TABLE II

OXIDATIONS BY THE MODIFIED OPPENAUER METHOD

Compound Oxidized	Product	Yield, %
α-Dihydrocaranine	α-Dihydrocaranone	65[a]
Caranine	a Phenanthridinium betaine	86[b]
Dihydroundulatine	Epioxodihydroundulatine	75[c]
Montanine	Dehydrococcinine	60[d]
Coccinine	Dehydrococcinine	35[d]
Dihydrobuphanamine	Oxodihydrobuphanamine	58[e]
Dihydrohaemanthamine	Fluorenylideneoxodihydrohaemanthamine	...[f]
Yohimbine	Yohimbinone	51[g]
β-Yohimbine	Yohimbinone	17[g]
Corynanthine	Yohimbinone	18[g]
Deoxyajmaline	Deoxyajmalone	85[h]
Dihydroambelline	Recovered starting material	81[i]
Falcatine	Recovered starting material	...[j]
Dihydrocrinine	Oxodihydrocrinine	51[k]
Cholesterol	Δ⁴-3-Cholestenone	44[l]
Crinamine	Recovered starting material	45[i]

[a] E. W. Warnhoff and W. C. Wildman, *J. Am. Chem. Soc.*, **79**, 2192 (1957). [b] H. M. Fales, E. W. Warnhoff, and W. C. Wildman, *ibid.*, **77**, 5885 (1955). [c] E. W. Warnhoff and W. C. Wildman, *ibid.*, **82**, 1472 (1960). [d] Y. Inubushi, H. M. Fales, E. W. Warnhoff, and W. C. Wildman, *J. Org. Chem.*, **25**, 2153 (1960). [e] H. M. Fales and W. C. Wildman, *ibid.*, **26**, 881 (1961). [f] H. M. Fales, personal communication. [g] M.-M. Janot, R. Goutarel, E. W. Warnhoff, and A. LeHir, *Bull. soc. chim. France*, 637 (1961). [h] M. F. Bartlett, R. Sklar, W. I. Taylor, E. Schlittler, R. L. S. Amai, P. Beak, N. V. Bringi, and E. Wenkert, *J. Am. Chem. Soc.*, **84**, 622 (1962). [i] E. W. Warnhoff, unpublished work. [j] W. C. Wildman, personal communication. [k] W. C. Wildman, *J. Am. Chem. Soc.*, **80**, 2567 (1958). [l] Present work.

close to the hydroxyl bearing carbon for hydride transfer, makes the reaction subject to stringent steric requirements, and there are several examples of amino alcohols not oxidized under these conditions (Table II, dihydroambelline, crinamine, and falcatine). In some of these cases (crinamine[8] and dihydroambelline[9]) the chromic acid–pyridine reagent has proved a successful alternative.

The potassium *t*-butoxide need not be freshly prepared as long as it has been protected from moisture and carbon dioxide. Commercially available alkoxide[10] should meet these requirements. The use of sublimed potassium *t*-butoxide is indicated whenever the alcohol to be oxidized contains a group which might react with the hydroxide or carbonate invariably present in unsublimed material (yohimbine, β-yohimbine, corynanthine, Table II).

The method is most readily applied to amino alcohols which can be separated by acid extraction from the fluorenone–fluorenol mixture. However, nonbasic alcohols, *e.g.*, cholesterol, can be oxidized and purified by chromatography, distillation, or sublimation. During the reaction even at room temperature some fluorenone is cleaved by base to 2-biphenylcarboxylic acid and this must be taken into account in isolation of acidic oxidation products.

Experimental

Reagents.—*t*-Butyl alcohol was distilled from sodium. Commercial fluorenone, benzophenone, and quinine were used without purification. Reagent grade benzene was dried over sodium.

Typical Oxidation Procedure.—Potassium metal (0.5 g., 0.012 g.-atom) was dissolved in 30 ml. of *t*-butyl alcohol. The excess alcohol was removed by distillation at atmospheric pressure and then at aspirator vacuum. The solid potassium *t*-butoxide was dried at 120–130° at aspirator vacuum for 15–30 min.

