Thiomethylation[1]

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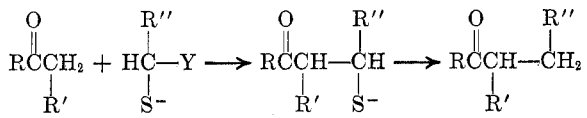
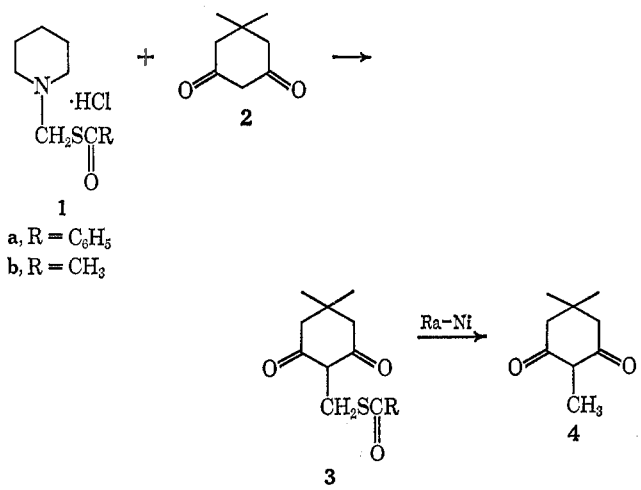
A method for the thiomethylation of active methylene compounds utilizing piperidinomethyl thiobenzoate hydrochloride (**1a**) and piperidinomethyl thioacetate hydrochloride (**1b**) is discussed. The scope and limitations of this reaction as a general alkylation method were investigated.

The common alkylation reactions involving active methylene type compounds usually involve modification of the system to be alkylated either by derivative formation (*e.g.*, eneamine) or by pretreatment with base. The utilization of an activated form of the alkylating agent which would require no modification of the compound to be alkylated and which could be used under very mild conditions appeared to be an attractive possibility. The ideal system would employ an activating group which could be removed during alkylation or which could be removed under neutral conditions after alkylation. A sulfur-containing system would meet these requirements since Raney nickel desulfurization following thioalkylation could be effected under mild conditions. The tentative scheme is given below.



Piperidinomethyl thiobenzoate hydrochloride (**1a**) was synthesized as a precursor for the preparation of "thioformaldehyde" in a thio-Prins reaction.[3] This compound was originally prepared[4] by the condensation of hydroxymethyl thiobenzoate with piperidine, and an alternate procedure was reported from these laboratories.[3]

When compound **1** was allowed to react with 5,5-dimethyl-1,3-cyclohexanedione (dimedone) (**2**), utilizing an excess of the latter, methylenebisdimedone was obtained. When a 1:1 molar ratio of the alkylating agent **1a** and dimedone were warmed in dioxane, a monothiomethylated product, 2-benzoylthiomethyl-5,5-dimethyl-1,3-cyclohexanedione (**3a**), formed as piperidine hydrochloride precipitated from the reaction solution. This compound was desulfurized to yield 2,5,5-trimethyl-1,3-cyclohexanedione (**4**).



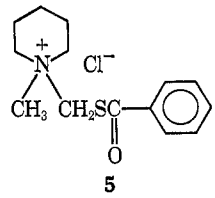
This method was utilized with a series of compounds (Chart I). In all cases, C-thioalkylation occurred with no O-alkylation being detectable. Proof of C-thioalkylation was obtained by desulfurization to the various methyl-alkylated systems. The use of benzenesulfonamide in this procedure yielded the N-thiomethylation product.

Attempts to thiomethylate cyclohexanone, malonic ester, phenol, and phloroglucinol under the conditions utilized for the successful alkylation of β-keto esters and β diketones failed to give the desired products. When the reaction time and/or the temperature were increased, the alkylating reagent, **1**, decomposed.[3]

An attempt at dialkylation by treating 3-benzoylthiomethyl-2,4-pentanedione (Chart I, eq 3) with 1 equiv of piperidinomethylthioacetate hydrochloride (**1b**) gave only starting material. Other modifications of the reagent and conditions were made in the hope of aiding in the elucidation of the mechanism. When the reagent **1** was utilized as the free base in the reaction with dimedone, no alkylated product was obtained.

