture was stirred at 0° for 70 minutes. The reaction product was acidified carefully with a mixture of 30 ml. of concentrated hydrochloric acid and 30 g. of ice, keeping the temperature of the mixture not higher than 0°. The aqueous layer was separated and extracted with 40 ml. of 5% sodium bicarbonate and the ether extract was dried over anhydrous magnesium sulfate. Careful fractionation with the 36″ wire gauze column[29] gave 9.5 g. (66.5%) of ethyl acetothiolacetate boiling at 110° (30 mm.), $n^{25}D$ 1.4942.

Anal. Calcd. for $C_8H_{10}O_2S$: C, 49.31; H, 6.90; S, 21.90. Found: C, 49.04; H, 6.76; S, 21.72.

***t*-Butyl Thiolacetate.**—Isopropylmagnesium bromide prepared from 4.0 g. (0.16 mole) of magnesium and 20.9 g. (0.17 mole) of isopropyl bromide in 41 ml. of ether was cooled to −20° and 19.8 g. (0.15 mole) of *t*-butyl thiolacetate[30] was added slowly. After the addition was complete the mixture was stirred at room temperature for 24 hr. and was then acidified with 30 ml. of concentrated hydrochloric acid and 30 g. of ice. The aqueous layer was separated and extracted with 20 ml. of ether. The ether extracts were combined, washed with 40 ml. of 5% sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Fractionation gave 5 g. (25%) of *t*-butyl thiolacetate and 4.1 g. (20%) of *t*-butyl acetothiolacetate, b.p. 55° (3 mm.), $n^{25}D$ 1.4808.

Anal. Calcd. for $C_8H_{14}O_2S$: C, 55.16; H, 8.10; S, 18.37. Found: C, 55.08; H, 8.09; S, 18.39.

Reaction of the *t*-Butyl Thiolacetate Grignard Reagent with Cyclohexanone.—The Grignard reagent from 4.5 g. (0.19 mole) of magnesium and 24.6 g. (0.20 mole) of isopropyl bromide in 60 ml. of ether was cooled to −25° and 21.1 g. (0.16 mole) of *t*-butyl thiolacetate was added slowly.

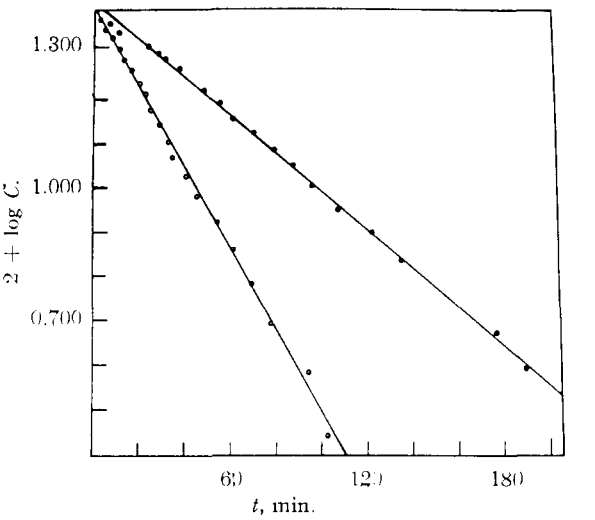

Fig. 1.—Knoevenagel reaction of benzaldehyde with ethyl malonate, ●, and ethyl dithiomalonate, ○; catalyst concentration halved for the thiolester.

TABLE I

CLAISEN CONDENSATIONS WITH ISOPROPYLMAGNESIUM BROMIDE

Reaction time	Temp., °C.	Yield, % β-keto ester	Ester, % recovered
	Ethyl thiolacetate		
1 hr.	−20	58	
1 hr.	−10	55	
1 hr.	−15 to −5	70	
1 hr.	−20 to 0	66	
	t-Butyl thiolacetate		
5 min.	0	..	80[a]
2 hr.	− 5	20	70
2 hr.	25	20	65
2 hr.	25	30	60
24 hr.	25	20	25

[a] The heat of reaction of the Grignard reagent with the thiolester to give the thiolester Grignard reagent, $BrMgCH_2COSC(CH_3)_3$, was noticeable immediately upon addition of the thiolester to the Grignard solution.

