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AZIRIDINES—IV[1]

CATALYTIC DECOMPOSITION OF PHENYLDIAZOMETHANE IN SCHIFF'S BASES[2]

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Abstract—Catalytic decomposition of phenyldiazomethane in Schiff's bases is found to proceed via formation of **trans**-1,3-dipole (azomethine ylide) as an intermediate product. Depending on the size and quantity of the substituents, the ylide undergoes either cyclization in controtatory sense to **cis**-aziridine or cycloaddition[2 + 3] to the C=N bond of imine. The reactivity of double bonds to ylide decreases in the order C=C > C=O > C=N.

In a series of recent studies we have been concerned with reactions of phenyldiazomethane with various types of double bond in the presence of phenylcarbenoid—generating catalysts.[1-3] In a previous work we reported on a new method of synthesizing tertiary aziridines with phenyldiazomethane and Schiff's bases in the presence of zinc iodide.[1] The process did not involve the formation of phenylcarbenoid, but was initiated by a nucleophilic addition of diazocompound to imine—ZnI_2 complex and subsequent elimination of nitrogen (Fig. 1).

Now we present the results of our studies on the reactions of phenyldiazomethane with imines in the presence of cuprous bromide. Until now several papers were published about the reactions of other carbenoids of this type with double C=N bonds,[4-7] but neither the extent nor the mechanism of the reaction has been studied in detail.

RESULTS AND DISCUSSION

Decomposition of phenyldiazomethane in imines. When dropping phenydiazomethane into a large excess of imine containing dissolved cuprous bromide, we observed rapid decoloration of the diazocompound and evolution of N_2. When the reaction was complete and the excess of imine removed, the composition of the mixture was subjected to ^{1}H NMR analysis and separated by column chromatography. In addition to catalytic decomposition, which was carried out at room temperature, thermal decomposition was effected for the sake of comparison by heating phenyldiazomethane in imine up to 120°. Under such conditions, diazocompound immediately decomposed. The results of catalytic and thermal investigations are presented in Table 1 below.

On the basis of ^{1}H NMR spectra of crude reaction mixtures (with excess imine removed), it was found that both in the catalytic and in the thermal method the aziridines **3** which are formed have **cis**-configuration only. Derivatives of imidazolidine **2**, which were formed only in catalytic experiments, had only the *r* − 2, *t* − 4, *t* − 5-configuration.[8] The structure of aziridines **3** and imidazolidines **2** was ascertained by comparison with the spectra of previously described compounds[1,9] or by comparison with authentic samples obtained in another way. Moreover, the **cis**-configuration of aziridine **3c** was confirmed by X-ray analysis.[10] Aziridines **3** and imidazolidine **2a** were isolated from the reaction mixtures with no secondary conversion of these compounds. The originally formed *r* − 2, *t* − 4, *t* − 5-imidazolidine **2b**, on the other hand, underwent complete inversion on the chromatographic column to *r* − 2, *c* − 4, *c* − 5-isomer[11] (Fig. 2).

Considering the kind and structure of the products formed, we suggest the following reaction mechanism: in the first stage, phenyldiazomethane decomposes and either phenylcarbenoid [PhCH:...CuBr] (catalytic decomposition) or "free" phenylmethylene [PhCH:] (thermal decomposition) is formed. Both these intermediate compounds react with a molecule of imine **1** giving rise to intermediate 1,3-dipole (azomethine ylide) with **trans**-configuration. Moreover, both carbenoid and "free" carbene dimerize or react with phenyldiazomethane,[12] with stilbene and benzalazine arising as side products. According to the

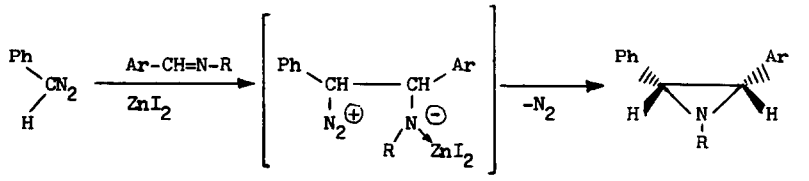


Fig. 1.

