On the Formation of Alcohols in the "Aprotic," Alkaline Decomposition of Certain Aldehyde Tosylhydrazones[1,2]

JAMES W. WILT, CHARLES A. SCHNEIDER, HENRY F. DABEK, JR., JOHN F. KRAEMER, AND WILLIAM J. WAGNER

Department of Chemistry, Loyola University, Chicago, Illinois 60626

Received November 5, 1965

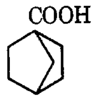
The tosylhydrazones of norbornane-1-carboxaldehyde, bicyclo[2.2.2]octane-1-carboxaldehyde, and nortricyclene-1-carboxaldehyde undergo a novel reaction to yield *alcohols* when subjected to the "aprotic" Bamford–Stevens reaction (alkaline decomposition of the tosylhydrazone in N-methylpyrrolidone at 180°). The alcohol yields are variable but reach *ca.* 45%. Other products commonly found in such reactions are also formed, such as sulfur compounds and, in one case, an N-tosylated hydrazone. No evidence for any hydrocarbon or sulfone products was obtained. A mechanism for alcohol formation is presented and discussed, the main feature of which is the unusual cleavage of *p*-toluenesulfinate esters to alcohols by the action of N-methylpyrrolidone. An argument is presented that this variation from the normal course of the aprotic Bamford–Stevens reaction is caused by the inability of the carbenes derived from these tosylhydrazones to undergo the usual intramolecular processes of hydride shifts, skeletal rearrangement and/or insertion. Such carbenes have been termed "constrained" carbenes.

There has appeared lately evidence that the alkaline decomposition of tosylhydrazones in "aprotic" solvents is a sensitive reaction.[3] Unless careful attention is paid to several reaction variables, the originally postulated[4] carbenic reaction pathway apparently changes to (or becomes mixed with) a cationic one. This variation has been blamed for a discrepancy reported in the literature concerning the products from such reactions.[5]

We report here some results that bear on this point, in that a study originally intended to be of carbenes has turned out rather to one of the corresponding carbonium ions, partly because of the reaction conditions chosen. The data substantiate the above idea of mechanistic switchover, but more than this, the chemistry described is of interest in other ways as well.

Results and Discussion

Literature methods were used for the synthesis of the acids **1**–**3**.[6–8] Conversion of these acids to the acid chlorides was followed by their reduction to the aldehydes using the acylaziridide method.[9] The tosylhydrazones **4**–**6** were then prepared in routine fashion. Because two of the carbenes from these tosylhydrazones, namely **7** and **8**, appeared to us to be incapable for structural reasons of undergoing any of the known[4] intramolecular processes of hydride shifts, skeletal rearrangement or insertion, just what would they do was a tempting question. The third case, that of **9**, afforded the possibility that it might cleave to 4-propargylcyclopentene, similarly to other cleavages of α-cyclopropylcarbenes reported.[4c,10] But otherwise for it, too, the normal intramolecular stabilization processes seemed unlikely.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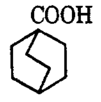
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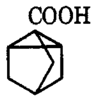
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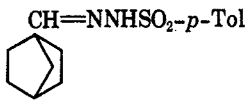
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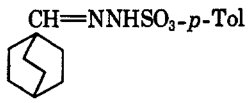
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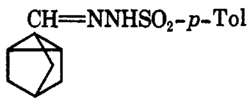
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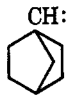
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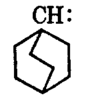
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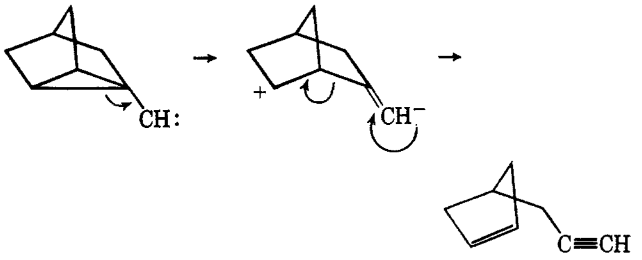

In the hope of preparing these carbenes, the tosylhydrazones **4**–**6** were decomposed in purified N-methylpyrrolidone solvent (NMP) at 180°, using sodium methoxide, according to some earlier directions of Friedman and Shechter.[4c,11] As the reactions were performed under "aprotic" conditions,[12] it was sur-

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[1] For a preliminary report of some of this work, *cf.* J. W. Wilt and C. A. Schneider, *Chem. Ind.* (London), 865 (1963).

[2] Taken in part from the dissertation of C. A. S., Loyola University, 1964, and the M.S. theses of H. F. D., Jr., and J. F. K., Loyola University, 1965.

[3] J. A. Smith, H. Shechter, J. Bayless, and L. Friedman, *J. Am. Chem. Soc.*, **87**, 659 (1965).

[4] (a) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959); (b) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); (c) *ibid.*, **82**, 1002 (1960); (d) *ibid.*, **83**, 3159 (1961).

[5] *Cf.* H. M. Frey and I. D. R. Stevens, *Proc. Chem. Soc.*, 144 (1964).

[6] W. R. Boehme, *J. Am. Chem. Soc.*, **81**, 2762 (1959).

[7] C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

[8] H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959).

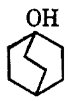
[9] H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **83**, 2016, 4549 (1961).

[10] (a) S. J. Cristol and J. K. Harrington, *J. Org. Chem.*, **28**, 1413 (1963); (b) D. M. Lemal and A. J. Fry, *ibid.*, **29**, 1673 (1964).

[11] It is now clear that the sparse detail given in the several short descriptions of carbene formation from tosylhydrazones can be misleading and that a more definitive literature is needed.

[12] Obviously this is a relative term. It is interesting to note that Powell and Whiting[4a] mention specifically that "apparently –NH– groups are ineffective in this sense"; *i.e.*, as proton donors. It is just this group that is responsible for the chemistry reported in this paper. There can exist a spectrum of "aprotic" character, of course, and intermediate diazo compounds (see text) can respond to different extents to various proton donors present in the reaction medium. This point has been mentioned by W. Kirmse in "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 48.

prising to find that *alcohols* were the major organic products. Furthermore, the alcohol products were present before the reactions were worked up and they were mixtures of rearranged as well as original structures. Thus, from the reaction of **4** there resulted the rearranged alcohol, bicyclo[2.2.2]octanol-1 (**10**) and norbornyl-1-carbinol (**11**) in the ratio of 5–7:1. From **5** there was formed a mixture of the rearranged bicyclo[3.2.2]nonanol-1 (**12**) and bicyclo[2.2.2]octyl-1-carbinol (**13**) in the ratio of 8:1. Reaction of **6** led to 6-hydroxynorcamphene (**14**) and nortricyclyl-1-carbinol (**15**) in the ratio of 1–2:1. Other products typical of tosylhydrazone decompositions were obtained also, though no consistent pattern of product formation other than alcohols emerged. From **4**, particularly upon longer reaction times, formation of *p*-tolyl *p*-toluenethiosulfonate (**16**) and *p*-tolyl disulfide (**17**) was observed. Though the matter was not investigated completely, such products were also probably formed from reactions of **5** and **6**. These are disproportionation products from the *p*-toluenesulfinate moiety of the tosylhydrazones and are not of great interest to the matter at hand.[13,14]



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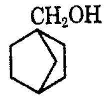

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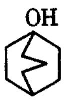

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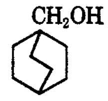

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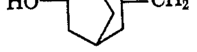

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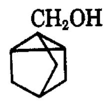

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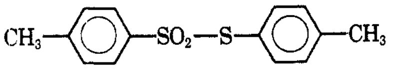

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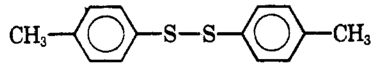

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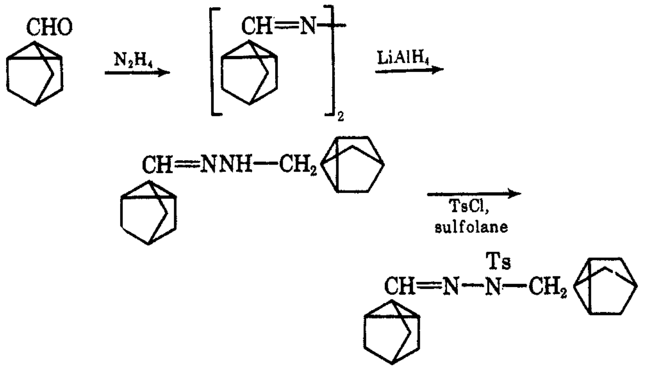
During the course of this work it was found that the methylene group of a carbinyl *p*-toluenesulfinate ester, *i.e.*, $-CH_2-O-SO-p$-tolyl, had its hydrogens magnetically nonequivalent in its nmr spectrum.[15] This observation led to uncovering these most significant and heretofore unreported intermediates in these reactions. The AB pattern of such esters (J = 10–12 cps) is readily observable and, in fact, such a pattern was seen (though it was weak) in the nmr spectrum of the unprocessed reaction material from **4** after a 5-min heating period under the above reaction conditions. After 15 min the pattern was gone. Comparison with a known sample proved that the signal in question arose from norbornyl-1-carbinyl *p*-toluenesulfinate (**18**). The signal was weak because from the alcohol products it was known that mostly bicyclo[2.2.2]octyl structures predominated in the reaction material. These of course would show no such nmr pattern. An extensive investigation of the infrared spectra of sulfinic esters then showed that even though the nmr AB pattern from **18** was weak, the characteristic infrared absorptions for sulfinic esters were strong in the reaction material from **4** (and also **5** and **6**) indicating the presence of another such ester, but one without a carbinyl methylene. This strengthened the belief that 1-bicyclo[2.2.2]octyl *p*-toluenesulfinate (**24**) was present in the reaction material from **4**. It seemed clear, then, that in all cases the two bicyclic alcohols formed as products from these tosylhydrazones were preceded in the reaction by their *p*-toluenesulfinate esters. That such was indeed the case was made quite likely by later experiments described below.