The solvent utilized for the reaction does not appear to be critical. Dimedone was thiomethylated with **1** in refluxing dioxane, ethanol, chloroform, and dimethylformamide. The optimum reaction conditions were those utilizing the reagent **1** and dioxane. Under these conditions piperidine hydrochloride precipitates as **1** reacts with the material to be alkylated. A minor disadvantage in utilizing the thioacetate **1b** is its insolubility in dioxane. When other solvents are employed, formation of piperidine hydrochloride can not be observed since it is soluble.

In order to determine if the stability and reactivity of the alkylating agent could be increased, various changes were made in the reagent. N-Methylpiperidine was allowed to react with chloromethyl thiobenzoate to produce piperidinomethyl thiobenzoate methochloride (**5**). This compound was utilized, under the conditions specified for the alkylating agent **1** with dihydroresorcinol and acetylacetone, for periods



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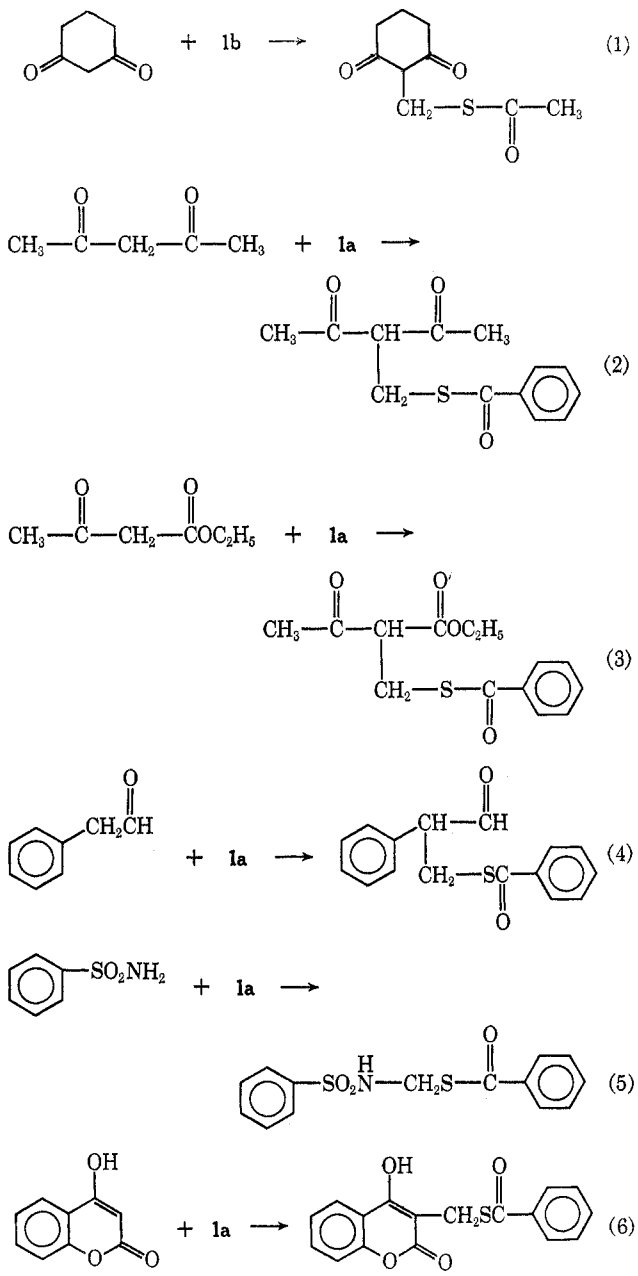
(1) Presented in part before the 1st Midwest Regional American Chemical Society Meeting, Kansas City, Mo., Nov. 4–5, 1965.

(2) Taken in part from the dissertations presented by J. R. J. Sorenson in Jan. 1965 and W. A. Albrecht in Dec 1965 to the Graduate School of the University of Kansas in partial fulfillment of the requirements for the Doctor of Philosophy Degree.

(3) E. E. Smissman and J. R. J. Sorenson, *J. Org. Chem.*, **30**, 300 (1965).