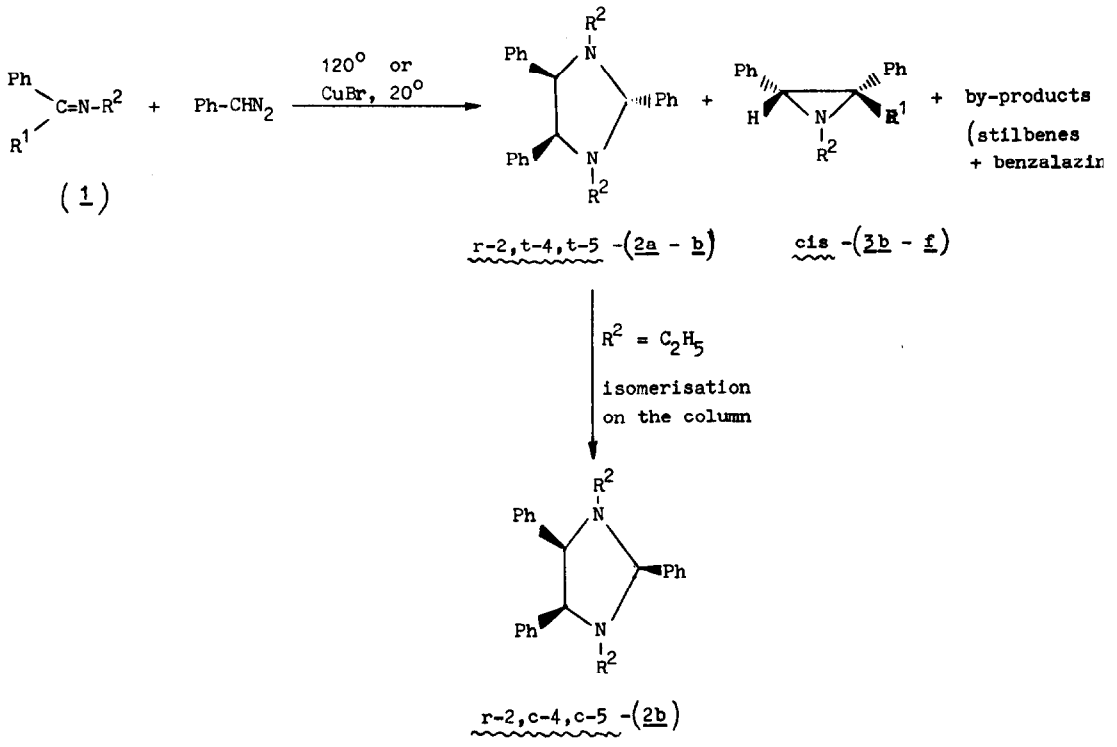


Fig. 2.

Table 1. Comparison of thermal (120°) and catalytic (Cu Br, 20°) decomposition of phenyldiazomethane in imines **1a–f**

Starting compounds			Products (Yield %) [a]			
			Thermal decomposition (120°)		Catalytic decomposition (CuBr, 20°)	
1	R^1	R^2	2	3	2	3
a	H	CH_3	not found	18	38	not found
b	H	C_2H_5	X[b]	X	8	10
c	H	$CH(CH_3)_2$	not found	6	not found	13
d	H	$C(CH_3)_3$	not found	traces	not found	5
e	CH_3	CH_3	X	X	not found	10
f	CH_3	C_2H_5	X	X	not found	7

[a] determined by integrating ^1H NMR spectra of crude reaction mixtures containing toluene as an internal standard of concentration.

[b] reaction was not performed.

Woodward–Hoffman rules, **trans**-ylide **4** undergoes conrotatory cyclization[13] forming appropriate **cis**-aziridines. If the ylide has a sufficiently long lifetime, it may undergo secondary cycloaddition[2 + 3] to a double C=N bond of imine giving imidazolidine derivatives. The stereospecific course of **cis**-aziridine **3** and *r* – 2, *t* – 4, *t* – 5-imidazolidines **2** formation shows that under the reaction conditions employed **trans**-ylide **4** does not isomerize. The small R^1 and R^2 substituents, which do not disturb the planarity of the ylide, extend its lifetime and make further [2 + 3 cycloaddition possible. The presence of cuprous br mide distinctly assists cycloaddition (Table 1) eith by stabilization of the ylide or by activating the imin We can thus propose the following scheme of tl processes leading to the formation of aziridine ar imidazolidine derivatives (Fig. 3).

Decomposition of phenyldiazomethane in imines the presence of other dipolarophiles (*3-component rea tions*). In order to obtain further confirmation of tl

