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Reactions of Tosylhydrazide Derivatives Having Olefinic Groups[1]

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When α,β-unsaturated ketone tosylhydrazones (**5**) were heated in 85% aqueous acetic acid, a smooth decomposition was induced and β-tosylketones (**4**) were obtained in fair yields. Tosylhydrazones, devoid of an olefinic group in the specified position, failed to undergo the present reaction. When allyl halides (**17**) were reacted with the anion of tosylhydrazide in DMSO, substitution occurred on the N-1 of tosylhydrazide, unlike as in the case of the reaction of chlorides with tosylhydrazide in pyridine, which effected the substitution on N-2. On warming in acetic acid, these 1-allyltosylhydrazides (**18**) afforded olefins (**19**) in fair yields, with a complete allylic rearrangement. A concerted cyclic mechanism was proposed for the **5**→**4** and **18**→**19** reactions.

It has been remarked that compounds derived from tosylhydrazide undergo many interesting reactions, and many of these reactions have been used for synthetic purposes.[2] The present paper will deal with two new types of reactions, one with α,β-unsaturated ketone tosylhydrazones, and the other with 1-allyltosylhydrazides.

a) α,β-Unsaturated Ketone Tosylhydrazone System. Since the article of Bamford and Stevens,[3] the base-induced thermal reactions of ketone tosylhydrazones have been extensively studied, but the reactions under acidic conditions have not attracted so much interest. Henry and Moore[4] thermolyzed several ketone tosylhydrazones in acetic acid, but the reaction proceeded in a complicated way and the product was a mixture of several compounds.

In connection with our studies of α,β-unsaturated ketone tosylhydrazones,[5] we carried out the reactions of these tosylhydrazones under acidic conditions. It has previously been established that these hydrazones afford pyrazole derivatives on treatment with alkoxides,[5-7] and conjugated dienes on treatment with alkyllithium.[8]

Henry and Moore[4] obtained β-tosylketone **4a** in a 29% yield by heating benzalacetophenone (**1**) and tosylhydrazide (**2**) in acetic acid. They proposed a mechanism of: (1) the decomposition of **2** into *p*-toluenesulfinic acid (**3**) and diimide, and (2) the 1,4-addition of **3** to benzalacetophenone to afford the product. The mechanism is reasonable because each step, both (1)[9] and (2)[10], is a known reaction. We thermolyzed benzalacetone tosylhydrazone (**5b**) in acetic acid and

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[1] The article has previously been reported in a preliminary form. T. Sato and I. Homma, Abstracts of papers presented at the 21st meeting of the Chemical Society of Japan, Osaka, April, 1968, Vol. III, p. 1814; T. Sato, I. Homma, and S. Nakamura, *Tetrahedron Lett.*, **1969**, 871.

[*1] Present address: Kao Soap Co., Ltd., Tokyo.

[2] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, John Wiley & Sons, New York (1967), p. 1185; *ibid.*, Vol. II, (1969), p. 417.

[3] W. R. Bamford and T. T. Stevens, *J. Chem. Soc.*, **1952**, 4735.

[4] R. A. Henry and D. W. Moore, *J. Org. Chem.*, **32**, 4145 (1967).

[5] T. Sato and S. Watanabe, This Bulletin, **41**, 3017 (1968).

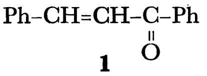
[6] R. K. Bartlett and T. S. Stevens, *J. Chem. Soc., C*, **1967,** 1964.

[7] H. A. Staab and H-A. Kurmeir, *Chem. Ber.*, **101**, 2697 (1968).

[8] W. G. Dauben, M. E. Lorber, N. D. Vietmeyer, R. H. Shapiro, J. H, Duncan, and K. Tomer, *J. Amer. Chem. Soc.*, **90**, 4762 (1968).

[9] R. S. Dewey and E. E. vanTamelen, *ibid.*, **83**, 3729 (1961).

[10] E. P. Kohler and M. Reimer, *Amer. Chem. J.*, **31**, 178 (1903).


