of dry tetrahydrofuran under nitrogen was added a solution of 0.535 g (3.3 mmol) of 1,1'-carbonyldiimidazole in 25 ml of dry tetrahydrofuran, and the resulting clear solution was stirred at 25° for 52 hr protected from moisture. Then 0.48 g (2.96 mmol) of diimidazole reagent was added and the reaction mixture was stirred for another 16 hr at 25°. The solvent was evaporated to give an oil which crystallized, recrystallization of which several times from dichloromethane–ether gave 0.5916 g (77%) of product, mp 159–163°. An analytical sample gave mp 160–163.5°. *Anal.* Calcd for $C_{12}H_{14}N_4O_2S$: C, 51.77; H, 5.08. Found: C, 51.92; H, 5.13. Nmr ($CDCl_3$) τ 1.6–3.4 (m, 6, ArH and ImH), 4.8 (broad s, 2, NH_2), 6.47 (s, 3, SCH_3), 7.67 (s, 3, $ArCH_3$).

1,6-Dimethyl-3-oxobenzo[*e*]-4*H*-1,2,4-thiadiazene Oxide (6).—A solution of 0.21 g (0.756 mmol) of the above imidazole derivative in 15 ml of *p*-dichlorobenzene was heated at 160–175° for 24 hr. The solvent was removed *in vacuo*, and the residue was dissolved in 100 ml of water and cooled. The resulting mixture was filtered, reduced to 30 ml, and cooled further to give 0.13 g (82%) of **6**, mp 295–300° dec. *Anal.* Calcd for $C_9H_{10}N_2O_2S$: C, 51.40; H, 4.80. Found: C, 51.66; H, 4.97. Ir (Nujol) 1650 (C=O), 1220 (O=S=N).

A sample of 2-(methyl-*N*-carboethoxysulfonimidoyl)-5-methylaniline (0.20 g, 0.782 mmol) was heated neat at 170–180° for 24 hr to give a solid residue which, when recrystallized from water, gave about 10 mg (6%) of **6**, mp 295–300° dec.

2-Methylsulfinyl-5-methylphenyl Azide (29).—To a solution of 0.30 g (1.63 mmol) of **25** in 5 ml of 2 N hydrochloric acid was added a 0.2 *M* solution of sodium nitrite (less than 2 equiv) until an excess of nitrous acid was present. The resulting yellow solution was stirred at 25° for 0.5 hr and then extracted to give an oil which solidified into 0.31 g (97%) of a yellow solid. Recrystallization of this solid from ether–pentane gave 0.17 g (53%) of **29**, mp 59–63°. *Anal.* Calcd for $C_8H_9N_3OS$: C, 49.20; H, 4.66. Found: C, 49.40; H, 4.47. Nmr ($CDCl_3$) τ 2.1–3.1 (m, 3, ArH), 7.25 (s, 3, SCH_3), 7.58 (s, 3, $ArCH_3$).

Registry No.—**1**, 34617-79-3; **2b**, 34617-80-6; (−)-(*R*)-**3**, 34617-81-7; **4**, 34617-82-8; **5**, 34617-83-9; **6**, 34662-87-8; **10a**, 36789-40-9; **10b**, 36789-41-0; **11**, 36789-42-1; **12**, 36870-61-8; **14**, 36789-43-2; **15**, 36789-44-3; **16a**, 36789-45-4; **16b**, 36789-46-5; **17**, 36789-47-6; **18**, 34617-85-1; **20**, 34662-88-9; **21**, 34617-86-2; **22**, 34617-93-1; **23**, 34617-94-2; **24**, 34617-87-3; **25**, 34617-88-4; **26**, 34617-90-8; **27**, 34617-89-5; **28**, 34617-91-9; **29**, 34617-92-0; **34**; 36789-27-2; **35**, 36789-28-3; **36**, 36789-29-4; 1-(2-methylthio-5-methyl)phenylthioacetylmorpholide, 36789-30-7; 1,4,4,6-tetramethyl-3-oxo-1,2-thiazanaphthalene oxide, 36789-31-8; 2-(methyl-*N*-carboethoxysulfonimidoyl)-5-methylaniline, 36789-32-9; 2-[methyl-*N*-(1-imidazolylcarbonyl)sulfonimodoyl]-5-methylaniline, 36789-33-0.

Thermal Reactions of Alkyl *N*-Carbomethoxysulfamate Esters

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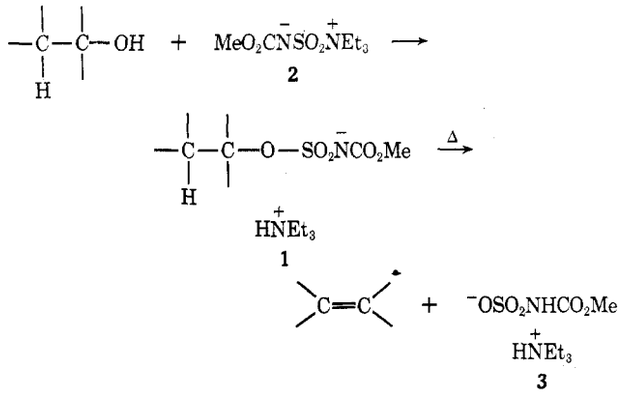
(Carboxysulfamoyl)triethylammonium hydroxide, inner salt, methyl ester was synthesized and shown to react with a broad spectrum of alcohols resulting in alkyl *N*-carbomethoxysulfamate esters. The scope and synthetic usefulness of the sulfamate ester function as a leaving group in thermolytic dehydration reactions was demonstrated by the facile conversion of tertiary and secondary alcohols to olefins and primary alcohols to urethanes. Stereochemically the reaction was established as a cis-stereospecific elimination by the formation of only protio-*trans*-stilbene from *threo*-2-deuterio-1,2-diphenylethyl-*N*-carbomethoxysulfamate triethylammonium salt and only α-deuterio-*trans*-stilbene from the corresponding erythro compound. The first-order rate constants for the diphenylethanol system were determined spectrophotometrically ($k_{35°} = 2.66 \times 10^{-6}$) and a small β-deuterium isotope effect was observed ($k_H/k_D = 1.05$ for erythro and 1.08 for threo compound). Activation parameters were calculated for the thermolysis with values $E_a = 22.4$ kcal/mol, $\Delta H^{\ddagger} = 21.7$ kcal/mol, $\Delta G^{\ddagger} = 22.8$ kcal/mol, $\Delta S^{\ddagger} = -3.3$ eu. These kinetic and stereochemical results are consistent with an initial rate-limiting formation of an ion pair followed by a fast cis β proton transfer to the departing anion at a rate greater than the interconversion of erythro- and threo ion pairs.

