A Convenient Synthesis of Ester *p*-Tosylhydrazones and Studies of the Thermal Decomposition of Some of Their Sodium Salts[1]

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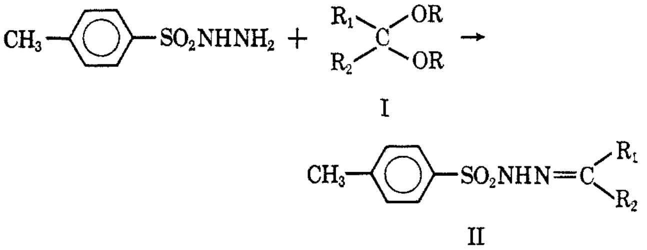
Ester *p*-tosylhydrazones are obtained in good yields from reactions of ortho esters and *p*-tosylhydrazine. The reactions of three of these ester *p*-tosylhydrazones, derived from methyl orthoformate, ethyl orthoacetate, and methyl orthobenzoate, with sodium hydride and the thermal decompositions of the product sodium salts are discussed. The products of these thermolyses are rationalized as being formed by two major reaction paths in the initial reactions with sodium hydride: (1) salt formation, the expected process; and (2) nucleophilic attack of hydride at carbon of the carbon–nitrogen double bond of the hydrazone. The substituent other than the alkoxyl group on this carbon atom is apparently the controlling factor as to which of these two routes predominates.

Our interest in preparing and examining 1-alkoxycarbenes was multipurpose: (1) to determine whether the attachment of oxygen to the carbenic carbon, which might be expected to enhance the stability of these carbenes, allows them to be more selective and possibly less electrophilic in their reactions[3]; (2) to study their decomposition products in aprotic solvents; and (3) to investigate their potential use in the synthesis of oxygen-substituted cyclopropanes.

Of the various procedures reported in which carbenes may be considered as intermediates, the thermal decomposition of α-alkoxydiazoalkanes formed *in situ* during thermolysis of salts of ester (*p*-toluenesulfonyl)hydrazones[4] appeared to offer the best promise of yielding α-alkoxycarbenes.

Synthesis of Ester *p*-Tosylhydrazones.—At the time we began our investigation a procedure for the preparation of ester *p*-tosylhydrazones was not available.[5] Literature reports of reactions of sulfonamides with ethyl orthoformate, forming N-ethoxymethylenesulfonamides,[6] and between *p*-toluenesulfonamide and ethyl orthocarbonate to yield diethyl N-(*p*-tosyl)imidocarbonate[7] suggested that an analogous reaction of orthocarboxylic esters and *p*-tosylhydrazine should occur to give the desired ester *p*-tosylhydrazones.

When *p*-tosylhydrazine is mixed with a slight excess of an orthocarboxylic ester (I) at room temperature, stirred for 45 min, and filtered, the precipitate is the ester *p*-tosylhydrazone (II). The yields, Table I, are all quite good, and the $\nu_{C=N}$ all appear at about 6.0 μ in the infrared spectra. A modification of this procedure, using methanol as solvent, produced IIe as a mixture of *syn* and *anti* isomers in 73% yield.[8] The material presently described is the high-melting isomer which has the *anti* configuration, if the previous assignment of *syn* stereochemistry to the isomer of mp 98–99° is correct.[8]



a, R = CH_3; R_1 = OCH_3; R_2 = H
b, R = C_2H_5; R_1 = OC_2H_5; R_2 = H
c, R = C_2H_5; R_1 = OC_2H_5; R_2 = CH_3
d, R = C_2H_5; R_1 = OC_2H_5; R_2 = C_2H_5
e, R = CH_3; R_1 = OCH_3; R_2 = C_6H_5
f, R = C_2H_5; R_1 = R_2 = OC_2H_5

TABLE I

Compd	Mp., °C	Yield, %	$\nu_{C=N}$
IIa	151.5–153	93	6.02
IIb	118.5–119.5	89	6.01
IIc	162–165	85	6.07
IId	151–152.5	74	6.03
IIe	141–143.5	86	6.05
IIf	86.5–87.5[a]	87	5.96

[a] Lit.[5] mp 85–86°.

The reaction of ethyl orthoacetate with *p*-tosylhydrazine gave initially a product with mp 86–89° which, after several recrystallizations from ethyl acetate, gave a material with mp 162–165°. There were considerable differences in their infrared spectra, but each had the characteristic 6.0-μ absorption associated with $\nu_{C=N}$. Both compounds, when treated with sodium hydride, gave the same sodium salt, according to infrared and nmr spectral analysis.

The nmr spectrum of the low-melting isomer in $DCCl_3$ appears to be that of a mixture. The spectrum shows a chemical shift difference of τ 0.06 between methylene quartets, a slightly larger difference of τ 0.08 between methyl triplets, and a τ 0.02 difference between the methyl singlets. Using the convention previously applied to IIe[8] would suggest that the pure isomer, mp 162–165°, has the *anti* configuration, and that the initial product of the reaction, mp 86–89°, is a mixture of isomers with the *syn* form in predominance.

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[1] A portion of this research appeared as a preliminary communication in *Tetrahedron Letters*, **No. 14**, 857 (1965).

[2] This represents a part of a dissertation presented by R. A. Krueger to the Graduate School of Kansas State University in partial fulfillment of the requirements of the degree of Doctor of Philosophy.

[3] A review of various reports of carbenes containing α-heteroatoms is given by W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, Chapter 9.

[4] In the previous report of some of these results[1] the nomenclature we used for these compounds was, for example, methyl N′-(*p*-tosyl)hydrazimidoformate for the structure *p*-$CH_3C_6H_4SO_2NHN{=}CHOCH_3$. In a letter from K. L. Loening, Director of Nomenclature, The Chemical Abstracts Service, the Chemical Abstracts name is methyl formate (*p*-tolylsulfonyl)hydrazone. Although we believe our initially adopted nomenclature is more in line with IUPAC, we are moved to accept that of Chemical Abstracts.

[5] Since that time R. J. Crawford and R. Raap [*Proc. Chem. Soc.*, 370 (1963)] reported the reaction of diethyl imidocarbonate and *p*-tosylhydrazine hydrochloride to yield diethyl carbonate *p*-tosylhydrazone.

[6] G. Tosolini, *Ber.*, **94**, 2731 (1961).

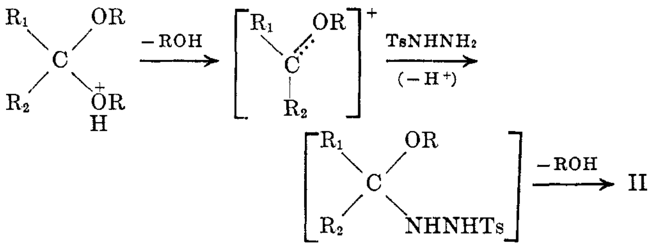
[7] R. F. Meyer, *J. Org. Chem.*, **28**, 2902 (1963).