To the dry *t*-butoxide was added 1.62 g. (5.0 mmoles) of dry quinine, 40 ml. of dry benzene (tetrahydrofuran or dimethyl sulfoxide), 4.50 g. (25 mmoles) of dry fluorenone, and a magnetic stirring bar. The reaction mixture was immediately put under a nitrogen atmosphere and stirred (with or without heating) for the period specified in Table I. The reaction mixture turned an opaque brown on mixing. The oxidation was terminated by the addition of 30–50 ml. of water, whereupon the color lightened to an orange-yellow.

The reaction mixture was diluted with 30–50 ml. of ether, and the two phases were separated. The aqueous layer was washed with two portions of ether. The combined organic layers were extracted with four portions of 5% hydrochloric acid. The combined aqueous acid solutions were washed twice with ether and poured into a mixture of ice and concentrated ammonium hydroxide solution. The white precipitate was extracted with three portions of ether. The ether extract was washed three times with saturated sodium chloride when the last wash was neutral. The dried (magnesium sulfate) ether solution was evaporated at reduced pressure. The yield of product varied from 70–97%.

The per cent of quininone in the product was determined from the ultraviolet extinction coefficient in absolute ethanol at 360 mμ. At this wave length pure quinine had no absorption while quininone had ε 3760. This analytical procedure was shown to be accurate to ±1% by measurements on known mixtures of quinine and quininone.

In the case of the reactions run in *t*-butyl alcohol, most of the alcohol was evaporated at reduced pressure before addition of water and ether and work-up.

The product from reaction 4, Table I, was chromatographed on 30 g. of alumina. Benzene–hexane (1:1) and pure benzene eluted **quininone**, m.p. 99–104° (hot stage), after recrystallization from cyclohexane.

When a reaction was carried out for 1 hr. at room temperature exactly as described above except that the quinine was omitted, there was recovered from the basic aqueous layer after acidification 0.59 g. of **2-biphenylcarboxylic** acid whose infrared spectrum in chloroform was identical with that of an authentic sample.

Oxidation of Cholesterol.—A mixture of the potassium *t*-butoxide prepared from 0.5 g. of potassium, 4.50 g. of dry fluorenone, 2.02 g. of dry cholesterol, and 40 ml. of dry benzene was put under nitrogen and stirred with a magnetic stirring bar for 1 hr. at room temperature. The reaction mixture was diluted with water and ether. The ether layer was separated, dried, and evaporated to leave 6.35 g. of yellow oil. Crystallization from cyclohexane removed 2.99 g. of fluorenone in three crops. The filtrate was then chromatographed on 100 g. of alumina. Pure benzene eluted **Δ⁴-3-cholestenone** which was recrystallized from cyclohexane to give 0.90 g. (44%), m.p. 80–82° undepressed on admixture with an authentic specimen.

(8) H. M. Fales and W. C. Wildman, *J. Am. Chem. Soc.*, **82**, 197 (1960)
(9) P. Naegeli, E. W. Warnhoff, H. M. Fales, R. E. Lyle, and W. C. Wildman, *J. Org. Chem.*, **28**, 206 (1963).
(10) MSA Research Corporation, Callery, Pa.

Cleavage–Elimination of Diphenylmethane from 7,7-Diphenylbicyclo[3.2.0]hept-2-en-6-one in Base[1]

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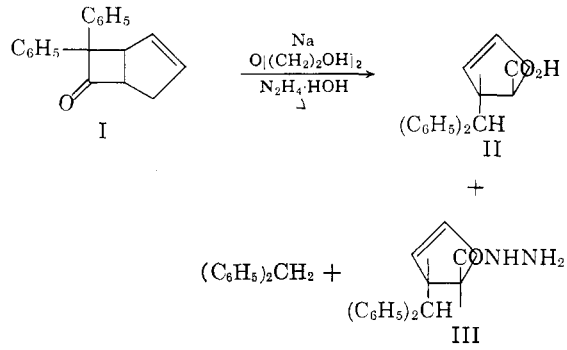
During an investigation into the synthesis and chemistry of certain strained bicyclic and polycyclic systems, we had occasion to study various methods of removing the carbonyl group from the product of the cycloaddi-

(1) From the M. S. thesis of A. C. Kovelesky, Kansas State University, 1962.

tion of diphenylketene and cyclopentadiene.[2,3] The structure of this product has been established as 7,7-diphenylbicyclo[3.2.0]hept-2-en-6-one (I) by two independent degradative sequences.[3,4]

When the ketone I was subjected to the Huang-Minlon modification[5] of the Wolff–Kishner reduction, three compounds were isolated, a hydrocarbon along with a mixture of *trans*-3-benzhydrylcyclopentene-4-carboxylic acid (II) and a small amount of the hydrazide of II (III). The initial basic cleavage of the cyclobutanone portion of the bicyclic ketone undoubtedly results in the formation of the *cis* acid which under the conditions of the reaction is isomerized to the thermodynamically more stable *trans* acid II. II is the only acid isolated.



