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STEREOCHEMISTRY IN THE 1,2-HYDROGEN MIGRATION TO A DIVALENT CARBON

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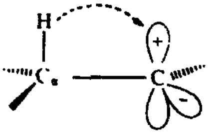
Abstract—The *trans/cis* ratios of the olefins obtained by both the carbenic and cationic decomposition of the diazo compounds $R_1CN_2CH_2R_2$, in which both R_1 and R_2 are the alkyl, aryl, or carboethoxy groups, have been determined. In the alkyl and aryl cases the *trans*-olefins were produced predominantly, whereas in the carboethoxy case the *cis*-olefin was formed preferentially. These stereochemical results were successfully explained by considering the conformations of the singlet carbene.

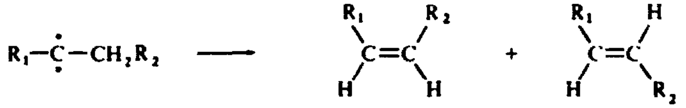
INTRODUCTION

IN THE previous papers,[1, 2] it has been shown that the intramolecular 1,2-hydrogen migration to a divalent carbon occurred in the singlet state, yielding an olefin: as shown in Scheme I, the H-bonded to C_α migrates to the vacant *p*-orbital of the sp^2-hybridized divalent carbon.



SCHEME I

It is well known[3] that the 1,2-hydrogen shift to a carbene gives a mixture of isomeric olefins (Eq 1).



(1)

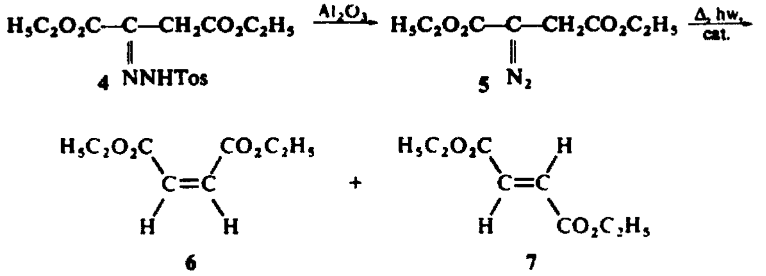
1   2 cis   3 trans

However, investigations[4] concerning to the stereochemical preference do not indicate whether **2** (*cis*) or **3** (*trans*) would be produced predominantly. It is of particular interest to determine the factors which control this point.

Consequently, we initiated a systematic investigation on the stereochemistry of the 1,2-hydrogen migration to carbenes. Thus, the diazo compounds or tosylhydrazones corresponding to the carbene **1**, in which both R_1 and R_2 are the alkyl, aryl, or ocarboethoxy groups, were decomposed by both a carbenic and cationic means. The *trans/cis* ratios of the olefins thus obtained were determined, and the discussion on the stereochemical results was undertaken using a model of Scheme I.

RESULTS

1. *Substituent effect of carboethoxy group*



(2)

Diethyl diazosuccinate (5) was prepared in a good yield by merely passing the corresponding tosylhydrazone (4) through a column of alumina. Treatment of 4 with base did not give pure 5.[*] The structure of 5 was confirmed by analytical and spectral data, and also chemically through the acetate derivative prepared by decomposition in acetic acid.

The thermal, photochemical, and acid-catalyzed decompositions of 5 gave both diethyl maleate (6) and diethyl fumarate (7) in good yields (Eq 2). The *cis/trans* ratios were determined by VPC, and these results are summarized in Table 1. The isomerization of the olefins was proved to be negligible in the processes of the decomposition, isolation, and VPC analysis, and this applies to all the cases described later.