One product other than alcohols and their sulfinic ester precursors was found from **6**, namely N-(nortricyclyl-1-carbinyl)nortricyclene-1-carboxaldehyde tosylhydrazone (**19**). This unusual compound was synthesized as shown. This is the method of Lemal and Fry[10b] who obtained a similar product in their work. Such compounds were also obtained by Nozaki and coworkers[14] and have been extensively studied by Dornow and Bartsch,[16] who showed their formation from diazoalkanes and aldehyde tosylhydrazones. All the other products (**10–18**) were identified through com-



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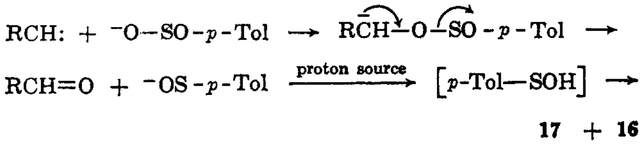
[13] It is of interest that **17** accelerates the conversion of *p*-toluenesulfinic acid to **16** [J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 2384 (1962)] though different conditions were used than those employed here. Perhaps a similar reaction occurred here, nonetheless. See also ref 14.

[14] *p*-Tolyl disulfide (**17**, 10%) has been detected in the alkaline, aprotic decomposition of benzaldehyde tosylhydrazone by H. Nozaki, R. Noyori, and K. Sisido, *Tetrahedron*, **20**, 1125 (1964). They ascribe its formation to an "obscure" oxidation–reduction reaction of *p*-toluenesulfinate ion with phenylcarbene, a process that yields benzaldehyde as well. The formation of **17** and aldehydes (again normally in low yields) in our work also probably involves such a reaction (see Table I), at least partially. We suggest the following course for this oxidation–reduction process. For the dispropor-



$$RCH\!: + {}^{-}O{-}SO\text{-}p\text{-}Tol \longrightarrow RCH{-}O{-}SO\text{-}p\text{-}Tol \longrightarrow RCH{=}O + {}^{-}OS\text{-}p\text{-}Tol \xrightarrow{\text{proton source}} [p\text{-}Tol{-}SOH] \longrightarrow \mathbf{17} + \mathbf{16}$$

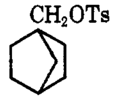
tionation of *p*-toluenesulfonic acid to **16** and **17**, see R. Connor, "Organic Chemistry," Vol. 1, H. Gilman, Ed., 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1943, p 920 ff. The apparently slight extent of this process might be ascribed to the preferential attack of sulfinate ion on a carbene at its *sulfur* atom rather than its *oxygen* atom, as above. See later in the text of the paper above for a discussion of this matter.

[15] J. W. Wilt and W. J. Wagner, *Chem. Ind.* (London), 1389 (1964). Others had noted this earlier; J. S. Waugh and F. A. Cotton, *J. Phys. Chem.*, **65**, 562 (1961); M. Öki and H. Iwamura, *Bull. Chem. Soc. Japan*, **35**, 1428 (1962). We thank Professors Cotton and Iwamura for drawing our attention to their work.

[16] A. Dornow and W. Bartsch, *Ann.*, **602**, 23 (1957). This germane paper has been largely overlooked by workers in the carbene field. It is interesting that these workers found that trimethylacetaldehyde tosylhydrazone did not undergo this reaction, presumably because of other rapid reactions. In fact, all the cases where N-tosylated products have been reported have involved carbenes that could not undergo the usual[4] processes readily.

parison with authentic samples available from independent synthesis or elsewhere.

The detection of these products and precursors led to the suspicion that either a carbene intermediate or a diazo compound was being protonated, even under these "aprotic" conditions, to cationic intermediates which then gave the observed products. Another line of evidence for cationic precursors was the similarity of these products to those formed in the hydrolysis of the tosylates **20**[17] and **21**[7] and the slightly alkaline hydrolysis of **22**.[8] All these *ionic* hydrolyses led to the same skeletal changes as did the tosylhydrazone reactions.



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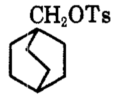

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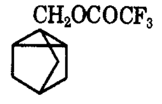

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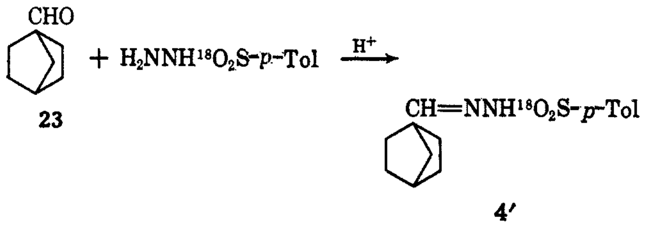
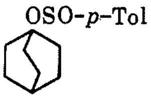
A provisional mechanism (see later) then dictated further experiments. Tosylhydrazone **4′** with ^{18}O in its sulfonyl group was prepared as shown. Its ^{18}O enrichment was 0.5% (above normal). This substance was treated identically as had been **4**, and the alcohol mixture (**10** + **11**) produced was isolated and analyzed by mass spectrometry. The ^{18}O enrichment in the alcohols was 0.4–0.6%, indicating that the oxygen atom of the alcohols originally was the sulfonyl oxygen of the tosylhydrazone. This finding, together with the spectral identification of sulfinic esters mentioned above, necessitated a study of the sulfinic esters themselves. These were prepared by reaction of the appropriate alcohol with *p*-toluenesulfinyl chloride in pyridine, affording **24** from **10** and **18** from **11**. *Each sulfinic ester was found to be converted smoothly to its alcohol with no detectable rearrangement upon being heated in NMP, with or without added sodium methoxide.*[18] Also, a mixture of **18** (1 part) and **24** (5.2 parts), when heated at 180° in NMP solvent in the absence of sodium methoxide, gave alcohols **10** and **11** in 72% yield and in the same proportion (*via* infrared analysis) as that obtained from the alkaline decomposition of **4**. With this dependence of alcohol formation on the NMP solvent being uncovered, some preliminary work was then done on the alkaline decomposition of **4** under "safer" aprotic conditions, namely, in hexadecane and diethyl Carbitol solvents. Two kinds of experiments were done, in air and under nitrogen. In air in the former solvent **4** yielded norbornane-1-carboxaldehyde (**23**) in 57% yield, together with sulfur-containing by-products. Under nitrogen, no volatile products were noted and the residue again showed "sulfone" infrared absorption indicating perhaps the presence of **16**. No aldehyde was formed here and in neither instance were alcohols produced. In reactions of **4** in hexadecane, precipitation of sodium *p*-toluenesulfinate was very rapid. This could account for the absence of any aldehyde formed by a carbene–sulfinate oxidation–reduction process.[14] The formation of **23** in air is unusual, but it could perhaps represent an alternative oxidation of carbene **7** by oxygen. Aryl carbenes (?) have been reported to be so oxidized,[19] but a question exists as to the spin states of such species. Other "carbenes" have also been reported to give carbonyl products with oxygen.[20] In any case, this oxidation pathway is certainly not common and, if true in this case, it reflects the unusual character of the carbene **7**. It should be mentioned, however, that the amount of aldehyde detected in these reactions did not always drop when a nitrogen atmosphere was employed (see Table I). Somewhat similar results were obtained when diethyl Carbitol was used. However, admixture of NMP in a molar amount equivalent to that of **4** again led to alcohol products.