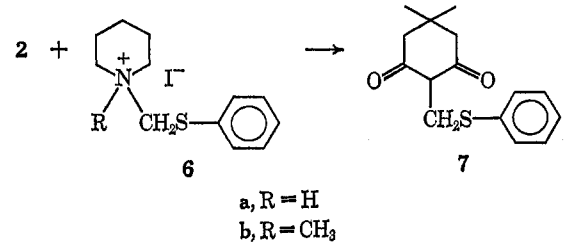
(4) H. Böhme, E. Nurnberg, and W. Schlephack, *Arch. Pharm.* (Weinheim), **292**, 585 (1959).

CHART I



up to 30 hr, but only starting material could be recovered.

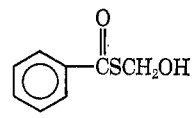
N-(Phenylthiomethyl)piperidine hydrochloride (**6a**) was prepared using the procedure of Grillot.[5] When it was refluxed with 1 equiv of dimedone in dioxane, an 89% yield of 2-phenylthiomethyldimedone (**7**) was obtained. Piperidine hydrochloride was observed in the reaction mixture within 2 min after mixing. However, N-(phenylthiomethyl)piperidine methiodide (**6b**) failed to alkylate dimedone.



6 **7**

a, R = H
b, R = CH_3

The thioalkylation of dimedone with hydroxymethyl thiobenzoate (**8**) in the presence of sulfuric acid has been reported.[6] In order to produce a more sensitive



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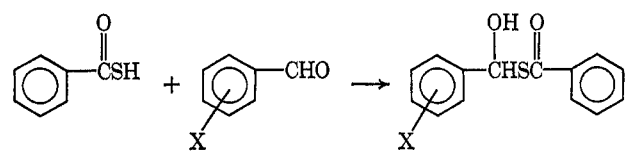
reagent which could be utilized under essentially neutral conditions and to study the possibility of extending the reaction beyond thiomethylation, it was decided to make derivatives of the alcoholic function.

Because of the ease of displacement of the tosyl group, it was selected as the derivative of choice of the hydroxymethyl thiobenzoate (**8**). Four other α-arylmethyl thiobenzoates (**9**) were prepared utilizing thiobenzoic acid and substituted benzaldehyde. The ease of condensation varied with the nature of the substituent on the aldehyde, the order for decreasing ease of condensation being *p*-NO_2 > *p*-Cl > *o*-Cl > *o*-Me > H. All attempts to prepare tosylate de-



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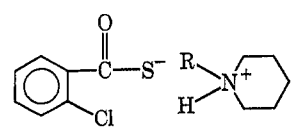
a, X = *p*-NO_2 c, X = *o*-Cl
b, X = *p*-Cl d, X = *o*-Me

rivatives of these thiobenzoates **9** failed. The condensation with α-naphthylisocyanate to give the corresponding α-naphthylurethans was successful; however, the latter compounds were unstable and tended to decompose to di-α-naphthylurea on recrystallization, on heating, or on standing at room temperature for 2–3 days.

Treatment of the α-hydroxy-α-arylmethyl thiobenzoates **9** with secondary amines resulted in the degradation of the benzoates to the corresponding aldehydes, and, in the case of the α-hydroxy-α-(chlorophenyl)methyl thiobenzoates, to the salt **10**.



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Since the formation of derivatives of the substituted thiomethyl alcohols failed, several attempts at condensing substituted α-hydroxymethyl thiobenzoates with diketones were made under both basic and acid conditions. In general, under the conditions used, the thiobenzoate reverts to the parent aldehyde and thiobenzoic acid.

(5) G. F. Grillot, H. R. Felton, B. R. Garrett, H. Greenberg, R. Green, R. Clementi, and M. Moskowitz, *J. Amer. Chem. Soc.*, **76**, 3969 (1954).

(6) H. Böhme, H. Bezzenberger, M. Clement, A. Dick, E. Nürnberg, and W. Schlephack, *Ann.*, **623**, 92 (1959).

Experimental Section[7]

Hydroxymethyl Thiobenzoate.—The literature procedure[6] was modified in the following manner. Thiobenzoic acid, 138 g (1.0 mol), and paraformaldehyde, 30 g (1.0 mol), were allowed to react at 100° for 2 hr under an atmosphere of nitrogen. The hot reaction mixture was filtered, and the filtrate solidified on cooling. The solid was recrystallized [ether–petroleum ether (bp 63–68°)] to give 135 g (80%) of product, mp 45–46° (lit.[6] mp 46°). The nmr spectrum showed peaks at 4.55, singlet, 1 H (-OH); 5.36, singlet, 2 H ($-SCH_2O$); 7.60, multiplet, 3 H (*meta* and *para* protons); 8.08, multiplet, 2 H (*ortho* protons).

