1-*p*-Chlorophenyl-3-propylurea (6).—A mixture of 1.00 g (7.8 mmoles) of propylcarbamoyl azide[4] and 1.55 g (7.8 mmoles) of sodium *p*-chlorobenzenesulfinate was heated for 1.5 hr in a 120° oil bath. The mixture was diluted with water, made strongly basic with 1 *N* sodium hydroxide, and filtered. The filtrate was acidified with 6 *N* hydrochloric acid, and the mixture was extracted with chloroform. The chloroform layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure to a yellow oil. Crystallization from ethanol gave 0.16 g (7% yield) of colorless crystals, mp 125–127° (lit.[11] mp 127–129°). The infrared spectrum was identical with that of an authentic sample.

N-Butylcarbamoyl-S-methyl-S-*p*-tolylsulfoximine (9). **A.**—A solution of 6.8 g (0.04 mole) of S-methyl-S-*p*-tolylsulfoximine[8] and 8.0 g (0.08 mole) of butyl isocyanate in 40 ml of glyme was heated under reflux for 2 hr. The solution was concentrated to a viscous, yellow liquid, which was twice crystallized from ether to provide 4.6 g (43% yield) of colorless prisms, mp 64–67°. Another recrystallization gave the analytical sample, mp 66–68°.

Anal. Calcd for $C_{13}H_{20}N_2O_2S$: C, 58.19; H, 7.51; N, 10.44; S, 11.93. Found: C, 58.41; H, 7.26; N, 10.24; S, 11.92.

The infrared spectrum (KBr disk) exhibits bands at 2.83 (NH), 6.15 (C=O), and 8.2, 8.7, and 9.1 μ (O=S=N).

B.—A mixture of 0.71 g (5.0 mmoles) of butylcarbamoyl azide[4] and 0.77 g (5.0 mmoles) of methyl *p*-tolylsulfoxide[7] was heated for 24 hr in a 135° oil bath; a gentle evolution of gas occurred. The resultant brown oil was chromatographed on 50 g of silica gel. The fraction eluted with a 4:1 chloroform–methanol mixture contained a yellow oil, which upon crystallization from ether provided 0.10 g (8% yield) of colorless prisms, mp 63–64°. The infrared spectrum was identical with that of the sample prepared in method A above.

S-*p*-Chlorophenyl-S-methyl-N-propylcarbamoylsulfoximine (10). **A.**—A solution of 12.7 g (0.07 mole) of S-*p*-chlorophenyl-S-methylsulfoximine [bp 134–136° (0.4 mm), prepared by the method of Misani, Fair, and Reiner[8]] and 11.9 g (0.14 mole) of propyl isocyanate in 100 ml of glyme was heated under reflux for 1 hr. The solution was concentrated to a solid, which upon recrystallization from ethyl acetate gave 5.5 g (29% yield) of colorless crystals, mp 99–102°. Recrystallization provided colorless prisms, mp 109–111°.

Anal. Calcd for $C_{11}H_{15}ClN_2O_2S$: C, 48.09; H, 5.46; Cl, 12.93; N, 10.20; S, 11.66. Found: C, 48.45; H, 5.54; Cl, 13.13; N, 10.06; S, 11.77.

The infrared spectrum (KBr disk) exhibits bands at 2.97 (NH), 6.10 (C=O), and 8.2, 8.8, and 9.2 μ (O=S=N). The nmr spectrum ($CDCl_3$) shows doublets at τ 2.07 and 2.48 (2 H each, J = 8 cps, phenyl), singlets at 4.68 (1 H, NH, broad) and 6.68 (3 H, SCH_3), a quartet at 6.88 (2 H, J = 6 cps, NCH_2), a multiplet at 8.53 (2 H, CCH_2C), and a triplet at 9.12 (3 H, J = 7 cps, CCH_3).

B.—A solution of 0.87 g (5.0 mmoles) of *p*-chlorophenyl methyl sulfoxide[7] and 0.65 g (5.0 mmoles) of propylcarbamoyl azide[4] was heated for 12 hr in a 115° oil bath. The resultant brown oil was chromatographed on 50 g of silica gel. The fraction eluted with a 49:1 benzene–methanol mixture contained an oily solid, which upon recrystallization from ethyl acetate gave 0.12 g (12% yield) of colorless crystals, mp 107–108°. The infrared spectrum was identical with that of the sample prepared by method A, above.