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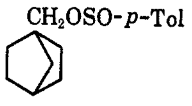

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TABLE I

ALCOHOL FORMATION FROM TOSYLHYDRAZONES

Tosylhydrazone[a]	Yield of alcohol, %[b]	Rearrangement ratio[c]	Other products (by number)[d]
4	44	5–7:1	23[e]
5	40	8:1	"X"[f]
6	42	1–2:1	19[g,h]

[a] N-Methylpyrrolidone solvent at 180° in the presence of sodium methoxide. For details, see Experimental Section. [b] Maximum yield obtained in the many reactions performed. The yields are based on gc analysis. Other methods usually gave lower results due to various interferences. [c] From infrared and nmr analysis; *e.g.*, from **4**, 5–7 parts of **10** to 1 part of **11**. [d] Compounds **16** and **17** were detected in most cases and occasionally isolated from **4**. No yield data was obtained. [e] Very dependent on conditions. In hexadecane in air the yield was 53–57%; under the given conditions, *ca.* 5–10%. [f] In one run this solid, mp 144–145°, was isolated in *ca.* 10% yield. See text. [g] Yield variable (16–50%). [h] Nortricyclene-1-carboxaldehyde was also isolated (*ca.* 4%). This yield was ncreased (by gc analysis) when the reaction of **6** was effected under nitrogen.

A question next arose as to whether a carbene could be otherwise detected from the decomposition of **4**. Advantage was taken in this regard of a recent demonstration that pyridine N-oxide is an efficient carbene trap.[21] Tosylhydrazone **4** was decomposed in pyridine N-oxide with sodium methoxide under conditions previously employed. The aldehyde **23** and pyridine were isolated in good yield, the latter as the picrate, indicating the probable presence of carbene **7**, as shown.

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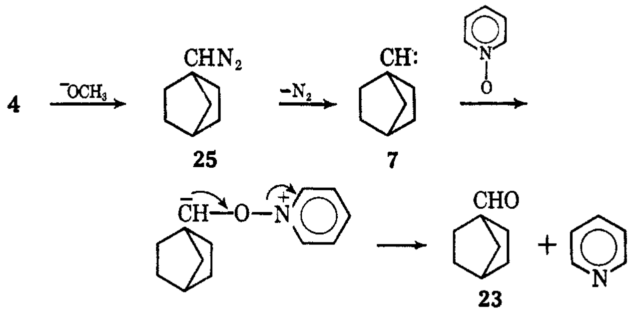
(17) C. A. Schneider, Dissertation, Loyola University, 1964. The ratio of **10**:**11** was 9:1 in acetone–water–collidine at 113°.

(18) The alcohol yields in this cleavage are high (70–85%) and the reaction appears to be general in solvents with the structural feature -CH-CO-Z:. The reaction is under investigation and the results will be published separately.

(19) For a review, *cf.* W. Kirmse, ref 12, Chapters 5 and 10.

(20) H. W. Wanzlick, *Angew. Chem., Intern., Ed. Engl.*, **1**, 75 (1962); R. W. Hoffmann and H. Häuser, *Tetrahedron Letters*, 197 (1964).

(21) E. E. Schweizer and G. J. O'Neill, *J. Org. Chem.*, **28**, 2460 (1963).



Though the presence of **7** in this reaction seems probable, it would undoubtedly be preceded by the diazo compound **25**, and either could be protonated to a carbonium ion precursor of the observed sulfinic esters. So the source of the protonation was next sought.

Reaction of **4** with a large excess of sodium methoxide in NMP at 180° failed to give alcohol products. Also, preformed sodium salt of **4** (from reaction of **4** with sodium hydride) in NMP at 180° produced no alcohol. Such findings implicated the tosylhydrazone itself as the proton source.[22] The free tosylhydrazone was by itself, however, not sufficient for reaction, as thermolysis of **4** in NMP at 180° gave no alcohol products. The conclusion was then drawn that there was involved a partial conversion of **4** to its anion in the presence of methoxide salt and that both **4** and its anion were necessary for alcohol formation in NMP solvent. Sodium methoxide is not immediately soluble in NMP and, as the reaction components were mixed and then swirled briefly in the reaction vessel before being placed in the 180° bath, incomplete conversion of **4** to its anion seems possible. In accord with this interpretation was the observation that if, instead of the slight excess of sodium methoxide commonly employed (0.12 mole excess), there was used a limited amount of base (0.1 equiv), alcohols again were formed and in about the same yield from **4**.

Lastly, a decomposition of **4** in the definitely protic solvent ethylene glycol using its sodium alkoxide as the base proceeded in an entirely different fashion, as would be expected. While the product was not fully characterized, its infrared spectrum was in agreement with 1-bicyclo[2.2.2]octyl 2-hydroxyethyl ether (**26**), a solvent-captured cationic product. Such products are known under these conditions.[4a]

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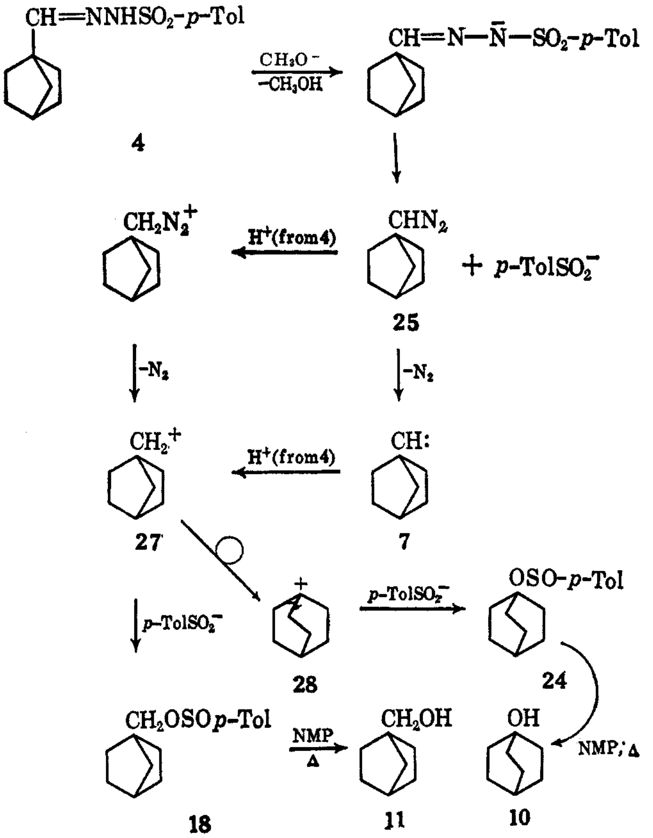
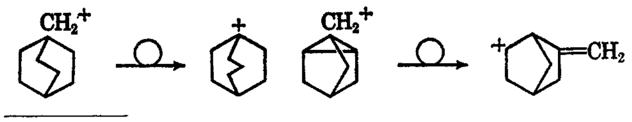
While the route to the alcohol products seemed established by all the above, mass balances for the reactions were not achieved and the complete description of these reactions is not available. Table I shows the yields of alcohol obtained, together with other information.

The data gathered in all these reactions can be largely interpreted in terms of a consistent mechanism for alcohol formation, shown in Scheme I for tosylhydrazone **4**. The intermediacy of diazo compounds such as **25** in such reactions is well supported[4] and whether the carbene **7** or diazo compound **25** is protonated by the parent tosylhydrazone, the resulting ion **27** is believed to rearrange quickly but not completely to the 1-bicyclo[2.2.2]octyl cation (**28**). Attack by *p*-toluenesulfinate ion on each of these ions then leads to the sulfinate esters (**18**, **24**) which are the first detectable intermediates in NMP solvent. From the ratio of alcohols produced from **4**, assuming equal rates of combination of the two cations with the sulfinate ion, the 1-norbornylcarbinyl cation (**27**) rearranges from five to seven times faster than it undergoes attack itself. The proposed mechanism explains the several points: why complete conversion of **4** to its anion precludes alcohol formation (the proton donor is absent); why aldehyde and pyridine result when pyridine N-oxide is solvent (the carbene **7** is trapped); why NMP solvent affords alcohols, while diethyl Carbitol and hexadecane solvents do not (sulfinic esters are cleaved by NMP but not by the latter two solvents, though it has not been shown that sulfinic esters are even formed in these other solvents); why a slight amount of methoxide suffices for alcohol formation (the carbene or diazo compound acts as the "base" toward **4** after initial reaction); and why ^{18}O is quantitatively transferred from the ^{18}O sulfonyl function to the alcohols (oxygen–sulfur cleavage in the sulfinic ester–NMP reaction[23]).