$\text{Ph-CH=CH-}\underset{\underset{\text{O}}{\parallel}}{\text{C}}\text{-Ph}$

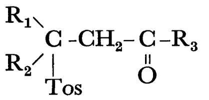
1


$\text{Tos}\overset{1}{\text{N}}\text{H}\overset{2}{\text{N}}\text{H}_2$

2

$p\text{-C}_7\text{H}_7\text{-SO}_2\text{H}$

3


$\text{R}_1\text{R}_2\underset{\text{Tos}}{\text{C}}\text{-CH}_2\text{-}\underset{\underset{\text{O}}{\parallel}}{\text{C}}\text{-R}_3$

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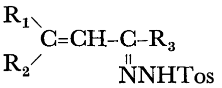
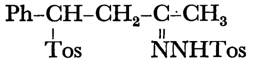

$\text{R}_1\text{R}_2\text{C=CH-}\underset{\underset{\text{NNHTos}}{\parallel}}{\text{C}}\text{-R}_3$

5

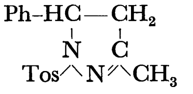
a: $\text{R}_1=\text{R}_3=\text{Ph}$
$\text{R}_2=\text{H}$

b: $\text{R}_1=\text{Ph}$
$\text{R}_2=\text{H}$
$\text{R}_3=\text{CH}_3$

c: $\text{R}_1=\text{R}_2=\text{R}_3=\text{CH}_3$


$\text{Ph-}\underset{\text{Tos}}{\text{CH}}\text{-CH}_2\text{-}\underset{\underset{\text{NNHTos}}{\parallel}}{\text{C}}\text{-CH}_3$

6



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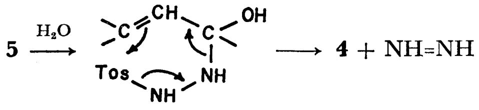
thus obtained Compounds **4b**, **6**, and **7** and the starting tosylhydrazone in 16%, 47% (stoichiometrically), 2.5%, and 5% yields, respectively. The formation of **6** is evidence that *p*-toluenesulfinic acid might intervene in the reaction.

We observed that a smooth decomposition was effected when the thermolysis was carried out in acetic acid *containing* 15% *of water.* The tosylhydrazones **5a**—**5c** afforded *β*-tosylketones **4a**—**4c** in yields of 76%, 68%, and 42%, respectively, no other products being isolated in the pure state. A concerted transfer of electrons in an intermediate **8** was presumed as the probable mechanism for the formation of **4** in view of the following observations. First, when **2** was heated under the present reaction conditions, a quantitative amount of 2-acetyltosylhydrazide (**9**) was obtained and no decomposition into diimide and *p*-toluenesulfinic acid was observed. 2-Acetyltosylhydrazide was a stable compound and was recovered unchanged on refluxing in an acetic acid-water mixture in the presence of benzalacetophenone. Second, when 3-methyl-2-cyclohexenone tosylhydrazone (**10**) was heated under the present reaction conditions, a quantitative amount of **9** was obtained. As 3-methyl-2-cyclohexenone and **3** afforded the *β*-tosylketone **11**, the failure of the **10**→**11** reaction could be ascribed to the incapability for **10** to take the cyclic configuration, as represented in **8**, which might be requisite for the tosyl migration. Acetophenone tosylhydrazone (**12**) also afforded **9** quantitatively under the same conditions. The formation of diimide in the reaction was evident because, when the reaction was carried out in the presence of azobenzene, 27% (on the basis of **5b**) of diacetylbenzidine (**13**) was obtained. It has been established that azobenzene is reduced by diimide to hydrazobenzene,[11] which then affords **13** by the reaction sequence of benzidine rearrangement and acetylation in acetic acid.[12]



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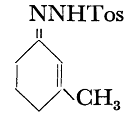
TosNHNHCOCH$_3$

9



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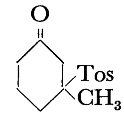

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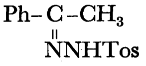
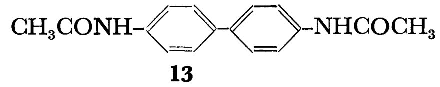
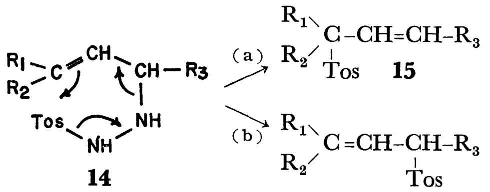

