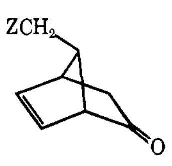
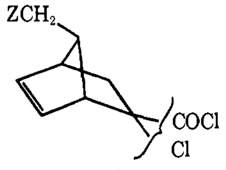
tion at 2250 cm^{-1} (*ca.* 30 min). Evaporation of solvent under reduced pressure (25°), addition of water, extraction with pentane, and removal of pentane afforded the bicyclic ketone Ia, 20.53 g (90.6%) of 97–98% purity by gas chromatographic (gc) analysis. The identity of this product with Ia prepared by the previously described route was established by spectroscopic, chromatographic, and chemical comparison.[15]



Ia, Z = $C_6H_5CH_2O$
Ib, Z = CH_3O
Ic, Z = C_6H_5CONH

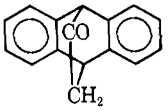


IIa, Z = $C_6H_5CH_2O$
IIb, Z = CH_3O
IIc, Z = C_6H_5CONH

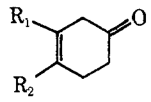
In a similar manner the Diels–Alder adduct IIb was prepared *via* 5-methoxymethylcyclopentadiene[6] and 2-chloroacrylyl chloride and transformed into the pure bicyclic ketone Ib[5–7] (yield 82%, based on chloromethyl methyl ether and thallous cyclopentadienide). The benzoylamino ketone Ic,[14] mp 125.5–126°, was also formed in good yield by the above described process from the adduct IIc, which in turn was obtained by alkylation of thallous cyclopentadienide by iodomethylbenzamide (in tetrahydrofuran) followed by addition to 2-chloroacrylyl chloride.

Cyclopentadiene and 2-chloroacrylyl chloride in ether (*ca.* 1.2 *M*) at 0° for 18 hr gave the expected mixture of exo and endo Diels–Alder adducts in 94% yield, and this mixture was converted *via* the Curtius route to 5-norbornen-2-one[14a] in 94% yield (gc analysis).

Anthracene and 2-chloroacrylyl chloride in dimethoxyethane solution (1 *M*) at reflux for 5 hr afforded the Diels–Alder adduct quantitatively, and this was transformed by the Curtius route to the ketone III, mp 146–147°,[14] in 87% overall yield from anthracene.



III



IV, $R_1 = H$; $R_2 = CH_3$
V, $R_1 = R_2 = CH_3$

The known ketone IV[14a] was obtained by the new method from isoprene in 83.5% overall yield, and the ketone V[14a] was prepared from 2,3-dimethylbutadiene (77%).[16]

The method described herein for the 1,4 addition of the $-CH_2CO-$ unit to 1,3-dienes is operationally simple, broadly applicable, and basically efficient. Many interesting uses can be foreseen for the synthesis of cyclic ketones.

Acknowledgment. We are grateful to the National Institutes of Health, the Agency for International Development, and the National Science Foundation for financial assistance.

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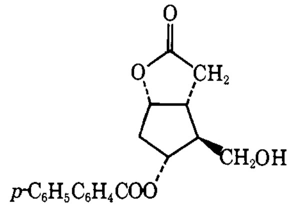
[15] Using this procedure in the route previously described [E. J. Corey, S. M. Albonico, U. Koelliker, T. K. Schaaf, and R. K. Varma, *J. Amer. Chem. Soc.*, **93**, 1491 (1971)], the key prostanoid intermediate i is obtained in a stereospecific process having an average yield per step of 95% and not involving chromatography.



i

[16] The Diels–Alder reactions with isoprene and 2,3-dimethylbutadiene were conducted at 0° for 16 hr. In the preparation of the ketones IV and V, the thermal rearrangement of the acyl azide was carried out in benzene at reflux for 1.5 hr. The hydrolysis of isocyanate was accomplished using a 1:1 mixture of tetrahydrofuran and 5% aqueous oxalic acid at 25° for 10 hr; under these conditions the β,γ-unsaturated ketones IV and V were obtained with little or no α,β isomer. The more stable conjugated isomers can be prepared by isomerization with 1 *N* hydrochloric acid at 25° for 15 hr.