SCHEME I



The mechanism given needs only the obvious structural changes when the other tosylhydrazones **5** and **6** are considered. The rearrangements shown must also



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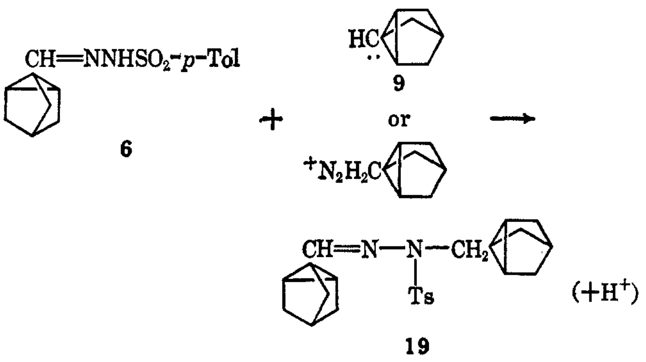
(22) *Cf.* ref 12. The possibility of protonation by parent tosylhydrazone has also been recently mentioned by others.[3]

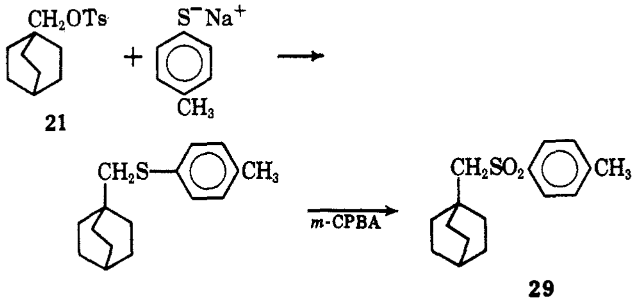
(23) This is inferred from the lack of rearrangement. Studies with ^{18}O and optically active sulfinates are underway. *Cf.* ref 18.

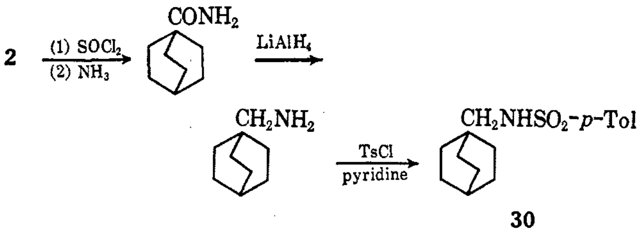
occur rapidly (but not equally so) relative to sulfinate ion capture under the conditions employed because of the extensive rearrangement found (see Table I). Two differences mark the reaction of tosylhydrazone **6**. First, alcohol **15** is easily converted *thermally* into its isomer **14**[24] and the exact proportions of each need not reflect the true kinetic composition of the product. A control experiment established, however, that pure **15** was not changed appreciably under the reaction conditions employed, so that the rearrangement ratio of Table I is probably close to the kinetic composition. Secondly, from **6** (although why only from **6** is not understood) the aforementioned product **19** was isolated. From literature data[10b,14,16] this compound probably arises from tosylhydrazone attack upon either the carbene **9** (insertion) or the diazonium compound (displacement followed by deprotonation) as shown. As all these species are present in the mechanism given, the formation of this product can be rationalized.



No cleavage of **9** to 4-propargylcyclopentene was observed, even though any volatile products from the reaction (at 180°) were sought through passage of the evolved nitrogen through cold traps. It is of interest that neither was fragmentation of 1-phenylcyclopropylcarbene (another α-cyclopropylcarbene) observed under these reaction conditions.[25] In the present case there may be an explanation for the absence of cleavage in that the nortricycyl system apparently has distinctly less overlap of its three-membered ring with a carbinyl carbon atom[26] and, therefore, the initial ring opening could be slower than in the other cases known[4c,10] and give the carbene **9** ample time for protonation and sulfinate capture.

Notable for their absence from these reactions were *sulfones*. On one occasion from **5** a very small amount of a crystalline substance (mp 144–145°) was obtained. This experiment inadvertently departed from the general procedure, so this product was considered somewhat of an artifact. It was not recovered **5**, but its nmr spectrum indicated (*inter alia*) the presence of one bicyclo[2.2.2]octyl ring and one *p*-tolyl function. Sulfonyl absorption seemed present from the infrared spectrum. Though the structure of this compound was not established even after lengthy research, an early belief based upon the spectra mentioned that it was bicyclo[2.2.2]octyl-1-carbinyl *p*-tolyl sulfone (**29**) was disproved by an alternative synthesis of **29**. After some failures by other methods, displacement by *p*-thiocresoxide ion on the tosylate shown,[27] followed by oxidation of the sulfide to the sulfone (mp 128.5–129°) with *m*-chloroperbenzoic acid succeeded. Spectral comparison confirmed that this sulfone was not the unknown. Speculation then arose that a compound akin to **19** had also formed from **5**. As cleavage of such N-tosylated hydrazones to *sulfonamides* is another reaction recorded in the encyclopedic paper of Dornow and Bartsch[16,28] there was the possibility that the unknown was N-bicyclo[2.2.2]octyl-1-carbinyl *p*-toluenesulfonamide (**30**). Synthetic **30** (mp 156.5–157.5°) was obtained by the scheme shown; however, it too, was not the unknown.





Even though mass balances were not achieved, it is interesting that sulfones were not detected. Such compounds are usually crystalline solids of easy isolation and it is doubtful that a significant amount of them would be missed over the many reactions performed on all three tosylhydrazones. The nondescript residues from these reactions invariably showed "sulfone" infrared absorption, but little credence was put in this, because one had tosylhydrazone, sulfinate, and thiosulfonate compounds possible as well. Indeed, the isolation of thiosulfonate **16** led us to suspect that these "sulfone" absorptions were caused by it primarily. Lemal and Fry[10b] and Nozaki, *et al.*,[14] first reported sulfone products under aprotic conditions of the Bamford–Stevens reaction.[29] The yields reported by both groups were always variable and Lemal asserts that the yield of sulfone (in this case 3-nortricyclyl *p*-tolyl sulfone) was best (*ca.* 50%) in a rigorously aprotic medium. Nozaki's sulfone (benzyl *p*-tolyl sulfone) was also formed in a number of aprotic solvents (11% in diethyl Carbitol, 2–4% in others, none isolated in water solvent). Nonetheless, Lemal suggests that the

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[24] H. Hart and R. A. Martin [*J. Am. Chem. Soc.*, **82**, 6362 (1960)] found the acetate of **15** to isomerize readily to that of **14** during gas chromatography.

[25] J. W. Wilt, J. M. Kosturik, and R. C. Orlowski, *J. Org. Chem.*, **30**, 1052 (1965).

[26] Literature reference in footnote 24.

[27] H. D. Holtz and L. M. Stock, *J. Am. Chem. Soc.*, **87**, 2404 (1965).

[28] Apropros to their work, a recent report by A. P. Krapcho and J. Diamanti [*Chem. Ind.* (London), 1847 (1965)] indicated azine formation from cyclododecanone tosylhydrazone in an aprotic Bamford–Stevens reaction. They did not mention the earlier work of Dornow and Bartsch[16] who, in fact, also reported aprotic azine formation.

[29] A. J. Fry, [*J. Am. Chem. Soc.*, **87**, 1816 (1965)] has recently reported another example of sulfone formation under aprotic conditions.

sulfone observed by Bamford and Stevens[30] probably represented a cation–sulfinate ion-capture process. In view of the findings from the reactions reported here, where cation–sulfinate ion-capture processes abound but where no sulfone was detected, we would suggest that the sulfone of Bamford and Stevens was indeed so formed, *but in a secondary fashion* from benzyl *p*-toluenesulfinate by thermal rearrangement. The known resistance of this ester to such rearrangement[31] could explain the low yield obtained (14%). Mechanistically one might expect an ambident nucleophile like *p*-toluenesulfinate ion to react with a carbonium ion at its oxygen atom, but with a neutral carbene at its sulfur atom. In the former case the driving force for reaction is the neutralization of charge and this is best achieved through attack by the most electron-rich site (oxygen) of the ambident sulfinate ion. The latter case is different because charge is dispersed, not destroyed, and such dispersal is easier in the α-sulfone carbanion that would result from attack by sulfur.[32] Thus the increased yield of Lemal's sulfone under more aprotic conditions (more carbene, less carbonium ion) could be explained. The absence of sulfone products in our case could then be explained as well. Sulfinate esters rather than sulfones were formed because carbonium ion substrates for sulfinate ion attack were involved, instead of carbenes. The sulfinic esters so formed were then simply cleaved by NMP to alcohols *faster* than they could rearrange to sulfones. In support of this are two points: first, the sulfinic ester cleavage reaction is quite fast;[33] and secondly, the synthesized sulfinic ester **18** showed no isomerization to a sulfone upon being heated in hexadecane (see Experimental Section).