$\text{Ph-}\underset{\underset{\text{NNHTos}}{\parallel}}{\text{C}}\text{-CH}_3$

12



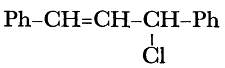
13

As a model for the intermediate **8**, a tosylhydrazide derivative, **14a**, was prepared from chloride **16** and **2** in pyridine. Although **14a** actually afforded **15a** on refluxing in ethanol, it was not possible, because of the symmetrical carbon skeleton of **14a**, to differentiate between the proposed cyclic mechanism (a) and the elimination-recombination mechanism on the same carbon atom (b). As an attempt to synthesize compound **14** with an unsymmetrical carbon skeleton, cinnamyl chloride (**17a**) and **2** were allowed to react under various reaction conditions, but the reaction mostly proceeded with nitrogen elimination, and cinnamyl *p*-tolyl sulfone resulted. In one case, when **17a** was treated with sodium salt of **2** in DMSO, nitrogen-elimination was avoided and a tosylhydrazide derivative was obtained. The product, however, proved not to be the expected **14b**, but an isomer, **18a**, as proved by the following observations. The IR spectrum of the compound showed a sharp band at 3400 cm^{-1} for NH$_2$, and two strong bands, at 1340 and 1150 cm^{-1}, for the tosyl group. The NMR spectrum showed a singlet at δ 3.5 corresponding to two protons for NH$_2$. The structure was further confirmed by deriving it to the benzal derivative **20a** by treatment with benzaldehyde. It is conceivable that the substitution occurred on the N-1 of **2** because the hydrogen on this nitrogen would be the most acidic and would ionize first when treated with sodium hydride. The reaction presented a sharp contrast to that of **2** with chlorides in pyridine, in which case substitution occurred on the more basic N-2, as in the case of **16**→**14a**. Although our attempts to synthesize **14b** were thus unsuccessful, we observed instead that compound **18a** underwent an interesting fragmentation when treated with acetic acid.



a: $\text{R}_1=\text{R}_3=\text{Ph}$
$\text{R}_2=\text{H}$

b: $\text{R}_1=\text{Ph}$
$\text{R}_2=\text{R}_3=\text{H}$


$\text{Ph-CH=CH-}\underset{\text{Cl}}{\text{CH}}\text{-Ph}$

16

b) 1-Allyltosylhydrazide System.[13] When **18a** was heated in acetic acid at 60°C, allylbenzene, **19a**, was unexpectedly obtained in a 66% yield. Allylbenzene was also obtained when **18a** was pyrolyzed at 110°C, but the yield was much lower in this case and

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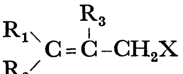
[11] E. E. vanTamelen, R. S. Dewey, and R. J. Timmons, *J. Amer. Chem. Soc.*, **83**, 3725 (1961).

[12] F. Sachs and C. M. Whittaker, *Ber.*, **35**, 1435 (1902).

[13] The authors are indebted to Mr. Shohei Nakamura for his helpful assistance.

the product was contaminated with toluene and other minor unidentified compounds. As an extension of this type of reaction, some allyl halides, **17b**—**17e**, were reacted with **2** by the NaH/DMSO method. The resulting compounds (**18b**—**18e**) were shown to have primary amino group from the IR and NMR spectra and by deriving them to benzalamino derivatives **20b**—**20d**. Compounds **18b**—**18d**, when warmed at 30—60°C in acetic acid, afforded **19b**—**19d** in 55—70% yields.

Two features of the acid fragmentation of the tosylhydrazides are noteworthy: 1. The reaction proceeds so as to isolate double bond from conjugation with the phenyl group or to cause the endocyclic double bond to migrate to the thermodynamically more unfavorable exocyclic double bond. 2. The reaction proceeds with a complete allylic rearrangement, no other double-bond isomers being detected in any product on analysis by gas chromatography and by a study of the NMR spectrum.



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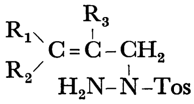

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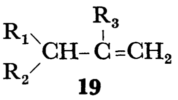

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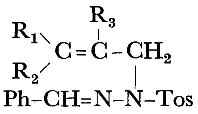
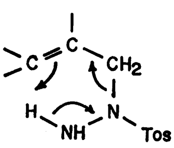


20

a: R_1=Ph, R_2=R_3=H, X=Cl
b: R_1=R_2=Ph, R_3=H, X=Br
c: R_1=R_3=Ph, R_2=H, X=Br
d: R_1, R_3=-$(CH_2)_4$-, R_2=H, X=Cl
e: R_1=R_2=R_3=H, X=Cl

The complete allylic rearrangement in the present reaction can be explained in terms of a concerted fragmentation of 1-allyltosylhydrazide **21**, or of the allyldiimide **22** formed *in situ* from **21**, by the elimination of *p*-toluenesulfinic acid.