[8] R. J. Crawford and R. Raap, *Can. J. Chem.*, **43**, 126 (1965).

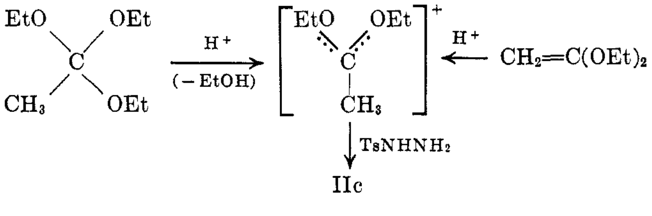
It had been previously reported[5] that IIf underwent decomposition on standing to a higher melting isomer when prepared from diethyl imidocarbonate and *p*-tosylhydrazine hydrochloride. When prepared by the present technique, IIf was reasonably stable, showing some melting point lowering to 81–83.5° but essentially no change in its infrared spectrum after 9 months storage.

This was not the case, however, for every compound of type II prepared by this method. In particular, IIc had a relatively short shelf life which apparently depended on the purity of the sample. In the cases where decomposition was observed, the sample had the odor of the corresponding carboxylic acid or its respective ester.

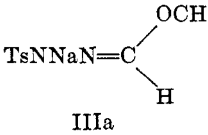
This method for preparing ester *p*-tosylhydrazones probably proceeds by protonation of an ether oxygen with elimination of a molecule of alcohol to give a stabilized carbonium ion which is then trapped by the nucleophilic amino function of another molecule of *p*-tosylhydrazine. Elimination of a second molecule of the alcohol will yield II.



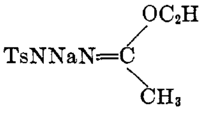
This would explain why our procedure occurs under milder conditions than those reactions involving sulfonamides which lack the nucleophilic group, and why reaction of *p*-tosylhydrazine with diethyl ketene acetal produces IIc rather than ketene *p*-tosylhydrazone. In this latter case, protonation of the methylene group would be expected to produce a more stable carbonium ion than protonation on oxygen and loss of a molecule of ethanol. It was also found that this method was successful with acetone dimethyl ketal to produce acetone *p*-tosylhydrazone (II, $R_1 = R_2 = CH_3$), but failed with formal and cyclopropanone diethyl ketal.



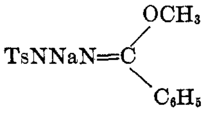
Thermal Decompositions of Sodium Salts of Ester *p*-Tosylhydrazones.—Since the thermal decomposition of the sodium salt of diethyl carbonate *p*-tosylhydrazone (IIf) had been reported in detail,[5] it was decided to investigate the thermal decompositions of sodium salts IIIa, IIIc, and IIIe derived from IIa, IIc, and IIe, respectively. Using this series of compounds, we could observe the effect of varying the second substituent on the carbenic center from hydrogen to methyl to phenyl.



IIIa



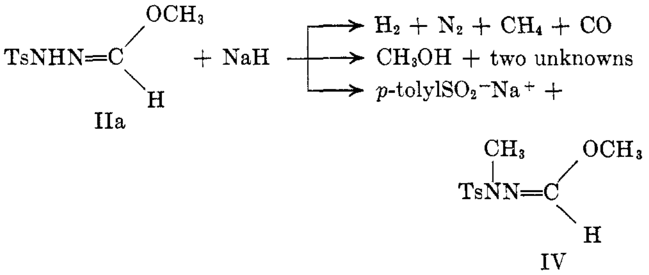
IIIc



IIIe

The three salts, IIIa, b, and c, as well as that derived from IIf, were prepared by mixing the ester *p*-tosylhydrazone with sodium hydride in an inert solvent, *i.e.*, tetrahydrofuran or monoglyme, while cooling the mixture in an ice bath. However, in order to isolate IIIa it was necessary to add the solid hydrazone IIa very slowly with efficient stirring to a dilute suspension of sodium hydride in tetrahydrofuran cooled in an ice bath.

When IIa was added in small portions to a suspension of sodium hydride in triglyme[9] at 5°, no gas was evolved. However, when the temperature of the reaction mixture warmed to about 25°, an exothermic reaction occurred with the temperature rising to 40°, and a vigorous evolution of gas was observed. During this time the color of the reaction mixture changed from an initial white suspension, to yellow with purple on the upper portions of the flask, to brown, and finally back to white. The gas liberated during this reaction contained hydrogen and nitrogen along with traces of methane and carbon monoxide.



Filtration of the reaction mixture gave sodium *p*-toluenesulfinate in 84% yield. Distillation of the filtrate under reduced pressure gave a liquid which was collected in the Dry Ice trap and contained 1.93 g (35% yield) of methanol along with two other components which were shown by vpc integration to be 1.3 and 5.5% of the liquid recovered in the trap.

The component present in smallest amount has not been isolated The other component has been separated and collected by vpc and has a fairly simple infrared spectrum. Its nmr spectrum also is quite simple, consisting of singlets at τ 1.75 and 5.71, which when integrated reveal a ratio of 1:3 protons, respectively. Elemental analysis[10] of this sample shows 28.88% carbon and 4.98% hydrogen, which does not appear to fit for any anticipated products.

The nmr spectrum suggested that this component may be either *cis*- or *trans*-1,2-dimethoxyethylene. These two compounds were prepared,[11] and vpc showed that neither of the above two components corresponds to the two isomeric 1,2-dimethoxyethylenes. A further possibility that we may be dealing with the two isomers of 1,2,3-trimethoxycyclopropane has not been checked, but this seems rather remote.

The residue from distillation of the solvent was found to contain 14% of starting hydrazone IIa and

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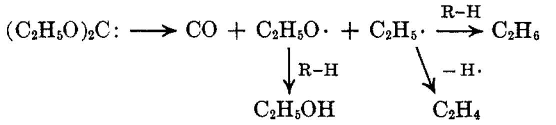
[9] This solvent was chosen since it was believed that the thermal decomposition of IIIa formed *in situ* could then be studied at some point below its boiling point.

[10] Owing to the very small amount of sample available, the purity of this sample cannot be assured and the analysis results cannot be considered binding.

[11] M. F. Fhostakovskii, N. V. Kuznitzov, and C.-M. Yang, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1685 (1965).