Hydroxymethyl Thioacetate.—The above procedure was followed except that purification was accomplished by distillation, bp 30–35° (15 mm) [lit.[6] bp 68–70° (20 mm)], yield 109 g (80%).

Piperidinomethyl Thiobenzoate Hydrochloride (1a).—Piperidine, 25.2 g (0.29 mol), was dissolved in ether and treated with a large excess of anhydrous magnesium sulfate. The mixture was cooled in an ice bath, and an ethereal solution of hydroxymethyl thiobenzoate, 50.0 g (0.296 mol), was added slowly with stirring. After the addition was complete, the mixture was stirred for an additional 15 min and filtered into 300 ml of ether saturated with 13.0 g (0.36 mol) of hydrogen chloride gas. The white solid was filtered and air-dried, yield 60.0 g (75%), mp 173–176° (lit.[4] mp 173°). The nmr and ir are in agreement with the structure.

The hydrochloride was converted to the hydriodide *via* ion exchange. The white crystalline material, mp 189–191°, was stable to air drying.

Anal. Calcd for $C_{13}H_{18}INOS$: C, 42.98; H, 4.99; N, 3.86. Found: C, 42.81; H, 4.98; N, 3.68.

Piperidinomethyl Thioacetate Hydrochloride (1b).—The above procedure was followed utilizing 4.7 g (0.056 mol) of piperidine and 6.0 g (0.056 mol) of hydroxymethyl thioacetate. The white precipitate was filtered and air-dried, mp 185°, yield 7.5 g (65%).

Piperidinomethyl Thiobenzoate Methiodide and Methochloride (5).—Piperidine, 5.0 g (0.06 mol), was dissolved in 50 ml of ether containing 10 g of anhydrous magnesium sulfate. An ethereal solution of 10.0 g (0.006 mol) of hydroxymethyl thiobenzoate was added, dropwise, to the amine solution with stirring. After removal of the magnesium sulfate by filtration, 10 ml (0.16 mol) of methyl iodide was added and the solution was allowed to stand for several days. The white crystalline solid was collected by filtration and recrystallized (methanol–ethyl acetate), yield 2.5 g, mp 163–164°.

Anal. Calcd for $C_{14}H_{20}INOS$: C, 44.57; H, 5.34; I, 33.64; N, 3.71. Found: C, 44.30; H, 5.31; I, 33.82; N, 3.52.

N-Methylpiperidine, 3.6 g (0.036 mol), and chloromethyl thiobenzoate, 6.7 g (0.036 mol), were dissolved in 50 ml of dry benzene. After refluxing for 18 hr, 2.4 g of product was isolated: mp 184–186°; nmr (D_2O) 1.95 (broad singlet, 6 H, $(CH_2)_3$); 3.47 (singlet, 3 H, NCH_3); 3.91 (broad singlet, 4 H, $-CH_2N-CH_2-$); 4.92 (singlet, 2 H); 5.76 (singlet, 2 H, SCH_2N); 7.73 and 8.15 (two multiplets, 5 H, aromatic).

N-Phenylthiomethylpiperidine (6a).—The procedure of Grillot[5] was used and 78.8 g (76%) of product was obtained by distillation, bp 112–114° (1.0 mm) [lit.[5] bp 138–141° (5–6 mm)].

An ethereal solution of 58 g (0.28 mol) of N-phenylthiomethylpiperidine was treated with hydrogen chloride at 0°. The ether was decanted and the semisolid product was washed with ethyl acetate to yield a white hygroscopic solid 116–118°. The nmr and ir spectra were as expected. All attempts to recrystallize the product caused decomposition. Because of its hygroscopicity, the elemental analysis was not obtained.

N-Phenylthiomethylpiperidine Methiodide (6b).—An ether solution of 19.5 g (0.095 mol) of N-phenylthiomethylpiperidine (**6b**) and 9.4 ml (0.15 mol) of methyl iodide was allowed to stand for 1 week in a stoppered flask at room temperature. The solid was filtered and recrystallized (methanol–ethyl acetate) to give 24 g (72%) of product, mp 179–180°. The nmr and ir spectra were as expected.