In conclusion, we feel it is worthwhile to point out that the original belief in the unusual character of carbenes **7–9** seemed warranted even though a study of these species in themselves was not achieved. Others[4e] have used NMP solvent and methoxide base on tosylhydrazones and obtained carbene reactions, so the conditions were not themselves solely responsible for the chemistry found here. Either the diazo compounds formed in the present study were unusually different from others (unlikely) or the carbenes from them were. We feel the latter is true and that the carbenes **7–9** are truly *constrained from intramolecular stabilization processes* and consequently are longer lived enough to undergo protonation and sulfinate ion capture with the eventual formation of alcohols. One might say that this work became a study of cationic intermediates more because of their carbene precursors than because of the conditions used, though certainly these did contribute.

Experimental Section

All melting points and boiling points are uncorrected for stem exposure. The former were taken routinely on a calibrated Fisher-Johns block but sealed capillary melting points were taken in an oil bath. Spectra were determined on Perkin-Elmer Model 21, Beckman IR-5A (infrared), Cary Model 14 (ultraviolet), and Varian A-60 (nmr) instruments. Infrared values are given in microns after the symbol λ. Not all absorptions for each compound are listed. The ultraviolet values are given in millimicrons after the symbol λ_{max}. The nmr spectra were generally taken on carbon tetrachloride solutions and all employed TMS as an internal standard. Unless the range is given, positions of multiplets are their centers. All integrations were in agreement with the assigned hydrogens. The nmr spectra of alcohols **12**, **13**, and their mixture were determined by Nuclear Magnetic Resonance Specialties, Inc., New Kensington, Pa. Gas chromatographic work was done on a Wilkens A-90-P Aerograph employing a helium gas flow. Signals were disk-integrated on a Sargent Model SR-GC recorder (1 mv). Retention times (t_r) are to the maxima of peaks. All microanalyses were done by Micro-Tech Laboratories, Skokie, Ill., unless otherwise stated. All critical solvents were redistilled to gc homogeneity. Many of the procedures were repeated a number of times with slight variations. The descriptions given are considered typical.

Norbornane-1-, bicyclo[2.2.2]octane-1-, and 1-nortricyclenecarboxylic acids (**1–3**, respectively) were prepared by literature methods: **1**[6] (melting point of various samples varied from 102 to 111°, lit.[6] mp 111–112°), **2**[7] (mp 134–137°, lit.[7] mp 140–142°), and **3**[8] (mp 118–119°, lit.[8] mp 119–120°).

Norbornane-1-, bicyclo[2.2.2]octane-1-, and 1-nortricyclenecarboxaldehydes were prepared by first converting the above acids into their acid chlorides with thionyl chloride in the usual fashion; acid chloride from acid: **1** (80%, bp 59–60° at 2 mm, lit.[34] 47–47.5° at 2.1 mm), **2** (86%, bp 61–63° at 0.5 mm), and **3** (97%, bp 68–70° at 3 mm). Hydrolysis of each acid chloride regenerated the pure parent acid, showing that no rearrangement occurred during its formation. The acid chlorides were used immediately in the next step, *viz.*, their conversion to N-acylaziridides through reaction with ethylenimine and triethylamine in ether.[9] Usually the N-acylaziridides were not isolated but were reduced *in situ* to the aldehyde with lithium aluminum hydride, as reported.[9] The aldehydes so formed were purified *via* their sodium bisulfite addition compounds. **Norbornane-1-carboxaldehyde** (**23**, 50%, mp 45–50°, λ^{KBr} 3.65, 5.78 (–CHO)) was a very volatile, colorless solid with a pleasant odor. It underwent air oxidation very readily. This volatility and autoxidation caused problems in its microanalysis.

Anal. Calcd for $C_8H_{12}O$: C, 77.40; H, 9.74. Found: C, 76.89; H, 9.72.

The burnt orange 2,4-dinitrophenylhydrazone derivative was recrystallized from ethanol–water and then benzene–hexane mixtures, mp 191–193° dec.

Anal. Calcd for $C_{14}H_{16}N_4O_4$: N, 18.47. Found: N, 18.23.

Bicyclo[2.2.2]octane-1-carboxaldehyde (83%, λ^{CCl_4} 3.74, 5.76, 5.87 (–CHO)) was similar in appearance to its norbornane analog, but even more volatile. It was therefore best characterized as its yellow 2,4-dinitrophenylhydrazone, mp 223–224° dec (from ethanol).

Anal. Calcd for $C_{16}H_{18}N_4O_4$: C, 56.59; H, 5.70. Found: C, 57.15; H, 6.02.

Nortricyclene-1-carboxaldehyde (31%, bp 45–55° at 1.5 mm, $n^{21.5}{}_D$ 1.4883, $d^{21.5}{}_4$ 1.048, λ^{neat} 3.63, 5.88 (–CHO), lit.[8] bp 83–87° at 14 mm) was also characterized as its red 2,4-dinitrophenylhydrazone, mp 224.5–225.5° (from ethanol–ethyl acetate, lit.[8] mp 218–219.5°). The aldehyde exhibited nortricyclene absorption[8] at 11.45 and 12.66 μ.

Norbornane-1-, bicyclo[2.2.2]octane-1-, and nortricyclene-1-carboxaldehyde tosylhydrazones (**4–6**, respectively) were prepared as described for **4**. Norbornane-1-carboxaldehyde (**23**, 8.05 g, 65 mmoles) was dissolved in methanol (125 ml), and glacial acetic acid (12 drops) and *p*-toluenesulfonylhydrazine (12.1 g, 65 mmoles) were added. The mixture was refluxed for 1 hr and allowed to stand overnight. The solution was well chilled and the crystalline precipitate collected. Concentration of the mother liquor afforded more material. The white, crystalline derivative was recrystallized from aqueous ethanol (14.4 g, 49.3 mmoles, 78%, mp 139–141°).

Anal. Calcd for $C_{15}H_{20}N_2O_2S$: C, 61.61; H, 6.90. Found: C, 61.50; H, 7.02.

The two analogs following were prepared as above, but with ethanol solvent: tosylhydrazone **5**, 77%, mp 142–143° (*Anal.* Calcd for $C_{16}H_{22}N_2O_2S$: C, 62.17; H, 7.23. Found: C, 62.58;

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[30] W. R. Bamford and T. S. Stevens [*J. Chem. Soc.*, 4735 (1952)] obtained benzyl *p*-tolyl sulfone from the alkaline decomposition of benzaldehyde tosylhydrazone under protic conditions (in ethylene glycol).

[31] A. H. Wragg, J. S. McFadyen, and T. S. Stevens, *ibid.*, 3603 (1958).

[32] For a discussion of these matters, see E. S. Gould, "Mechanism and Structure in Organic Chemistry," H. Holt and Co., New York, N. Y., 1959, p 296 ff; R. Gompper, *Angew. Chem.*, **76**, 412 (1964).

[33] J. W. Wilt and R. Stein, unpublished work.

[34] F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).

H, 7.42.); and tosylhydrazone **6**: 71.5%; mp 131–132°; $\lambda_{max}^{CH_3CN}$ 218 (18,500), 255 (7930), 273 (2920) (*Anal.* Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.25. Found: C, 61.96; H, 6.48.). The various spectra of these tosylhydrazones were in accord with their structures.