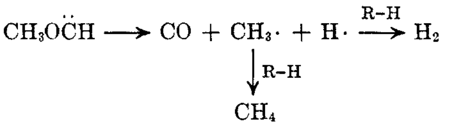
2% of methyl formate N′-methyl-p-tosylhydrazone (IV). The latter compound was identified by its infrared and nmr spectra, and its elemental analysis.

The production of the relatively large quantity of methanol was unexpected. Crawford and Raap,[5] in studying the thermal decomposition of the sodium salt of diethyl carbonate p-tosylhydrazone, observed large amounts of ethanol, ethylene, and ethane as products. These were rationalized by homolysis of the intermediate diethoxycarbene. Assuming the formation of methoxycarbene in the present case, it



$$(C_2H_5O)_2C: \longrightarrow CO + C_2H_5O\cdot + C_2H_5\cdot \xrightarrow{R-H} C_2H_6$$
$$C_2H_5O\cdot \xrightarrow{R-H} C_2H_5OH \qquad C_2H_5\cdot \xrightarrow{-H\cdot} C_2H_4$$

seems unlikely that homolysis would result in methoxyl radicals. The most reasonable homolytic fission of this carbene would appear to result in carbon monoxide and methane, and probably hydrogen. The former two compounds are observed as gaseous



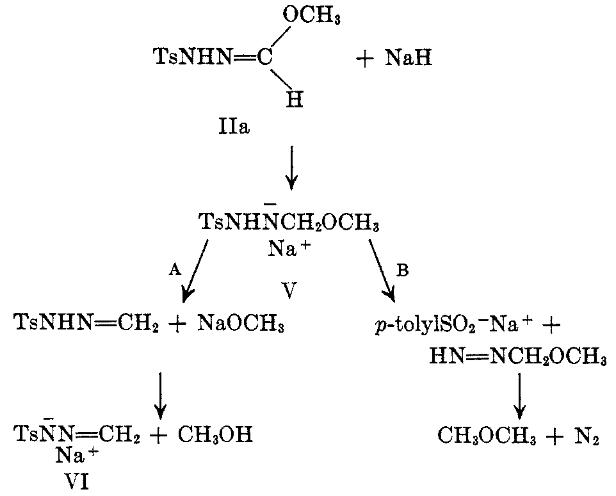
$$CH_3O\ddot{C}H \longrightarrow CO + CH_3\cdot + H\cdot \xrightarrow{R-H} H_2$$
$$CH_3\cdot \xrightarrow{R-H} CH_4$$

products of the reaction, while the formation of hydrogen formed in this manner is masked by that produced in salt formation with sodium hydride. Heterolytic fissions likewise do not appear reasonable to account for the methanol.

The fact that hydrazone IIa decomposes at room temperature when added to a suspension of sodium hydride in triglyme suggests that some reaction(s) other than normal salt formation to IIIa is occurring. This is supported by the experimental evidence that when IIIa is prepared in dilute tetrahydrofuran solution it must be heated in triglyme to 220° before decomposition takes place as shown by gas evolution.

Consideration of other parts of structure IIa which might be attacked by sodium hydride leads one to the conclusion that the carbon–nitrogen double bond appears to be particularly vulnerable. There appear to be no reports of addition reactions of sodium hydride with carbon–nitrogen double bonds. However, the similarity in behavior of carbon–nitrogen and carbon–oxygen double bonds in reactions with Grignard reagents, sodium bisulfite, and hydrogen cyanide has been shown.[12] Further support of this proposal may be found in the report that sodium hydride in boiling xylene adds to benzophenone, a relatively unreactive carbonyl group, giving benzhydrol after hydrolysis, and catalyzes the conversion of benzaldehyde to benzyl benzoate.[13]

If sodium hydride was to add to the carbon–nitrogen double bond (to be referred to as the *abnormal* process)[14]



giving V, two modes of decomposition of this intermediate appear reasonable. An alternative to path A would be a 1,2-proton shift of the acidic hydrogen leading to VII which could eliminate methanol to yield salt VI.

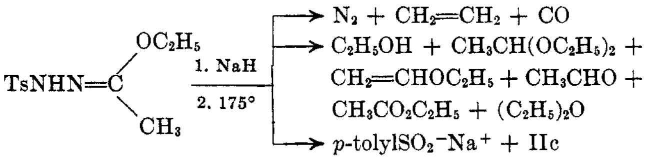
$Ts\bar{N}NHCH_2OCH_3Na^+$

VII

During the warming of this exothermic reaction VI would decompose to methylene, *via* diazomethane, which is expected to insert mainly into the ethereal solvent. Insertion of some methylene in the N–H bond of IIa could readily account for the small amount of the N′-methylhydrazone IV formed.

Route B does not appear to be operative in this reaction, since dimethyl ether was not observed. This ether would be expected by analogy with the report of the decomposition of N′-(2-phenyl-2-butyl)-N-(p-tosyl)hydrazide in alcoholic potassium t-butoxide to give 2-phenylbutane in 83% yield.[15,16]

When ethyl acetate p-tosylhydrazone (IIc) was added in small portions to a stirred, cooled suspension of sodium hydride in triglyme, more than the theoretical amount of gas was collected. Analysis by vapor phase chromatography indicated hydrogen and nitrogen, but no hydrocarbon gases. When the resulting reaction mixture was heated to 175° for 2.5 hr, additional gas was collected, which contained nitrogen, ethylene, and carbon monoxide in the ratio of 365:3:1. This was calculated to be about a 0.6% yield of ethylene and 0.2% yield of carbon monoxide. The yield of nitrogen from this thermal decomposition was 77%.



IIc

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(12) C. G. Overberger and A. V. DiGiulio, *J. Am. Chem. Soc.*, **80**, 6562 (1958), and references cited therein.

(13) F. W. Swamer and C. R. Hauser, *ibid.*, **68**, 4627 (1946).

(14) (a) The likelihood of an addition reaction of this type occurring in this system of surface reactions on the insoluble base, sodium hydride, would appear to be better than if one were to use a soluble base, such as methyllithium in ether. This should be considered to be a recommendation for the use of soluble bases for the preparation of salts of p-tosylhydrazones. (b) An alternate path to this *abnormal* process might be the α elimination of the elements of methanol in a manner analogous to the reports of W. R. Hertler and E. J. Corey [*J. Org. Chem.*, **23**, 1221 (1958)] and I. Ugi and R. Meyr [*Chem. Ber.*, **93**, 239 (1960)] in their conversions of formamides to isonitriles. This path, however, does not explain the large amounts of ethanol produced from IIc or the abnormal products from IIc and IIe.

(15) D. J. Cram and J. S. Bradshaw, *J. Am. Chem. Soc.*, **85**, 2677 (1965).

