mixture containing 34% cyclohexenone as shown by the ultraviolet spectrum or 39% by gas chromatographic analysis; the other larger peak in the gas chromatograph corresponded in position to cyclohexanone.

C. Over Glass Helices Employing Recycling Apparatus.—The same recycling pyrolysis apparatus was employed except that the pyrolysis column was packed with clean $^3/_{16}$-in. i.d. Pyrex glass helices.

The distillation flask was charged with 60 g. of 2-acetoxycyclohexanone, b.p. 113–114° (8 mm.), the oil bath maintained at 170°, system pressure at 10 mm., fractionating column temperature at 85°, and pyrolysis column temperature at 450°. Under these conditions the product distilled at a rate of about 3 drops per min. at a still head temperature of 60°. Over half the material had pyrolyzed in 3 hr.; after 6 hr. only about 5 ml. of material was left in the flask and at the end of 19 hr. it was dry.

The receiver contained 47.57 g. of a slightly yellow liquid, and the Dry Ice traps contained 8.8 g. of liquid, also slightly yellow. The apparatus was washed out thoroughly with ether to give 1.75 g. of brown residue for a material balance of 58.12 g. (97%). There was no charring evident in the pyrolysis column. Gas chromatography of the combined 47.57- and 8.8-g. material showed only two peaks, one corresponding to acetic acid, the other to cyclohexenone. Careful distillation of this material through a 2-ft. stainless steel saddle-packed column gave 33.40 g. (90.5% yield) of cyclohexenone, b.p. 60.5–62° (10 mm.), $\lambda_{max}^{95\%\ C_2H_5OH}$ 224 mμ (ε 10,600), 2,4-dinitrophenylhydrazone, m.p. 162.6–164°. Reported values are b.p. 61–63° (14 mm.), 2,4-dinitrophenyl hydrazone, m.p. 163°.[2]

Pyrolysis of Cyclohexenone. A. Over Glass Helices.—A 40.3-g. sample of cyclohexenone, b.p. 72–74° (24 mm.), n^{25}_D 1.4830, $\lambda_{max}^{95\%\ C_2H_5OH}$ 225 mμ (ε 9370), was passed through the pyrolysis apparatus described above during a period of 3.25 hr. at 510–520° in a slow stream of nitrogen (which was prepurified by passage through 20% sodium hydroxide solution, two bottles of Fieser's solution, two bottles of lead acetate, concentrated sulfuric acid, and a calcium chloride tower). Both Dry Ice traps were empty. Distillation of the material collected in the ice-cooled trap through a semimicro column[19] gave the following fractions: No. 1, 1.28 g., b.p. 50–70° (26 mm.), n^{25}_D 1.4730; 2, 16.95 g., b.p. 70–73° (26 mm.), n^{25}_D 1.4810; 3, 12.15 g., b.p. 73–77° (26 mm.), n^{25}_D 1.4850; 4, 3.17 g., boiling point to about 100° (forced) (26 mm.), n^{25}_D 1.4990. These fractions appeared to be mainly unchanged starting material.

B. Over Carbon.—An 8.7-g. sample of 2-cyclohexenone, b.p. 61–62° (15 mm.), was pyrolyzed at 20 mm. in the recycling apparatus. The pyrolysis column was packed with lump coconut charcoal; and the column temperature was maintained at 450°. After 4 hr. the distillation flask was empty and a solid crystalline material had collected in the fractionating head condenser. The liquid nitrogen-cooled traps contained no material boiling below 100° and an infrared spectrum of the product (1.8 g.) collected in these traps indicated the presence of cyclohexenone, a small amount of a saturated ketone, and phenol. The pyrolysis apparatus, including the fractionating head condenser, was washed out with ether, and the ether was removed by distillation to give 2.2 g. of a light yellow oil. The infrared spectrum of this oil indicated the presence of only two components, phenol, and cyclohexenone. The 1.8 g. from the traps was combined with the 2.2 g. from the apparatus, diluted with ether, and extracted with 5% sodium hydroxide solution. These aqueous extracts were acidified to Congo red with hydrochloric acid and the turbid solution was extracted with ether. The ether extracts were combined, dried over anhydrous sodium sulfate, and the ether was distilled to give 2.4 g. of a clear oil. The infrared spectrum of this clear oil was identical in all respects with the infrared spectrum of a sample of authentic phenol.