TABLE 1. DECOMPOSITION OF DIETHYL DIAZOSUCCINATE (5)

			Relative yield (%)		Ratio
Thermal	Solvent	Olefin (%)	*cis*-6	*trans*-7	*cis/trans*
	Mesitylene	93	88	12	7
	Xylene	68	90	10	9
	Anisole	91	91	9	10
	Di-n-buthyl-ether	91	95	5	19
	Diglyme	86	97	3	32
Photochemical	n-Hexane	96	88	12	7
Catalyzed	CuCl	89	67	33	2
	$AlCl_3$	46	89	11	8
	HCl	33	80	20	4
	AcOH	32	92	8	12

Unexpectedly, the thermodynamically unstable[7] *cis*-olefin 6 was produced in preference to the thermodynamically stable *trans*-olefin 7 in any decomposition method used, as apparent from Table 1. It can be seen that the *cis* component of the olefin was ca. 90–97 % in the thermal decomposition, and 80 % in the HCl-catalysis. A marked solvent effect was observed in the thermal decomposition: the more polar the solvent, more preferential the *cis*-olefin formation. For example, the *cis/trans* ratio was found to be only 7 in mesitylene, whereas in more polar diglyme the ratio increased to 32, and the *cis*-6 comprised 97 % of the olefin.

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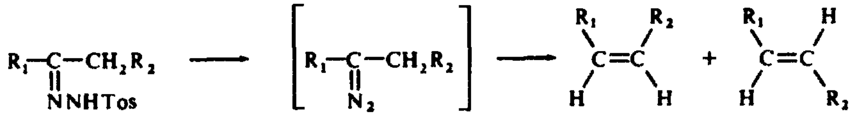
[*] The usual Bamford-Stevens method would lead to the hydrolysis of the ester group,[5] and see Ref. 6.

2. *Substituent effect of alkyl groups*


(3)

8a,b,c **9a,b,c** **10a,b,c** **11a,b,c**

a: $R_1 = C_2H_5, R_2 = CH_3$; b: $R_1 = CH_3, R_2 = C_2H_5$; c $R_1 = t\text{-Bu}, R_2 = CH_3$

The tosylhydrazones (**8a, b, c**) substituted by alkyl groups were decomposed, without the isolation of the diazo compounds (**9a, b, c**)* which were unstable at room temperature, under the two distinct conditions. It has been generally accepted that the decomposition of a diazo compound or tosylhydrazone proceeds *via* the carbene intermediate in an aprotic solvent, while it proceeds *via* the diazonium and/or carbonium ion in a protic medium.[9] Thus, the decomposition was carried out in both aprotic (diglyme) and protic (ethylene glycol)[9] media in the presence of sodium methoxide as base.

Pentan-3-one tosylhydrazone (**8a**) was decomposed with sodium methoxide in aprotic diglyme at 140°. The colour of the solution changed temporarily to pink, presumably the colour of the diazo **9a**, and vanished after vigorous and approximately quantitative evolution of nitrogen. The products were isolated and purified by preparative VPC, and characterized by comparison with authentic samples. Thus, we obtained pent-2-ene in an 89% yield, and the *trans*(**11a**)/*cis*(**10a**) ratio was found to be 3. On the other hand, a similar decomposition of **8a** in protic ethylene glycol gave pent-2-ene (48%)† and a trace of pent-1-ene, and the ratio decreased to 1·4.

It is notable that the thermodynamically stable[7] *trans*-olefin was formed in preference to the *cis*-olefin in the decomposition of **9a**, contrary to the carboethoxy case **5** in which the thermodynamically unstable *cis*-olefin was produced predominantly, and the *trans*/*cis* ratio decreased in the protic solvent. These tendencies were also observed in the other alkyl and aryl substituted carbenes as described later.

The decomposition of pentan-2-one tosylhydrazone (**8b**) in dry diglyme gave pent-2-ene (86%) and pent-1-ene (4%). The **11b**/**10b** ratio was found to be 4·7. On the other hand, in ethylene glycol it gave pent-2-ene (32%) and pent-1-ene (15%), and the ratio decreased to 1·3.

The similar decomposition of 2,2-dimethylpentan-3-one tosylhydrazone (**8c**) substituted with a bulky *t*-Bu group gave 2,2-dimethylpent-3-ene (80%) in diglyme, and the **11c**/**10c** ratio was found to be 249, while in ethylene glycol the ratio decreased down to 17.

3. *Substituent effect of aryl group*

In connection with the results of **8**, desoxybenzoin tosylhydrazone (**12**) was directly decomposed with sodium methoxide in dry diglyme at 160°. Stilbene was obtained in a 76% yield, and the *trans*-**14**/*cis*-**13** ratio was found to be 13. In ethylene glycol the ratio decreased to 2. This tendency is the same as that of the alkyl substituted cases.