(16) Decomposition *via* route B readily explains the formation of benzaldehyde dimethyl acetal reported recently by R. J. Crawford and R. Raap [*Can. J. Chem.*, **43**, 356 (1965)] in the reaction of methyl benzoate p-tosylhydrazone and sodium methoxide. In this case, normal salt formation to IIIe and methanol is an equilibrium and route A is a reaction which leads nowhere. This plus the present data may indicate that route A, or its alternate, is favored over B under normal conditions.

A Dry Ice trap connected to the reaction vessel contained ethanol (22.2%), acetal (24.3%), ethyl vinyl ether (10%), diethyl ether (1.4%), acetaldehyde (1.1%), and ethyl acetate (0.2%). Filtration of the reaction mixture gave sodium *p*-toluenesulfinate in 95% yield. Distillation of the filtrate left a residue from which was isolated IIc in 1.5% yield.

Here the products appear to require that the reaction of IIc and sodium hydride follow both the normal salt formation to IIIc, which thermally decomposes to α-ethoxydiazoethane and can account for several of the products (Chart I), as well as the abnormal addition which eventually ends up in the production of ethanol and methyl carbene (Chart II). In Chart I we cannot exclude the possibility of protonation of the diazo compound to a diazonium salt and its subsequent decomposition to products. It is to be noted that in both the normal and abnormal processes minor oxidation of the carbene apparently occurs. This may be from contamination of oxygen in the nitrogen atmosphere employed before IIc is treated with sodium hydride or arise by some other mechanism.[17]

CHART I

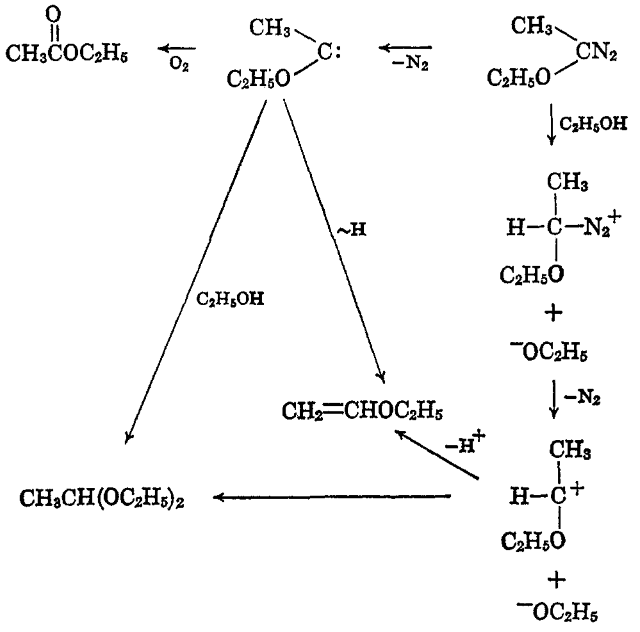
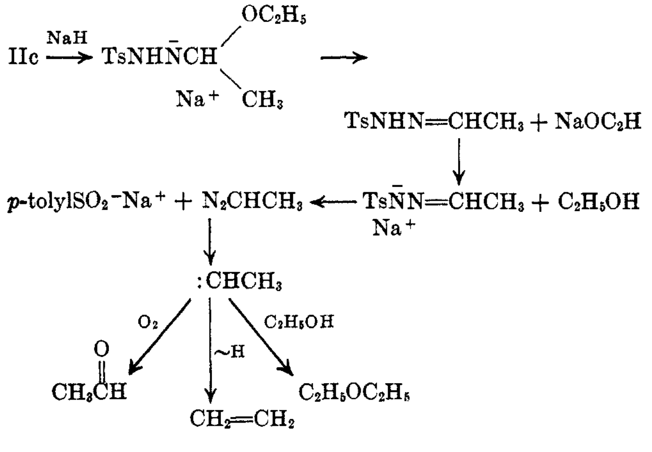
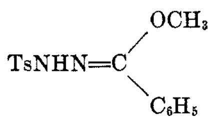


CHART II



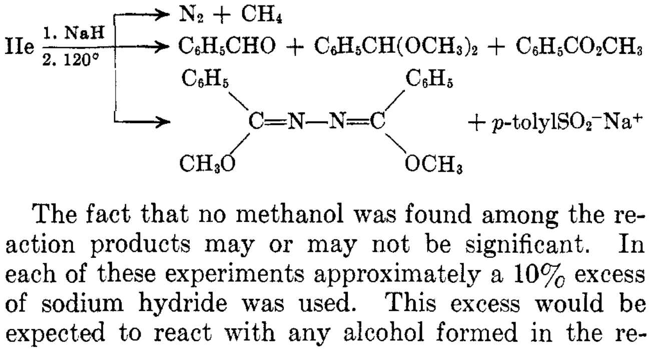
If a diimide of the type proposed previously as route B was an intermediate, it would be expected to decompose under the reaction conditions, or certainly before the temperature of the reaction mixture reached 175°. The gases collected during the addition of IIc to sodium hydride contained only a small amount of nitrogen, indicating that route B was playing a minor role in this reaction.

The preparation of sodium salt IIIe of methyl benzoate *p*-tosylhydrazone (IIe) was carried out as before with sodium hydride in diglyme. When the resulting mixture was heated at 120° for 2.5 hr, nitrogen and methane (65:1) were liberated and 79% of the theoretical amount of sodium *p*-toluenesulfinate was isolated. The liquid fraction isolated from the reaction mixture contained benzaldehyde (1.4%), benzaldehyde dimethyl acetal (2.1%), and methyl benzoate (3.6%), as shown by vapor phase chromatography. Methoxybenzalazine was isolated in 66% yield.



$\text{TsNHN}{=}\text{C}(\text{OCH}_3)(\text{C}_6\text{H}_5)$

IIe



The fact that no methanol was found among the reaction products may or may not be significant. In each of these experiments approximately a 10% excess of sodium hydride was used. This excess would be expected to react with any alcohol formed in the reaction to give the sodium alkoxide. Thus, an amount of alcohol in excess of that required to react with the sodium hydride would have to be formed before the presence of the alcohol would be observed.

Again in this case it appears necessary to involve the normal and abnormal processes in the initial reaction of IIe with sodium hydride, and the normal process greatly predominates. The formation of benzaldehyde dimethyl acetal and methyl benzoate are explained by reaction of the α-methoxyphenylcarbene with methanol and oxygen, respectively, and benzaldehyde by oxidation of phenylcarbene, the abnormal carbene product.[18]

No accounting of the small amount of methane seems reasonable by the above. One speculation as to its origin might be hydride attack on the methoxyl methyl group of IIe which might produce benzoyl diimide. This could decompose to nitrogen and benzaldehyde, both of which are observed products.