Immediately after the addition of the thiolester 14.7 g. (0.15 mole) of cyclohexanone was added slowly enough so that the temperature did not rise above −20°. After the mixture had been stirred for an hour at −20° it was allowed to come to room temperature and was then stirred for twelve hours. After acidification with 40 ml. of concentrated hydrochloric acid and 40 g. of ice, the ether was separated, the acid solution was washed with ether and the combined ether extracts were washed with sodium bicarbonate solution and were dried over anhydrous magnesium sulfate. Fractionation of the product gave 22.5 g. (65%) of *t*-butyl 1-hydroxycyclohexylthiolactate, b.p. 106° at 2 mm., $n^{25}D$ 1.4951.

Anal. Calcd. for $C_{12}H_{22}O_2S$: C, 62.58; H, 9.63; S, 13.90. Found: C, 63.03; H, 9.75; S, 13.32.

TABLE II

CONDENSATION OF CYCLOHEXANONE WITH $BrMgCH_2COSC(CH_3)_3$

Reacn. time, hr.	Temp., °C.	Yield, % β-hydroxy thiolester
1	0–5	21
2	0–5	35
4	25	70, 71, 65, 67
12	25	65

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(30) We wish to thank the Phillips Petroleum Co., Bartlesville, Oklahoma for a generous supply of this ester.

Hydrolysis of 1.0 g. of the ester in 20 ml. of 8% sodium hydroxide for one hour and crystallization of the acid from ligroin gave 0.4 g. (85%) of 1-hydroxycyclohexaneacetic acid, m.p. 61° (lit.[31] 62–64°).

Desulfuration of *t*-Butyl 1-Hydroxycyclohexylthiolacetate.—*t*-Butyl 1-hydroxycyclohexylthiolacetate (2.2 g.) was heated for an hour in refluxing *t*-butyl alcohol with 40 g. of Raney nickel which had been washed with *t*-butyl alcohol. Removal of the nickel and alcohol and evaporative distillation (at 140° (12 mm.)) of the residue gave 1.1 g. (80%) of 2-(1-hydroxycyclohexyl)-ethanol, $n^{18}D$ 1.4900.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.66; H, 11.19. Found: C, 66.31; H, 11.01.

Rate of Reaction of Ethyl Dithiolmalonate with Benzaldehyde.—The ethyl dithiolmalonate[32] was prepared by reaction of malonic acid with thionyl chloride followed (without purification of the acid chloride) by the addition of ethyl mercaptan. Careful fractionation gave a 25% yield of a nearly colorless product, b.p. 110–112° (2 mm.), $n^{25}D$ 1.5203.

Anal. Calcd. for $C_7H_{12}O_2S_2$: C, 43.72; H, 6.29; S, 33.35. Found: C, 43.77; A, 6.32; S, 33.18.

The rate of reaction was determined by using the procedure described by Pratt and Werble.[23] A repetition of their rate determination was made with 500 ml. of benzene solution of 0.25 *M* in benzaldehyde and 0.25 *M* in ethyl malonate containing 64 units[33] of the piperidine–caproic acid catalyst and there was obtained a rate constant of 9.95×10^{-3} liters moles^{-1} min.$^{-1}$ which agrees quite well with the value of 9.96×10^{-3} obtained by Pratt and Werble.

The reproducibility of the measurements was improved by prior treatment of the inside of the water separator with diphenyldichlorosilane in order to prevent wetting of the glass by the water droplets.

Since the rate of reaction of the thiolester (0.25 *M* in a total volume of 500 ml. with benzaldehyde (0.25 *M*) was found in preliminary experiments to be considerably faster than the malonic ester reaction, the catalyst concentration was halved to 32 units. The plot of log *c vs. t* (Fig. 1) is in good agreement with the assumed first-order dependence of the reaction rate on thiolester concentration and a rate constant of 20.8×10^{-3} liters mole^{-1} min.$^{-1}$ was obtained. This gives a relative rate of reaction of about 4:1 for ethyl dithiolmalonate compared with ethyl malonate.

The ethyl benzaldithiolmalonate underwent considerable decomposition during fractionation. There was obtained 24 g. (68%) of the condensation product, b.p. 177–179° (1 mm.), $n^{25}D$ 1.6180.