The dehydration of alcohols *via* a first-order thermolytic Ei decomposition of a derived ester has been a valuable method in the portfolio of practiced synthetic organic reactions. When compared to solvolytic elimination, the cis-β hydrogen geometrical constraint and the absence of α-carbon carbonium ion character (and thus skeletal rearrangements) in the transition state of such eliminations provide a predictable and therefore strategically useful step in a directed synthetic sequence. A variant of the Ei mechanism timing exists in which ionization of the α carbon attached group results in an ion pair whose collapse involves transfer of the β hydrogen from the cation to anion. This mechanism is especially important in cases of elimination with good leaving groups in nonpolar media. Such an ion-pair mechanism may show the kinetic order and stereospecificity of an Ei scheme but in many cases carbonium ion rearrangements are observed.

In order to minimize such rearrangements but preserve the stereospecificity of a solution (for operational convenience) Ei reaction in a synthetic step, the reacting system should be of such a design as to reduce the degree of ion-pairing character. To meet this requirement the departing anionic group should have a good incipient proton nucleophilicity in solvents of low polarity. Furthermore, if the developing anion has multiple proton acceptor sites the $\Delta G^{\ddagger}$ will be decreased owing to an increased positive entropy contribution. Finally, the formation of the requisite alcohol derivative should be facile even in the presence of severe steric factors.[1] With such criteria in mind we have examined the thermolytic behavior of alkyl *N*-carbomethoxysulfamate salts, **1**, as intermediates in a potential synthetic method for the conversion of alcohols to alkenes.

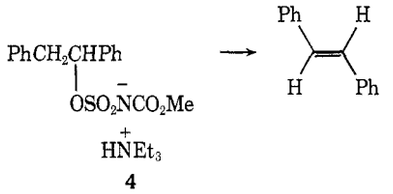
The triethylammonium *N*-carbomethoxysulfamates (**1**) employed in this study were generated by the interaction of methyl(carboxysulfamoyl)triethylammonium hydroxide inner salt (**2**) with the candidate alcohols

(1) For example, mesylates of alcohols are more readily formed than tosylates, since the former result from an addition to a reactive sulfene generated from the dehydrohalogenation of the precursor methanesulfonyl chloride.



neat or in hydrocarbon solvent at 30° or below. The above inner salt was prepared as previously reported[2] from carbomethoxysulfamoyl chloride and triethylamine. The triethylammonium gegenion of these sulfamate esters was readily exchanged for either a sodium cation or a proton. If a dry tetrahydrofuran solution of an alkyl *N*-carbomethoxysulfamate triethylammonium salt was treated with 1 equiv of sodium hydride and the solvent and liberated triethylamine were evaporated, an infusible sulfamate ester sodium salt was obtained. The free base resulted from rapid washing of a benzene solution of the triethylammonium salt with a cold 2% aqueous hydrochloric acid solution. In the case of *tert*-alkyl sulfamate esters the salts were sufficiently labile at room temperature as to preclude isolation. However, all the *sec*- and *tert*-alkyl derivatives studied smoothly decomposed at temperatures between 30 and 80° in a variety of solvents to provide reasonable yields of isolated alkenes and the water-soluble salt **3**.

In order to delineate the mechanistic details of the elimination reaction the observed exclusive conversion of 1,2-diphenylethyl-*N*-carbomethoxysulfamate triethylammonium salt to *trans*-stilbene was chosen as a model system for further study. When the correspond-

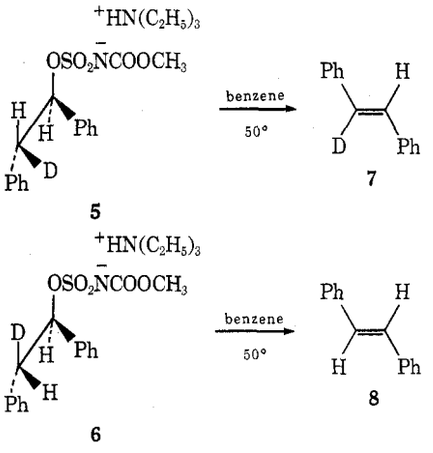


ing *erythro*- and *threo*-2-deuterio-1,2-diphenylethyl-*N*-carbomethoxysulfamates[3] were allowed to decompose in benzene solution at 50° the former provided α-deuterio-*trans*-stilbene (**7**) which contained a minimum of 0.97 deuterium atoms per molecule as demonstrated by mass spectral analysis, while the latter gave only protio-*trans*-stilbene (**8**). These stereochemical results were *unchanged* by substituting for benzene the more basic solvent, dimethylformamide, and indicate that a cis elimination is operative over a wide range of solvent basicities.[4]

(2) G. M. Atkins, Jr., and E. M. Burgess, *J. Amer. Chem. Soc.*, **90**, 4744 (1968).

(3) The precursor deuterated alcohols were derived by reduction from the appropriate stilbene oxides: D. Y. Curtin and D. B. Kellom, *ibid.*, **75**, 6011 (1953).

(4) The competition for proton removal between basic solvents and gegenion and the result on E1 stereochemistry has been reported: P. S. Skell and W. L. Hall, *ibid.*, **85**, 2851 (1963).



A kinetic study of the elimination reaction of **4**, **5**, and **6** in 95% aqueous ethanol was performed by following product development spectrophotometrically at 295 nm (see Table I).