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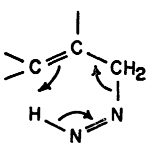
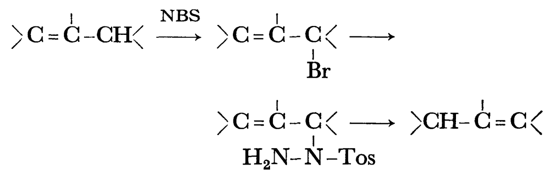


22

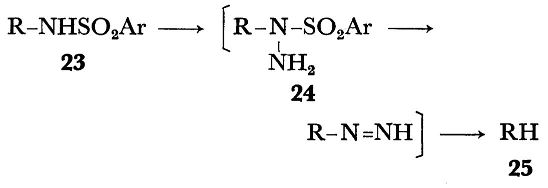
Similar types of double-bond migrations have been reported in the cases of: (1) the reaction of allylamines with difluoroamine,[14] (2) the unusual Wolff-Kishner reduction of α,β-unsaturated carbonyl compounds,[15] and (3) the reaction of allylmercuric derivatives with hydrogen chloride.[16] However, reactions (1) and (2) have limited general applicability because, in the former case, a special experimental technique is necessary for handling difluoroamine and, in the latter case, the reaction frequently gives the product as a mixture of double-bond isomers or proceeds in another directions.

The present reaction could be used for causing the double bond to migrate by the sequence of reactions shown in Scheme 1:

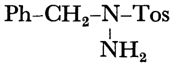


Scheme 1

Nickon and Hill[17] showed that the treatment of *N*-substituted sulfonamides, **23**, with an excess of hydroxylamine-*O*-sulfonic acid in the presence of aqueous alkali yielded the corresponding hydrocarbons, **25**, and proposed a scheme involving 1-substituted arylsulfonylhydrazides (**24**) as the possible pathway. As an example, they obtained toluene from *N*-benzyltosylamide, **23** (Ar=p-C_7H_7, R=$PhCH_2$), in a good yield. Similar types of reactions under alkaline conditions were

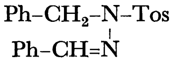


also reported by Cram.[18] With the intention of comparing the present reaction (in acetic acid) with the reaction under alkaline conditions, the base-induced decomposition of **18a** and **18b** was investigated. When **18a** was treated with sodium methoxide, allylbenzene and 1-phenylpropene were obtained in a ratio of 71:29, as determined from the relative area under each peak on the gas chromatogram. In the same way, **18b** gave a 55:45 mixture of 3,3-diphenylpropene (**19b**) and 1,1-diphenylpropene. As it was confirmed in a separate experiment that allylbenzene (**19a**) was isomerized to 1-phenylpropene to an extent of only 12.5% under the same conditions, it was evident that a portion of the 1-phenylpropene was formed directly from **18a**, instead of *via* allylbenzene (**19a**), under alkaline conditions. Presumably, fragmentations with and without the allylic rearrangement of **18a** occur competitively.



$Ph\text{-}CH_2\text{-}N(NH_2)\text{-}Tos$

26



$Ph\text{-}CH_2\text{-}N(N{=}CH\text{-}Ph)\text{-}Tos$

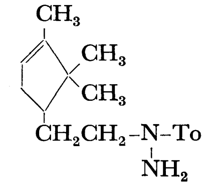
27

$Ph\text{-}CH_2\text{-}N{=}NH$

28

$Ph\text{-}CH{=}N\text{-}NH_2$

29



30

It is most probable that an olefinic group in the specified position is requisite for this type of fragmen-

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[14] C. L. Bumgardner and J. P. Freeman, *J. Amer. Chem. Soc.*, **86**, 2233 (1964).

[15] I. Elphimoff-Felkin and M. Verrier, *Tetrahedron Lett.*, **1968**, 1515, and the references cited therein.

[16] P. D. Sleezer, S. Winstein, and W. G. Young, *J. Amer. Chem. Soc.*, **85**, 1890 (1963).

[17] A. Nickon and A. S. Hill, *ibid.*, **86**, 1152 (1964).

[18] D. J. Cram and J. S. Bradshaw, *ibid.*, **85**, 1108 (1963).

tation to occur. When 1-benzyltosylhydrazide (**26**) was treated with acetic acid, a benzalamino derivative **27** was obtained in a 54% yield (calculated stoichiometrically). Obviously, the lack of an olefinic group in **26** forced the reaction to proceed in a way other than the one described above. A reasonable scheme for the formation of **27** would involve three steps: a) the elmination of *p*-toluenesulfinic acid from **26**, thus affording benzyldiimide (**28**), b) the tautomerization of the diimide into benzaldehyde hydrazone (**29**), and c) the reaction of the hydrazone, or the benzaldehyde formed therefrom, with the starting material, **26**. No smooth reaction proceeded with a compound in which the olefinic group was located in a position remote from the tosylhydrazide group, as in **30**. Under severer conditions, **30** afforded an unidentifiable mixture as the product.

Experimental

*Tosylhydrazones, **5a**, **5b**, **10**, and **12**.* The hydrazones were prepared by refluxing equivalent quantities of the ketones and tosylhydrazide (**2**) in methanol containing a trace amount of conc. hydrochloric acid for 1 hr. The details are summarized in Table 1.