Acknowledgment.—This study was supported in part by grants from the National Institutes of Health, the National Science Foundation, and the Wisconsin Alumni Research Foundation.

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The *n*-Butylthiomethylene Blocking Group[1]

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The chemical and physical properties of several representative 2-*n*-butylthiomethylene ketones are described, together with methods of preparation of this derivative. The use of the *n*-butylthiomethylene grouping as a "blocking group" during ketone methylation reactions is delineated. Several of the blocked ketones have been converted to α-methyl ketones by reductive desulfurization of the derivative.

In considering approaches to the total synthesis of polycyclic natural products, such as the di- and triterpenes, we adopted a plan[3-5] that would construct first the A/B ring system, which could then be elaborated further to the desired end product. Such a general scheme has not only been successful in our hands[4,5] but has also led to the syntheses of α-onocerin,[6] olean-11,12;13,18-diene,[7] and pentacyclosqualene[8] by other workers. One[3] of the paths we chose for the preparation of such an A/B ring system necessitated the intro-

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(2) Public Health Service Research Fellow of the National Heart Institute, 1958–1960.

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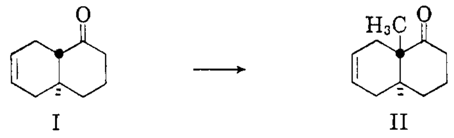
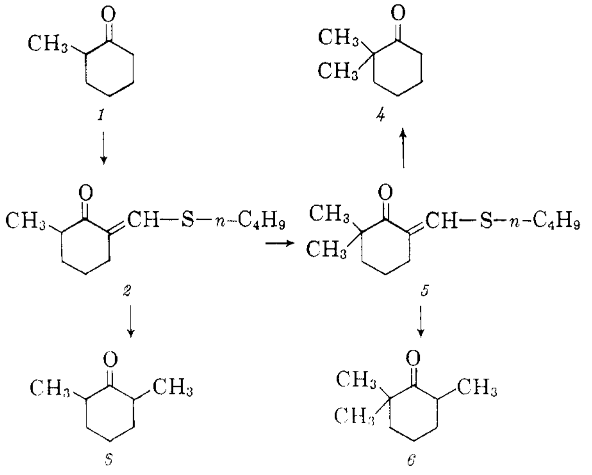


duction of an angular methyl group into *trans*-Δ^6-octalone-1 (I). The difficulty of this task is obvious when it is realized that direct methylation of such ketones as decalone-1 invariably introduces the methyl group at the more accessible C-2-methylene position rather than at the angular C-9 methine.[9] This problem has been faced and solved in the past by Robinson (*N*-methylanilinomethylene)[10] and Johnson (benzylidene[11] and isopropoxymethylene[12]) by using an unreactive grouping to render the C-2 methylene group inert during methylation at the C-9 position. More recently, other methods for blocking one side of a ketone have been employed by Woodward—*i.e.*, the dithioketal[13] and conjugation of the ketone with a quaternary carbon through a double bond.[14] To our knowledge neither method has been applied to the problem at hand, and the latter is obviously not applicable here. The dithioketal grouping has been found to render the ketone group very inert in other cases in these laboratories[15] (probably due to a steric effect) and was, therefore, not considered for this work.

The requirements that we set down for the blocking group that we were to use were somewhat different than those of previous workers. First, the grouping must be readily introduced and equally readily removed under mild conditions without ring cleavage. Second, the grouping must not deactivate the ketone either by a conjugative or steric effect. Third, we desired to develop a grouping that could not only serve to block the C-2 methylene position but also could be used further in the direct synthetic sequence, if possible. This last requirement meant that we needed a grouping that was relatively stable toward the conditions for work-up of the methylation reaction. These requirements limited our attention to derivatives of the 2-hydroxymethylene ketones, since the operations involved in introducing and removing these derivatives could be expected to be facile.[10,12] The use of such derivatives also offered the possibility for their reduction and rearrangement to α,β-unsaturated aldehydes—intermediates that have proved useful in our synthetic work[3-5]—by the procedure of Seifert and Schinz.[16]

In our hands, the amine derivatives of the 2-hydroxymethylene ketones[10] were unsatisfactory. In particular, the pyrrolidinomethylene ketones rendered the ketone inert toward methylation. The 2-alkoxymethylene ketones,[12] while not quite as inert toward methylation, were quite sensitive to moisture, and thus we were not able to isolate pure ketones after methylation reactions. As a result, we decided to investigate the 2-alkylthiomethylene ketones and were pleased to find that, in particular, the *n*-butylthiomethylene grouping came close to satisfying all our desires.