TABLE I

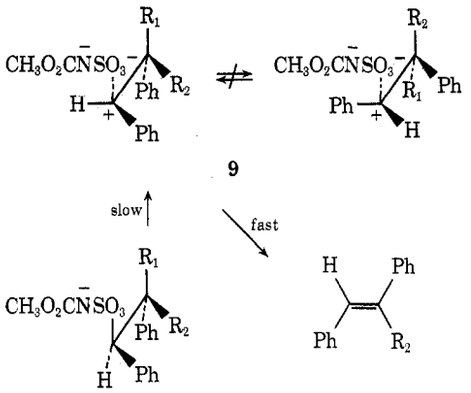
THERMOLYSES OF **4**, **5**, AND **6** IN 95% AQUEOUS ETHANOL[a]

Compd	Temp, °C	Concn × 10⁵, mol/l.	*k* × 10⁶, sec⁻¹
4	52	4.00	16.9
		3.00	15.5
		2.00	16.4
	46	4.00	9.13
		3.00	9.05
		2.00	9.20
	35	4.00	2.65
		3.00	2.63
		2.00	2.71
5	35	4.00	2.57
		2.00	2.51
6	35	4.00	2.43
		2.00	2.49

[a] First-order kinetics were displayed up to 60% reaction with a rate constant at 35° of 2.66 ± 0.03 × 10^{-6} sec^{-1} for **4** and activation parameters of E_a, +22.4 ± 0.5 kcal/mol; $\Delta H^{\ddagger}$, +21.7 ± kcal/mol; $\Delta G^{\ddagger}$, +22.8 ± 0.5 kcal/mol; and $\Delta S^{\ddagger}$, −3.3 eu. The β-deuterium isotope effect determined from this data had k_H/k_D = 1.05 ± 0.02 and 1.08 ± 0.03 at 35° for the erythro and threo isomers, respectively.

The product analysis, the first-order kinetics, the activation parameters, and the isotope effect data are consistent with a mechanism with an initial rate-limiting formation of an ion pair followed by a fast cis-β-proton transfer to the departing anion at a rate greater than the interconversion of the erythro- and threo-derived ion pairs (**9a**, **9b**). The departing anion must compete effectively with the solvent as a base in dimethylformamide to further account for the stereochemical result. Whether the proton is transferred to nitrogen or oxygen of this anion is unclear, but from a statistical and thermodynamic (based on bond energies) viewpoint, the transition state forming an O–H bond is energetically more favorable. Although the thermolysis of **4** does not represent the mechanism for all the examples investigated, it does provide a basis upon which the other results may be rationalized.

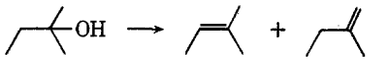
The Saytzeff rule would be expected to be operative in such an ion-pair elimination and this thesis is borne out by the observed conversion of 2-methyl-2-butanol



9

a, R_1 = H; R_2 = D
b, R_1 = D; R_2 = H

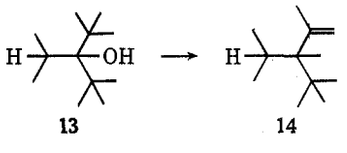
(**10**) to 2-methyl-2-butene (**11**) and 2-methyl-1-butene (**12**) in a ratio of 2.4:1.[5,6] In addition, such an ion-



10 **11** **12**

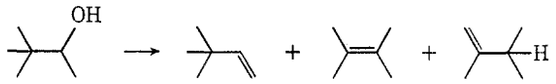
pairing mechanism would predict that, in favorable cases, skeletal rearrangement would occur in the carbonium ion component. In order to assess the scope of this possibility we have examined the alkene product distribution from a selected number of alcohols.

3-*tert*-Butyl-2,2,4-trimethyl-3-pentanol (**13**) was prepared by treating ethyl isobutyrate with 2 equiv of *tert*-butyllithium in pentane at −78° and the structure was verified by its infrared, nmr, and mass spectral display. Upon treatment with **2** in acetonitrile solution at 50°, **13** gave only 3-*tert*-butyl-2,3,4-trimethyl-1-pentene (**14**) identified through the following data.



13 **14**

The ir spectrum had absorption at 1645 cm^{-1} (C=CH_2) and nmr signals (60 MHz, $CDCl_3$) appeared at δ 4.90–4.82 (m, 2 H), 1.03 (d, J = 7 Hz, 6 H), 1.92 (q, J = 7 Hz, 1 H), 1.80 (d, J = 2 Hz, 3 H), 0.97 (s, 3 H), 0.92 (s, 9 H). Although here the mechanistic sequence requires (as is often observed) conversion of one *tert*-neopentyl cation to another by methyl rather than hydried migration (to give 3-*tert*-butyl-2,4,4-trimethyl-1-pentene) the cis-β proton conformation required for elimination without rearrangement would not be energetically accessible owing to eclipsing of the methyl and *tert*-butyl groups.[7] The dehydration of 3,3-dimethyl-2-butanol (**15**) *via* the sulfamate ester sodium salt in benzene solution at 70° afforded the Wagner–Meerwein rearranged alkenes **16** and **17** as well as **18** in a ratio of



15 **18** **16** **17**

3:1.5:1. The absence or presence of solvents with diverse dielectric constants produced no significant variation on this product distribution (Table II). The

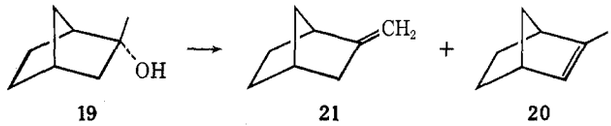
TABLE II
THERMOLYSES OF 3,3-DIMETHYL-2-BUTYL *N*-CARBOMETHOXYSULFAMATE SODIUM SALT

Temp, °C	Solvent	Products ratio[a] 18	16	17
60	Triglyme	1	3	1.2
70	Benzene	1	3	1.5
100	Neat	1	4	1.2

[a] Determined by gas chromatography.

amount of unrearranged alkene produced is surprising, since the competition between Wagner–Meerwein rearrangement and β-proton removal usually lies completely in the direction of the former.