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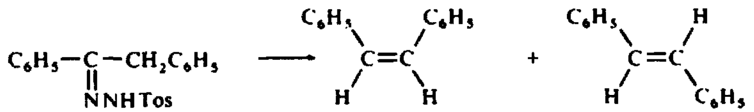
* It is well known that the thermal decomposition of the tosylhydrazone in aprotic solvents gives the free carbene *via* the diazo compound.[8]

† The decrease in yield will be due to the side reaction of the carbene with the protic solvent; cf Ref. 11.



12 **13** **14**

DISCUSSION

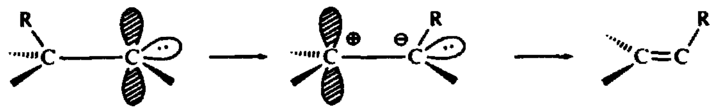
The above results obtained can be summarized by stating that: (i) the thermodynamically favourable *trans*-olefin was preferentially obtained in the alkyl or aryl substituted carbene, whereas unexpectedly in the carboethoxy substituted compound the thermodynamically less favourable *cis*-olefin was formed in preference to the *trans*-olefin, (ii) in the alkyl substituted carbenes, more bulky the alkyl group, the more preferential the *trans*-olefin; if the substitution group was changed from an Et to a Bu group, the *trans*/*cis* ratio increased from 3 to 249, (iii) in the alkyl and aryl cases, the *trans*/*cis* ratio in the protic decomposition (cationic process) was smaller than in the corresponding aprotic solvent (carbenic one), while in the carboethoxy case the ratio in the cationic pass was larger than in the carbenic one, (iv) the solvent effect was observed in the thermal carbenic decomposition of diethyl diazosuccinate (Table 1); the formation of the *cis*-olefin was more preferential in a polar solvent than in a nonpolar medium.

TABLE 2. THE *trans*/*cis* RATIOS IN THE CARBENIC AND CATIONIC DECOMPOSITION

	R_1/R_2	Et/Me	Me/Et	t-Bu/Me	Ph/Ph	COOEt/COOEt
Carbenic	*trans*/*cis*	3	4·7	249	13	0·03
Cationic	*trans*/*cis*	1·4	1·3	17	2	0·3[a]

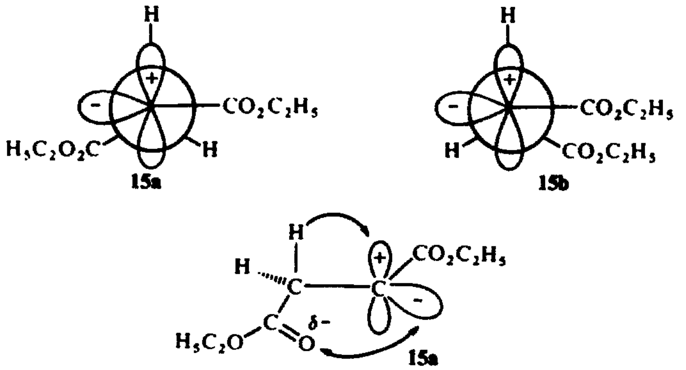
[a] This is the value in HCl-catalyzed decomposition. In ethylene glycol, the decomposition products of 5 and the solvent could not be separated.

The i, ii, and iii are summarized and shown in Table 2. The above four points can not be explained merely by the thermodynamical stability of the products. Kirmse and Buschhoff pointed out[4] that the conformation of the carbene must be considered on the stereochemistry of the olefin formation reaction in the carbenic decomposition of a diazo compound (Scheme II). However, they assumed *a priori* that the migration (migration group R = H, Alkyl, or Alkoxyl) proceeds not through the triplet state but the singlet state.



SCHEME II

Now, as we have already clarified that the hydrogen migration occures in the singlet state,[1, 2] we can safely and reasonably explain the above results by considering the singlet conformations. Scheme III depicts the Newman projection of Scheme I in the carboethoxy case.