Identification of the hydrazide III was accomplished by elemental analysis, infrared and proton magnetic resonance[6] spectra. In the latter spectrum, the compound showed three exchangeable hydrogens when equilibrated with deuterium oxide at room temperature. III was also synthesized from the acid chloride of II or by refluxing the bicyclic ketone I with excess hydrazine hydrate, thereby establishing its stereochemistry and origin.

The hydrocarbon formed in 30–35% yield was found to be diphenylmethane by its boiling point, and infrared and proton magnetic resonance[6] spectra. The formation of diphenylmethane must result from a cleavage process, and it appeared reasonable that this might arise from a conjugate elimination[7] involving the *trans* acid II, or its carboxylate anion.

To test this proposal, *trans*-3-benzhydrylcyclopentene-4-carboxylic acid (II) was treated with alkali under conditions comparable to those employed in the modified Wolff–Kishner reduction. As the amount of diphenylmethane isolated in these experiments was small (See Table I in Experimental), it appears that a conjugate elimination from II or its anion is unlikely. Our efforts to prepare the pure *cis* isomer of acid II have been unsuccessful.[8,9] It would have been of interest to examine the *cis* acid, *cis*-3-benzhydrylcyclopentene-4-carboxylic acid, to determine whether it might be the precursor to the diphenylmethane.[10]

Experimental[11]

7,7-Diphenylbicyclo[3.2.0]hept-2-en-6-one (I).—This ketone was prepared according to the method of Smith and co-workers[3] by the cycloaddition of diphenylketene and cyclopentadiene, m.p. 86–88°, yield 75–88% (reported[3] m.p. 88–89°).

Attempted Modified Wolff–Kishner Reduction of 7,7-Diphenylbicyclo[3.2.0]hept-2-en-6-one.—To a solution of 4.9 g. (0.21 mole) of sodium in 200 ml. of diethylene glycol was added 18.3 g. (0.070 mole) of bicyclic ketone and 21 ml. of hydrazine hydrate. The mixture was refluxed for 10 hr. After cooling to room temperature, the reaction mixture was diluted with water, extracted with ether, and the combined extracts dried over sodium sulfate. Evaporation of the solvent and fractional crystallization of the residue from petroleum ether (b.p. 60–70°) gave 3.5 g. (30%) of diphenylmethane and 0.4 g. (2%) of *trans*-3-benzhydrylcyclopentene-4-carboxylic acid hydrazide. The diphenylmethane was identified by its infrared and n.m.r. spectra, and its b.p. of 131–135° (15 mm.) [reported[12] b.p. 141° (27 mm.)].

The *trans*-3-benzhydrylcyclopentene-4-carboxylic acid hydrazide was recrystallized from aqueous ethanol and sublimed at 130° (0.1 mm.), m.p. 159–160°. The n.m.r. spectrum indicated twenty protons with three labile ones as determined by equilibration at room temperature with deuterium oxide. The infrared spectrum had bands at 2.88, 3.0, and 6.1 μ attributable to the acylhydrazide structure IV.

Anal. Calcd. for $C_{19}H_{20}N_2O$: C, 78.08; H, 6.85; N, 9.59. Found: C, 78.31; H, 7.19; N, 9.70.

The basic aqueous layer remaining after ether extraction was acidified with dilute hydrochloric acid and extracted with ether. The ether extracts were dried over sodium sulfate and the solvent evaporated to yield 12.0 g. (61%) of a colorless solid, m.p. 145–149°, whose infrared spectrum identified it as *trans*-3-benzhydrylcyclopentene-4-carboxylic acid. The *trans* acid could be purified by fractional crystallization from petroleum ether, followed by recrystallization from aqueous methanol, m.p. 148–149° (reported[13] m.p. 148–149°).