The major product, α-methoxybenzalazine, we believe results from the trapping of α-methoxyphenylcarbene by its diazo precursor. This is by analogy

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(17) J. Wilt and C. A. Schneider [*Chem. Ind.* (London), 865 (1963)] and J. Wilt, C. A. Schneider, and C. F. Parsons [Abstracts of the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, p 44S] reported that *p*-toluenesulfinate anion serves as the "oxidant" in the thermal decomposition of the salt of norbornane-1-carboxaldehyde *p*-tosylhydrazone to yield bicyclo[2.2.2]octan-1-ol and 1-norbornane-1-methanol.

(18) We failed to find any benzyl methyl ether, the product of reaction of phenylcarbene and methanol, which may be the result of only very small amounts of this alcohol being formed.

with the recent report[19] that a number of carbenes react with diphenyldiazomethane to yield the corresponding azines. It was also shown that the thermal decomposition of diphenyldiazomethane is first order in diazo compound.

Summarizing the results of the reactions of ester *p*-tosylhydrazones with sodium hydride, it appears that two initial paths are followed. One path (normal) results in the formation of the sodium salt of the *p*-tosylhydrazones. The other (abnormal) appears to involve hydride attack at the carbon atom of the carbon–nitrogen double bond. The substituent on this carbon atom is apparently the controlling factor as to which of these two routes predominates.

From steric considerations, the importance of hydride attack at the carbon atom of the carbon–nitrogen double bond might be anticipated to decrease in the order methyl formate *p*-tosylhydrazone (IIa) > ethyl acetate *p*-tosylhydrazone (IIc) > methyl benzoate *p*-tosylhydrazone (IIe). This order is observed. Likewise, from electronic considerations, a similar order would be anticipated. The electrophilic character of the carbon atom of the carbon–nitrogen double bond is expected to be greatest for the hydrogen-substituted *p*-tosylhydrazone ester, IIa, and least for the phenyl-substituted compound, IIe. This is borne out by the results.

Several attempts were made to trap the intermediate carbenes. It was found that IIIa did not decompose in *n*-propylketene dimethyl acetal at 170°. When IIa was added to a suspension of sodium hydride in ketene diethyl acetal and the mixture was heated to 95–100°, distillation gave ketene diethyl acetal (36%), ethyl orthoacetate (1%), ethyl β-ethoxycrotonate (19%), with IIIa (17%), and IIa (5%) being recovered from the residue. The formation of ethyl orthoacetate and ethyl β-ethoxycrotonate can best be explained by allowing for some hydrolysis of the ketene diethyl acetal prior to its use as solvent in this reaction.

Heating of IIIe in ketene diethyl acetal gave a 68% yield of sodium *p*-toluenesulfinate. Distillation of the reaction mixture at reduced pressure gave fractions which contained benzaldehyde (1.2%), methyl benzoate (2.4%), and a third component which could not be purified either by vpc or distillation. The last three fractions collected from the distillation were redistilled to give a 1% yield of 1,2-dimethoxy-1,2-diphenylethane and considerable methoxybenzalazine. The formation of 1,2-dimethoxy-1,2-diphenylethane may be explained as a hydrogen atom abstraction by α-methoxyphenylcarbene, which probably results from the thermal decomposition of α-methoxybenzalazine during distillation, with hydrogen atom abstraction and subsequent dimerization of the α-methoxybenzyl radicals. A somewhat analogous explanation was used when this product was formed in the photolysis of diphenyldiazomethane in the presence of benzyl methyl ether.[20]

We have found the relatively electron-rich double bonds of the ketene acetals to be of no value as traps for the proposed intermediate carbenes. The report that 1-decene acts as a poor trap in the thermal decomposition of the potassium salt of IIe while diethyl fumarate gives a 62% yield of the corresponding cyclopropane derived from α-methoxyphenylcarbene[21] coupled with our data serves to indicate that this carbene is relatively nucleophilic.

Experiments are presently underway to test further this proposed abnormal pathway in the reactions of sodium hydride, as well as other bases, with *p*-tosylhydrazones.

Experimental Section[22]

Methyl Formate *p*-Tosylhydrazone (IIa).—To 10.6 g (0.10 mole) of methyl orthoformate was added 14.8 g (0.08 mole) of *p*-toluenesulfonylhydrazine with stirring. Within 15 min solution had occurred, but shortly a precipitate again appeared. After 40–60 min a solid mass had formed which was washed with petroleum ether (bp 30–60°), leaving 16.6 g (93%) of a crystalline product, mp 88–93°. Recrystallization from benzene–methanol (50:50) gave a product melting at 151.5–153°.

Anal. Calcd for $C_9H_{12}N_2O_3S$: C, 47.36; H, 5.30. Found: C, 47.11; H, 5.01.

Preparation of the Sodium Salt of Methyl Formate *p*-Tosylhydrazone.—To a rapidly stirred mixture of 1.95 g (0.043 mole) of a 53.5% sodium hydride suspension in mineral oil in 100 ml of dry tetrahydrofuran, cooled in an ice bath, was slowly added 9.89 g (0.043 mole) of hydrazone IIa. During the addition the mixture turned light yellow. Stirring was continued for an additional 1 hr, after which the reaction mixture was filtered and the solid recrystallized from ethanol and water to give 7.25 g (67%) of the salt. The infrared and nmr spectra showed the loss of the N-H function.

Ethyl Formate *p*-Tosylhydrazone (IIb).—The same procedure was followed as in the synthesis of IIa, using 22.2 g (0.15 mole) of ethyl orthoformate and 18.6 g (0.10 mole) of *p*-toluenesulfonylhydrazine to yield 20.0 g (87%) of IIb, mp 116–118°. Recrystallization from benzene–Skellysolve B (75:25) gave a colorless crystalline product, mp 118.5–119.5°.

Anal. Calcd for $C_{10}H_{14}N_2O_3S$: C, 49.57; H, 5.82; mol wt, 242. Found: C, 49.64; H, 5.96, mol wt, 242 (osmometer, ethanol solvent).

Preparation of the Sodium Salt of Ethyl Formate *p*-Tosylhydrazone.—To a solution of 2.4 g (0.01 mole) of IIb in 100 ml of dry tetrahydrofuran cooled in an ice bath, was added with stirring 0.28 g (0.01 mole) of a 53.5% sodium hydride dispersion in mineral oil. The mixture was stirred for 1 hr, a few drops of ethanol were added to destroy any remaining sodium hydride, and the mixture was filtered. The precipitate was washed with ether to give 2.7 g (100%) of the salt. The infrared and nmr spectra of the product showed the loss of N-H.