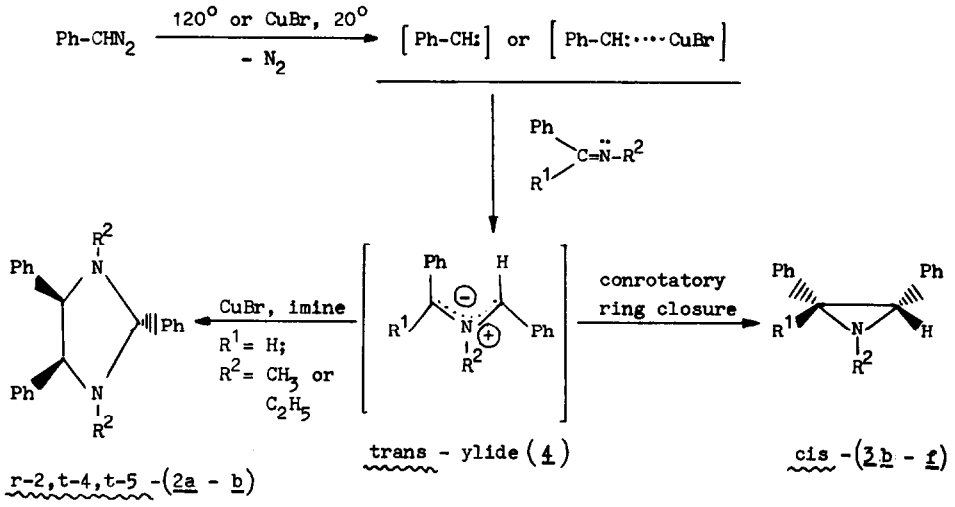


Fig. 3.

presence of *trans*-ylide **4** in the reactions of phenylcarbenoid with imines, catalytic decomposition of phenyldiazomethane in N-benzylidenemethylamine (**1a**) was carried out by adding to it small amount of another dipolarophile: dimethyl maleate or benzaldehyde. It turned out in both cases that the ylide had been completely captured by the dipolarophiles and appropriate cycloadducts formed with good yields. In the reaction with dimethyl maleate, a pyrrolidine derivative **5** was formed with $r-2, t-3, t-4, t-5$-configuration.[14] The addition of *cis*-1-methyl-2,3-diphenylaziridine (**3a**) to dimethyl maleate in boiling xylene gave the same isomer **5** (Fig. 4).

Still further confirmation was obtained from synthesis of **5** from cycloadduct **9**. The latter arises when aziridine **3a** is heated with maleic anhydride in boiling xylene. The action of diazomethane on **9** yields the same isomer of **5** which was obtained in the reaction of phenylcarbenoid with **1a** and dimethyl maleate. On the other hand, aziridine **3a**, kept with dimethyl maleate in the presence of cuprous bromide at room temperature, did not change its concentration even after several days. These experiments demonstrate that, contrary to the suggestion of Baret,[4] the reaction of copper carbenoid with imine first leads to the formation of azomethine ylide and then to aziridine

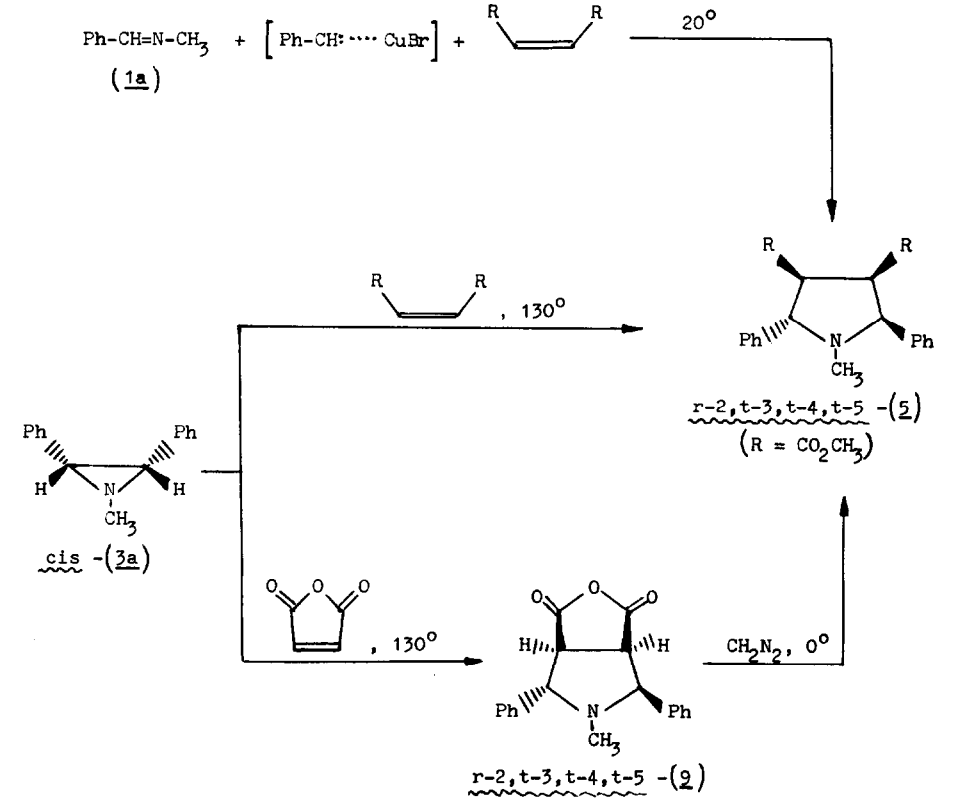


Fig. 4.