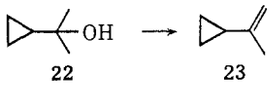
An acetonitrile solution of 2-*endo*-methylbicyclo[2.2.1]heptan-2-ol (**19**), when treated with **2** at 50°, afforded an 80% yield of the cycloalkenes, 2-methyltricyclo[2.2.1]heptene (**20**) and 2-methylbicyclo[2.2.1]-hept-2-ene (**21**) in a ratio of 1:1.[8] As expected, no



19 **21** **20**

rearrangement products were found; however, in this case from consideration of the cis stereochemical constraint and Saytzeff correlation observed in aliphatic cases (see **10** → **11** + **12**) the unexpected greater rate of formation of **21** relative to **20** may be due to the relatively increased strain energy content of the latter. In addition, the steric effect of the endo C-5 hydrogen would interfere with formation of the ion-pair geometry necessary for subsequent endo C-3 hydrogen removal.[9]

When neat 2-cyclopropyl-2-propanol (**22**) was treated with **2** an exothermic reaction ensued from which a moderate yield of 2-cyclopropylpropene[5,10] (**23**) was



22 **23**

isolated. No evidence for the formation of 2-cyclopropylidene propane was found and this observation is consistent with the proposed[11] "bisected" geometry for the cyclopropylcarbinyl cationic component of the ion pair in which the β-cyclopropyl hydrogen would be orthogonal to the departing group and thus sterically unavailable for elimination.

In order to study a further example in a similar system, 3,4-epoxy-2-methyl-2-butanol (**24**) was subjected to the action of **2** at 55°. Only 3,4-epoxy-2-

(5) Determined by gas chromatography and nmr spectral comparison with authentic samples.

(6) This ratio is smaller than that obtained from a solvolytic elimination of the corresponding halides: H. C. Brown and M. Makagawa, *J. Amer. Chem. Soc.*, **77**, 3610 (1955).

(7) It has been reported that upon melting di-*tert*-butylneopentylcarbinyl *p*-nitrobenzoate gives tri-*tert*-butylethylene as well as a rearranged terminal alkene similar to **14**. Ion pairing was invoked as a mechanistic rationalization to account for these products: G. J. Abruscato and T. T. Tidwell, *J. Amer. Chem. Soc.*, **92**, 4125 (1970); P. D. Bartlett and T. T. Tidwell, *ibid.*, **90**, 4421 (1968).

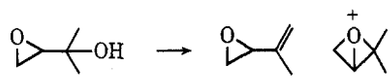
(8) The nmr spectra observed are identical with those reported for **20** and **21**: R. A. Finnegan and R. S. McNeese, *J. Org. Chem.*, **29**, 3234 (1964); H. Krieger, *Suom. Kemistilehti B*, **38**, 260 (1965).

(9) This effect is pronounced in the E2 syn *vs.* anti elimination mode observed in *endo*- and *exo*-bicyclo[2.2.1]heptyl chlorides: J. Sicker, *Angew. Chem., Int. Ed. Engl.*, **11**, 200 (1972).

(10) V. A. Slabey, *et al.*, *ibid.*, **71**, 1518 (1949).

(11) C. V. Pittman and G. A. Olah, *ibid.*, **87**, 2998 (1965).

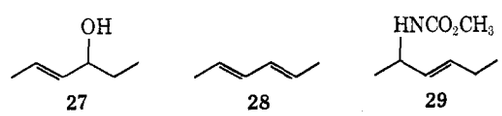
methyl-1-butene (**25**) was isolated and identified by characteristic nmr (60 MHz, $CDCl_3$) signals at δ 5.17 (m, 1 H, J = 1 Hz), 3.35 (m, 1 H, J = 3 Hz), 2.75 (m, 2 H, J = 3 Hz), 1.63 (d, 3 H, J = 2 Hz), and an exact mass determination. This reaction contrasts sharply with the solvolysis of the corresponding tosylate, which provides a 3-oxetanol tosylate *via* internal return to the 1-oxabicyclobutonium cation (**26**).[12] If such a cation is one component of the ion-pair intermediate in the conversion of **24** to **25** it must undergo



24 **25** **26**

rapid proton transfer to the anion from the methyl-substituted face before any geometrical realignment of the ion-pair components occurs.

In another example, either the sodium or triethylammonium salt of the *N*-carbomethoxysulfamate derivative of 4-hexen-3-ol (**27**) underwent elimination in triglyme solution at 75° to afford only 2,4-hexadiene (**28**).[5] However, if the sodium salt was decomposed as a solid at 80° and the reaction mixture was treated with water, the rearranged urethane, methyl-*N*-(2-hex-3-enyl)carbamate (**29**), was isolated in high yield. The

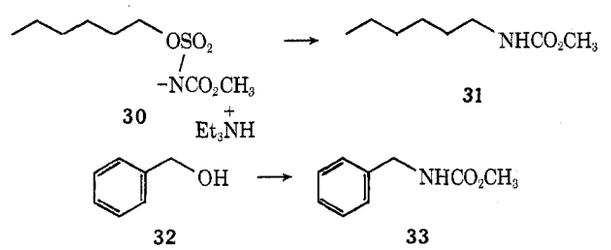


27 **28** **29**

structure of **29** was established by the observed nmr (60 MHz, $CDCl_3$) signals at δ 5.55 (m, 2 H), 4.10 (s, 1 H), 3.60 (s, 3 H), 2.00 (m, 1 H), 1.65 (m, 2 H), 1.05 (m, 6 H), and ir ($CHCl_3$) absorption at 3440 (NH), 1720 (C=O), and 1675 cm^{-1} (C=C). The latter reaction course may be a result of a solid-state configuration favorably disposed for an SNi′ rearrangement in which negligible charge separation requiring solvent stabilization develops.

With primary alkyl *N*-carbomethoxysulfamate salts a SN2 pathway becomes energetically more favorable as compared to the Ei counterpart and urethanes result from thermolyses of these salts. For example, when 1-hexanol is treated directly with **2** and after the initial exothermic formation of **30** is complete the reaction mixture is heated to 95°, a 75% yield of methyl *N*-hexylcarbamate[5] (**31**) is obtained after treatment with water.

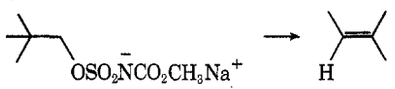
Benzyl alcohol (**32**) was likewise converted to *N*-benzylcarbamate[5] (**33**) in 80% yield.



30 **31** **32** **33**

In a contrasting reaction, the neat free base derived from **30** upon thermolysis at 150° provides a 1:1 mixture of 1- and 2-hexenes[5] in what is probably an autocatalyzed elimination resulting from the presence of the acidic carbomethoxylsulfamoyl proton, which also promotes the observed isomerization of the initially produced terminal alkene.