Employing the classic models for such work, we prepared the 2-*n*-butylthiomethylene derivatives of 2-methylcyclohexanone (*1*) (95%) and decalone-1 (84%) by acid-catalyzed azeotropic removal of water from a benzene solution of the corresponding hydroxymethylene derivative[12] and *n*-butyl mercaptan. *n*-Butyl mercaptan was chosen simply because it boils high enough not to be removed from the reaction mixture by distillation, yet low enough so that any excess mercaptan could be conveniently stripped from the product. The stability of these derivatives to storage over a period of several months proved to be an added dividend.



These 2-*n*-butylthiomethylene ketones were readily enolized by strong base. In fact, the best conditions for methylation allowed the ketone to be in contact with the base alone for only three to five minutes at room temperature. If methyl iodide was not then added or if the basic enolate solution was heated, the yields of methylated material dropped appreciably. By using these mild conditions we were able to methylate the cyclohexanone derivative (*2*) in 84% yield and the decalone derivative in 85% yield. In each case, the blocking group was sufficiently stable to the reaction conditions and work-up to permit easy isolation of the methylated, blocked ketones.

While the *n*-butylthiomethylene group was labile toward acidic conditions (all the blocked ketones gave slowly developing ferric chloride tests), we felt it would be advantageous if basic conditions could be found for removal of the

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(13) R. B. Woodward and A. A. Patchett, *J. Chem. Soc.*, 1131 (1957).

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blocking group. After some experimentation, it was found that aqueous sodium hydroxide in diethylene glycol would readily remove the blocking group, and that in the case of the model compounds, the free ketone could be isolated by steam distillation. Thus, the methylated cyclohexanone derivative (*5*) afforded 2,2-dimethylcyclohexanone (*4*) in 77% yield, and the corresponding decalone derivative gave a 60:40 mixture of *cis*- and *trans*-9-methyldecalone-1 in 78% yield.

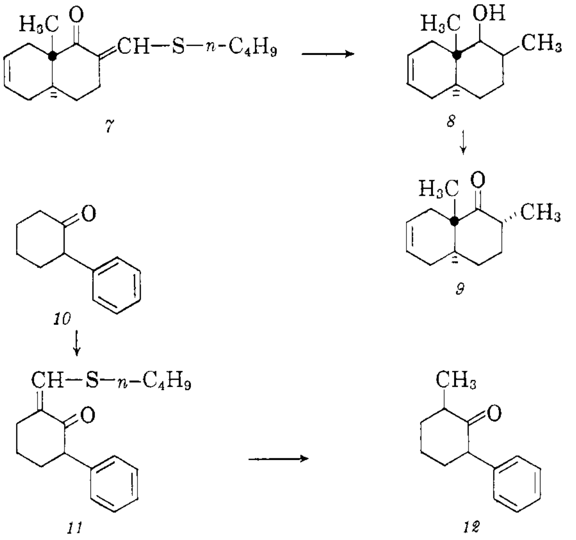
Thus the work with the model compounds suggested that our primary aims could be satisfied by the n-butylthiomethylene group, and we have applied the method to *trans*-Δ^6-octalone-1 (I). The results were equally satisfying, and we were able to realize a 63% over-all yield of a 1:3 mixture of *cis*- and *trans*-9-methyl-Δ^6-octalone-1.[3]

Turning our attention to the possible other uses of the n-butylthiomethylene group, we were able to demonstrate its ready conversion to an α,β-unsaturated aldehyde[3-5] by reduction and then acid-catalyzed rearrangement.[16,17] The synthetic utility of this and similar related transformations is amply confirmed by the syntheses accomplished using the alkoxymethylene group.[4,5,18]

By virtue of the presence of the sulfur atom, the n-butylthiomethylene group offered a unique opportunity to introduce a methyl group by desulfurization. It was felt that under the reductive conditions necessary to desulfurize the compound, any of the primarily formed methylene ketones would be reduced further to a methyl group. Thus this reaction would provide a method for introducing one, *and only one*, methyl group on the C-2 methylene position.