(but not the other way round). Additional confirmation of this was obtained by demonstration that aziridine **3a** does not react with benzaldehyde under conditions of catalytic reaction (CuBr, 20°).

The reaction of N-benzylidenemethylamine (**1a**) with phenylcarbenoid in the presence of benzaldehyde leads to unstable oxazolidine **6a** with configuration $r-2$, $t-4$, $c-5$. Kept for a few days at room temperature, this compound transformed into thermodynamically more stable isomer $r-2$, $c-4$, $t-5$.[15] The isomerization proceeded rapidly during separation of the reaction mixture on the chromatographic column. The primary product obtained in the reaction of N-(*p*-methoxybenzylidene)-methylamine (**1g**) with phenylcarbenoid in the presence of *p*-anisaldehyde behaved in the same way. The ^{1}H NMR spectrum of the crude mixture in this last case showed that cycloaddition of ylide **4g** proceeds in a stereospecific and also regiospecific manner (with nonsymmetric ylide participating in this case). The only product of the reaction was unstable isomer **r-2, t-4, c-5** of 3-methyl-2-phenyl-4,5-di-(*p*-methoxyphenyl)oxazolidine (**6g**) in which the aryl groups of imine and aldehyde occupy neighbouring positions 4 and 5 (Fig. 5).

The configurations of stable isomers $r-2$, $c-4$, $t-5$-**6a** and **6g** have been confirmed by X-ray studies.[16,17] The 3-component reactions of phenylcarbenoid with imine and dipolarophile described above were conducted in a large excess of imine used as solvent. The formation of pyrrolidine or oxazolidine derivatives instead of imidazolidine demonstrates that the intermediate azomethine ylide exhibits considerably greater reactivity with respect to the C=C and C=O bonds than to the C=N bond. To establish the relative reactivity of ylide **4** with respect to this bonds, an experiment was carried out in which benzaldehyde and dimethyl maleate were used simultaneously. The reaction was carried out in an excess of imine **1a**. The only product of cycloaddition was pyrrolidine **5**. This indicates that the reactivity of double bonds relative to ylide decreases in the order C=C > C=O > C=N. An identical order of reactivity was found in the case of ylide thermally generated from aziridine. Heating aziridine **3a** with dimethyl maleate or benzaldehyde in boiling xylene gave appropriate cycloadducts (**5** or **6a**) with very good yield, while no cycloaddition product was formed with imine **1a** (similarly as in the case of thermal decomposition of phenyldiazomethane in imines, Table 1).

In all the reactions described above, the ylide participating in them had the *trans*-configuration of phenyl groups. This was naturally so in the case of the ylide generated from *cis*-aziridine, but also in the case of the ylide arising from the addition of phenylcarbenoid to imine. In none of the reactions did we

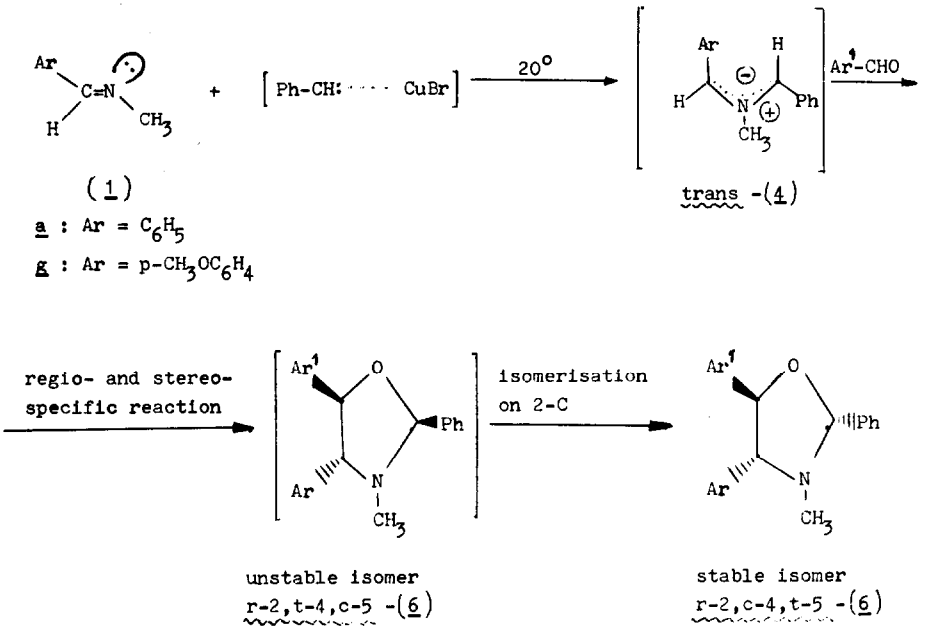


Fig. 5.