*Mesityl Oxide Tosylhydrazone **5c**.* The compound was prepared according to the method reported by Closs.[19] Mp 118—122°C, Lit[19]: mp 105—110°C.

*Thermolysis of Tosylhydrazones **5a**, **5b**, **5c**, **10**, and **12** in Aqueous Acetic Acid.* A solution of 1g of hydrazone in 15 m*l* of 85% aqueous acetic acid was heated as specified in Table 2 for 3 hr. The subsequent evaporation of the solvent and the recrystallization of the residual solid afforded the product.

*β-Tosylketones **4a**, **4b**, **4c**, and **11**.* An aqueous solution of sodium *p*-toluenesulfinate was neutralized with dilute hydrochloric acid and shaken with ether. To the resulting ether solution was added an equivalent amount of ketone, and the separated solid was recrystallized. The details are summarized in Table 3.

*Thermolysis of Benzalacetone Tosylhydrazone (**5b**) in Acetic Acid.* A solution of 2g of benzalacetone tosylhydrazone (**5b**) in 25 m*l* of freshly-distilled acetic acid was refluxed for 3 hr. The solvent was removed *in vacuo*. The resulting oil solidified on treatment with a small amount of ether. The solid was washed with ether several times (ether-insoluble solid: named A). The ether washings were combined and the ether was removed. The residual solid (0.3 g) afforded crystals of mp 142°C when recrystallized from methanol. The compound was identified as **4b** by comparison with an authentic sample (IR spectrum, mp, and mixed mp). When

TABLE 1

Ketone	Product	Mp (Lit)	Crystn solvent		C(%)	H(%)	N(%)
Benzalaceto-	**5a**	146—148	Methanol	Found:	70.11	5.27	7.44
phenone	$C_{22}H_{20}N_2O_2S$	(156-157)[7]		Calcd :	70.20	5.36	7.44
Benzalacetone	**5b**	185—187	Dioxane-	Found:	64.80	5.65	8.89
	$C_{17}H_{18}N_2O_2S$	(195)[6]	water	Calcd :	64.95	5.77	8.91
3-Methyl-2-	**10**	134—135	Methanol-	Found:	60.72	6.69	10.33
cyclohexenone	$C_{14}H_{18}N_2O_2S$		water	Calcd :	60.42	6.52	10.07
Acetophenone	**12**	148	Ethanol	Found:	62.30	5.63	9.62
	$C_{15}H_{16}N_2O_2S$	(148)[3]		Calcd :	62.49	5.59	9.72

TABLE 2

Tosylhydrazone	Reaction condition	Product	Yield (%)	Crystn solvent
5a	Reflux	**4a**	76	Methanol
5b	Reflux	**4b**	68	Acetone-methanol-water
5c	95°C	**4c**	42	Methanol-water
5c	Reflux	**9**	92	Water
10	85°C	**9**	95	Water
12	Reflux	**9**	90	Water

TABLE 3

Tosylketone	Mp	(°C) (Lit)	Found C(%)	Found H(%)	Calcd C(%)	Calcd H(%)
4a	176—177	(169—170)[10]	72.71	5.32	72.51	5.53
$C_{22}H_{20}O_3S$		(170—171)[4]				
4b	143	(147—148)[10]	67.58	6.01	67.54	6.00
$C_{17}H_{18}O_3S$						
4c	88—89	(94)[20]	61.32	7.30	61.40	7.14
$C_{13}H_{18}O_3S$						
11[a]	90—91		63.24	6.97	63.14	6.81
$C_{14}H_{18}O_3S$						

a) This compound was also obtained by heating the starting components in 85% aqueous acetic acid.

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19) G. L. Closs, L. E. Closs, and W. A. Böll, *J. Amer. Chem. Soc.*, **85**, 3796 (1963).

20) C. L. Arcus and J. Kenyon, *J. Chem. Soc.*, **1938**, 684.

the solid A was recrystallized from ethanol, 0.7 g of crystals with a mp of 140—142°C was obtained. The compound was identified as **6** by comparison with an authentic samle (IR spectrum, mp and mixed mp). From the mother liquor of the recrystallization process, 0.1 g of the starting tosylhydrazone, **5b**, and 0.05 g of crystals of **7** (mp 156—157°C) were obtained. On recrystallization from ethanol, the mp rose to 159—159.5°C (Lit[6]: mp 164—165°C).

Found: C, 64.72; H, 5.68; N, 8.89%. Calcd for $C_{17}H_{18}N_2O_2S$: C, 64.95; H, 5.77; N, 8.91%.