Preparation of Reference Alcohols. Bicyclo[2.2.2]octanol-1 (**10**) was prepared by the sequence of Grob, *et al.*[7] (in sealed capillary mp 210–215°, lit.[7] mp 211–215°): nmr (δ), 1.33 s (O*H*), 1.6 s (all ring protons);[35] λ^{CS_2} 2.77, 2.98 (O–H), 9.11, 9.22 (C–O). **Norbornyl-1-carbinol** (**11**) was synthesized according to Bixler and Niemann[37] by the reduction of **1** with lithium aluminum hydride (78.5%, mp 52–56°, lit[37] mp 59.0–60.2°): nmr (δ), 1.07–1.67 m (ring CH_2 groups) with 1.71 s (O*H*), 2.23 m (bridgehead *H*), 3.73 s (CH_2OH); λ^{CS_2} 2.71, 2.91 (O–H), 9.52 sh, 9.65, 9.78 (C–O). **Bicyclo(3.2.2)nonanol-1** (**12**) resulted from the hydrolysis of bicyclo[2.2.2]octyl-1-carbinyl tosylate (**21**, *vide infra*) in dioxane–water at 140° as reported[7] (48%, mp 193–197° in sealed capillary, lit.[7] mp 199–201°): nmr (δ), 1.33–2.00 m (all ring protons),[38] 2.4 s (O*H*); λ^{CCl_4} 2.71, 2.90 (O–H), λ^{CS_2} 9.19, 9.56 (C–O). **Bicyclo(2.2.2)octyl-1-carbinol** (**13**) was the product of reduction of acid **2** with lithium aluminum hydride[7] (86%, waxy solid, bp 68–69° at 0.5 mm, lit.[7] bp 98–99° at 10 mm); nmr (δ), 1.08–1.83 m (all ring protons),[36] 3.07 (CH_2O*H*, these two singlets are separated by about 1.5 cps); λ^{CCl_4} 2.71, 2.87 (O–H), λ^{CS_2} 9.66 (C–O). **6-Hydroxynorcamphene** (**14**, *endo* or *exo* unknown) was prepared as a colorless oil by the isomerization of **15** (*vide infra*).[24] Passage of **15** through a column of silicone rubber (SE-30, 20% on firebrick, 5 ft × 0.25 in.) at 130–200° with a helium flow of 60 ml/min led to the formation of **14**, collected as the peak following that of **15**: nmr (δ), 1.1–2.83 m (ring CH_2 groups), 3.0–3.4 m (bridgehead protons), 3.7, 3.8 m (<C*H*-OH, *endo* + *exo*?), 4.63 m, 4.9 m (<C=CH_2). An unsaturated aldehyde contaminant was present to a small extent (δ 9.65, -C*H*O, as well as other small signals at δ 5.2 and 6.0, -C*H*=C<). The contaminant was not investigated further; λ^{neat} 2.95 (O–H), 3.2, 5.96, 6.00, 11.35 (>C=CH_2), 9.39 (C–O). The aldehyde contaminant appeared weakly at 5.77 (C=O). The acetate of **14**[24] has been reported to have λ 5.97, 6.02, and 11.30, while **14** itself (probably)[24] has λ 11.30, bp 55–58° at 0.8 mm. **Nortricyclyl-1-carbinol** (**15**) was prepared as reported[8] by the reduction of **3** with lithium aluminum hydride (80%, bp 65° at 1.1 mm, n^{19}D 1.4948, d^{24}_4 1.03, lit.[8] bp 50–54° at 0.8 mm, n^{25}D 1.4941, phenylurethan mp 115–116°, lit.[8] 117.5–118°): nmr (δ), 1.03 (cyclopropyl protons of nortricyclyl ring), 1.3 (ring CH_2 groups), 2.0 (bridgehead *H*), 3.3 (-O*H*), 3.7 (CH_2OH). The signals were all apparent singlets, except δ 1.3 (a thin multiplet) and δ 2.0 (a broad envelope); λ^{neat} 2.95 (O–H), 3.21, 11.72, 12.69 (nortricyclyl), 9.79 (C–O). The alcohol could be successfully chromatographed on a Carbowax 20M column (one peak) below 155° (column temperature) with injector temperatures below 165°. Above these temperatures on this column, or above 130° on SE-30 columns, isomerization to **14** occurred. Curiously, **15** did not isomerize to **14** to any appreciable extent (infrared analysis) when heated in NMP at 180° for 15 min.

Analysis of Alcohol Mixtures.—The alcohols formed in the decompositions of the tosylhydrazones were identified and analyzed instrumentally. Alcohol pairs **10–11** and **12–13** were not resolved during gas chromatographic attempts on various columns, although a slight separation of the latter pair was achieved on a Carbowax 2000 column at 190° [t_r (retention time): **12**, 6.8 min; **13**, 7.7 min; 60 cc/min helium flow rate]. Alcohols **14** and **15** were resolvable; *e.g.*, on a Carbowax 20M column (5 ft × 0.25 in.) at 138° (60 cc/min helium flow rate) **14** had t_r 46.7 min, **15** had t_r 41.3 min. Integration of these peaks coupled with comparison with calibration curves for each pure alcohol then gave the yield and composition of this alcohol pair. Infrared analysis of the alcohol pairs was performed by mixing known amounts of the pure alcohols and comparing the infrared spectra of these mixtures to that of the gc collected alcohol mixture from the tosylhydrazone decompositions (*vide infra*). Particular attention was paid to the C–O stretch absorption region.[39] Thus, *e.g.*, comparison of the 9.1–9.2-μ region *vs.* the 9.5–9.8-μ region afforded a measure of the **10**:**11** alcohol ratio (3° C–O *vs.* 1° C–O). Use was also made of the characteristic >C=CH_2 absorptions in **14** in analyzing the **14–15** mixture. Nmr analysis of the alcohol mixtures used the characteristic -CH_2OH resonance of the carbinols (**11**, **13**, **15**) to calculate the mole ratios of components, assuming binary mixtures (and no evidence was found for third components in the alcohols from these reactions). Thus, the resonances at δ 3.73, 3.07, and 3.7 for **11**, **13**, and **15**, respectively, allowed a particularly satisfying method of identification and (*via* integration calculations) composition analysis. This nmr method was the best used, but the other methods agreed fairly well with it.

N-(Nortricyclyl-1-carbinyl)nortricyclene-1-carboxaldehyde Tosylhydrazone (**19**).—The procedures followed closely those of Lemal and Fry,[10b] so detailed descriptions will be omitted. **Nortricyclene-1-carboxaldehyde azine** was prepared from the aldehyde (18 mmoles) and anhydrous hydrazine (9 mmoles) in ethanol (absolute, 4.2 ml) and acetic acid (1 drop) by refluxing the mixture under nitrogen for 2 hr. The precipitated azine was recrystallized from ethanol (colorless solid, 58%; mp 143–143.5°); nmr (δ), 1.4–1.6 m (all ring protons except C-4 H), 2.05 m (C-4 protons), 7.7 s (-C*H*=N–); λ^{KBr} 3.29 (cyclopropyl C–H of nortricyclyl ring), 6.15 (>C=N–), 11.5, 12.55 (nortricyclyl).

Anal.[40] Calcd for $C_{16}H_{20}N_2$: C, 79.95; H, 8.39. Found: C, 79.82; H, 8.24.

The azine (1 g) was converted into **N-(nortricyclyl-1-carbinyl)-nortricyclene-1-carboxaldehyde hydrazone** by reduction with lithium aluminum hydride in ether under nitrogen. The white semisolid product was not characterized due to the reported[10b] ease of air oxidation of a similar compound, but rather it was treated with *p*-toluenesulfonyl chloride (4.2 mmoles) and triethylamine (4.2 mmoles) in freshly distilled sulfolane (17.5 ml) under nitrogen. The homogeneous mixture was heated at 140–150° for 3 hr. The material was then flooded with water and extracted with four 25-ml portions of ether. This solution was washed, dried, and evaporated. The solid product, **19**, was recrystallized from pentane–ether mixtures or ethanol to give white plates (0.76 g, 46%, mp 126–127°): nmr (δ), 0.9–1.7 m (a well-resolved multiplet, all nortricyclyl ring protons except C-4 H), 1.93 m, 2.1 m (the nortricyclyl C-4 protons are at slightly different values), 2.4 s (Ar–CH_3), 3.35 s (–CH_2–N<), 7.1–7.75 (aromatic *H*), 7.8 s (-C*H*=N–); $\lambda^{KB.r}$ 6.24 (>C=N–), 7.44, 7.51, 8.48 (br), 8.63 (all are due to $-SO_2-$), 11.45, 12.78 (nortricyclyl), 14.1; $\lambda_{max}^{CH_3CN}$ 220 (20,900), 257 (9880), 275 (2820).

Anal. Calcd for $C_{23}H_{28}N_2O_2S$: C, 69.66; H, 7.12. Found: C, 69.61, 69.93;[40] H, 7.28, 7.18.[40] This material was identical in every way with the **19** isolated from decomposition of **6**.

Preparation of Miscellaneous Substances Involved in This Study. ***p*-Tolyl *p*-toluenethiosulfonate** (**16**) was prepared by the oxidation of ***p*-tolyl disulfide** (**17**, Aldrich Chemical Co., Inc.) with hydrogen peroxide in acetic acid (mp 74–75°, lit.[41] mp 78°, λ^{Nujol} 7.52, 8.75 ($-SO_2-$)). **Norbornyl-1-carbinyl *p*-toluenesulfinate** (**18**) and **1-bicyclo[2.2.2]octyl *p*-toluenesulfinate** (**24**) were prepared as follows. The appropriate alcohol (20 mmoles) and a slight excess of *p*-toluenesulfinyl chloride[42] were mixed in dry ether (20 ml) containing pyridine (20 mmoles) in a vessel cooled in a hydrochloric acid–ice mixture. The reaction mixtures were refrigerated for 12 hr and then processed by washing the ether phase with water, sodium bicarbonate solution, dilute hydrochloric acid, and again with water to neutrality. Removal of the ether left the esters (90–100%) which were clarified with Norit or by passage through a column of alumina. Attempted distillation of these esters in a Hickman still at less than 0.1 mm decomposed them. The esters were characterized spectrally and were fairly pure, though slight contamination with the parent alcohol was evident at times. **18** (n^{15}D 1.5477, d^{23}_4 1.145) was a mobile, pale yellow oil; nmr (δ), 1.1–1.5 m (ring CH_2 groups), 2.1–2.3 m (bridgehead *H*), 2.38 s (Ar–CH_3), 3.38, 3.99 (–CH_2–OSO–*p*-tolyl, these are the midpoints of the lines 1–4 of an AB

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[35] The chemical shifts of the ring hydrogens in some (but not all[36]) bicyclo[2.2.2]octyl compounds appear to be the same, giving rise to a singlet about 3 cps wide at half-height. See also ref 27.