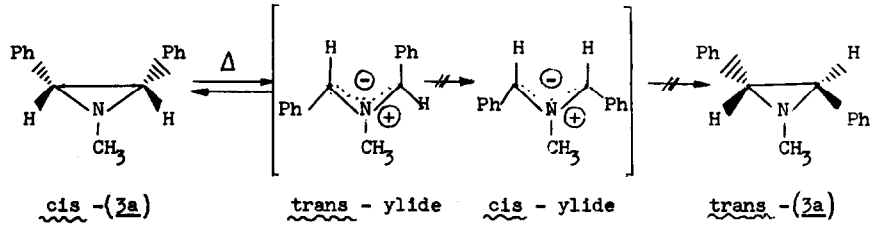


Fig. 6.

observe the formation of products related to *cis*-ylide which proves that the *trans*-ylide to *cis*-ylide inversion barrier is to high to be attained under the reaction conditions. This was also observed when *cis*-aziridine **3a** was heated in boiling mesitylene. No isomerization of aziridine **3a** was observed, although it is well known that under such conditions some aziridines undergo opening to ylide[18,19] (Fig. 6).

Unfortunately, *trans*-aziridine **3a** was not available and we were thus unable to investigate the reverse process. The formation of *trans*-ylide in the addition of phenylcarbenoid to imine may be due to steric factors. Phenylcarbenoid attack is at the lone electron pair of nitrogen, i.e. in the plane of C=N bond of *anti*-imine,[21] with bulky phenyl groups occupying distant positions, which leads to the formation of *trans*-ylide (Fig. 7).

Synthesis of model imidazolidine **2** *and oxazolidine* **6** *derivatives.* In order to confirm the structure of the products described above, we synthesized some of them in an independent way. For the same reason we synthesized different isomers of previously obtained compounds to rule out their presence in the reaction mixtures. The isomers of 1,3-dialkyl-2,4,5-triphenylimidazolidines **2** were obtained by heating *meso* or *dl*-diamines **7** with benzaldehyde. In the case of *meso*-diamines **7a-b**, 2:5 mixtures of isomers $r-2$, $t-4$, $t-5$ and $r-2$, $c-4$, $c-5$ were obtained (Fig. 8). It was impossible to separate the two isomers chromatographically, and during distillation isomer $r-2$, $t-4$, $t-5$ underwent total conversion to isomer $r-2$, $c-4$, $c-5$.[11]

The reaction with *dl*-diamines **7a-b** yielded isomer $r-2$, $t-4$, $c-5$ (Fig. 9). Isomers $r-2$, $c-4$, $t-5$ and $r-2$, $c-4$, $c-5$ of oxazolidine **6a** were obtained by reacting *threo* or *erythro*-aminoalcohols **8** with benzaldehyde (only one isomer was observed in each reaction). The first of these isomers $r-2$, $c-4$, $t-5$ is identical to the one obtained from phenylcarbenoid, imine **1a** and benzaldehyde (Fig. 10). Similarly as in the earlier case of isomer $r-2$, $c-4$, $t-5$,[16] the structure of isomer $r-2$, $c-4$, $c-5$ was confirmed by X-ray studies.[20]

EXPERIMENTAL

M.ps were determined in open capillary tubes and are uncorrected. ^{1}H NMR spectra were obtained using a Tesla BS 476 (60 MHz) instrument. Chemical shifts are reported in ppm downfield from internal TMS(δ). IR spectra were measured on a Perkin–Elmer 325 instrument. Mass spectra (MS) were determined on an LKB-2091 spectrometer (70 eV). The identity of the compounds compared was ascertained on the basis of the absence of any differences in ^{1}H NMR and IR spectra.

Imines **1**. These compounds were prepared using well-known reactions; *Compounds* **1a**: b.p. 68°/10 mm (lit.[22] b.p. 92°/34 mm); **1b**: b.p. 72°/9 mm (lit.[23] b.p. 92°/28 mm); **1c**: b.p. 42°/0.2 mm (lit.[24] b.p. 64°/8 mm); **1d**: b.p. 48°/0.2 mm (lit.[25] b.p. 90°/11 mm); **1e**: b.p. 57–58°/0.7 mm (lit.[26] b.p. 57–58°/0.65 mm); **1f**: b.p. 68–70°/0.5 mm (lit.[26] b.p. 44°/0.13 mm); **1g**: b.p. 113–14°/14 mm (lit.[27] b.p. 133/20 mm). The imines were kept in an ethereal soln (with appropriate amine added) over KOH pellets; before use they were distilled under argon.