2-Acetyltosylhydrazide (9). An acetic-acid solution of tosylhydrazide (**2**) was refluxed for 2 hr. The solvent was then removed *in vacuo*, and the solid was recrystallized from water. Mp 146—147°C (Lit[21]: mp 151°C).

Found: C, 47.19; H, 5.01; N, 12.36%. Calcd for $C_9H_{12}N_2O_3S$: C, 47.37 ; H, 5.30; N, 12.28%.

4-Phenyl-4-tosyl-2-butanone Tosylhydrazone (6). a) An aqueous solution of 1 g of sodium *p*-toluenesulfinate was neutralized with dilute hydrochloric acid, and free *p*-toluenesulfinic acid was extracted with ether . To the resulting ether solution, we then added 1.6 g of benzalacetone tosylhydrazone (**5b**). The solid was filtered and recrystallized from ethanol. Mp 144—146°C. b) A methanol solution containing 1.5 g of **4b**, 1 g of tosylhydrazide (**2**), and a trace amount of conc. hydrochloric acid was refluxed for 2 hr. On cooling, a solid separated which was then recrystallized from ethanol. Mp 144—146°C. The compounds obtained from the two processes, a) and b), were identical.

Found: C, 61.41; H, 5.55; N, 6.01%. Calcd for $C_{24}H_{26}N_2O_4S_2$: C, 61.27; H, 5.57; N, 5.96%.

Thermolysis of Benzalacetone Tosylhydrazone (5b) in Aqueous Acetic Acid in the Presence of Azobenzene. A solution of 3g of benzalacetone tosylhydrazone (**5b**) and 1.7 g of azobenzene in 27 m*l* of acetic acid and 3 m*l* of water was refluxed for 5 hr. The solvent was evaporated *in vacuo*, and the residue was washed with petroleum ether (the petroleum ether-insoluble oil: named B). From the petroleum-ether washing, 0.7 g of azobenzene was recovered. The oil B partially crystallized when a small amount of chloroform was added. The solid was filtered (mother liquor: named C), and recrystallized from acetic acid. Crystals of diacetylbenzidine (**13**) (0.7 g) were thus obtained. Mp 328°C (Lit[12]: mp 330—331°C). Found: C, 71.62; H, 6.11; N, 10.21%. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44%. The work-up of the mother liquor of the recrystallization process of **13** afforded other crystals. Recrystallization from ethanol afforded a pure sample of 4-tosylazobenzene (0.3 g); mp 218—220°C. (Lit[22]: mp 224—225°C). Mixed mp with the authentic sample: 220°C. From the mother liquor, C, **4b** was obtained.

1,3-Diphenyl-2-propen-1-ol. To a solution of 20 g of benzalacetophenone in 50 m*l* of ethanol, we added, portion by portion, 1 g of sodium borohydride. The solution was stirred at room temperature for 3 hr, and then the ethanol was evaporated *in vacuo*. A small amount of acetic acid was added to decompose the excess borohydride, and water was added. The solution was shaken with ether and dried over sodium sulfate. The evaporation of the solvent afforded crystals which were recrystallized from ether-petroleum ether. Mp 56°C (Lit[23]: mp 58—59°C).

2-(1,3-Diphenyl-2-propen-1-yl)tosylhydrazide (14a). Thionyl chloride (7.5 m*l*) was added, drop by drop, to 18 g of 1,3-diphenyl-2-propen-1-ol with cooling by ice water, after which the resulting mixture was warmed at 80°C. After gas evolution had ceased, the excess thionyl chloride was removed *in vacuo*. The resulting oil (**16**) was added to a solution of 16 g of tosylhydrazide in 100 m*l* of pyridine with cooling by ice water, and the solution was stirred for 2 hr at room temperature. When the solution was poured into a cold hydrochloric acid (1:1), a solid separated. This was filtered, washed with ether, and recrystallized from ethanol. Prolonged heating in ethanol caused decomposition. Crystals of **14a** were obtained (8 g). Mp 132°C.

Found: C, 69.78; H, 5.84; N, 7.48%. Calcd for $C_{22}H_{22}N_2O_2S$: C, 69.82; H, 5.86; N, 7.40%.

Thermolysis of 14a. A small amount of **14a** was dissolved in ethanol and refluxed for 20 min. On cooling, a solid crystallized out; it was identified as **15a** by comparison with an authentic sample (IR spectrum, mp, and mixed mp).

1,3-Diphenyl-3-tosylpropene (15a). The crude chloride **16** obtained above and an equivalent quantity of *p*-toluenesulfinic acid was dissolved in benzene and refluxed for 2 days. The solvent was removed *in vacuo*, and the residual solid was recrystallized from ethanol. Mp 157—158°C.