Ethyl Acetate *p*-Tosylhydrazone (IIc).—In the same manner as for IIa, 16.2 g (0.1 mole) of ethyl orthoacetate and 14.9 g (0.08 mole) of *p*-toluenesulfonylhydrazine were mixed together to give 20.5 g (85%) of the desired compound, mp 86–89°. Repeated recrystallizations from ethyl acetate gave a product, mp 162–165°.

Anal. Calcd for $C_{11}H_{16}N_2O_3S$: C, 51.54; H, 6.29, mol wt, 256. Found: C, 51.73; H, 6.33; mol wt, 259 (osmometer, chloroform solvent).

Preparation of the Salt of Ethyl Acetate *p*-Tosylhydrazone.—To 3.59 g (0.08 mole) of a 53.5% suspension of sodium hydride in mineral oil in 30 ml of diglyme cooled with an ice bath was added dropwise 20.5 g (0.08 mole) of IIc, mp 86–89°, dissolved in 125 ml of diglyme. Stirring was continued for 1 hr. Owing to the fineness of the precipitate, the product was centrifuged and washed twice with ether to give 17.5 g (84%) of the sodium salt. The loss of the N-H function was indicated in the infrared and nmr spectra of this product.

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[19] H. Reimlinger, *Ber.*, **97**, 339 (1964).

[20] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4675 (1952).

[21] See ref 16.

[22] All melting points were taken on a Kofler hot stage and are corrected. Boiling points are uncorrected. Infrared absorption spectra were determined on a Perkin-Elmer Model 137 double-beam recording spectrophotometer. Nmr spectra were determined on a Varian A-60 recording spectrometer using carbon tetrachloride as solvent (unless otherwise stated) and tetramethylsilane as the internal standard. Ultraviolet absorption spectra were determined on a Cary Model 11 recording spectrophotometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Molecular weights were obtained with a Mechrolabs osmometer, Model 301 A, or with a Bendix Time-of-Flight mass spectrometer. Gases were analyzed by vapor phase chromatography on a Molecular Sieve 5A column.

Ethyl Propionate *p*-Tosylhydrazone (IId).—Nine grams (0.05 mole) of *p*-toluenesulfonylhydrazine was added to 30.0 g (0.17 mole) of ethyl orthopropionate as in the preparation of IIa. The isolated product weighed 9.9 g (74%), mp 145–148°, which when recrystallized from ethanol melted at 151–152.5°.

Anal. Calcd for $C_{12}H_{18}N_2O_3S$: C, 53.31; H, 6.71; mol wt, 270. Found: C, 53.57; H, 6.72; mol wt, 271 (osmometer, chloroform solvent).

Preparation of Sodium Salt of Ethyl Propionate *p*-Tosylhydrazone.—To a mixture of 1.3 g (0.005 mole) of IId in 10 ml of cold dry monoglyme was added 0.28 g (0.006 mole) of a 53.5% sodium hydride dispersion in mineral oil. The mixture was stirred for 1 hr, filtered, and recrystallized from ethanol, yielding 1.46 g (77%) of the desired salt. The nmr and infrared spectra of this compound showed the loss of N–H.

Methyl Orthobenzoate.—The method of McElvain and Venerable[23] was followed in the preparation of this compound: bp 112–113.5° (24 mm), 136.5 g (75% yield), $n^{20}D$ 1.4888 [lit.[23] bp 114–115° (25 mm), 86% yield, $n^{25}D$ 1.4858].

Methyl Benzoate *p*-Tosylhydrazone (IIe).—Preparation of this compound followed the procedure for IIa, using 18.6 g (0.1 mole) of *p*-toluenesulfonylhydrazine and 21.6 g (0.12 mole) of methyl orthobenzoate to yield 26.3 g (86%), mp 139–143°, of the desired compound. Recrystallization from methanol afforded the compound with a melting point of 141–143.5°.

Anal. Calcd for $C_{15}H_{16}N_2O_3S$: C, 59.19; H, 5.30. Found: C, 59.34; H, 5.37.

Preparation of the Sodium Salt of Methyl Benzoate *p*-Tosylhydrazone.—A solution of 3.97 g (0.013 mole) of IIe in 30 ml of dry tetrahydrofuran was cooled in an ice bath. To this was added in small portions, 0.58 g (0.013 mole) of a 53.5% mineral oil suspension of sodium hydride. The mixture was stirred for 30 min, filtered, washed with petroleum ether, and dried, yielding 3.98 g (93.5%) of the desired salt. The nmr and infrared spectra indicate the loss of the N–H group.

Ethyl Orthocarbonate.—This compound was prepared according to the procedure of Roberts and McMahon[24]: bp 158–161°, 43% yield, $n^{20}D$ 1.3920 (lit.[24] bp 158–161°, 46–49%, $n^{25}D$ 1.3905–1.3908).

Diethyl Carbonate *p*-Tosylhydrazone (IIf).—This compound was prepared in the same manner as IIa, using 9.6 g (0.05 mole) of ethyl orthocarbonate and 7.4 g (0.04 mole) of *p*-toluenesulfonylhydrazine to give 11.1 g (97%) of IIf. The product was recrystallized from ethanol, 10.0 g (87%), mp 86.5–87.5° (lit.[5] mp 85–86°).

Anal. Calcd for $C_{12}H_{18}N_2O_4S$: C, 50.34; H, 6.34; mol wt, 286. Found: C, 50.16; H, 6.26, mol wt, 275 (osmometer, chloroform solvent).

Preparation of the Sodium Salt of Diethyl Carbonate *p*-Tosylhydrazone.—This salt was prepared in the same manner as the sodium salt of IIb, using 20 ml of diglyme as the solvent, 5.5 g (0.019 mole) of IIf, and 0.85 g (0.019 mole) of sodium hydride as a 53.5% dispersion in mineral oil. The resulting precipitate was filtered and washed with ether, 5.3 g (86%). The infrared and nmr spectra indicate the loss of the N–H function.

Acetone *p*-Tosylhydrazone.—To 5.0 g (0.05 mole) of 2,2-dimethoxypropane was added with stirring 4.82 g (0.026 mole) of *p*-toluenesulfonylhydrazine. The mixture was placed in the refrigerator for 2 hr and filtered to give 5.09 g (87%) of product, mp 145–146°, which when recrystallized from ethanol had a melting point of 157–158° (lit.[25] mp 156°).

Ketene Diethyl Acetal.—This compound was prepared according to the procedure of McElvain and Kundiger[26]: bp 83–86° (200 mm), 67–72% [lit.[26] bp 83–86° (200 mm), 67–75%).