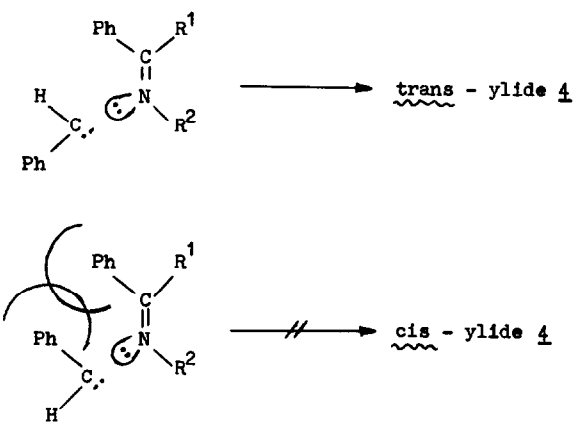


Fig. 7.

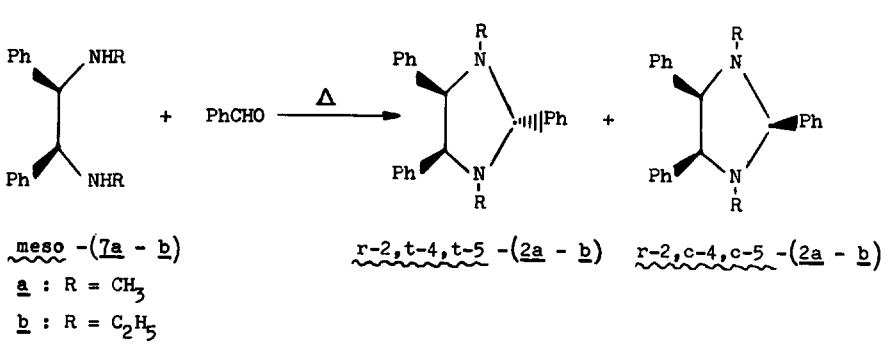
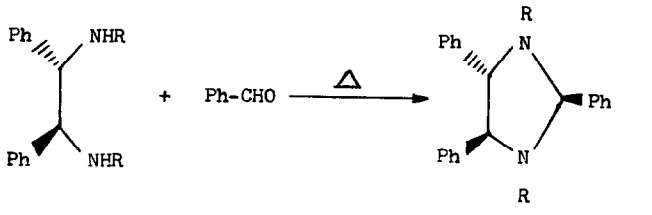


Fig. 8.



dl -(7a - b) r-2,c-4,t-5 -(2a - b)

Fig. 9.

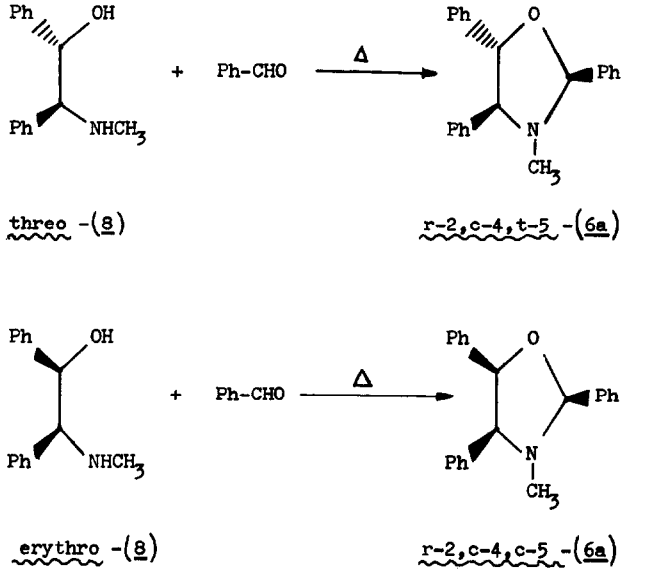


Fig. 10.

Phenyldiazomethane was prepared from benzaldehyde tosylhydrazone by the Bamford–Stevens reaction in the version described by Farnum.[27] It was used without further purification.