Found: C, 75.87; H, 5.77%. Calcd for $C_{22}H_{20}O_2S$: C, 75.84; H, 5.79%.

The reaction of Cinnamyl Chloride with Tosylhydrazide. A solution of 2 g of tosylhydrazide and 0.5 g of cinnamyl chloride in 10 m*l* of pyridine was warmed to 70°C. The evolution of gas was observed. After the gas evolution had ceased, the solution was poured into a cold hydrochloric acid (1:1). The solid filtered and recrystallized from aqueous methanol (0.8 g). Mp 112—113°C. The compound was identified as cinnamyl *p*-tolyl sulfone by comparison with an authentic sample (IR spectrum, mp, and mixed mp).

Cinnamyl p-*Tolyl Sulfone.* Equivalent quantities of sodium *p*-toluenesulfinate and cinnamyl chloride in DMSO were kept at 80°C for 5 hr. Water was then added, and the mixture was shaken with ether. Thereafter ether was removed, and a mixture of benzene and ligroin was added. A solid separated on standing in a refrigerator; it was recrystallized from aqueous methanol. Mp 118—119°C (Lit[24]: mp 126—126.5°C).

Found: C, 70.03; H, 5.83%. Calcd for $C_{16}H_{16}O_2S$: C, 70.57; H, 5.92%.

1-Chloromethylcyclohexene (17d).[25] Into a solution of 5.2 g of 2-methylenecyclohexanol (bp 82—85°C/23 mmHg, prepared from ethyl 2-cyclohexanonecarboxylate[26]) in 100 m*l* of ether, we stirred 3.4 m*l* of thionyl chloride. When the solution was refluxed for 10 hr and poured into ice water, an ether layer was separated. The ether solution was washed with cold water and dried over calcium chloride. The ether was removed, and the residue was distilled. Bp 62—64°C/11 mmHg. The IR spectrum showed no band assignable to exo-methylene ($\rangle C=CH_2$).

1-Allyltosylhydrazides 18a, 18b, 18c, 18d, and 18e, and 1 Benzyltosylhydrazide (26). To a solution of 1.86 g of tosylhydrazide (**2**) in 20 m*l* of DMSO, we added 0.5 g of sodium hydride (50%) with stirring and external cooling. After the gas evolution had subsided, an equivalent amount of halide was added, little by little, with cooling. The reaction mixture was then stirred for an additional 10 min and poured into ice water. The solid was filtered, washed with cold water several times, and recrystallized from benzene-

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TABLE 4

Halide	Product	Mp(°C)	Yield(%)		C (%)	H (%)	N (%)
17a	**18a**	105—107	80	Found:	63.74	5.96	9.52
	$C_{16}H_{18}N_2O_2S$			Calcd :	63.56	6.00	9.27
17b[27)]	**18b**	109	65	Found:	69.95	5.80	7.46
	$C_{22}H_{22}N_2O_2S$			Calcd :	69.82	5.86	7.40
17c[28)]	**18c**	109	87	Found:	69.93	6.11	7.29
	$C_{22}H_{22}N_2O_2S$			Calcd :	69.82	5.86	7.40
17d	**18d**[a)]	92	75	Found:	60.14	7.43	10.10
	$C_{14}H_{20}N_2O_2S$			Calcd :	59.98	7.19	9.99
17e	**18e**	87—89	84	Found:	53.29	6.28	12.38
	$C_{10}H_{14}N_2O_2S$			Calcd :	53.09	6.24	12.38
$PhCH_2Cl$	**26**	120—121[b)]	73	Found:	61.12	5.51	10.32
	$C_{14}H_{16}N_2O_2S$			Calcd :	60.86	5.84	10.14

a) Characteristic NMR signals: δ 5.64 (broad singlet, 1H) for =CH–; δ 3.58 (broad singlet, 2H) for $-CH_2-N$; δ 3.51 (sharp singlet, 2H) for $-NH_2$.

b) Lit[29)]: mp 127.5—128.5°C.

TABLE 5

Benzal deriv.	Mp(°C)	Found			Calcd		
		C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
20a $C_{23}H_{22}N_2O_2S$	128—129	70.87	5.61	7.22	70.75	5.68	7.18
20b $C_{29}H_{26}N_2O_2S$	147	74.47	5.55	6.12	74.66	5.62	6.01
20c $C_{29}H_{26}N_2O_2S$	166	74.38	5.42	5.87	74.66	5.62	6.01
20d $C_{21}H_{24}N_2O_2S$	109—110	68.07	6.58	8.18	68.46	6.57	7.60
27 $C_{21}H_{20}N_2O_2S$	108—109[a)]	69.21	5.75	7.96	69.21	5.53	7.69

ligroin. The details are summarized in Table 4.