SCHEME III

From **15a** the *trans*-olefin is produced, and the *cis*-olefin comes from **15b**. Although sterically **15a** is more stable than **15b**, electrostatically *vice versa*, because the electrostatical repulsion between the lone pair of the sp^2-hybridized divalent carbon and the carbonyl oxygen atom is greater in **15a** than in **15b**.[10] Consequently, the dominance of the electrostatical rather than the sterical factors would favour the *cis*-isomer.

Furthermore, these ionic intermediates agree with the observation of the solvent effect. The electrostatic repulsion becomes more effective in a polar solvent than in a nonpolar one, the *cis*-olefin increases as the solvent is changed from the nonpolar to polar one.

On the other hand, in the alkyl and aryl cases the electrostatic attraction rather than repulsion between the lone pair and R_2 would act,* and then **16a** is more stable than **16b** both electrostatically and sterically (Scheme IV). This leads to the preference of the *trans*-olefin.

SCHEME IV
R_1, R_2 =
alkyl or aryl

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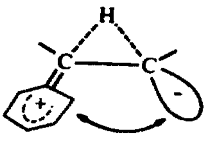
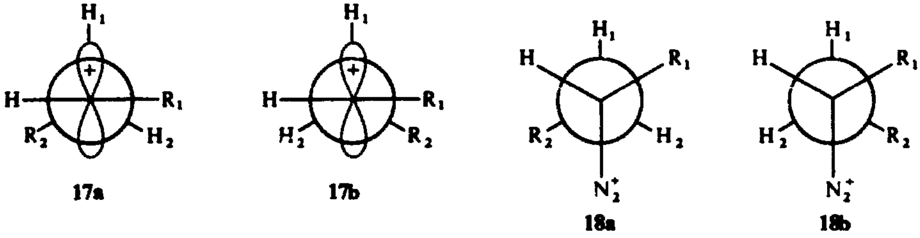
* Alkyl groups should push out the electron and bear a positive charge.
In the aryl case, also, there should be the electrostatical attraction as shown in the diagram.



In the alkyl cases, the more bulky alkyl group favours the sterically stable **16a**. Thus, the *trans/cis* ratio is 3 and 4·7 in **9a** and **9b** respectively, and increases up to 249 in **9c**.

Finally, in the cationic process, the intermediate carbonium ion (**17a** and **17b**) and/or diazonium ion (**18a** and **18b**) were considered. (Scheme V).



17a **17b** **18a** **18b**

SCHEME V

The olefin is formed either by the elimination of H_1^+ from **17** or by the concerted *trans*-elimination of N_2 and H_1^+ from **18**.[11] Thus, **17a** or **18a** gives the *trans*-olefin and **17b** or **18b** does the *cis*-olefin. Contrary to **16** in the carbenic process, the lone pair is absent in **17** or **18**, so, the stereochemistry of the olefin thus obtained would be governed by only the steric factor. In the alkyl and aryl cases, the proportion of **17a** or **18a** *versus* **17b** or **18b** respectively is lower than that of **16a** *versus* **16b**, because **16a** is advantageous with respect to both the electrostatical and sterical factors. Therefore, the *trans/cis* ratio in the cationic decomposition is smaller than in the corresponding carbenic one (Table 2).

On the other hand, in the carboethoxy case, the displacement of the lone pair into a H atom in **15a** will lead to the loss of the electrostatic repulsion, causing an increase in the *trans*-olefin. In fact, the *cis/trans* ratio in HCl-catalyzed decomposition (completely cationic process[6]) becomes smaller than is the case in the thermal carbenic decomposition (Table 1).*

In conclusion, it has been found that the stereochemistry should depend on both the steric and electrostatic factors. The former will act so as to give the thermodynamically favourable olefin, while the latter, if the carbene is substituted with the electronegative group such as carboethoxy, will afford the thermodynamically disfavoured compound.