Catalytic decomposition of phenyldiazomethane in imines **1**

General procedure. 60 ml of freshly distilled **1** and 100 mg of cuprous bromide[28] were placed in a flask equipped with condenser, dropping funnel and magnetic stirrer. After passing argon through the apparatus and protecting it against moisture, a 1.2 g (*ca.* 10 mmole) of phenyldiazomethane in 10 ml imine was dropped in at the rate of 5–6 drops a minute. Throughout that time the contents of the flask was vigorously stirred, and the stirring continued for 30 min after the dropping had been completed. To remove cuprous bromide, 100 ml of ether were added and the obtained soln was shaken with 5% soln of ammonia. The organic layer was dried ($MgSO_4$), the ether was evaporated and the excess of imine was removed using oil pump. The remainder was subjected to ^{1}H NMR analysis determining quantitatively the content of the components with the use of an internal concentration standard (measured quantity of toluene). The components of the mixture were separated on a chromatographic column (neutral Al_2O_3, hexane–ether).

Thermal decomposition of phenyldiazomethane in imines **1**

General procedure. The reaction was carried out as in the catalytic method. Phenyldiazomethane soln was dropped into imine (under N_2) heated to 120° (oil bath) and the mixture was stirred at that temp. for 30 min. Following cooling, the excess of imine was removed under vacuum and subjected to the same treatment as before. The yields obtained (based on the crude phenyldiazomethane) are given in the Table. The physical properties and spectral data for **3a-f** can be found in our earlier paper.[1]

1,3-*Dimethyl-r* − 2, *t* − 4, *t* − 5-*triphenylimidazolidine* (*r* − 2, *t* − 4, *t* − 5-**2a**), colourless crystals, m.p. 117–19° (from EtOH-H_2O); ^{1}H NMR ($CDCl_3$) 2.0 (6, s, CH_3), 4.58 (2, s, 4-H + 5H), 5.2 (1, s, 2-H), 7.0–7.5 (15, m, Ph); MS(*m/e*) 327 (M^+, 26%), 209 (100%). (Found: C, 84.3; H, 7.4; N, 8.6. $C_{23}H_{24}N_2$ requires: C, 84.1; H, 7.4; N, 8.5%).

Dihydrochloride, colourless crystals, m.p. 283–84° (from EtOH).

1,3-*Diethyl-r* − 2, *t* − 4, *t* − 5-*triphenylimidazolidine* (*r* − 2, *t* − 4, *t* − 5-**2b**) (unstable isomer)[29]; ^{1}H NMR ($CDCl_3$) 0.8 (6, t, CH_3), 2.45 (4, q, CH_2), 4.65 (2, s, 4 − H + 5 − H), 5.28 (1, s, 2-H), 7.0–7.5 (15, m, Ph).

1,3-*Diethyl-r* − 2, *c* − 4, *c* − 5-*triphenylimidazolidine* (*r* − 2, *c* − 4, *c* − 5-**2b**), colourless crystals, m.p. 51–52° (from EtOH); ^{1}H NMR ($CDCl_3$) 0.62 (6, t, CH_3), 2.5 (4, q, CH_2), 4.03 (1, s, 2-H), 4.1 (2, s, 4-H + 5-H), 6.7–7.7 (15, m, Ph); MS(*m/e*) 355 (M^+, 11%), 193 (100%). (Found: C, 84.1; H, 7.8; N, 7.5. $C_{25}H_{28}N_2$ requires: C, 84.1; H, 7.9; N, 7.8%).

Three-component reactions

(1) *With dimethyl maleate.* The reaction was carried out in the same way as the catalytic decomposition of phenyldiazomethane (see above); 0.7 g (*ca.* 5 mmole) of dimethyl maleate were dissolved in **1a**. Cycloadduct **5** was identified in the mixture from ^{1}H NMR spectrum (after removal of excess N-benzylidenemethylamine).

(2) *With aromatic aldehydes.* The reaction was carried out in the same way as the decomposition of phenyl-

diazomethane catalyzed by cuprous bromide; 35 mmole of appropriate aldehyde were added to **1a** or **1g**. After excess imine had been removed (oil pump), the remainder was subjected to ^{1}H NMR analysis. Stable isomers *r* − 2, *c* − 4, *t* − 5 of **6a** and **6g** were separated on a chromatographic column (neutral Al_2O_3, hexane–ether).

3-*Methyl-r* − 2, *t* − 4, *c* − 5-*triphenyloxazolidine* (*r* − 2, *t* − 4, *c* − 5-**6a**) (unstable isomer)[29], ^{1}H NMR ($CDCl_3$) 1.9 (3, s, CH_3), 3.95 (1, d, J = 8 Hz, 4-H), 5.05 (1, d, J = 8 Hz, 5-H), 5.73 (1, s, 2-H), 7.0–7.5 (15, m, Ph).