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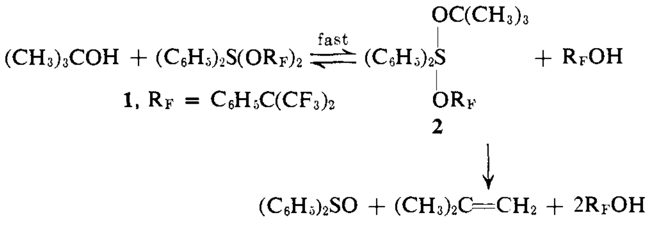
Sulfuranes. III. A Reagent for the Dehydration of Alcohols

Sir:

The use of stable, crystalline sulfurane **1** as a dehydrating agent for the conversion of alcohols to alkenes was suggested by our preliminary observation[1] that the alkoxy ligands of **1** rapidly exchange with added alcohols, and by the earlier observation[2] of isobutylene in the product mixture from a perester decomposition postulated to give a sulfurane as an intermediate. We here report results which suggest that **1** is indeed a dehydrating agent with unique properties, potentially of great synthetic utility.



$$(CH_3)_3COH + \underset{\mathbf{1},\ R_F\,=\,C_6H_5C(CF_3)_2}{(C_6H_5)_2S(OR_F)_2} \xrightleftharpoons{\text{fast}} \underset{\mathbf{2}}{(C_6H_5)_2\overset{OC(CH_3)_3}{\underset{OR_F}{S}}} + R_FOH$$

$$\downarrow$$

$$(C_6H_5)_2SO + (CH_3)_2C{=}CH_2 + 2R_FOH$$

The dehydration of *tert*-butyl alcohol by sulfurane **1** in chloroform at −50° is complete within seconds to yield isobutylene. We suggest that the ionization of sulfurane **2** to give the *tert*-butoxysulfonium ion (perhaps catalyzed by a molecule of the acidic R_FOH) is followed by rapid abstraction of a β proton. Secondary alcohols, which dehydrate more slowly, give nmr evidence for the postulated rapidly equilibrating mixtures of sulfuranes at −50°.

Earlier attempts to dehydrate tricyclopropylcarbinol (**3**) using sulfuric acid or phosphorus pentoxide failed to yield any of olefin **4**.[3] Dehydration with sulfurane **1**, however, gives 32% (by nmr, 25% by isolation) of **4** in a striking demonstration of the synthetic utility of this new dehydrating agent. The method used for isolation of **4** is of rather general applicability. The acidic R_FOH is removed by washing with 10% aqueous sodium hy-

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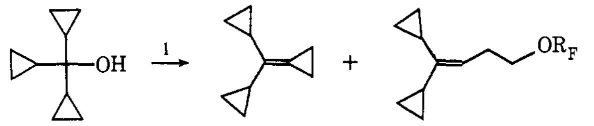
[1] For earlier papers in this series, see J. C. Martin and R. J. Arhart, *J. Amer. Chem. Soc.*, **93**, 2339, 2341 (1971).

[2] W. G. Bentrude and J. C. Martin, *ibid.*, **84**, 1561 (1962); D. L. Tuleen, W. G. Bentrude, and J. C. Martin, *ibid.*, **85**, 1938 (1963); see also C. Walling and M. J. Mintz, *J. Org. Chem.*, **32**, 1286 (1967).

[3] H. Hart and P. A. Law, *J. Amer. Chem. Soc.*, **84**, 2462 (1962).

droxide. Solvent chloroform is removed by distillation; then **4** is removed from the less volatile diphenyl sulfoxide and **5** by flash distillation at 10^{-2} mm, pot temperature 60°. Variations of this procedure using recrystallization or column chromatography to separate nonvolatile olefins from the polar sulfoxide, or using glpc to separate volatile olefins, are also useful.



3 **4** (32%) **5** (68%)

The product yields in Table I were determined by nmr using the aromatic proton peak integrals (from a known amount of **1** added to a known amount of alcohol) as an internal standard. All nmr peaks outside the aromatic proton region were identified using 220-MHz nmr and authentic samples of products. In every case the total yields of identified products, determined by careful integrations of completely resolved product peaks, were within ±5 mol % of the amount of alcohol added. The yields quoted assume 100% of identified products. New compounds were identified by nmr (using homonuclear and heteronuclear spin decoupling where appropriate) and glpc–mass spectrometry.