[36] In this bicyclo[2.2.2]octyl derivative, contrary to others,[35] the ring hydrogens differ enough to broaden the signal a good deal and to allow multiplet splittings to be seen.

[37] R. L. Bixler and C. Niemann, *J. Org. Chem.*, **23**, 742 (1958).

[38] The bicyclo[3.2.2]nonyl ring hydrogens are not like those of the bicyclo[2.2.2]octyl case,[35] in that a multiplet results. This multiplet, however, is not as resolved (at 60 Mc) as in other cyclic molecules and actually appears as a broad, sharply tapering signal.

[39] *Cf.* L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, pp 94–96.

[40] Analyses by Galbraith Laboratories, Inc., Knoxville, Tenn.

[41] O. Hinsberg, *Ber.*, **41**, 2836 (1908).

[42] F. Kurzer, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 937.

pattern[15] of which J_{AB} = 10 cps), 7.13–7.53 (aromatic *H*); λ^{neat} 8.77, 10.58, 13.32. The latter two absorptions are broader than the first. Absorptions in these areas have been found in all the alkyl *p*-toluenesulfinic esters studied in this work and are believed to be characteristic for them. The 8.77-μ absorption is fairly constant regardless of the alkyl group while the others vary between 10.2–11.0 and 13.0–13.8 μ; **24** ($n^{21.5}{}_{\text{D}}$ 1.5524, $d^{27}{}_4$ 1.100) was also a pale yellow oil: λ^{neat} 8.76, 10.95, 13.05. **Norbornyl-1-carbinyl tosylate** (**20**) was prepared as described[37] (83%, mp 76–79°, lit.[37] mp 78.9–80°). Its solvolysis in acetone–water–collidine will be described separately.[17] **Bicyclo[2.2.2]octyl-1-carbinyl tosylate** (**21**) was similarly prepared[7] (61%, mp 68–69°, lit.[7] mp 73°). Its conversion to sulfone **29** is described later (*vide infra*). **Bicyclo[2.2.2]octyl-1-carbinyl *p*-tolylsulfone** (**29**). Two methods of synthesis failed. Displacement by sodium *p*-thiocresoxide on tosylate **21** (*vide supra*) in diethyl Carbitol at 170° gave recovered tosylate. In the second method, ***p*-tolyl bicyclo[2.2.2]octane-1-thiolcarboxylate** was prepared by reaction of bicyclo[2.2.2]octane-1-carboxylic acid chloride with *p*-thiocresol at 25° for 3 days in the presence of pyridine. The reaction mixture was poured into water and the precipitated solid was recrystallized from ethanol–water (white crystals, mp 80.5–81°, 83%, λ^{KBr} 5.98 (R*C*O–SR')).

Anal. Calcd for $C_{16}H_{20}OS$: C, 73.80; H, 7.74. Found: C, 74.03; H, 7.69.

A reduction of this thioester to the corresponding sulfide was attempted by the method of Eliel and Daignault[43] employing the addition of lithium aluminum hydride to the ester and boron trifluoride in ether. No sulfide product was detected, the seeming result being complete reduction to alcohol **13**. Sulfone **29** was obtained successfully as follows.[44] Tosylate **21** (1.47 mmoles) was mixed in ethanol (absolute, 10 ml) with sodium *p*-thiocresoxide (made by treating sodium, 5.84 g-atom, with the alcohol, followed by the addition of *p*-thiocresol, 5.84 mmoles). The mixture was sealed in an ampoule and heated at 74° for 6 hr. The cooled ampoule was opened and the contents filtered into 5% aqueous potassium hydroxide. The aqueous solution was thoroughly extracted with ether and the extracts evaporated. The semisolid residue (sulfide) was dissolved in chloroform (10 ml) and added dropwise to *m*-chloroperbenzoic acid (Aldrich Chemical Co., Inc., 85%, 2.94 mmoles) in further chloroform (10 ml) at 0°. After 12 hr the solution was washed thoroughly with sodium carbonate solution (10%) and water, dried, and finally evaporated. Separation of **29** from unchanged **21** (10% of this was recovered) was achieved by chromatography on alumina (benzene–petroleum ether, 2:1), the sulfone eluting last. The chromatography was easily monitored as **21** had $-SO_2-$ absorption at 7.41, 8.41, and 8.55 μ. The sulfone was recrystallized from benzene–petroleum ether (white crystals, 14%, mp 129–129.5°): nmr (δ), 1.63 s (all alicyclic ring protons[35]), 2.42 s (Ar–C*H*$_3$), 2.72 s (–C*H*$_2$SO$_2$–), 7.2–7.8 (aromatic *H*); λ^{KBr} 7.7, 7.76, 8.78 ($-SO_2-$).

Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.02; H, 7.97. Found: C, 68.95; H, 7.97.

N-(Bicyclo[2.2.2]octyl-1-carbinyl)-*p*-toluenesulfonamide (**30**). **Bicyclo[2.2.2]octane-1-carboxamide** was prepared by treating the acid chloride with dry ammonia gas in ether (55%, mp 169–171°, lit.[45] mp 177–178°). Reduction of this amide (4.6 mmoles) was achieved with lithium aluminum hydride (5.3 mmoles) in the usual manner in dry ether. The reaction mixture was decomposed with sodium hydroxide (6 *N*) and the ether phase processed to obtain **bicyclo[2.2.2]octyl-1-carbinylamine** (93%, reacts rapidly with CO_2 in air, mp 80–90° on block, dec without melting up to 200° in a sealed tube, λ^{KBr} 2.9 (N–H), 5.98 (N–H bend)). The amine (1.8 mmoles), tosyl chloride (1.9 mmoles), and pyridine (10 ml) were heated in a test tube atop a steam bath for 1.5 hr and then poured into cold, dilute hydrochloric acid. The precipitated **30** was recrystallized several times from aqueous ethanol (white crystalline solid, about 90%, mp 156.5–157.5°): nmr (δ), 1.0–1.77 m (bicyclic ring protons), 2.42 s (Ar–C*H*$_3$), 2.56 d (–C*H*$_2$–NH–, J_{AX} = 7 cps), 4.57–4.87 m (–N*H*–), 7.2–7.8 (aromatic *H*); λ^{KBr} 3.04 (sharp, N–H), 7.59, 7.62, 8.7 ($-SO_2-$).

Anal. Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90. Found: C, 65.42; H, 7.96.

Decomposition of Tosylhydrazones 4–6 in N-Methylpyrrolidone. —Most of the reactions were performed by premixing dry tosylhydrazone and freshly prepared sodium methoxide and adding freshly distilled N-methylpyrrolidone (a generous gift from the General Aniline and Film Corp.). The scale of the experiments ranged from 0.1 to *ca.* 5 g of tosylhydrazone. The sodium methoxide was normally 1.1–1.2 equiv relative to the tosylhydrazone. The solvent volume was about 15–20 ml/g of tosylhydrazone. The initially light purple colored solutions (which often contained suspended sodium methoxide) were swirled briefly and then immersed in an oil bath held at 180°. Nitrogen was evolved rapidly (3–5 min) and usually in nearly quantitative amount. The evolved nitrogen was collected in an azometer after having been passed through Dry Ice traps to condense any volatile products (of which none was detected in any of the thirty-odd reactions performed). The reactions were held at 180° for 15–30 min, then poured into excess water and extracted with pentane. The pentane extracts were dried and concentrated and processed *via* gc. The gc traces showed only pentane solvent and at times traces of parent aldehyde and incompletely removed N-methylpyrrolidone in addition to the product alcohols under the conditions described above. Thorough washing to remove NMP was important as it had a gc retention time close to those of the alcohols. The alcohols were usually not resolved on various columns (*vide supra*) and were collected as mixtures by successive injections. Their structure and composition analysis has been described earlier. Other details may be found in Table I.

From **4** a mixture of **10** and **11** was obtained as a fragrant white solid (mp 197–201 or 208–210° in a sealed tube depending upon the rate of heating).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.99; H, 11.00.

From **5**, a mixture of **12** and **13** was obtained, again as a crystalline, fragrant solid (mp 160–180° in a sealed tube).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.14; H, 11.63.

From **6** the liquid mixture of **14** and **15** was collected and identified by infrared and nmr methods only (*vide supra*).