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Elimination Reactions of *endo*-2-Norbornyl Brosylate

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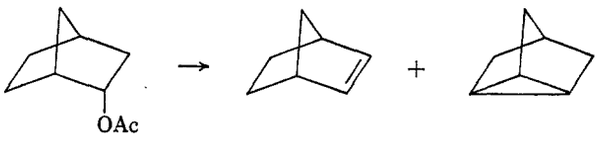
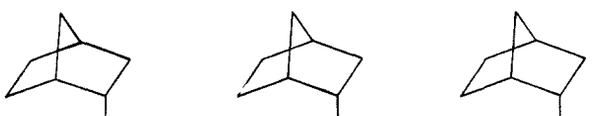
In the course of another investigation, it was necessary to convert *endo*-2-norborneol-2,3,3-d_3 or its derivative to 2,3-dideuterionorbornene without skeletal rearrangement; yet there are only a few reports in the literature[2,3] of elimination of substituents in the *endo*-2 position in the bicyclo[2.2.1]heptane series. Thus a study of such elimination reactions was undertaken.

When *endo*-2-norbornyl acetate (1) was pyrolyzed[4] at 600–615°, the major olefin product was not norbornene (2) but nortricyclene (3) in a ratio of 7:93 as



1 2 3

determined by vpc analysis. Pyrolysis[5] of methyl *endo*-2-norbornyl sulfite (4) at 250° afforded 2 and 3 in the ratio 16:84. It is interesting to note that subjection of *endo*-2-dimethylaminonorbornane (5) to either the Hofmann or Cope elimination conditions led only to the formation of norbornene (2).[3]



4 5 6

Treatment of *endo*-2-norbornyl brosylate (6) with various bases gave varying results (Table I). The bulkiest tertiary alkoxide yielded the least amount of nortricyclene (3). Under solvolytic conditions[6] (nitrobenzene) the ratio of 2 to 3 was 24:76, a ratio which is nearly the same as the equilibrium ratio using a silica–alumina catalyst at the reflux temperature.[7] Under more forcing conditions in which the *endo*-brosylate was heated with sodium iodide in acetone at 110° in a sealed tube,[8] the resulting ratio of 2 to 3

TABLE I

ELIMINATION REACTIONS OF *endo*-2-NORBORNYL BROSYLATE (6)[a]

		Composition ratio[b]	
Reaction	Solvent	2	3
1	*t*-Hexanol[c]	94	6
2	*t*-Hexanol[c,d]	92	8
3	*t*-Butyl alcohol[c]	62	38
4	α-Terpineol[c]	54	46
5	2-Octanol[c]	39	61
6	Nitrobenzene	24	76
7	*s*-Collidine	22	78
8	Acetone[e]	19	81
9	Quinoline	12	88

[a] All reactions except 8 were swept with nitrogen to collect the olefins in a Dry Ice–isopropyl alcohol bath. All reactions were run at 100–120° for 3 hr, except 8 which was run at 110° in a sealed tube for 24 hr. [b] Determined by vpc analysis using a 10% diisodecyl phthalate (8 ft × 0.25 in.) column at 45°. [c] The potassium salt was formed *in situ*. [d] Some *p*-cymene was added. [e] Sodium iodide was added.

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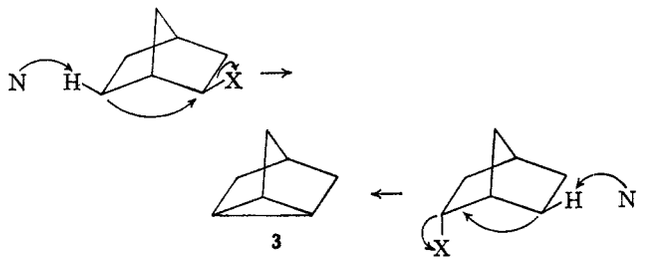
was 19:81; dehydrobrosylation in *s*-collidine and quinoline resulted in a 22:78 and a 12:88 ratio, respectively. Low yields (5–15%) of olefinic product were obtained using the *endo*-brosylate and *t*-hexoxide, a method reported[9] to give 53–59% yields with the *exo*-brosylate. However, the poor yield was not unexpected in light of the fact that the *exo*-dimethylaminonorbornane provided yields of 65–77% while the *endo* epimer **5** afforded yields of 2–4%.[3]