Table I. Reactions of Alcohols with **1** in Chloroform-*d* at Room Temperature

Alcohol	Products	% yield[c]
tert-Butyl alcohol[a]	Isobutylene	100
tert-Amyl alcohol	2-Methyl-2-butene	41
	2-Methyl-1-butene	59
1-Methylcyclohexanol	1-Methylcyclohexene	90
	Methylenecyclohexane	10
Tricyclopropylcarbinol	**4**	32
	5	68
2-Cyclopropyl-2-propanol	2-Cyclopropylpropene	100
2-Butanol	*cis*- and *trans*-2-butene	44
	1-Butene	56
Cyclohexanol	Cyclohexene	100
cis(27%)- and *trans*(73%)-4-*tert*-butylcyclohexanol	4-*tert*-Butylcyclohexene	100
cis-2-Methylcyclohexanol	1-Methylcyclohexene	75
	3-Methylcyclohexene	25
trans-2-Methylcyclohexanol	3-Methylcyclohexene	100
Methanol[a]	CH_3OR_F	100
Ethanol	$CH_3CH_2OR_F$	100
Isobutyl alcohol	$(CH_3)_2CHCH_2OR_F$	100
Neopentyl alcohol[b]	$(CH_3)_3CCH_2OR_F$	67
	2-Methyl-2-butene	9
	2-Methyl-1-butene	24
3-Hydroxypropionitrile	Acrylonitrile	100
Isoborneol	Camphene	59
	Tricyclene	41
exo-2-Norborneol	Nortricyclene	100

[a] At −50°. [b] Neat at 90°. [c] Product yields based on nmr (see text). Ratios of products are accurate to ±3%; total yields of products (unisolated) to ±5%.

Tertiary alcohols (Table I) form dehydration products instantaneously when treated with **1** in chloroform-*d* at room temperature. Most secondary alcohols also undergo quantitative and rapid dehydration when treated with **1** at room temperature. For example, *cis*- and *trans*-4-*tert*-butylcyclohexanols are converted to 4-*tert*-butylcyclohexene, with the cis isomer reacting with **1** at least 150 times more rapidly than the trans. This evidence for a preferred trans diaxial disposition of leaving groups is reinforced by results of competitive dehydrations of mixtures of the *cis*- and *trans*-2-methylcyclohexanols. The cis isomer, with its favored axial-hydroxyl conformation, is completely destroyed by **1** before loss of the more slowly reacting trans isomer can be detected. The only products are those expected for a trans diaxial elimination.[4]

Methyl alcohol reacts rapidly and quantitatively with **1** at −50° to give R_FOCH_3. Ethanol and isobutyl alcohol also give only the corresponding unsymmetrical ethers,[5] no olefins. The rate of ether formation in the case of isobutyl alcohol is noticeably slower than that for methanol, and neopentyl alcohol shows a drastically retarded rate (>5 hr at 90°). The order of reactivity is that expected[7] for an S_N2 displacement on the alkoxysulfonium ion.[8] In addition to the unsymmetrical neopentyl ether typical carbonium ion products, 2-methyl-2-butene (9%) and 2-methyl-1-butene (24%), are formed.

If the β proton of a primary alcohol is sufficiently acidic, elimination will occur in preference to etherification, as in the case of 3-hydroxypropionitrile.

The carbonium ion character in the dehydration of secondary and tertiary alcohols with sulfurane is illustrated by the formation of rearrangement products camphene (59%) and tricyclene (41%) upon dehydration of isoborneol. The complete absence of the unrearranged bornylene in the product mixture again points up the strong preference for trans coplanar geometry in the transition state for this elimination reaction. The treatment of *exo*-2-norborneol with **1** gives only nortricyclene, in a reaction of some synthetic utility. This also suggests the intermediacy of carbonium ions.[10]

The dehydration of 2-methyl-2-propanol-*1,1,1,3,3,3*-d_6 with **1** at 25° shows an intramolecular kinetic isotope effect (k_H/k_D = 1.54) which is similar to that seen[11] indirectly for other E1 eliminations.

Dehydrations of secondary and tertiary carbinols with sulfurane **1** proceed under unusually mild conditions, tertiary alcohols by a mechanism near the E1 end of the spectrum, and secondary alcohols by a mechanism with considerable E2 character as evidenced by the strong preference for trans coplanar geometry in olefin

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(4) For related observations of dehydration reactions in this series see G. Vavon and M. Barbier, *Bull. Soc. Chim. Fr.*, **49**, 567 (1931); H. J. Schaeffer and C. J. Collins, *J. Amer. Chem. Soc.*, **78**, 124 (1956); H. L. Goering, R. Reeves, and H. H. Espy, *ibid.*, **78**, 4926 (1956); H. Pines and C. N. Pillai, *ibid.*, **83**, 3270 (1961); K. Kochloefl, M. Kraus, C. Chin-Shen, L. Beránek, and V. Bažant, *Collect. Czech. Chem. Commun.*, **27**, 1199 (1962); and E. J. Blanc and H. Pines, *J. Org. Chem.*, **33**, 2035 (1968).