All these alcohols were detected also by direct injection of the NMP reaction material into the gas chromatograph, establishing the fact that the processing described above did not of itself produce these products. No significant difference in either yield or composition of alcohol product was noticed. Compound **19** settled out from the pentane solutions containing the products from the decomposition of **6** upon standing overnight. It was collected and recrystallized from ethanol–water, mp 124.5–125°. A mixture melting point and identical infrared spectrum identified it with the authentic material (*vide supra*). Its yield was variable (16–50%), the most consistent results being obtained by differential infrared techniques on the pentane solution using the 8.63 and 14.1-μ absorptions of **19** and comparison with known mixtures. From all the decompositions small amounts of parent aldehyde (usually 1–4% by gc, occasionally as high as 10%) were detected, both during gc analysis at times and through recovery as the 2,4-DNP derivatives (identified by mixture melting point). On evaporating the pentane solutions further, particularly those from longer reaction time decompositions of **4**, it proved possible to isolate small amounts of **16** and **17**. These were identified by mixture melting point determinations and comparison of spectra with knowns. No attempt was made to determine their yield.

The several variations in the above description of these decompositions generally were processed as mentioned. The variations were: *time* (reactions processed after 5 min were compared to those after 15 min); *reagents* (results with about 30 equiv of sodium methoxide down to 0.1 or none at all were compared to those using the normal amount); and *atmosphere* (reactions under nitrogen were compared to those under air; in the former no nitrogen evolution percentage was measured). Certain of the varied studies warrant a bit more description, however. Conversion of **4** to its sodium salt with sodium hydride was followed by a "routine" decomposition as given above. Only a trace of alcohol products was observed. The preparation of **4'** with ^{18}O sulfonyl was achieved through reaction of **23** with *p*-toluenesulfonyl-^{18}O-hydrazine, as mentioned earlier. The latter was prepared as follows. In a vessel cooled in an ice bath, *p*-tolyl disulfide (**17**, 25 g, 0.101 mole) was stirred with water slightly enriched in ^{18}O (Yeda Research and Development Co., Ltd., Rehovoth, Israel, 500 ml) while chlorine gas was rapidly passed in at such a rate that the temperature remained below 10°. After 2 hr, ether (200 ml) was added and the stirring continued

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(43) E. L. Eliel and R. A. Daignault, *J. Org. Chem.*, **29**, 1630 (1964).

(44) We thank Mr. P. Chenier for this preparation.

(45) H. P. Fischer and C. A. Grob, *Helv. Chim. Acta*, **47**, 564 (1964).

for 15 min. The separated etherphase was washed with aqueous solutions of sodium bisulfite and sodium carbonate and then dried. Removal of the ether left crude p-toluenesulfonyl-^{18}O chloride (28.4 g, 74%). It was recrystallized four times from petroleum ether (bp 30–60°) and formed a white crystalline mass (23.5 g, mp 66–67°, lit.[46] mp 69°). The sulfonyl chloride was then converted to p-toluenesulfonyl-^{18}O-hydrazine (86%, mp 107–108°, lit.[47] mp 112°) by reaction with hydrazine (95%) in benzene. The product was recrystallized from ether. Mass spectral analysis of **4′** indicated it contained 0.5% atom excess of ^{18}O. Reaction of **4′** with sodium methoxide in NMP gave **10** and **11** as before. The alcohols were collected during gc analysis and a mass spectral analysis of them gave an ^{18}O atom excess of 0.4 and 0.6% in two trials.

Decomposition of Tosylhydrazone 4 in Other Solvents. (a) Decomposition of **4** (1 g, 3.42 mmoles) in hexadecane (15 ml) at 180° using sodium methoxide (0.2 g, 3.76 mmoles) *under air* for 15 min led to the precipitation of sodium p-toluenesulfinate (positive mercuric chloride test). Gc analysis of the reaction material *directly* indicated aldehyde **23** (53.5–57% over several runs), but *no* alcohols **10** or **11**. Another reaction as above (but on a one-fifth scale) *under nitrogen* again gave sodium p-toluenesulfinate, but *no* volatile products other than solvent were detected by gc analysis of the unprocessed material. (b) Identical experiments on **4** using diethyl Carbitol yielded similar results. An experiment using a mixed solvent of diethyl Carbitol and an amount of NMP equivalent to **4**, however, again yielded alcohols **10** and **11**, though the yield was lowered to 25%. (c) Tosylhydrazone **4** (1 g), sodium methoxide (0.2 g), and pyridine N-oxide (10 g) were held at 180° for 20 min and then poured into excess dilute hydrochloric acid. The acidic solution was thoroughly extracted with petroleum ether and the extracts were dried and concentrated. Treatment with 2,4-DNP reagent afforded the derivative of **23**, which was recrystallized from ethanol, mp 187–188° (*vide supra*, mp 191–193°). The previously mentioned acidic solution was made alkaline (odor of pyridine) and again extracted with petroleum ether. The extracts were combined, dried, and concentrated. Upon the addition of a concentrated ethanolic solution of picric acid, pyridinium picrate formed (mp 145–150°, unchanged upon repeated recrystallizations from ethanol, lit.[48] mp 167°). The infrared spectra of the derivatives were identical with knowns. The yields of the derivatives were high, but not measured. (d) Reaction of **4** (1 g) with sodium ethylene glycolate (1 *N*, 5 ml) at 180° was complete within 2 min with quantitative evolution of nitrogen. The material was poured into water and extracted with petroleum ether. Isolation of the major gc peak material gave a colorless oil, λ^{neat} 2.9 (O–H), 8.99 (>C–O) 9.4 (br, –CH$_2$–O–), which was neither **10** nor **11**. Its spectrum suggests it was **26**, though the compound was not investigated further to prove this.

Cleavage of Sulfinic Esters.—While the complete description of these reactions will be published later,[18,33] one critical experiment may be described. Sulfinic esters **18** (60.4 mg) and **24** (314 mg) were heated *alone* in NMP (about 0.5 ml) for 2 min. The black reaction mixture was transferred quantitatively with acetone to a 10-ml volumetric flask and diluted to the mark with further acetone. Quantitative gc analysis (using peak area *vs.* micromoles calibration curves for each alcohol) indicated a yield of **10** and **11** of 73.8, 70.1, 71.9, and 73.7% (four separate analyses, av 72.4%). The infrared spectrum of the collected alcohols matched that of the alcohol mixture from **4** excellently, leading to the ratio (Table I) of 5.2 parts of **10** to 1 part of **11**. Nmr analysis gave a ratio closer to 7 parts of **10** to 1 part of **11**. Heating ester **18** (400 mg) in hexadecane (5 ml) at 180° for 15 min yielded no detectable sulfone **29** nor p-toluenesulfinic acid (failure of mercuric chloride test on aqueous wash). No alcohol was observed by infrared methods at this time, but later work[33] has shown the alcohol is formed to a slight extent (*ca.* 3% by gc). The failure to observe sulfone formation is in keeping with literature results[49] where only those sulfinic esters capable of yielding more stable carbonium ions by C–O cleavage are rearranged thermally to sulfones.

Acknowledgment.—We are deeply indebted to those who, from no less than five laboratories, provided us with most of the nmr spectra reported here; in particular, to Drs. R. S. Bly, R. K. Bly, S. J. Lapporte, R. C. Miller, C. G. Miller, and R. R. Sauers. The mass spectra were determined and interpreted by S. Meyerson, American Oil Co., Whiting, Ind., to whom we express our appreciation and thanks.

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Heterogeneous Defluorination of Carbon

WAYNE C. SOLOMON, LOUIS A. DEE, AND DONALD W. SCHULTS

Air Force Rocket Propulsion Laboratory, Research and Technology Division, Air Force Systems Command, Edwards, California

Received August 27, 1965

A variety of fluorinated olefins have been found to undergo halogen interchange in the presence of a solid Lewis acid. Cyclic olefins such as perfluorocyclobutene are converted to their perchloro analogs by the action of aluminum chloride with particular ease. This same reaction does not appear to proceed in the homogeneous phase.

During a search for methods of cleavage of the very strong carbon–fluorine bonds, a route which appears to have some generality has been examined. The early literature indicates that dichlorodifluoromethane in benzene evolves hydrogen fluoride upon addition of aluminum chloride.[1] Trichlorofluoromethane forms carbon tetrachloride very rapidly in the presence of aluminum chloride. Aluminum chloride has been shown to produce a variety of fluorochloropropenes when it is treated with hexafluoropropene.[2,3] A Lewis acid such as boron tribromide has been found to replace all of the chlorine or tetrachlorocyclopropene.[4] Although the latter reaction involves cleavage of the carbon–chlorine bond rather than the carbon–fluorine bond, it appears to be related to the preceding examples in a general way.

The present study concerns the reaction of acyclic and cyclic fluorine containing olefins with Lewis acids. We have observed that interconversion of halogen takes place rapidly when cyclic fluorine containing olefins are mixed with either aluminum bromide or aluminum chloride.

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