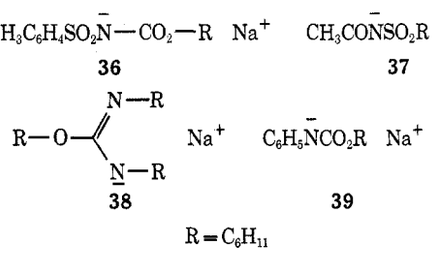
When a primary sulfamate ester is examined in which severe steric restrictions to a bimolecular displacement reaction are operative, only an Ei pathway is important at the higher temperature required for decomposition. To exemplify, the sodium salt of the carbomethoxysulfamate ester of 2,2-dimethyl-1-propanol (**34**) when decomposed as a solid at 110° affords only 2-methyl-2-butene (**35**).[5] The conversion of primary alcohols to



34 **35**

urethanes *via* the sulfamate ester salts is complementary to the reported[13] SNi reaction of *N*,*N*-dimethylsulfamate esters of allylic and benzylic alcohols to give dimethyl derivatives of amines, and both provide an important synthetic alternative to the more usual methods of alcohol to amine transformation. In a further synthetic application the treatment of *syn*-benzaldehyde oxime with **2** at 100° with subsequent hydrolysis provided the Beckmann rearrangement product, formanilide, in modest yield.

It was of interest to determine how other groups might compare in potential Ei reactivity to salts of *N*-carbomethoxysulfamate esters, and to this end a number of derivatives of cyclohexanol were prepared by addition of this alcohol to the appropriate heterocumulene followed by treatment with sodium hydride. Thermolysis of **36**, **37**, **38**, and **39** between 100 and



36 **37** **38** **39**

$R = C_6H_{11}$

150° provided no evidence for the formation of cyclohexene, although the free base derived from **36** in *tertiary* systems has been reported[14] on pyrolysis to be a basis for a general alkene synthesis.

Experimental Section[15]

(Carboxysulfamoyl)triethylammonium Hydroxide Inner Salt Methyl Ester (2).—Anhydrous methanol (18.80 g, 0.550 mol) in

(12) H. G. Richey, Jr., and D. V. Kinsman, *Tetrahedron Lett.*, 2505 (1969).

(13) E. H. White and C. A. Elliger, *J. Amer. Chem. Soc.*, **87**, 5261 (1965).

(14) L. C. Roach and W. H. Daly, *J. Chem. Soc. D*, 606 (1970).

(15) Melting points are uncorrected and the microanalyses were performed by Huffman Laboratories, Wheatridge, Colo. Infrared spectra were obtained using a Perkin-Elmer Model 457 spectrometer fitted with sodium chloride optics. The nmr spectra were determined with a Varian A-60 spectrometer (TMS internal standard) and mass spectra were measured on a Varian M-66 spectrometer. Ultraviolet spectra were obtained from a Cary Model 14 recording spectrophotometer using 1-cm quartz cells and 95% aqueous ethanol solvent. Gas–liquid phase chromatography for collection of analytical samples was performed using an F & M Model 700 dual-column gas chromatograph fitted with a silicon rubber column (4 ft) with helium as the carrier gas. General analytical data were obtained using a Hewlett-Packard Model 402 dual column gas chromatograph fitted with a UCON polar column (4 ft) using nitrogen as the carrier gas. The apparatus used in the thermolyses consisted of a U-shaped glass tube with standard taper glass joints at each end. At the end to be inserted into the reaction vessel was a gas inlet tube which admitted a flow of nitrogen and the other end of the U-tube was fitted to a Dry Ice cooled trap.

25 ml of benzene was added dropwise to a solution of chlorosulfonyl isocyanate (65.72 g, 0.500 mol) in 200 ml of benzene in a 500-ml flask fitted with a 50-ml addition funnel. The mildly exothermic reaction was controlled with a cool water bath. After the addition was complete (30 min), the solvent and excess methanol were removed from the reaction mixture under reduced pressure. The resulting white, crystalline mass was crystallized once from toluene to give colorless needles (61.00 g, 91.9%) of carbomethoxysulfamoyl chloride, mp 70–71°.

Anal. Calcd for $C_2H_4ClNO_4S$: C, 13.88; H, 2.33; N, 8.10; S, 18.49. Found: C, 13.76; H, 2.53; N, 8.13; S, 18.72.

Carbomethoxysulfamoyl chloride (3.47 g, 0.020 mol) dissolved in 50 ml of benzene was added dropwise to a solution of triethylamine (4.60 g, 0.045 mol) in 25 ml of benzene in a 250-ml three-neck round-bottom flask fitted with a 125-ml addition funnel under a nitrogen atomsphere at ambient temperature. After the addition was complete (1 hr), the precipitate of triethylamine hydrochloride (0.56 g, 96%) was removed by filtration, and the solvent was evaporated under reduced pressure to afford a residual colorless oil which solidified on standing. Crystallization from toluene yielded colorless needles (3.87 g, 81%) of (carboxysulfamoyl)triethylammonium hydroxide inner salt methyl ester (**2**): mp 71–72°; nmr ($CDCl_3$) δ 3.66 (s, 3 H), 3.29 (q, 6 H, J = 7 Hz), and 1.15 (t, 9 H, J = 7 Hz).

Anal. Calcd for $C_8H_{18}N_2O_4S$: C, 40.32; H, 7.62; N, 11.72; S, 13.43. Found: C, 40.04; H, 7.54; N, 11.51, S, 13.36.

Dehydration of 1,2-Diphenylethanol.—1,2-Diphenylethanol (3.96 g, 0.020 mol) in 15 ml of benzene was added dropwise to a solution of **2** (5.00 g, 0.021 mol) in 20 ml of benzene in a 50-ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atomsphere of dry nitrogen. After the addition was complete (30 min), the temperature was raised to 50° and mintained for 30 min. Water (10 ml) was added and the benzene layer was separated, dried over anhydrous sodium sulfate, and evaporated to yield a white, crystalline solid. Crystallization from ethanol gave colorless plates (3.42 g, 95%) of *trans*-stilbene, mp 124° undepressed upon admixture with an authentic sample. In another example, the reaction was repeated in exact proportions using *N*,*N*-dimethylformamide as the solvent. After the temperature was maintained at 50° for 30 min, water (10 ml) was added and the reaction mixture was extracted three times with 10-ml portions of ether. The ether extracts were combined, washed three times with 25-ml portions of water, dried overy anhydrous sodium sulfate, and evaporated to afford a white, crystalline solid. Crystallization from ethanol gave 3.45 g (96%) of pure *trans*-stilbene.