(5) The formation of ethers from primary alcohols is formally, and perhaps mechanistically, analogous to the formation of 1-dimethylaminoalkanes from the reaction of primary alcohols with hexamethylphosphorictriamide,[6] a reaction which possibly involves a phosphorane intermediate.

(6) R. S. Monson, *Tetrahedron Lett.*, 567 (1971).

(7) F. C. Whitmore and G. H. Fleming, *J. Amer. Chem. Soc.*, **55**, 4161 (1933); I. Dostrovsky and E. D. Hughes, *J. Chem. Soc.*, 157 (1946).

(8) An alternative formulation as an electrocyclic reaction, which is suggested by the unexpectedly[9] large amount of unsymmetrical ether formed from neopentyl alcohol, is made less likely by the product diversion from unsymmetrical ether to diethyl ether upon addition of potassium ethoxide to a reacting mixture of **1** and ethanol.

(9) W. Kirmse and K. Horn, *Tetrahedron Lett.*, 1827 (1967).

(10) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Amer. Chem. Soc.*, **87**, 376 (1965); H. C. Brown and K. T. Liu, *ibid.*, **92**, 200 (1970); H. Kwart, T. Takeshita, and J. L. Nyce, *ibid.*, **86**, 2606 (1964).

(11) V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953); G. J. Frisone and E. R. Thornton, *ibid.*, **90**, 1211 (1968).

formation. Primary alcohols form unsymmetrical ethers in the absence of structural features increasing the acidity of β protons.

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The Reaction of Representative Organic Azides with Triethylborane. A New Route to Secondary Amines

Sir:

A wide variety of organic azides react readily with triethylborane in refluxing xylene. Nitrogen is evolved and an intermediate is produced which undergoes facile methanolysis or hydrolysis to the corresponding secondary amine (eq 1). This reaction opens up a new route to secondary amines.

$$\begin{array}{l} RN_3 + BEt_3 \xrightarrow{\Delta} REtNBEt_2 \\ \qquad\qquad\qquad \downarrow CH_3OH \\ \qquad\qquad\qquad REtNH + Et_2BOCH_3 \end{array} \tag{1}$$

Trialkylboranes react readily with carbenes and carbenoid intermediates.[1] Nitrenes are isoelectronic with carbenes, but no reaction between organoboranes and nitrenes has yet been described. Consequently, we decided to explore this possibility.

Nitrenes are produced in the thermal decomposition of organic azides[2] (eq 2). Such a nitrene might be expected to react with an organoborane with migration of an alkyl group from carbon to nitrogen (eq 3). Such intermediates are known to undergo ready solvolysis to the corresponding secondary amines[3] (eq 4).

$$RN_3 \xrightarrow{\Delta} R\ddot{N}: + N_2 \tag{2}$$

$$R\ddot{N}: + BR'_3 \longrightarrow RR'NBR'_2 \tag{3}$$

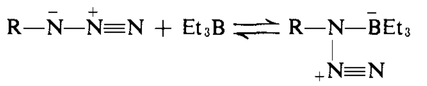
$$RR'NBR'_2 + CH_3OH \longrightarrow RR'NH + R'_2BOCH_3 \tag{4}$$

Accordingly, a 1.0 *M* solution of triethylborane in tetrahydrofuran (THF) was heated under nitrogen with an equimolar quantity of *n*-butyl azide in an autoclave at 170°. After 3 hr the reaction mixture was oxidized with 30% hydrogen peroxide and 3 *M* sodium hydroxide to destroy residual organoborane. Analysis of the dried extract by glpc indicated a 55% yield of *n*-butylethylamine.