***trans*-3-Benzhydrylcyclopentene-4-carboxylic Acid Hydrazide (IV).** A.—A solution of 3.6 g. (0.014 mole) of 7,7-diphenylbicyclo[3.2.0]hept-2-en-6-one in 25 ml. of 85% hydrazine hydrate was heated under reflux for 18 hr. After cooling to room temperature the solution was poured into water and extracted with ether. The combined ether extracts were washed with water and dried over magnesium sulfate. Evaporation of the solvent gave 3.4 g. (86%) of the hydrazide. After recrystallization from aqueous ethanol and sublimation of 130° (0.05 mm.), the colorless solid melted at 157–159°. The infrared spectra of this and the material isolated from the Wolff–Kishner reduction was identical and mixture melting point showed no depression.

B. ***trans*-3-Benzhydrylcyclopentene-4-carboxylic acid**, 2.3 g. (0.008 mole), and thionyl chloride, 1.5 g. (0.012 mole), were allowed to stand at room temperature for 3 hr. and heated on a steam bath for 1 hr. Excess thionyl chloride was removed under reduced pressure and the residual acid chloride solidified.

This was dissolved in 50 ml. of chloroform which was slowly added to 8.3 g. (0.017 mole) of hydrazine hydrate cooled in an

(2) H. Staudinger, *Ann.*, **356**, 94 (1907); H. Staudinger and E. Suter, *Ber.*, **53B**, 1092 (1920).

(3) L. I. Smith, C. L. Agre, R. M. Leekley, and W. W. Prichard, *J. Am. Chem. Soc.*, **61**, 7 (1939).

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(5) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(6) The authors wish to express their appreciation to Dr. Donald P. Hollis, Varian Associates, for determination of the p.m.r. spectrum on the A-60 spectrometer.

(7) G. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955), have discussed a number of conjugate or 1,4-eliminations. Further examples of such eliminations are given by S. Searles, Jr., R. G. Nickerson, and W. K. Witsiepe, *J. Org. Chem.*, **24**, 1839 (1959), and examples cited therein.

(8) We wish to express our appreciation to Mr. Jerry Reed, a participant in a National Science Foundation Undergraduate Participation Program, for further efforts to obtain the *cis* acid II.

(9) We have not been able to duplicate the reported[3] hydroxide cleavage of 7,7-diphenylbicyclo[3.2.0]hept-2-en-6-one (I) in refluxing methanol to yield a mixture of acids II and III. Varying reaction times and amounts of reactants lead in almost every case to the isolation of only the *trans* acid III.

(10) The other possible conjugate elimination products, carbon dioxide and cyclopentadiene, have not been observed, probably due to the basic reaction medium. Efforts were made to find cyclopentadiene after acidification of the diluted reaction mixture but were without success.

(11) All melting points were taken on a Kofler hot stage. Boiling points are uncorrected. Infrared absorption spectra were determined on a Perkin-Elmer Model 137 double beam recording spectrophotometer.

(12) A. Klages and P. Allendorff, *Ber.*, **31**, 999 (1898).

(13) E. H. Farmer and M. O. Farooq, *J. Chem. Soc.*, 1925 (1938).

ice bath. After warming to room temperature, the two layers were separated, the aqueous layer extracted with chloroform, and the combined extracts dried over sodium sulfate. Evaporation of the chloroform yielded 2.1 g. (87%) of the hydrazide which after recrystallization from dilute ethanol and sublimation at 130° (0.1 mm.) gave colorless product, m.p. 157–159°.

trans-**3-Benzhydrylcyclopentene-4-carboxylic Acid (III).**—This acid was prepared by the hydrolytic fission of 7,7-diphenylbicyclo-[3.2.0]hept-2-en-6-one.[13] In the majority of experiments the melting points of the product indicated that almost pure *trans* acid was isolated rather than the mixture as reported by Farmer and Farooq.[13] Reducing the amount of base and reaction time did not alter the product melting point significantly. The pure *trans* acid was obtained by recrystallization once from petroleum ether then from methanol, m.p. 148–149°.

Elimination Studies of *trans*-3-Benzhydrylcyclopentene-4-carboxylic Acid.—The general procedure is exemplified by the following experiment. To a solution of 2.72 g. (0.0413 mole) of potassium hydroxide pellets in 50 ml. of diethylene glycol was added 4.5 g. (0.0162 mole) of *trans*-3-benzhydrylcyclopentene-4-carboxylic acid and the mixture heated at 180° for 2 days. After cooling and diluting with water the mixture was extracted with ether and the extracts dried over magnesium sulfate. Evaporation yielded the diphenylmethane.