EXPERIMENTAL

All temps are uncorrected. IR spectra were recorded with a Hitachi-S2 spectrophotometer; NMR spectra were obtained by a Japan Electron Optics JNM-4H-100 spectrometer. Chemical shifts are given in τ-scale together with splitting patterns and relative integrated area. UV spectra were measured with a Hitachi EPS-2U spectrophotometer. VPC analyses were carried out on a Yanagimoto 5DH using a 5·25 m × 0·3 cm column packed with 30% $AgNO_3$-$C_6H_5CH_2CN$ on firebrick. Alternatively employed was a Japan Electron Optics JDT 650 TP using a 2 m × 0·6 cm column packed with Microwax on celite.

Diethyl oxalacetate tosylhydrazone (4)

A soln of 49·5 g (0·25 mol) diethyl oxalacetate,[12] 50 g (0·27 mol) *p*-toluenesulfonylhydrazine, and 300 ml

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* Although the *trans*-olefin increased in the cationic decomposition, it did not exceed over the *cis*-olefin. This is the subject for a future study.

EtOH was refluxed for 1 hr, then ca. 200 ml EtOH was evaporated on a water bath. The white ppt formed was removed by filtration and air dried. The crude diethyl oxalacetate tosylhydrazone, 47·9 g (54%), was recrystallized twice from benzene–ligroin; m.p. 91–92°; IR (Nujol) 3260, 1730, 1600, 1380, 1350, 1310, 1130, 1110, 710, and 690 cm^{-1}. (Found: C, 50·68; H, 5·60; N, 7·95. Calc. for $C_{15}H_{20}O_6N_2S$: C, 50·56; H, 5·66; N, 7·86%).

Diethyl diazosuccinate (5)

Compound 4 (4·7 g) was chromatographed on a column of 60 g of alumina. Elution with benzene (200 ml) resulted in the yellow oil. Distillation of the oil under reduced press gave 1·0 g diethyl diazosuccinate (40%); b.p. 103–105° (3 mm); n_D^{25} 1·467; IR (neat) 2120, 1745, 1695, 1375, 1310, 1200, 1115, and 1030 cm^{-1}; NMR (in CCl_4) 5·63–6·03 (quadriplet–quadriplet, 4), 6·78 (s, 2), 8·55–8·85 (t, 6); $UV_{max}^{C_6H_{12}}$ 221, 257, 405 mμ. The decomposition of 5 in AcOH gave 1,2-dicarboethyoxy-1-acetoxyethane in a 64% yield: b.p. 107–108° (2 mm); IR (neat) 1750, 1376, 1280, 1210, 1180, 1098, 1070, and 1028 cm^{-1}; NMR (in CCl_4) 4·67–4·82 (t, 1), 5·73–6·00 (m, 4), 7·22–7·32 (d, 2), 7·94 (s, 3), 8·64–8·84 (triplet–triplet, 6). (Found: C, 51·68; H, 7·03. Calc. for $C_{10}H_{16}O_6$: C, 51·72; H, 6·94%).

Decomposition of 5

(a) *Thermal decomposition.* A yellow soln of 0·2 g of 5 in 15 ml dry abs solvent, such as mesitylene, xylene, anisole, di-n-butylether, and diglyme, was heated at 170° in an oil bath. After few min, nitrogen was evolved quantitatively, and the yellow colour disappeared. The resulted soln was directly analyzed by the VPC (Microwax, 170°) in order to determine the *cis/trans* ratio. This analytical procedure was used also in the other decomposition methods.

(b) *Photochemical decomposition.* A soln of 0·2 g of 5 in 20 ml abs n-hexane was irradiated for 1 hr at 0° using Eikosha high press mercury lamp equipped with the filter soln[13] (3650–3663 Å) in order to avoid the isomerization of the olefins formed.

(c) CuCl *and* $AlCl_3$ *catalyzed decomposition.* To a soln of 0·2 g of 5 in 10 ml of dry ether, 0·5–1·0 g of the catalyzer was added at room temp.

(d) *Acid-catalyzed decomposition.* To a soln of 1·0 g of 5 in 50 ml ether and 20 ml water, 10 ml acid (conc HCl or AcOH) was added at room temp. After the decomposition ceased, the organic layer was separated rapidly, and washed with water several times, and dried over Na_2SO_4.