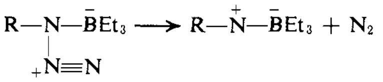
This result was encouraging. However, it would be far more convenient if the reaction could be carried out at atmospheric pressure in a suitable high boiling solvent. To our surprise, even solvents boiling in the range of 135° were satisfactory. We finally selected xylene as a convenient solvent for the reaction.

n-Butyl azide proved to be quite stable in this solvent at reflux. Thus no significant nitrogen evolution was observed over 15 hr. However, the addition of an equimolar quantity of triethylborane to the refluxing solution of *n*-butyl azide resulted in a relatively rapid evolution of gas. Over a period of 6 hr 1 mol equiv of the gas, presumably nitrogen, was given off. Hydrolysis of the reaction mixture gave a 72% yield of *n*-butylethylamine.

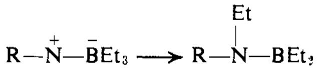
Clearly the reaction does not involve an initial decomposition of the azide into the nitrene and nitrogen (eq 1). The rate of evolution of nitrogen follows second-order kinetics. The results, therefore, are in better agreement with a mechanism involving reversible coordination of the azide with triethylborane (eq 5), followed by loss of nitrogen from the intermediate (eq 6), with subsequent (or concurrent) migration of the ethyl group from boron to nitrogen (eq 7). Solvolysis produces the corresponding secondary amine (eq 4).



$$R{-}\bar{N}{-}\overset{+}{N}{\equiv}N + Et_3B \rightleftharpoons \underset{\overset{|}{{}_{+}N\equiv N}}{R{-}N}{-}\bar{B}Et_3 \tag{5}$$



$$\underset{\overset{|}{{}_{+}N\equiv N}}{R{-}N}{-}\bar{B}Et_3 \longrightarrow R{-}\overset{+}{N}{-}\bar{B}Et_3 + N_2 \tag{6}$$



$$R{-}\overset{+}{N}{-}\bar{B}Et_3 \longrightarrow R{-}\overset{\overset{Et}{|}}{N}{-}BEt_2 \tag{7}$$

Phenyl azide and several representative alkyl azides were examined with triethylborane. The reaction rates for the more hindered azides were somewhat slower. However, all gave comparable yields, 72–80%, of the corresponding secondary amine. The results are summarized in Table I.

Table I. The Reaction of Representative Organic Azides with Triethylborane

Organic azide[a] RN_3	Time, hr	Product[b]	Yield,[c] %
n-Butyl	6	*n*-Butylethylamine	72
Isobutyl	6	Isobutylethylamine	78
sec-Butyl	24	*sec*-Butylethylamine	80
Cyclopentyl	15	Cyclopentylethylamine	77
Cyclohexyl	24	Cyclohexylethylamine	73
Phenyl	9	*N*-Ethylaniline	78

[a] 10 mmol of RN_3 and 10 mmol of Et_3B in 10 ml of xylene, heated under reflux in a nitrogen atmosphere. [b] All products were isolated by glpc and exhibited analytical and spectral data in accordance with the assigned structures. [c] By glpc analysis, based on organic azide.

The reaction exhibits some features similar to those previously noted for the reaction of organoboranes with diazo compounds.[4] The diazo reactions exhibit considerable sensitivity to steric effects. This is also noted in the present azide reaction. Thus, organoboranes from α-olefins react smoothly with *n*-butyl azide. For example, yields of 80 and 73%, respectively, were

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(1) D. Seyferth and B. Prokai, *J. Amer. Chem. Soc.*, **88**, 1834 (1966); G. Köbrich and H. R. Merkle, *Angew. Chem., Int. Ed. Engl.*, **6**, 74 (1967); G. Köbrich and H. R. Merkle, *Chem. Ber.*, **100**, 3371 (1967); A. Suzuki, S. Nozawa, N. Miyaura, M. Itoh, and H. C. Brown, *Tetrahedron Lett.*, 2955 (1969); H. C. Brown, B. A. Carlson, and R. H. Prager, *J. Amer. Chem. Soc.*, **93**, 2070 (1971).

(2) P. Walker and W. A. Waters, *J. Cnem. Soc.*, 1632 (1962); W. H. Saunders and J. C. Ware, *J. Amer. Chem. Soc.*, **80**, 3328 (1958).

(3) H. Steinberg and R. J. Brotherton, "Organoboron Chemistry," Vol. II, Wiley, New York, N. Y., 1966, p 27.

(4) J. Hooz and S. Linke, *J. Amer. Chem. Soc.*, **90**, 5936, 6891 (1968); J. Hooz and D. M. Gunn, *Chem. Commun.*, 139 (1969); J. Hooz and G. F. Morrison, *Can. J. Chem.*, **48**, 868 (1970).