Reaction of Ketene Diethyl Acetal with *p*-Toluenesulfonylhydrazine.—To 5.0 g (0.05 mole) of ketene diethyl acetal was added with stirring 4.2 g (0.023 mole) of *p*-toluenesulfonylhydrazine. The mixture was stirred for 30 min and filtered, and the precipitate was washed three times with petroleum ether to give 5.5 g (86%) of a white crystalline precipitate, mp 81–86°. The infrared and nmr spectra were identical with those of IIc.

Reaction of Methyl Formate *p*-Tosylhydrazone with Sodium Hydride.—To a stirred mixture of 8.79 g (0.20 mole) of sodium hydride (as a 53.5% suspension in mineral oil) in 300 ml of dry triglyme cooled to 5° in an ice bath was added in small portions 38.9 g (0.17 mole) of IIa. During this addition no gas was liberated. However, when the temperature of the reaction mixture was allowed to warm to approximately 25°, a vigorous evolution of gas was observed. During this time the temperature of the reaction mixture rose to 41° and the color of the reaction mixture changed from its initial white suspension to yellow with purple at the upper edges of the reaction mixture. Then the mixture became brown, and finally returned to white. The mixture was stirred for 7 hr, and after this time 5880 cc of gas had been collected The reaction mixture was heated to 110° for 1 hr, during which time an additional 190 cc of gas was collected. The gas was shown by vapor phase chromatography to contain nitrogen and hydrogen, and a trace of methane and carbon monoxide.

The reaction mixture was cooled to room temperature and filtered. The precipitate was dissolved in water and washed three times with ether. The water was removed from the layer under reduced pressure to yield 30.9 g (84%) of sodium *p*-toluenesulfinate dihydrate.

The triglyme solvent was distilled from the reaction mixture filtrate at 61° (0.4 mm). The Dry Ice trap in the distillation system contained 2.39 g of a liquid which on vapor phase chromatography on a 6 ft × 0.25 in. Carbowax column was shown to be 81.9% of methanol (35.3% yield), 8.2 min; 1.3% on an unidentified component having a retention time of 17.9 min; 5.5% of a liquid of unassigned structure having a 24.4-min retention time; and 10.7%, 0.256 g, of water, probably obtained from the atmosphere backing into the trap during manipulations. The nmr spectrum of the peak having a retention time of 24.4 min consists of singlets at τ 1.75 and 5.71 integrating for 1 and 3 protons, respectively. The presence of methanol was proven by comparison of retention times with an authentic sample and by collection of a sample from the vapor phase chromatograph and comparison of its infrared spectrum with an authentic sample.

The residue from the distillation was washed with ether. The infrared spectrum of the ether-insoluble portion showed it to be IIa (5.7 g, 14%). The ether was removed from the ethereal solutions and, on standing, crystals formed in the residue. The crystals were filtered off and recrystallized from heptane to give 0.74 g (2%) of methyl formate N′-methyl-*p*-tosylhydrazone (IV), mp 96–98°. The infrared and nmr spectra of IV were consistent with the assigned structure.

Anal. Calcd for $C_{10}H_{14}N_2O_3S$: C, 49.57; H, 5.82; N, 11.56. Found: C, 49.78; H, 6.05; N, 11.31.

Dimethoxyethylene.—This compound was prepared from 1,1,2-trimethoxyethane as previously reported in the literature.[11] The reaction product was purified by gas chromatography on a 6 ft × 0.25 in. Carbowax 20 M column. Three components were observed: the two isomers of dimethoxyethylene (1:3.4) and 1,1,2-trimethoxyethylene. Correcting the yield for recovered starting material, the olefins were obtained in 41% yield [lit.[11] 18% yield, bp 97–99° and 103° (1:3.5)]. The nmr spectra of the two olefins were identical, showing peaks at τ 3.68 and 6.54 in the ratio of 1:3.

Thermal Decomposition of IIIc, the Sodium Salt of Ethyl Acetate *p*-Tosylhydrazone.—IIc (35.9 g, 0.14 mole) was added slowly to a stirred mixture of 8.1 g (0.18 mole) of sodium hydride (as a 53.5% suspension in mineral oil) in 300 ml of dry triglyme. A small amount of nitrogen was liberated along with the hydrogen (3510 cc). After stirring for 1 hr, the mixture was heated to 175° for 2.5 hr. The total gas volume, 6020 cc, was collected over water and was shown by vapor phase chromatograph integration to contain nitrogen, ethylene, and carbon monoxide in the ratio of 365:3:1, respectively.

The reaction mixture was cooled to 95° and placed under vacuum (25 mm) to remove the volatile products from the reaction mixture into a Dry Ice trap attached to the reaction flask. The trap contained 4.08 g of material consisting of 39% ethanol (22.2%), 26% acetal (24.3%), 27% ethyl vinyl ether (10%), 5% diethyl ether (1.4%), 2% acetaldehyde (1.1%), and 1% ethyl acetate (0.2%). These products were separated by vapor phase chromatography using a 6 ft × 0.25 in. β,β-oxidipropionitrile on Chromosorb W column at 50°. The retention time of each component, with the exception of acetal, was checked with an authentic sample. In every case, except with acetaldehyde, diethyl ether, and ethyl acetate, a sample of the component

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[23] S. M. McElvain and J. T. Venerable, *J. Am. Chem. Soc.*, **72**, 1661 (1950).

[24] J. D. Roberts and R. E. McMahon, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 457.

[25] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

[26] S. M. McElvain and D. Kundiger, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p 506.

was collected and its infrared spectrum was compared with that of an authentic sample. The nmr spectrum of acetal was identical with that previously published.[27]

The nonvolatile liquid slurry was filtered and the precipitate was washed three times with 100-ml portions of ether. The precipitate was dissolved in water and extracted four times with 100-ml portions of ether. The ethereal washings were dried over anhydrous sodium sulfate, and the ether was distilled off to yield only triglyme. The water was removed from the aqueous solution at reduced pressure, yielding 28.5 g (95%) of sodium *p*-toluenesulfinate dihydrate.

The triglyme was distilled from the reaction filtrate at reduced pressure, leaving a residue which was filtered. The purity of the triglyme was assured by vapor phase chromatography. The precipitate was dissolved in water and washed five times with 50-ml portions of ether. The ethereal extracts were combined and dried over sodium sulfate, and the ether was distilled off, leaving a mixture of triglyme and mineral oil. The aqueous solution was evaporated, leaving 2.18 g of a dark oil which, when chromatographed on alumina using benzene as the eluent, gave 0.53 g (1.5%) of IIc.