The basic solution remaining after ether extraction was acidified with dilute hydrochloric acid, extracted with ether, and the combined extracts dried. Removal of the solvent yielded the residual starting *trans* acid.

The results of the elimination studies are given in Table I.

TABLE I

ELIMINATION STUDIES WITH *trans*-3-BENZHYDRYLCYCLOPENTENE-4-CARBOXYLATE SALTS

Weight of acid, g.	Solvent	Reaction time, hr.	Temp.	Ph_2CH_2, g. (yield)	Acid recovery, g.
4.5[a]	Ethylene glycol	48	180°	0.1 (4%)	4.2
4.2[a]	Diethylene glycol	29	200–250°	.1 (4%)	4.1
2.2[a]	Diethylene glycol	8	250°	.05 (4%)	2.0
5.4[a]	Diethylene glycol	8	280–300°	.2 (6%)	5.2
4.7[b]	Diethylene glycol	9.5	200–250°	.2 (7%)	4.3

[a] Reaction mixture contains an excess of potassium hydroxide (see Experimental). [b] Preprepared sodium salt.

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Reaction of 1-Alkynes with Organometallic Compounds. XI. The Reactivity of Dialkylmagnesiums toward 1-Hexyne

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It was reported in the first paper[3] of this series that the relative reactivities toward 1-hexyne of diethyl ether solutions of alkylmagnesium halides (as determined from reaction half-lives) were in the order isopropyl > ethyl > *n*-propyl > methyl. This order was correlated with the number of β-hydrogens on the alkyl group, and it was suggested that this might be evidence for anionic hyperconjugation.[3,4]

The purpose of the present paper is to report results which show that the reactivities of diethyl ether solutions of some dialkylmagnesiums follow the same order as that observed for the Grignard reagents, and, therefore, the same correlation with the number of β-hydrogens applies. These dialkylmagnesium reactivities are in terms of rate constants corresponding to a two-step, competitive, consecutive, second-order mechanism. The agreement between this mechanism and the experimental data does not rule out the possibility that the mechanism is actually more complicated (for example, that dimers of the dialkylmagnesium may be present).

Kinetic Theory.—One would expect that the reaction of a dialkylmagnesium with 1-hexyne would involve at least two competitive, consecutive steps, and, if the dialkylmagnesium is dimerized in ether a four-step reaction would be involved. The nonlinear differential equations for any number of competitive, consecutive, second-order steps can be made linear and solved in terms of a time variable θ used by French.[5] For the reaction here under consideration, θ can be defined by

$$\theta = \int_0^t (b - P)dt \qquad (1)$$

where b is the initial concentration of 1-hexyne, and P is the moles of hydrocarbon gas produced per liter of solution. θ can be calculated easily by graphical integration of the experimental curve for P *vs.* t. For a single reaction of any number of competitive, consecutive, second-order steps the integrated rate law takes the form

$$P/a = f(\theta) \qquad (2)$$

where, for the case here under consideration, a is the initial concentration of alkyl groups (*i.e.*, twice the initial molarity of R_2Mg). According to equation 2, P/a does not depend upon a or b explicitly. For the two-step reaction with rate constants k_1 and k_2, equation 2 is

$$\frac{P}{a} = \frac{1}{2(k_1 - k_2)}[(2k_2 - k_1)e^{-k_1\theta} - k_1e^{-k_2\theta}] + 1 \qquad (3)$$

Becker, *et al.*,[6] concluded, from vapor pressure data and from the kinetics of the reaction with benzonitrile, that diethylmagnesium dimerizes in tetrahydrofuran. If there are present in ethyl ether both monomers, R_2Mg, and dimers, $R_2Mg \cdot R_2Mg$, then the reaction with 1-hexyne would no longer be a single reaction. Equation 2, in general, would not hold, and P/a could depend explicitly upon both a and b.

Results

The experimental results for the reactions of three dialkylmagnesiums with 1-hexyne in ethyl ether are shown as plots of P/a *vs.* θ in Fig. 1 and 2. The values of a and b are given in Table I. Theoretical

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(2) To whom inquiries should be sent.
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