Anal. Calcd for $C_{13}H_{20}INS$: C, 44.70; H, 5.77; N, 4.01. Found: C, 44.77; H, 5.69; N, 3.96.

(7) Melting points were obtained on a calibrated Thomas–Hoover Unimelt and are corrected. Ir data (μ) were recorded on Beckman IR-8 and IR-10 spectrometers. Nmr data (ppm, δ) were recorded on Varian Associates Model A-60 and A-60A spectrometers (TMS). Microanalyses were conducted by Huffman Laboratories, Inc., Wheatridge, Colo., and on an F & M Model 185 analyzer, University of Kansas.

2-Benzoylthiomethyl-5,5-dimethyl-1,3-cyclohexanedione.—Dimedone, 2.8 g (0.02 mol), was added to a refluxing solution of piperidinomethyl thiobenzoate hydrochloride, 5.4 g (0.02 mol), dissolved in 100 ml of *p*-dioxane. Almost immediately solid material precipitated, and after 14 min the reaction mixture was cooled and filtered. The residue weighed 2.4 g and was identified as piperidine hydrochloride, mp 244°. The dioxane solution was treated with twice its volume of ether and 5.0 g (86%) of product was collected by filtration and recrystallized from chloroform–carbon tetrachloride, mp 170–171°. The nmr and ir spectra were as expected.

Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 65.72; H, 6.40.

3-Benzoylthiomethyl-2,4-pentanedione.—Acetylacetone, 1.0 g (0.01 mol), was dissolved in 25 ml of *p*-dioxane and the solution was heated to reflux. Piperidinomethyl thiobenzoate hydrochloride, 2.7 g (0.01 mol), was added to the solution with stirring and heating for 5 min. Piperidine hydrochloride, 1.2 g, was collected by filtration, and the filtrate was reduced in volume to 5 ml. The oil was crystallized from ethanol–water to yield 1.3 g (52%) of product, mp 61–62°. The nmr and ir spectra were as expected.

Anal. Calcd for $C_{13}H_{12}O_3S$: C, 62.37; H, 5.64. Found: C, 62.29; H, 5.63.

2-Benzoylthiomethyl-2-phenylacetaldehyde.—Piperidinomethyl thiobenzoate hydrochloride, 5.44 g (0.02 mol), was dissolved in 70 ml of refluxing *p*-dioxane. A solution of 2.4 g (0.02 mol) of freshly distilled phenylacetaldehyde dissolved in 10 ml of *p*-dioxane was added, and the reaction mixture was heated at reflux for 10 min. After cooling, 2.39 g of piperidine hydrochloride was collected by filtration. The filtrate was concentrated to about 5 ml and chromatographed on 40 g of silica gel. Elution was accomplished with carbon tetrachloride followed with dichloromethane. Upon evaporation of the latter solvent, 2.8 g of an orange oil was obtained. The nmr and ir spectra were as expected. The product was analyzed as its 2,4-DNP derivative, mp 161–162°.

Anal. Calcd for $C_{22}H_{18}N_4O_5S$: C, 58.66; H, 4.03; N, 12.44. Found: C, 59.06; H, 4.27; N, 12.30.

N-Benzoylthiomethylbenzenesulfonamide.—Piperidinomethyl thiobenzoate hydrochloride, 2.72 g (0.01 mol), was dissolved in 30 ml of refluxing dioxane. Benzenesulfonamide, 1.57 g (0.01 mol), was added, the reaction mixture was cooled, and 1.2 g (theoretical amount 1.2 g) of piperidine hydrochloride was collected by filtration, mp 244°. The filtrate was poured into 100 ml of ice water and the white precipitate was filtered and air-dried. Recrystallization from carbon tetrachloride gave 1.6 g (52%) of product, mp 84°. The nmr and ir spectra were as expected.

Anal. Calcd for $C_{14}H_{13}NO_3S_2$: C, 54.70; H, 4.26; N, 4.56. Found: C, 54.70; H, 4.35; N, 4.54.