Dehydration of *erythro*-2-Deuterio-1,2-diphenylethanol.—The above procedure was carried out using *erythro*-2-deuterio-1,2-diphenylethanol[3] (3.36 g, 0.016 mol) in 10 ml of benzene and **2** (4.30 g, 0.018 mol) in 20 ml of benzene. Recrystallization from ethanol gave colorless plates (2.89 g, 94%) of α-deuterio-*trans*-stilbene (**7**): mp 124° (lit.[16] mp 124°); nmr ($CDCl_3$) δ 7.34 (m, 10 H), 6.99 (s, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 182 (14), 181 (97), 180 (100). For comparison *trans*-stilbene had mass spectrum (70 eV) *m/e* (rel intensity) 181 (14), 180 (100). For **7** the minimum deuterium atom/molecule is 0.97.

In another example, the reaction was repeated in exact proportions using *N*,*N*-dimethylformamide as the solvent. Using the same work-up as for diphenylethanol in *N*,*N*-dimethylformamide, 2.91 g (95%) of **7** was obtained with an identical mass spectrum.

Dehydration of *threo*-2-Deuterio-1,2-diphenylethanol.—The above procedure was carried out using the threo isomer[3] (3.36 g, 0.017 mol) in 10 ml of benzene and **2** (4.30 g, 0.018 mol) in 20 ml of benzene. Recrystallization from ethanol gave 2.83 g (92%) of *trans*-stilbene containing no deuterium by mass spectroscopy.

In another example, the reaction was carried out in exact proportions using *N*,*N*-dimethylformamide as the solvent. Again, using the same work-up as for diphenylethanol in this solvent, 2.86 g (93%) of *trans*-stilbene containing no deuterium by mass spectroscopy was isolated.

Dehydration of 2-Methylbutan-2-ol (10).—2-Methylbutan-2-ol (2.30 g, 0.025 mol) was added neat to **2** (7.50 g, 0.032 mol) at ambient temperature in a 50-ml round-bottom flask connected to a cold trap by a glass U-tube. Within 5 min of the addition an exothermic reaction developed, the reaction mixture became homogeneous, and a clear, colorless liquid distilled into the cold trap. The reaction mixture was flushed with a stream of dry nitrogen for 1 hr, after which the collected distillate was analyzed by gas chromatography and nmr spectral comparison. The alkenes (2.00 g, 95%) were shown to consist of 2-methyl-2-butene (70%) (**11**) and 2-methyl-1-butene (30%) (**12**) by comparison with an authentic mixture.

Dehydration of 3-*tert*-Butyl-2,2,4-trimethylpentan-3-ol (13).—A solution of 1.7 *M* *tert*-butyllithium (122 ml, 10.01 g, 0.16 mol) in pentane in a 500-ml three-neck round-bottom flask fitted with a 125-ml addition funnel under a nitrogen atmosphere was cooled to −78° with a Dry Ice and acetone bath. Ethyl 2-methylpropanoate (8.13 g, 0.07 mol) in 50 ml of diethyl ether was added dropwise and the reaction mixture was allowed to stir for 1 hr at −78°. After the reaction was allowed to warm to room temperature, the excess *tert*-butyllithium was destroyed by the slow addition of water. The reaction was neutralized with 30% aqueous hydrochloric acid and extracted three times with 25-ml portions of ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to yield a colorless oil which crystallized on standing. Crystallization from benzene–hexane gave colorless needles (12.37 g, 95%) of 3-*tert*-butyl-2,2,4-trimethylpentan-3-ol (**13**): mp 24–25°; ir ($CHCl_3$) 3620 (OH), 2950, 2920, and 2880 cm^{-1}, no C=O band; nmr ($CDCl_3$) δ 3.58 (s, 1 H), 1.92 (m, 1 H, J = 7 Hz), 1.02 (d, 6 H, J = 7 Hz), 0.092 (s, 18 H); exact mass determination—theoretical 186.340, found 186.342.

3-*tert*-Butyl-2,2,4-trimethylpentan-3-ol (**13**) (3.00 g, 0.016 mol) in 10 ml of acetonitrile was added dropwise to a solution of **2** (4.75 g, 0.020 mol) in 25 ml of acetonitrile in a 50-ml round-bottom flask fitted with a reflux condenser. The temperature was raised to 50° and maintained for 1 hr, after which the reaction was cooled, treated with water, and extracted three times with 10-ml portions of ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to afford a colorless liquid (1.88 g, 70%) which was shown by glc to be homogeneous and identified as 3-*tert*-butyl-2,3,4-trimethylpent-1-ene (**14**): nmr ($CDCl_3$) δ 4.90 (m, 1 H), 4.82 (m, 1 H), 1.82 (m, 1 H, J = 7 Hz), 1.80 (d, 3 H, J = 2 Hz), 1.03 (d, 6 H, J = 7 Hz), 0.97 (s, 3 H), 0.92 (s, 9 H); mass spectrum (70 eV) *m/e* (rel intensity) 168 (1.0), 112 (100), 97 (95), 69 (90), 57 (85), 43 (65), 41 (83).

Anal. Calcd for $C_{12}H_{24}$: C, 85.71; H, 14.29. Found: C, 85.60; H, 14.21.

Dehydration of 3,3-Dimethylbutan-2-ol (15).—3,3-Dimethylbutan-2-ol (3.00 g, 0.029 mol) in 5 ml of triglyme was added dropwise to a solution of **2** (7.50 g, 0.032 mol) in 25 ml of triglyme in 50-ml round-bottom flask connected to the thermolysis apparatus at ambient temperature under a stream of dry nitrogen. The reaction mixture was treated with sodium hydride (0.77 g, 0.032 mol) (prepared from 1.35 g of sodium hydride–mineral oil dispersion by several washings with dry hexane) and maintained at ambient temperature until hydrogen evolution ceased. The temperature was raised to 60° and a clear, colorless liquid distilled into the cold trap. Glc and nmr analysis of the distillate showed the presence of three components which were identified as 3,3-dimethylbut-1-ene (**18**) (18%), 2,3-dimethylbut-2-ene (**16**) (55%), and 2,3-dimethylbut-1-ene (**17**) (27%) by comparison with authentic samples. The total yield of olefinic products was 2.28 g (85%).