The elimination of a substituent in the *exo* position results in the formation of nortricyclene with smaller amounts of norbornene. Formation of **5** can be easily rationalized by the nucleophilic attack on the *exo* proton



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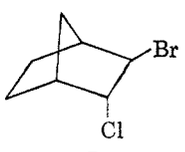
attached to C-6. However, the formation of **3** from the isomer is not readily understood since consideration of electronic and stereochemical factors should make such attack unfavorable.

Reagents which add to the norbornene double bond under a variety of conditions without undergoing skeletal rearrangement do so to afford the *exo–cis* product (see for example, oxymercuration,[10] hydroboration,[11] deuteration,[12,13] hydrocarboxylation,[14] nitrosylation,[15] and diimidization[16]). The preference for *exo–cis* elimination in *exo*-2-substituted norbornanes has been demonstrated[17] from the fact that 2-chloro- and 2-bromonorbornene are obtained from the reaction of *exo*-2-bromo-3-*endo*-chloronorbornane (**7**) and *exo*-2-chloro-3-*endo*-bromonorbornane (**8**), respectively, with alkoxide. The formation of norbornene (**2**) from either



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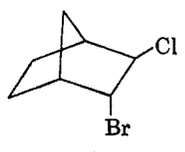

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an *exo* or *endo* leaving group is readily apparent; however, the *endo–cis* elimination is a much slower and a less favorable process.

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Experimental Section

General Procedure.—To 50 ml of the alcohol employed was added 1.0 g of potassium metal. After solution occurred 3.31 g (0.01 mole) of *endo*-2-norbornyl brosylate, mp 59–60° (lit.[18] mp 60.0–61.7°), was added and the system was heated at 100–120° for 3 hr while being swept with nitrogen. The trap cooled in Dry Ice–isopropyl alcohol was analyzed by vpc for the products (see Table I). Reactions in solvents such as nitrobenzene, quinoline, and *s*-collidine were carried out in an analogous manner except that no potassium was added.

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Alkyl-1,3,4-oxadiazoles

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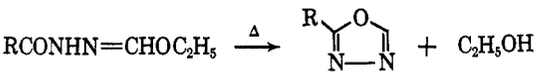
Although 2,5-diaryl- and alkylaryl-1,3,4-oxadiazoles have been known for a long time, the first monosubstituted 1,3,4-oxadiazoles were reported in 1955 by two independent laboratories.[2] Since 1955 other workers[3] have extended this reaction.

This paper describes unreported monoalkyl-1,3,4-oxadiazoles, 2,5-dialkyl-1,3,4-oxadiazoles, and details related to the preparation of unsubstituted 1,3,4-oxadiazole.[4] The monosubstituted 1,3,4-oxadiazoles listed in Table I were prepared by heating 1-acyl-2-ethoxymethylenehydrazines (Table II) that were made from alkylcarboxylic acid hydrazides and triethyl orthoformate. Reaction of alkylcarboxylic acid hydrazides,



and triethyl orthoacetate furnished the 2-alkyl-5-methyl-1,3,4-oxadiazoles (see Table I). The nmr data for these compounds are included in Table I.

It was found during the study of the reaction of triethyl orthoformate and carboxylic acid hydrazides that the ethoxymethylene intermediate, RCONHN=$CHOC_2H_5$, and the carboxylic acid hydrazide reacted further to form the bis compound, RCONHN=CHNHNHCOR.[3b,5] The reaction of the bis compound and triethyl orthoformate also gave the 1,3,4-oxadiazole system. These reactions are operative for both the alkyl- and arylcarboxylic acid series.

The above reactions are envisioned in terms of reversible equations similar to those proposed by Roberts and DeWolfe[6] for aryl amines and triethyl orthoformate and confirmed by us.[7]

The condensation products formed by reaction of formic acid hydrazide and triethyl orthoformate were

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