*Benzal Derivatives **20a**, **20b**, **20c**, **20d**, and 17.* An ethanol solution of equivalent amounts of 1-substituted tosylhydrazide (**18a**—**18d**, and **26**) and benzaldehyde was kept at 70°C for 1 hr, and then at room temperature overnight. The crystals which thus separated were filtered and recrystallized from methanol. The details are summarized in Table 5.

*Thermolysis of 1-Allyltosylhydrazides **18a**, **18b**, **18c**, and **18d**, and 1-Benzyltosylhydrazide (**26**) in Acetic Acid.* Two grams of the hydrazide were dissolved in 15 m*l* of acetic acid, and the solution was heated. A gas evolution started at 30°C and became vigorous at 40—70°C. The solution was kept at the temperature specified in Table 6 until the gas evolution ceased. Excess water was then added, and the solution was shaken with ether. The ether layer was washed with an aqueous solution of sodium bicarbonate and dried over sodium sulfate. On the evaporation of the ether, an oil remained; it was then distilled. A gas-chromatographic investigation of the crude oil indicated that this oil was not contaminated with any of the isomers.

*Base-induced Decompositon of **18a**.* A solution of 0.8 g of **18a** and 2 g of sodium methoxide in 50 m*l* of ethanol was refluxed until no gas evolution was observed (40 min). Most of the ethanol was evaporated *in vacuo*, and water was added. The mixture was shaken with ether, and the ether solution was washed with water and dried over sodium sulfate. The oil which remained on the evaporation of ether was distilled under a vaccum (20 mmHg). All the materials which had distilled at the bath temperature of 70—80°C were collected and analyzed by gas chromatograpy. From the retention time and the relative area of each peak in the gas chromatogram, it was determined that the oil consisted of allylbenzene and 1-phenylpropene (71% and 29% respectively).

*Base-induced Decompositiom of **18b**.* A solution of 1 g of **18b** and 2 g of sodium methoxide in 50 m*l* of ethanol was refluxed for 5 hr. After the evaporation of the ethanol *in vacuo*, water was added and the mixture was shaken with ether. The ether layer was washed with water, and the ether was removed. The oil which remained was distilled under a vacuum (3 mmHg). All the materials which had been distilled before the bath temperature reached 170°C were collected and analyzed by gas chromatography. It was determined that the oil consisted of 3,3-diphenylpropene (**19b**) and 1,1-diphenyl-1-propene (55% and 45% respectively).

Base Treatment of Allylbenzene. A solution of allylbenzene (0.6 g), sodium *p*-toluenesulfonate (0.91 g), and sodium methoxide (4 g) in 100 m*l* of ethanol was refluxed for 40 min. A work-up of the reaction mixture in the way described above, and subsequent gas-chromatographic analysis, indicated that the reaction product consisted of two components (Fractions 1 and 2) (87.5% and 12.5% respectively). Each fraction was then collected. Fraction 1 was found to be allylbenzene by comparison with an authentic

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TABLE 6

Tosylhydrazide	Product	Yield (%)	Reaction condn(°C)	Identification
18a	**19a**	66	60	Identical with the authentic sample[30]
18b	**19b**	55	32—43	IR: 1630, 990, 910 cm^{-1} (–CH=CH$_2$); NMR: Identical with the reported one[31]
18c	**19c**	70	50—60	Identical with the authentic sample[32]
18d	**19d**	60	40	IR: Identical with the reported one[33]
26	**27**	54	70	Described above

sample (IR spectrum and retention time on gas chromatography). Fraction 2 was identified as 1-phenylpropene from its IR spectrum (955 cm^{-1} for the *trans* olefin).

*1-[2-(1,5,5-Trimethylcyclopenten-4-yl)ethyl]tosylhydrazide (**30**).* Into a DMSO solution of the tosylhydrazide anion, prepared in the way described above, we stirred an equivalent amount of 2-(1,5,5-trimethylcyclopenten-4-yl)ethyl tosylate[34] at room temperature. After 20 min, water was added and the mixture was shaken with ether. The evaporation of the ether afforded a solid which was then recrystallized from petroleum ether. Mp 83—84°C.

Found: C, 63.23; H, 8.05; N, 8.60%. Calcd for $C_{17}H_{26}N_2O_2S$: C, 63.33; H, 8.13; N, 8.69%.

Benzalamino derivative; mp 119—120°C. Found: C, 70.44; H, 7.52; N, 6.96%. Calcd for $C_{24}H_{30}N_2O_2S$: C, 70.22; H, 7.37; N, 6.82%.

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