In another example the reaction as described above was run using benzene as a solvent. The distillate had the same components in slightly different proportion: **18** (19%), **16** (58%), and **17** (23%). The total yield of olefinic products was 2.25 g (84%).

In yet another example, tetrahydrofuran was used as the solvent. After hydrogen evolution had ceased, solvent was removed *in vacuo* to yield a white solid which when heated to 100° to yield a clear, colorless distillate with the composition **18** (16%), **16** (65%), and **17** (20%). The total yield of olefinic products was 2.30 g (86%).

Dehydration of *endo*-2-Methylbicyclo[2.2.1]heptan-2-ol (19).—Methyl iodide (11.36 g, 0.08 mol) dissolved in 25 ml of anhydrous diethyl ether was added dropwise to a mechanically stirred suspension of magnesium turnings (1.82 g, 0.075 mol) in 25 ml of diethyl ether. The resulting solution was treated dropwise with norcamphor (5.50 g, 0.05 mol) dissolved in 25 ml of diethyl ether. After this addition was complete (15 min), the reaction mixture was allowed to stir for 1 hr, after which it was hydrolyzed with a saturated aqueous solution of ammonium chloride and extracted with three 10-ml portions of diethyl ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to yield colorless prisms (5.51 g, 89%) of *endo*-2-methylbicyclo-[2.2.1]heptan-2-ol (**19**): mp 30–31° (lit.[8] mp 31.5–32°); ir

(16) M. Schlosser, *Chem. Ber.*, **97**, 3219 (1964).

($CHCl_3$) 3620 (OH), 2950 and 2870 cm^{-1}, no C=O band; nmr ($CDCl_3$) δ 2.73 (s, 1 H), 1.68 (complex m, 10 H), 1.30 (s, 3 H).

endo-2-Methylbicyclo[2.2.1]heptan-2-ol (4.20 g, 0.032 mol) in 10 ml of acetonitrile was added dropwise to a solution of **2** (9.00 g, 0.038 mole) in 20 ml of acetonitrile in a 50-ml round-bottom flask fitted with a reflux condenser and calcium chloride drying tube. The temperature was raised to 50° and maintained for 1 hr, after which the reaction mixture was cooled, treated with 15 ml of water, and extracted with three 10-ml portions of ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to give a colorless liquid (2.76 g, 80%) which was shown by glc to contain two components.

Separation was affected by collection from a gas–liquid chromatograph (20% Carbowax column, injector temperature 220°, detector temperature 220°, column temperature 65°). The peak of shorter retention time (47% of the mixture) was identified[8] as 2-methylbicyclo[2.2.1]hept-2-ene (**20**): nmr ($CDCl_3$) δ 5.42 (m, 1 H), 2.71 (m, 1 H), 2.54 (m, 1 H), 1.68 (d, 3 H, J = 2 Hz); exact mass determination—theoretical, 108.172; found, 108.169. The other component was identified[8] as 2-methylenebicyclo-[2.2.1]heptane (**21**): nmr ($CDCl_3$) δ 4.78 (m, 1 H), 4.52 (m, 1 H), 2.66 (m, 1 H), 2.33 (m, 1 H), 2.00 (m, 1 H); exact mass determination—theoretical, 108.172; found, 108.173.

Dehydration of Dimethylcyclopropylcarbinol (22).—Dimethylcyclopropylcarbinol (3.00 g, 0.034 mol) was added neat to **2** (9.50 g, 0.040 mol) in a 50-ml round-bottom flask connected to the thermolysis apparatus at ambient temperature under a stream of dry nitrogen. After 10 min an exothermic reaction ensued, the reaction mixture became homogeneous, and a clear, colorless liquid distilled into the cold trap. Glc and nmr analysis of the distillate (1.20 g, 66%) showed one component which was identified as 2-cyclopropylpropene (**23**): nmr ($CDCl_3$) δ 4.67 (m, 2 H), 1.64 (d, 3 H), 1.10 (complex t, 1 H), 0.56 (m, 4 H), identical with that of an authentic sample.[10]

Dehydration of 3,4-Epoxy-2-methylbutan-2-ol (24).—3,4-Epoxy-2-methylbutan-2-ol[17] (3.00 g, 0.029 mol) was added neat to **2** (9.50 g, 0.040 mol) in a 50-ml round-bottom flask connected to the thermolysis apparatus at ambient temperature under a stream of dry nitrogen. The reaction mixture was warmed to 55° for several minutes while a rapid distillation of a clear, colorless liquid into the cold trap occurred. Glc analysis of the distillate (1.41 g, 69%) showed one component which was subsequently identified as 3,4-epoxy-2-methylbut-1-ene (**25**): nmr ($CDCl_3$) δ 5.17 (m, 1 H, J = 1 Hz), 3.35 (m, 1 H, J = 3 Hz), 2.75 (complex m, 2 H, J = 3 Hz), 1.63 (d, 3 H, J = 2 Hz), identical with that previously reported;[18] exact mass determination: theoretical 84.119, found, 84.120.

Dehydration of 4-Hexen-3-ol (27).—4-Hexen-3-ol (4.38 g, 0.044 mol) was added to **2** (10.70 g, 0.045 mol) in 25 ml of triglyme in a 50-ml round-bottom flask connected to the thermolysis apparatus at ambient temperature under a stream of dry nitrogen. The temperature was raised to 75° and a clear, colorless liquid distilled into the cold trap. Glc and nmr analysis of the distillate (2.62 g, 73%) showed one component which was identified as 2,4-hexadiene (**28**) when compared to an authentic sample.