Anal. Calcd. for $C_{14}H_{16}O_2S_2$: C, 59.96; H, 5.75; S, 22.87. Found: C, 59.94; H, 5.76; S, 23.02.

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(32) J. E. Purvis, H. D. Jones and H. S. Tasker, *J. Chem. Soc.*, **97**, 2287 (1910).

(33) A solution of 16.6 g. of piperidine and 45.4 g. of caproic acid made up to 200 ml. with benzene contains 1 unit catalyst/ml. (9.76×10^{-4}) mole/ml. of piperidine and $2(9.76 \times 10^{-4})$ mole/ml. of caproic acid.

PORTLAND, OREGON

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE AND ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Rearrangements in Carbonium Ion-Type Reactions of C^{14}-Labeled Dehydronorbornyl Derivatives[1]

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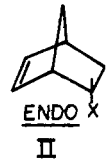
RECEIVED OCTOBER 11, 1954

Solvolysis of *exo*- and *endo*-dehydronorbornyl-2,3-C_2^{14} *p*-bromobenzenesulfonates in acetic acid and formic acid solutions and nitrous acid deaminations of *endo*-dehydronorbornyl-3-C^{14}-amine in acetic acid and aqueous fluoboric acid were found to yield 4–17% of dehydronorbornyl derivatives with 30–48% of the C^{14} located at other than the 2,3-positions. The C^{14}-rearrangements are discussed in terms of unsymmetrical "dehydronorbornium" intermediates.

In conjunction with our investigation of rearrangements in carbonium ion-type reactions of C^{14}-labeled norbornyl derivatives,[3] studies were made of solvolyses of *exo*- and *endo*-dehydronorbornyl-2,3-C_2^{14} *p*-bromobenzenesulfonates (Ia and IIa) and nitrous acid deamination of *endo*-2-amino-$\Delta^{5,6}$-norbornene-3-C^{14} (*endo*-dehydronorbornyl-3-C^{14}-amine, IIb).

I



II

Ia, IIa, X = *p*-$BrC_6H_4SO_3$–
Ib, IIb, X = $-NH_2$
Ic, IIc, X = $-OH$
Id, IId, X = $-OAc$
Ie, IIe, X = $-O_2CH$

Synthetic Procedures and Experimental Results

A mixture of *exo*- and *endo*-dehydronorborneols-2,3-C_2^{14} (Ic and IIc) was obtained by the lithium aluminum hydride reduction of mixed labeled dehydronorbornyl acetates (Id and IId) from the Diels–Alder reaction between cyclopentadiene and vinyl-1,2-C_2^{14} acetate.[3] Equilibration of the alcohol mixture in refluxing toluene with sodium and fluorenone effected enrichment in the *exo*-isomer,[3,4] the latter amounting to 47% of the recovered product. With *p*-bromobenzenesulfonyl chloride in pyridine,[5] the alcohols yielded the desired sulfonates Ia and IIa.

The stereoisomeric *p*-bromobenzenesulfonate mixtures were not separated for the solvolysis experiments since the published[6] relative solvolysis rates of Ia and IIa indicated that Ia easily can be solvolyzed preferentially at 45° in the presence of IIa. Acetolysis of Ia or IIa gave principally 3-acetoxynortricyclene (IIIa) with lesser amounts of *exo*-dehydronorbornyl acetate (Id).[6] Conversion of the product mixtures to the corresponding alcohols and hydrogenation gave mixtures of 3-hydroxynortricyclene (IIIb) and *exo*-norborneol (IV). The hydro-

(1) (a) Supported in part by the joint program of the Office of Naval Research and the U. S. Atomic Energy Commission. (b) Presented in part at the Symposium on Reaction Mechanisms at the 75th Anniversary Meeting of the American Chemical Society, September 7, 1951.

(2) Gates and Crellin Laboratories, California Institute of Technology, Pasadena 4, Calif.

(3) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., THIS JOURNAL, **76**, 4501 (1954).

(4) (a) W. v. E. Doering and T. C. Aschner, *ibid.*, **71**, 838 (1949); (b) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950), erroneously infer that the equilibrium product is substantially pure *exo*-dehydronorborneol.

(5) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(6) S. Winstein, H. M. Walborsky and K. Schreiber, THIS JOURNAL, **72**, 5795 (1950).