Pentan-3-one tosylhydrazone (8a)

Compound 8a was prepared in 73% yield from pentan-3-one and tosylhydrazine in a manner similar to that described for 4; m.p. 98·5–99·5°; IR (Nujol) 3260, 1644, 1600, 1376, 1335, 1165, 820, and 690 cm^{-1}. (Found: C, 56·61; H, 7·08; N, 11·24. Calc. for $C_{12}H_{18}O_2N_2S$: C, 56·68; H, 7·14; N, 11·02%).

Pentan-2-one tosylhydrazone (8b)

Compound 8b was prepared in 82% yield from pentan-2-one and tosylhydrazine in a manner similar to that described for 4; m.p. 85·5–86°; IR (Nujol) 3260, 1642, 1600, 1388, 1335, 1170, 930, 815, and 670 cm^{-1}; NMR (in $CDCl_3$) 1·87–2·60 (A_2B_2 type, 4), 2·57 (s, 1), 7·43 (s, 3), 7·53–7·86 (t, 2), 8·14 (s, 3), 8·20–8·63 (m, 2), 9·00–9·30 (t, 3). (Found: C, 56·80; H, 7·17; N, 11·13. Calc. for $C_{12}H_{18}O_2N_2S$: C, 56·68; H, 7·14; N, 11·02%).

2,2-*Dimethylpentan-3-one tosylhydrazone* (8c)

Compound 8c was obtained in 40% yield from 2,2-dimethylpentan-3-one[14] and tosylhydrazine in a manner similar to that described for 4; m.p. 131–132°; IR (Nujol) 3260, 1630, 1600, 1380, 1342, 1170, 972, 910, 818, and 685 cm^{-1}; NMR (in $CDCl_3$) 2·04–2·67 (A_2B_2 type, 4), 2·60 (s, 1), 7·47 (s, 3), 7·54–7·93 (quadriplet, 2), 8·75–9·04 (t, 3), 8·92 (s, 9). (Found: C, 59·26; H, 7·82; N, 9·94. Calc. for $C_{14}H_{22}N_2O_2S$: C, 59·55; H, 7·85; N, 9·92%).

Decomposition of 8a, 8b, and 8c

A mixture of 5 g of 8a, 8b, or 8c, 1·2 g of NaOMe, and 15 ml dry diglyme (carbenic decomposition) or ethylene glycol (cationic one) was heated at 140° in an oil bath. After the decomposition ceased, the temp of the oil bath was raised to evaporate the solvent (< ca. 170°). Then, the volatile materials were collected and analyzed by VPC ($AgNO_3$-$C_6H_5CH_2CN$). The authentic *cis*-, *trans*-pent-2-ene, and pent-1-ene were commercial grade, and *trans*-4,4-dimethylpent-2-ene was prepared according to a known procedure;[15] b.p. 76–77° (lit.[15] 76°); n_D^{20} 1·3980 (lit.[15] 1·3986); NMR (in CCl_4) 4·65 (singlet having satellite peaks, 2), 8·36–8·42 (d, 3), 8·93 (s, 9). The *cis*-isomer was obtained by partial hydrogenation (Pd-BaSO$_4$) of the corresponding acetylene: b.p. 79–80° (lit.[16] 80°); n_D^{20} 1·4030 (lit.[16] 1·4022); NMR (in CCl$_4$) 4·78 (singlet having satellite peaks, 2), 8·28–8·35 (d, 3), 8·93 (s, 9).

Desoxybenzoin tosylhydrazone (12)

Compound **12** was prepared in 92% yield from desoxybenzoin and tosylhydrazine in a manner similar to that described for **4**: m.p. 134–135°; IR (Nujol) 3200, 1635, 1600, 1375, 1170, and 695 cm^{-1}. (Found: C, 69·23; H, 5·71; N, 7·78. Calc. for $C_{21}H_{20}N_2O_2S$: C, 69·21; H, 5·53; N, 7·69%).

Decomposition of 12

A mixture of 3·6 g of **12**, 0·6 g of NaOMe, and 15 ml dry diglyme or ethylene glycol was heated at 160° in an oil bath. After the evolution of N$_2$ ceased, the resulted mixture was poured into water, and extracted twice with ether and dried over CuCl. After the evaporation of ether, the residual material was analyzed by VPC (Microwax).

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