3-Benzoylthiomethyl-4-hydroxycoumarin.—To 5.44 g (0.02 mol) of piperidinomethyl thiobenzoate hydrochloride dissolved in 100 ml of refluxing *p*-dioxane was added 3.4 g (0.02 mol) of 4-hydroxycoumarin. The reaction mixture was refluxed for 10 min. After cooling, 2.35 g of piperidine hydrochloride was collected by filtration. The filtrate was poured into 150 ml of ice water, and the resulting precipitate was filtered and crystallized from acetone–water to yield 5.4 g (87%) of product, mp 166–167°. The nmr and ir spectra were as expected.

Anal. Calcd for $C_{17}H_{12}O_4S$: C, 65.37; H, 3.87. Found: C, 65.61; H, 4.04.

2-Acetylthiomethyl-5,5-dimethyl-1,3-cyclohexanedione. A.—To a solution of 3.08 g (0.0147 mol) of piperidinomethyl thioacetate hydrochloride dissolved in 35 ml of dimethylformamide (DMF) was added 2.065 g (0.0147 mol) of dimedone. The solution was stirred and heated at 100° for 2 hr. On cooling, piperidine hydrochloride, 1.65 g, precipitated. Evaporation of the filtrate gave, after recrystallization from carbon tetrachloride, 2.9 g (86%) of 2-acetylthiomethyl-5,5-dimethyl-1,3-cyclohexanedione, mp 135°. The nmr and ir spectra were as expected.

B.—Dimedone, 1.4 g (0.01 mol), and piperidinomethyl thioacetate hydrochloride, 2.1 g (0.01 mol); were dissolved in 25 ml of chloroform and refluxed for 1 hr. Carbon tetrachloride, 25 ml, was added to the solution and the chloroform was removed by heating the open flask on a steam bath. The hot carbon tetrachloride was filtered to remove 1.3 g of piperidine hydrochloride. The product crystallized, after cooling the filtrate, to give 1.76 g (78%), mp 134–135°.

2-Acetylthiomethyl-1,3-cyclohexanedione.—A solution of 1.1 g (0.01 mol) dihydroresorcinol and 2.1 g (0.01 mol) piperidinomethyl thioacetate hydrochloride dissolved in 50 ml of chloroform was refluxed for 1 hr. The chloroform solution was reduced to half its volume, and 100 ml of ether was added to precipitate piperidine hydrochloride, 1.55 g (100%). The solvent was removed to give an orange semisolid which was recrystallized from dichloromethane–petroleum ether (bp 63–68°) to yield 1.1 g (55%) of product, mp 132°. The nmr and ir spectra were as expected.

Anal. Calcd for $C_9H_{12}O_3S$: C, 54.00; H, 6.04. Found: C, 53.72; H, 5.94.

2-Phenylthiomethyl-5,5-dimethyl-1,3-cyclohexanedione.—To 25 ml of refluxing *p*-dioxane was added 2.4 g (0.01 mol) of N-phenylthiomethylpiperidine hydrochloride. Dimedone, 1.4 g (0.01 mol), was then added to the refluxing solution. Within 2 min, a white precipitate was observed. After cooling the reaction mixture, 1.1 g of piperidine hydrochloride was collected by filtration. The filtrate was poured into 100 ml of ice water and allowed to stand overnight. The precipitate was filtered and air-dried to yield 2.3 g (89%) of product. The solid was recrystallized from acetone–petroleum ether (bp 63–68°), mp 139°. The nmr and ir spectra were as expected.

Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.91. Found: C, 68.65; H, 6.90.

Desulfurization Procedure.—Raney nickel, the catalyst, was prepared by the method of Pavlic and Adkins.[8] Examples of the general procedure follow.

2,5,5-Trimethyl-1,3-cyclohexanedione.—2-Benzoylthiomethyl-5,5-dimethyl-1,3-cyclohexanedione, 2.9 g (0.01 mol), was dissolved in 125 ml of ethyl acetate at 65–70°. About 20 g (wet weight) of Raney nickel was added to the solution with stirring and heated for 1 hr. The reaction mixture was filtered while hot and the residue was washed with three 50-ml portions of hot ethyl acetate. The washings and original filtrate were combined, and the solvent was removed to yield 0.96 g (62%) of product melting at 163–165° (lit.[9] mp 163°). An authentic sample was prepared by the method of Desai.[9] The melting point and infrared spectra were identical with those of the desulfurized product.