When 2,2-dimethyl-6-n-butylthiomethylenecyclohexanone (*5*) was stirred and heated with W-2 Raney nickel,[19] there resulted an 82% yield of 2,2,6-trimethylcyclohexanone (*6*). From a survey of available laboratory procedures[20] for the preparation of this ketone, this method would appear to be one of the most convenient. Similarly, the same Raney nickel treatment of the monomethyl derivative (*2*) led to a 62% yield of the equally difficult to prepare 2,6-dimethylcyclohexanone (*3*). It is of ancillary interest that through the agency of the n-butylthiomethylene group, convenient procedures have also been developed for the preparation of both of the dimethylcyclohexanones (*3*) and (*4*) and trimethylcyclohexanone (*6*) from 2-methylcyclohexanone (*1*).

On Raney nickel treatment, 2-n-butylthiomethylenedecalone-1 was converted to 2-methyldecalone-1 in 82% yield,[21] and 6-phenyl-2-n-butylthiomethylenecyclohexanone (*11*), prepared in 80% yield from 2-phenylcyclohexanone (*10*) by the standard method, was transformed into 6-phenyl-2-methylcyclohexanone (*12*) in 94% yield. In the latter case this high yield method could be quite useful, as direct methylation of 2-phenylcyclohexane will introduce the first methyl group at the highly active 2-position in preference to the C-6 methylene.



As might be expected when this desulfurization procedure was applied to 9-methyl-2-n-butylthiomethylene-*cis*-*trans*-Δ^6-octalone-1 (*7*),[3] the product was found to have suffered reduction of the 6,7-double bond as well as reductive desulfurization of the 2-n-butylthiomethylene. This difficulty was, however, overcome by reducing the thioenol ether with sodium in liquid ammonia, whereupon a 31–37% yield[27] of the Δ^6-octalol-1 (*8*) was realized. The octalol (*8*) was then oxidized to the corresponding dimethyloctalone (*9*) in 80% yield with Jones reagent.[22] While both the octalol (*8*) and the octalone (*9*) behaved as pure liquids, experience had shown[3] that the starting thioenol ether (*7*) was a 1:3 mixture of the *cis*- and *trans*-fused systems. The formation of a crystalline semicarbazone of the dimethyloctalone (*9*) in high yield but melting over a wide range (m.p. 188–198°) attested to the fact that this ketone, too, was a mixture of *cis* and *trans* isomers. Obviously, the reduction-oxidation sequence applied here was not as successful in removing the undesired *cis* isomer as was the reduction-rearrangement sequence leading to the α,β-unsaturated aldehyde.[3]

The chemical reduction of the n-butylthiomethylene group may prove to be a useful adjunct to the

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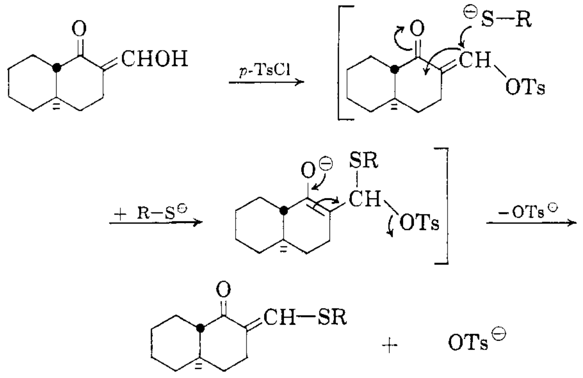
[22] K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946); see also C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

Raney nickel procedure in cases where catalytically reducible groupings are also present.

At this point one further problem presented itself in connection with another project where it was necessary to block the methylene adjacent to a ketone in an acid-labile molecule. Since the acidic conditions of the benzene azeotropic procedure were not applicable, a method was developed whereby the hydroxymethylene ketone was first tosylated in pyridine solution and then treated with the mercaptan in the same solution. This procedure relies on the mercaptan displacing the tosylate and probably involves first addition of mercaptide, followed by an irreversible elimination of more stable tosylate anion, as follows:



A similar phenomenon is probably involved when the alkylthiomethylene group is removed in aqueous potassium hydroxide solution. In this case, the mercaptide anion is the more stable of the two and is eliminated. The final basic cleavage of the resulting β-keto aldehyde, of course, renders this latter sequence irreversible.