In another example, **27** (3.00 g, 0.030 mol) in 10 ml of tetrahydrofuran was added dropwise to a solution of **2** (7.50 g, 0.032 mol) and 20 ml of tetrahydrofuran in a 50-ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atmosphere of dry nitrogen. After the addition was complete (20 min) the reaction mixture was treated with sodium hydride (0.72 g, 0.030 mol, prepared from 1.27 g of sodium hydride–mineral oil dispersion by several washings with dry hexane) and maintained at ambient temperature until hydrogen evolution had ceased. The solvent was removed under reduced pressure to afford a white solid which was heated to 80° for 30 min. Water (10 ml) was added and the reaction was extracted three times with 10-ml portions of ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to give a pale yellow oil (2.28 g, 94%) which glc showed to be one component, and was subsequently identified as methyl *N*-2-hex-3-enylcarbamate (**29**): ir ($CHCl_3$) 3440 (NH), 2960, 2900, 1720 (OCON), and 1675 cm^{-1} (C=C); nmr ($CDCl_3$) δ 5.55 (complex m, 2 H), 4.10 (broad s, 1 H), 3.60 (s, 3 H), 2.00 (complex m, 1 H), 1.65 (m, 2 H), 1.05 (m, 6 H); exact mass determination—theoretical 157.215; found 157.217.

Anal. Calcd for $C_8H_{15}NO_2$: C, 61.15; H, 9.55; N, 8.92. Found: C, 60.92; H, 9.50; N, 8.75.

(17) G. B. Payne, *J. Org. Chem.*, **27**, 3819 (1962).

(18) M. N. Sheng and J. G. Zajacek, *ibid.*, **35**, 1839 (1970).

Methyl N-Hexylcarbamate (31).—1-Hexanol (3.00 g, 0.029 mol) was added neat to **2** (7.40 g, 0.031 mol) in a 50-ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atmosphere of dry nitrogen. After a mild exothermic reaction the resultant viscous yellow oil was heated to 95° for 30 min. Water (10 ml) was added and the reaction mixture was extracted three times with 10-ml portions of ether. The ether layer was separated, dried over anhydrous sodium sulfate, and evaporated to yield 4.25 g (91%) of a colorless oil which was identified as methyl *N*-hexylcarbamate (**31**) by nmr and ir spectral comparison with an authentic sample.

In another example, 1-hexanol (1.96 g, 0.019 mol) was added neat to **2** (5.00 g, 0.021 mol) at ambient temperature under an atmosphere of nitrogen. After the mild exothermic reaction had ceased, the reaction mixture was dissolved in 20 ml of benzene and rapidly washed with a cold aqueous solution of 2% hydrochloric acid. The benzene layer was separated, dried over anhydrous sodium sulfate, and evaporated to give a viscous oil: ir ($CHCl_3$) 3325 (NH), 3000, 1740 (C=O), 1330, and 1160 cm^{-1} (SO_2N); nmr ($CDCl_3$) δ 8.15 (broad s, 1 H), 4.30 (t, 2 H), 3.70 (s, 3 H), 1.25 (m, 8 H), 0.90 (t, 3 H).

When placed in the thermolysis apparatus and subjected to a temperature of 150°, the oil gave a clear, colorless distillate which on glc analysis and comparison with an authentic mixture showed two components, 1-hexene (50%) and 2-hexene (50%). The total yield of olefinic products was 1.14 g (70%).

Methyl N-Benzylcarbamate.—Benzyl alcohol (2.16 g, 0.020 mol) was added neat to **2** (5.95 g, 0.025 mol) in a 50-ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atmosphere of dry nitrogen. The resulting exothermic reaction produced a homogeneous reaction mixture. Reducing the pressure to 0.55 Torr and raising the temperature to 115° caused distillation of a pale yellow liquid (2.64 g, 80%) which was identified as methyl-*N*-benzylcarbamate by ir spectral comparison with an authentic sample.

Dehydration of 2,2-Dimethylpropan-1-ol.—2,2-Dimethylpropan-1-ol (1.76 g, 0.020 mol) in 10 ml of benzene was added dropwise to a solution of **2** (5.95 g, 0.025 mol) and 20 ml of benzene in a 50-ml round-bottom flask fitted with a reflux condenser at ambient temperature under an atmosphere of dry nitrogen. The benzene was removed under reduced pressure and the residue was dissolved in 25 ml of tetrahydrofuran. The solution was treated with sodium hydride (0.53 g, 0.022 mol, prepared from 0.93 g of sodium hydride–mineral oil dispersion by several washings with dry hexane) and maintained at ambient temperature until hydrogen evolution had ceased. The tetrahydrofuran was evaporated to yield a white solid, which was thermolyzed at 110° for 30 min. A clear, colorless liquid distilled (1.17 g, 84%) which was identified as 2-methyl-2-butene (**35**) by nmr spectral and glc comparison with an authentic sample.

Beckmann Rearrangement of *syn*-Benzaldehyde Oxime.—*syn*-Benzaldehyde oxime (2.42 g, 0.020 mol) was added to **2** (5.00 g, 0.021 mol) in a 50-ml round-bottom flask fitted with a reflux condenser at ambient temperture under an atmosphere of dry nitrogen. After an exothermic reaction, the resulting viscous oil was heated to 90° for 30 min, cooled, dissolved in 20 ml of benzene, washed once with 10 ml of a saturated aqueous sodium chloride solution, dried over anhydrous sodium sulfate, and evaporated to yield 1.36 g (75%) of formanilide, mp 45–46°, undepressed upon admixture with an authentic sample.

Registry No.—**2**, 29684-56-8; **4**, 36917-28-9; **5**, 36912-48-8; **6**, 36912-49-9; **7**, 3947-92-0; **10**, 75-85-4; **13**, 5457-42-1; **14**, 36917-30-3; **15**, 464-07-3; **19**, 3212-16-6; **21**, 497-35-8; **26**, 930-39-2; **27**, 4663-22-3; **28**, 19482-44-1; **29**, 7437-61-8; **31**, 4798-58-7; **33**, 36914-89-3; **35**, 22139-32-8; 3,3-dimethyl-2-butyl *N*-carbomethoxysulfamate sodium salt, 36914-91-7; carbomethoxysulfamoyl chloride, 36914-92-8; 1,2-diphenylethanol, 614-29-9; bicyclo[2.2.2]octan-2-ol, 24848-12-2; 2,2-dimethylpropen-1-ol *syn*-benzaldehyde oxime, 75-84-3.

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