3-Methyl-4-hydroxycoumarin.—The above procedure was followed to desulfurate 2.1 g (0.0067 mol) of 3-benzoylthiomethyl-4-hydroxycoumarin dissolved in 80 ml of ethyl acetate using 14 g (wet weight) of Raney nickel. Upon removal of the solvent, 0.86 g (74%) of product was isolated and recrystallized from chloroform–carbon tetrachloride, mp 225–228° (lit.[10] mp 231°).

(8) A. A. Pavlic and H. Adkins, *J. Amer. Chem. Soc.*, **68**, 1471 (1946).

Registry No.—Hydroxymethyl thiobenzoate, 23853-33-0; **1a** (HI), 23853-34-1; **1b** (HCl), 876-24-4; **5** (methiodide), 23853-36-3; **5** (methochloride), 23853-37-4; **6b**, 23853-38-5; 2-benzoylthiomethyl-5,5-dimethyl-1,3-cyclohexanedione, 23853-39-6; 3-benzoylthiomethyl-2,4-pentanedione, 23853-40-9; 2-benzoylthiomethyl-2-phenylacetaldehyde (2,4-DNP), 23853-41-0; N-benzoylthiomethylbenzenesulfonamide, 23853-42-1; 3-benzoylthiomethyl-4-hydroxycoumarin, 23853-43-2; 2-acetylthiomethyl-5,5-dimethyl-1,3-cyclohexanedione, 23853-44-3; 2-acetylthiomethyl-1,3-cyclohexanedione, 23853-45-4; 2-phenylthiomethyl-5,5-dimethyl-1,3-cyclohexanedione, 23853-46-5.

Acknowledgment.—The authors gratefully acknowledge support of this project by the National Institutes of Health Grants GM-9254 and GM-14,467.

(9) R. G. Desai, *J. Chem. Soc.*, 1079 (1932).
(10) K. Sen and P. Bagchi, *J. Org. Chem.*, **24**, 316 (1959).

Additions to Bicyclic Olefins. II. A Convenient Synthesis of Apobornene and Apocamphor[1]

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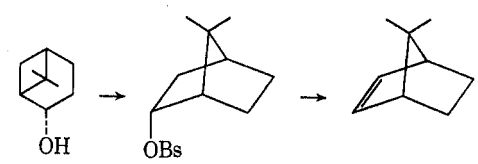
A convenient five-step synthesis of apobornene (7,7-dimethylnorbornene) from the readily available camphenilone (3,3-dimethylnorcamphor) has been developed in an overall yield of 30%. This procedure makes possible the synthesis of apobornene in relatively large quantities in purities of 98% or better. Through minor modifications the synthesis can be directed to the preparation of apocamphor.

A considerable quantity of pure apobornene (7,7-dimethylnorbornene) was required for our studies of the stereochemical aspects of additions to bicyclic systems.[3] The synthesis of apobornene has been described previously.[4,5] However, the procedures do not lend themselves to the preparation of apobornene in appreciable quantity or in the desired purity. Consequently, we undertook to develop a more satisfactory procedure.

The most direct procedure would be the Diels–Alder reaction of 5,5-dimethylcyclopentadiene with ethylene. However, the synthesis of the diene appeared to offer severe difficulties.[6] Another possibility was the conversion of β-nopinol into apobornyl brosylate,[7] followed by an elimination (eq 1). However, β-nopinol is not



(1)

easily synthesized.[8] Solvolytic methods can be used to obtain apoisoborneol as a mixture with isomeric alcohols.[9] However, we observed that the isolation of pure alcohol on a large scale was quite time consuming.

After examining a number of such approaches we decided that the most convenient procedure appeared

(1) Graduate research assistant on grants (G 19878 and GP 6492 X) supported by the National Science Foundation.
(2) Postdoctorate research associate on Grant GM 10937 from the National Institutes of Health.
(3) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 1990 (1970).
(4) (a) G. Komppa and T. Hasselstrom, *Ann. Acad. Sci. Fenn. Ser. A9*, **24**, 3 (1925); (b) G. Komppa and T. Hasselstrom, *Ann.*, **497**, 116 (1932); (c) G. Komppa and R. H. Roschier, *ibid.*, **429**, 175 (1922).
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(9) (a) See ref 8; (b) S. Beckmann and R. Bamberger, *Ann.*, **574**, 73 (1951); (c) Y. Chretien-Bessiere and J. P. Monthiard, *Compt. Rend.*, **258**, 937 (1964).