When this basic pyridine procedure was applied to 2-hydroxymethylenedecalone-1 using benzyl mercaptan, the benzylthiomethylene derivative resulted in 60% yield. Similarly, it was possible to realize a 64% yield of 2-*n*-butylthiomethylene-*trans*-Δ^6-octalone[3] under these conditions and using *n*-butyl mercaptan. While the yields of the pyridine sequence are not as good as those observed by the benzene azeotropic procedure, they are still good, and the method serves a useful purpose when highly labile ketones must be blocked.

Experimental[23]

2-Alkylthiomethylene Ketones: (1) Benzene Azeotropic Procedure. (a) 2-*n*-Butylthiomethylene-6-methylcyclohexanone (*2*).—The hydroxymethylene derivative, b.p. 97–99° (23 mm.) was prepared from 76 g. (0.675 mole) of 2-methylcyclohexanone in 78% yield by the procedure of Johnson and Posvic.[12] A solution of this derivative (72.6 g., 0.52 mole) in 400 ml. of benzene containing 54.0 g. (0.6 mole) of *n*-butyl mercaptan in 100 mg. of *p*-toluenesulfonic acid was refluxed under a Dean-Stark water separator in a nitrogen atmosphere. After 5 hr., 9.5 ml. of water had collected, and the reaction mixture was cooled, washed with 50 ml. of 10% aqueous potassium bicarbonate, water, and dried (Na_2SO_4). After removal of the solvent at reduced pressure, distillation of the residue afforded 99 g. (95%) of yellow thioenol ether (*2*), b.p. 93–95° (0.05 mm.). The analytical sample, obtained by redistillation, boiled at 95° (0.05 mm.).

Anal. Calcd. for $C_{12}H_{20}OS$: C, 67.87; H, 9.49; S, 15.10. Found: C, 67.54; H, 9.61; S, 15.29. Ultraviolet $\lambda_{max}^{C_2H_5OH}$ 313 (18,000). Infrared: λ_{max}^{film} 6.01 μ and 6.46 μ (alkylthiomethylene ketone).

(b) 2-*n*-Butylthiomethylenedecalone-1.—In the same fashion 27 g. (0.15 mole) of 2-hydroxymethylenedecalone-1[12] was converted to its thioenol ether with 15.5 g. (0.17 mole) of *n*-butyl mercaptan. The product, obtained in 84% yield, boiled at 129° (0.05 mm.).

Anal. Calcd. for $C_{15}H_{24}OS$: C, 71.37; H, 9.58; S, 12.70. Found: C, 71.38; H, 9.56; S, 12.81.

(c) 2-*n*-Butylthiomethylene-6-phenylcyclohexanone (II).—In the same fashion, 87 g. (0.43 mole) of 2-hydroxymethylene-6-phenylcyclohexanone,[1] b.p. 108–111° (0.1 mm.) was converted to the thioenol ether (*11*) in 88% yield with 48.5 ml. (40.5 g., 0.45 mole) of *n*-butyl mercaptan. The analytical sample boiled at 166–168° (0.1 mm.) and melted at 78–79°.

Anal. Calcd. for $C_{17}H_{22}OS$: C, 74.40; H, 8.08; S, 11.69. Found: C, 74.39; H, 8.08; S, 11.72.

(2) Pyridine Method: (a) 2-Benzylthiomethylenedecalone-1.—To a solution of 5.6 g. (0.031 mole) of 2-hydroxymethylenedecalone-1[12] in 25 ml. of pyridine at 0° under nitrogen was added 6.5 g. (0.034 mole) of *p*-toluenesulfonyl chloride. The reaction mixture was stirred at 0° under nitrogen for 0.5 hr. and then 4.3 g. (4.0 ml., 0.034 mole) of benzyl mercaptan was added. The mixture was allowed to stand at 0° for 20 hr. and was then poured into 200 ml. of 1% aqueous sodium hydroxide solution. The mixture was extracted four times with 75-ml. portions of ether, and the combined ethereal extracts were washed with water, 25% aqueous potassium hydroxide solution, water, saturated salt solution, and dried (Na_2SO_4). After removal of the solvents at reduced pressure, the residue was crystallized from ethyl alcohol affording 5.3 g. (60%) of yellow needles, m.p. 76–78°. Several recrystallizations from the same solvent afforded the analytical sample which melted at 79–80°.

Anal. Calcd. for $C_{18}H_{22}OS$: C, 75.48; H, 7.74; S, 11.19. Found: C, 75.68; H, 7.96; S, 11.24.