Thermal Decomposition of IIIe, the Sodium Salt of Methyl Benzoate *p*-Tosylhydrazone.—To a mixture of 7.18 g (0.16 mole) of sodium hydride (as a 53.5% suspension in mineral oil) in 200 ml of dry diglyme, cooled in an ice bath, was added with stirring 44.3 g (0.145 mole) of IIe. After the addition was complete, the reaction mixture was allowed to warm to room temperature and stirred for an additional 2 hr. The mixture was then heated at 120° for 2.5 hr. The gas liberated during the reaction contained nitrogen and methane in relative amounts of 65:1, respectively.

The reaction mixture was filtered, and the precipitate was dissolved in water and extracted with three 100-ml portions of ether. The water was removed at reduced pressure from the aqueous solution, yielding 24.5 g (79%) of sodium *p*-toluenesulfinate dihydrate.

The filtrate and ethereal extracts were combined, dried over anhydrous sodium sulfate, and distilled at reduced pressure. Vapor phase chromatography of the distillates indicated the presence of benzaldehyde (1.4%), benzaldehyde dimethyl acetal (2.1%), and methyl benzoate (3.6%). Further proof of the presence of these compounds was obtained by collection of each component and comparison of its infrared and nmr spectra with those of authentic samples. These separations were accomplished on a 20 ft × 0.25 in. diisodecyl phthalate on Chromosorb W column.

The residue from the distillation solidified on standing and was recrystallized from petroleum ether to yield 16.17 g (66%) of α-methoxybenzalazine, mp 73.5–74°. The ultraviolet absorption spectrum of this compound has λ_{max} 269 mμ (ϵ 12,000) in 95% ethanol. The nmr spectrum showed two multiplets centered at τ 2.11 and 2.66 and a singlet at τ 6.20 which integrated for 2:3:3 protons, respectively. Attempts to chromatograph the reaction product on Woelm neutral alumina (activity I) resulted in decomposition of the azine.

Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44; mol wt, 268. Found: C, 71.43; H, 5.63; N, 10.63; mol wt, 264 (osmometer, ethanol solvent).

Reaction of Methyl Formate *p*-Tosylhydrazone with Sodium Hydride in Ketene Diethyl Acetal.—To a well-stirred suspension of 7.64 g (0.17 mole) of sodium hydride (53% in mineral oil) in 64.4 g (0.55 mole) of ketene diethyl acetal was added in small portions 38.5 g (0.17 mole) of IIa. No color had developed after the addition of a small amount of IIa so the reaction was heated at 95–100° during the addition of the remaining *p*-tosylhydrazone (1 hr). The reaction mixture was then distilled at reduced pressure to yield 23.3 g (36%) of ketene acetal, 1.1 g (1%) of triethyl orthoacetate, and 8.3 g (19%) of ethyl β-ethoxycrotonate. The infrared and nmr spectra of the crotonate were compatible with the structure of the compound.

The residue from the distillation was taken up in water and extracted five times with ether. The ethereal extracts were dried over sodium sulfate, the ether was distilled, and the residue (13.6 g) was heated to 130° (0.05 mm) without any material distilling out of the liquid. The water was removed from the aqueous solution, leaving 33.2 g of a mixture, which was washed with ethanol. In this manner 7.37 g (17%) of IIIa was recovered. The solvent was removed from the ethanol-soluble portion, leaving a dark tar which on standing gave 1.85 g (5%) of the starting material. The infrared spectra of samples of the reaction product before and after chromatography on neutral alumina indicated that decomposition occurred on the alumina.

Thermal Decomposition of the Sodium Salt of Methyl Benzoate *p*-Tosylhydrazone in the Presence of Ketene Diethyl Acetal.—A well-stirred mixture of 40.5 g (0.38 mole) of ketene diethyl acetal, 28.3 g (0.087 mole) of IIIe, and 75 ml of diglyme was heated at 125° for 1.5 hr at which time 74% of the theoretical amount of nitrogen had been collected. The reaction mixture was cooled and the solid was filtered to yield 15.5 g (68%) of sodium *p*-toluenesulfinate. The excess ketene diethyl acetal was distilled from the filtrate. Water was added to the residue from the distillation, and the resulting mixture was extracted twice with ether. The ethereal extracts were dried over sodium sulfate and the ether was distilled. The resulting dark red oil, weighing 9.9 g, was fractionated through a spinning-band distillation column. Vapor phase chromatography, using an Apiezon L 6 ft × 0.25 in. column, of the first three fractions, which boiled from 34 (0.15 mm) to 67° (0.08 mm), indicated three major components having retention times of 5.95, 8.15, and 13.15 min. Using the integrated areas of each peak to determine the amount of each component present in each of the fractions and then collecting each component to determine its identity by comparison of its infrared spectrum with that of an authentic sample, the components were shown to be 0.11 g (1.2%) of benzaldehyde, 0.28 g (2.4%) of methyl benzoate, and 1.27 g of an unidentified mixture.

This latter mixture has not been resolved by any of several columns. When large amounts ($\sim$50 μl) of this material are chromatographed, a shoulder appears on the peak. The infrared spectrum of this material indicates it to be an α,β-unsaturated ester (5.81 μ) and the nmr spectrum ($CDCl_3$) indicates the presence of aromatic protons, a singlet at τ 2.65, a multitude of peaks from τ 5.20 to 7.50 with a sharp singlet at τ 6.79, and another series of peaks in the region from τ 8.37 to 9.29.

The last three fractions boiling from 98 (0.05 mm) to 120° (0.02 mm) were combined and redistilled. On standing, one fraction, bp 85–105° (0.02 mm), gave 0.1 g of 1,2-dimethoxy-1,2-diphenylethane, mp 142–143° (lit.[25] mp 140–142°). The nmr spectrum in $CDCl_3$, using an external tetramethylsilane standard, consisted of singlets at τ 2.52 (5), 5.46 (1), and 6.61 (3). Another fraction, bp 121 (0.04 mm) to 120° (0.02 mm), 2.2 g (18%), was shown by its infrared spectrum to be methoxybenzalazine. The infrared spectrum of the residue from the distillation, 2.64 g, indicated that it contained mostly methoxybenzalazine.

Dichlorocyclopropanone Diethyl Acetal.—This compound was prepared according to the procedure of McElvain and Weyna[28]: bp 65 (8 mm) to 63° (6 mm), 17.5 g, 44% yield [lit.[28] bp 69–70° (9 mm), 68% yield].

Cyclopropanone Diethyl Acetal.—The procedure used for the preparation of this compound was identical with that used by Gassman and Pape[29] for the lithium dechlorination of 7,7-dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-ene. The desired compound was isolated: bp 119–120°, 4.47 g (39%), $n^{20}D$ 1.4004 (lit.[28] bp 120–121°, $n^{25}D$ 1.3980). Vapor phase chromatography of the crude reaction product indicated a 54% yield of cyclopropanone diethyl acetal.

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[29] P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).