(b) 2-*n*-Butylthiomethylene-*trans*-Δ^6-octalone-1.—In the same manner 3.55 g. (0.02 mole) of 2-hydroxymethylene-*trans*-Δ^6-octalone,[3] b.p. 58–59° (0.07 mm.), was converted to the thioenol ether,[3] m.p. 62–64°, in 64% yield with 3.8 g. (0.02 mole) of *p*-toluenesulfonyl chloride and 2.31 ml. (1.98 g., 0.022 mole) of *n*-butyl mercaptan.

Methylation of *n*-Butylthiomethylene Ketones: (a) 2,2-Dimethyl-6-*n*-butylthiomethylenecyclohexanone (*5*).—A solution of 16 g. (0.4 mole) of potassium metal was dissolved in 400 ml. of dry *t*-butyl alcohol. To this clear solution under a nitrogen atmosphere was added 25.2 g. (0.1 mole) of the thioenol ether (*2*), and the mixture was stirred for 3–5 min. at room temperature. The mixture was then chilled in an ice bath, and 40 ml. of methyl iodide was added all at once. After the initial reaction had subsided, the reaction mixture was refluxed for 2 hr.; most of the solvent removed at reduced pressure, and 150 ml. of water was added to the residue. The resulting mixture was extracted with ether, and the ethereal extract washed successively with water and saturated salt solution. After drying (Na_2SO_4), the ethereal solution was concentrated, and the resulting residue distilled. In this manner there was obtained 18.9 g. (84%) of the dimethylthioenol ether (*5*), b.p. 89–91° (0.07 mm.), as a mobile, light yellow liquid.

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[23] Melting points were taken on a Kofler hot stage and are corrected. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Infrared spectra were recorded on a Perkin-Elmer Infracord Model 137 and ultraviolet spectra were taken on a Cary recording spectrophotometer, Model 11.

The analytical sample, obtained by redistillation, boiled at 90° (0.07 mm.).

Anal. Calcd. for $C_{13}H_{22}OS$: C, 68.97; H, 9.80; S, 14.16. Found: C, 68.85; H, 9.82; S, 14.18.

(b) **9-Methyl-2-*n*-butylthiomethylenedecalone-1.**—In the same fashion 25.2 g. (0.1 mole) of 2-*n*-butylthiomethylenedecalone-1 was methylated in 85% yield with 16 g. (0.4 mole) of potassium and 40 ml. of methyl iodide in 400 ml. of dry *t*-butyl alcohol. The analytical sample boiled at 121° (0.07 mm.).

Anal. Calcd. for $C_{16}H_{26}OS$: C, 72.12; H, 9.84; S, 12.03. Found: C, 72.07; H, 9.83; S, 12.14.

Removal of the *n*-Butylthiomethylene Group: (a) 2,2-Dimethylcyclohexanone (*4*).—A mixture of 16.4 g. (0.0725 mole) of 2,2-dimethyl-6-*n*-butylthiomethylenecyclohexanone (*5*), 50 ml. of 25% aqueous potassium hydroxide, and 50 ml. of diethylene glycol was refluxed under nitrogen for 15 hr. The camphorous-smelling mixture was then steam distilled until 100 ml. of distillate had been collected. The distillate was saturated with salt and extracted with three 60-ml. portions of ether. The combined ethereal extracts were washed with two 10-ml. portions of 25% potassium hydroxide, two 50-ml. portions of saturated salt solution, and dried (Na_2SO_4). The ether was removed by distillation on a water bath at atmospheric pressure through a 50-cm. Vigreux column. Distillation of the residue afforded 7.0 g. (77%) of 2,2-dimethylcyclohexanone (*4*), b.p. 170–172° (750 mm.) [reported,[24] b.p. 170–171° (760 mm.)]. The ketone (*4*) formed a semicarbazone, m.p. 194–195°, in 92% yield (reported[24] 193°).

(b) **9-Methyldecalone-1.**—In the same manner 14.4 g. (0.054 mole) of 9-methyl-2-*n*-butylthiomethylenedecalone-1 was cleaved in 78% yield in 80 ml. of 12.5% aqueous diethyleneglycolic potassium hydroxide. This material, b.p. 124–127° (25 mm.),[12] was shown to be a mixture of two components in the ratio 60:40 by vapor phase chromatography on an Apiezon L-firebrick column at 195°.

Desulfurization of the *n*-Butylthiomethylene Group: (1) With Raney Nickel. (a) 2,2,6-Trimethylcyclohexanone (*6*).—To a suspension of 300 g. of W-2 Raney nickel catalyst[19] in 1 l. of ethanol was added 50 g. (0.22 mole) of the thioenol ether (*5*) in 50 ml. of ethanol. This rapidly stirred suspension was heated at 65° for 45 min., and then the catalyst was removed by filtration. The filtrate was combined with that from the reduction of another 50-g. batch of thioenol ether (*5*), and the ethanol removed by slow distillation through a 75-cm. Vigreux column. The residue was taken up in ether, washed with 50 ml. of water, 50 ml. of saturated salt solution, and dried (Na_2SO_4), and distilled. There was obtained 50.4 g. (82%) of 2,2,6-trimethylcyclohexanone b.p. 168–170° (735 mm.) [reported,[20] b.p. 178.7–179° (767 mm.)] (semicarbazone, m.p. 206–208° alone or on admixture with an authentic specimen prepared by the procedure of Sobotka and Chanley[20]).

(b) **2,6-Dimethylcyclohexanone** (*4*).—In a similar fashion, when 53.4 g. (0.251 mole) of 2-*n*-butylthiomethylene-6-methylcyclohexanone (*2*) was desulfurized with 320 g. W-2 Raney nickel catalyst[19] in 1000 ml. of ethanol, there was obtained 19.6 g. (62%) of 2,6-dimethylcyclohexanone (*3*), b.p. 172.5–173° (751 mm.) [reported,[25] b.p. 172–173°]. The semicarbazone, prepared in 89% yield, melted at 194–196° [reported,[26] m.p. 196°].

(c) **2-Methyldecalone-1.**—In the same manner, 2.5 g. (0.01 mole) of 2-*n*-butylthiomethylenedecalone-1 afforded 1.35 g. (82%) of 2-methyldecalone-1, b.p. 98° (8 mm.) [reported,[9] b.p. 111° (12 mm.)], with 30 g. of W-2 Raney nickel catalyst[19] in 40 ml. of ethanol. The oxime, prepared in 85% yield, melted at 151–152.5° [reported,[9] m.p. 148–149.5°].

(d) **2-Methyl-6-phenylcyclohexanone** (*12*).—In the same manner, 10 g. (0.0365 mole) of the thioenol ether (*11*) was desulfurized in 94% yield to the ketone (*12*), b.p. 92° (0.12 mm.); m.p. 51–52°, with 40 g. of W-2 Raney nickel catalyst[19] in 300 ml. of ethanol.

Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.90; H, 8.63.

(2) **By Lithium–Ammonia Reduction: 2,9-Dimethyl-trans-Δ^6-octalone-1** (*9*).—When a solution of 26.75 g. (0.105 mole) of 9-methyl-2-*n*-butylthiomethylene-*cis-trans*-Δ^6-octalone-1[8] in 150 ml. of dry ether was added to 1 l. of liquid ammonia, a yellow suspension resulted. Sodium (55 g.; 2.4 g.-atoms) and ethanol (450 ml.) were added intermittantly over a period of 4 hr., and then the ammonia and most of the ethanol removed in an air jet on the steam bath. The residue was treated with 200 ml. of water and steam distilled until 1.5 l. of distillate was collected. The distillate was saturated with salt and extracted with ether. The ethereal solution was washed with saturated salt solution, dried (Na_2SO_4), and distilled. There resulted 6.50 g. (34%)[27] of 2,9-dimethyl-*cis-trans*-Δ^6-octalol-1(8), b.p. 118–119° (6 mm.).

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 79.84; H, 11.09.

When 10.9 g. (0.0605 mole) of the alcohol (*8*) was oxidized with 16.5 ml. of Jones reagent[22] in 100 ml. of acetone, there was obtained 8.5 g. (80%) of the dimethyloctalone (*9*), b.p. 114–115° (10 mm.).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.17. Found: C, 80.79; H, 10.11.

The **semicarbazone,** prepared in 88% yield according to the procedure of Fieser, melted over the range 188–198°. The melting range of this material could not be diminished by further crystallization from methanol.

Anal. Calcd. for $C_{13}H_{21}O$: C, 66.35; H, 9.00; N, 17.86. Found: C, 66.25; H, 8.89; N, 17.89.

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[27] The yields of this reaction were consistently between 31–37%; the originally reported[1b] 64% yield was obtained only once and could not be repeated.