3-*Methyl-r* − 2, *c* − 4, *t* − 5-*triphenyloxazolidine* (*r* − 2, *c* − 4, *t* − 5-**6a**), yield 1.35 g (43%), colourless needles, m.p. 88–89° (from MeOH); ^{1}H NMR ($CDCl_3$) 2.07 (3, s, CH_3), 3.37 (1, d, J = 8.5 Hz, 4-H), 4.9 (1, d, J = 8.5 Hz, 5-H), 5.0 (1, s, 2-H), 7.0–7.7 (15, m, Ph); MS(*m/e*) 315 $M^{+\cdot}$, 0.35%), 209 (100%). (Found: C, 83.8; H, 6.9; N, 4.4. $C_{22}H_{21}NO$ requires: C, 83.8; H, 6.7; N, 4.4%).

3 - *Methyl* - *r* − 2 - *phenyl* - *t* − 4, *c* − 5 - *di* - (*p* - *methoxyphenyl*)*oxazolidine* (*r* − 2, *t* − 4, *c* − 5 - **6g**) (unstable isomer),[29] ^{1}H NMR ($CDCl_3$) 1.83 (3, s, CH_3), 3.6 (6, s, OCH_3), 3.7 (1, d, J = 7.5 Hz, 4-H), 4.8 (1, d, J = 7.5 Hz, 5-H), 5.6 (1, s, 2-H), 6.7–7.5 (13, m, Ar).

3-*Methyl-r* − 2-*phenyl-c* − 4, *t* − 5-*di*-(p-*methoxyphenyl*) *oxazolidine* (*r* − 2, *c* − 4, *t* − 5-**6g**), yield 1.80 g (48%), colourless needles, m.p. 96–97° (from EtOH); ^{1}H NMR ($CDCl_3$) 1.95 (3, s, CH_3), 3.11 (1, d, J = 7.5 Hz, 4-H), 3.63 (6, s, OCH_3), 4.7 (1, d, J = 7.5 Hz, 5-H), 5.0 (1, s, 2-H), 6.4–7.5 (13, m, Ar). (Found: C, 76.8; H, 6.9; N, 3.5. $C_{24}H_{25}NO_3$ requires: C, 76.8; H, 6.7; N, 3.7%).

Decomposition of phenyldiazomethane in imine **1a** *in the presence of both dimethyl maleate and benzaldehyde.* The reaction was carried out in the same way as the catalytic decomposition of phenyldiazomethane in **1a**; 35 mmole of benzaldehyde and 35 mmole of dimethyl maleate were simultaneously added to imine. After the removal of excess of reagents (oil pump) it was found by an ^{1}H NMR analysis that the only product of cycloaddition is *r* − 2, *t* − 3, *t* − 4, *t* − 5-pyrrolidine **5**.

*Cycloaddition of cis-*1-*methyl-*2, 3-*diphenylaziridine* (**3a**) *to double bonds.* 2 mmole of appropriate dipolarophile (**A**-dimethyl maleate, **B**-maleic anhydride, **C**-benzaldehyde, **D**-N-benzylidenemethylamine) were added to the soln of 0.42 g (2 mmole) of **3a** in 10 ml of xylene. The mixture was heated for 10 hr under argon to b.p.. The xylene was evaporated and remainder was subjected to ^{1}H NMR analysis. Cycloadducts were formed in experiments **A**, **B**, and **C**, while no imidazolidine was found to arise in experiment **D**. The reaction products were purified by crystallization.

1-*Methyl-r* − 2, *t* − 5-*diphenylpyrrolidine-t* − 3, *t* − 4-*dicarboxylic acid dimethyl ester* (*r* − 2, *t* − 3, *t* − 4, *t* − 5-**5**), yield 630 mg (89%), colourless crystals, m.p. 106–108° (from MeOH); ^{1}H NMR ($CDCl_3$) 1.75 (3, s, CH_3), 3.07 (3, s, OCH_3), 3.33 (1, m, 3-H), 3.47 (3, s, OCH_3), 3.60 (1, m, 4-H), 4.56 (1, d, J = 7 Hz, 5-H), 4.93 (1, d, J = 7 Hz, 2-H), 7.2 (10, m, Ph); IR (KBr) $\nu_{C=O}$ 1732 and 1722 cm^{-1}. (Found: C, 70.5; H, 6.7; N, 3.9; $C_{21}H_{23}NO_4$ requires: C, 71.4; H, 6.6; N, 3.9%).

1-*Methyl-r* − 2, *t* − 5-*diphenylpyrrolidine-t* − 3, *t* − 4-*dicarboxylic acid anhydride* (*r* − 2, *t* − 3, *t* − 4, *t* − 5-**9**), yield 490 mg (70%), colourless needles (from benzene–petroleum ether); ^{1}H NMR ($CDCl_3$) 1.89 (3, s, CH_3), 2.28 (1, m, 3-H), 2.78 (1, m, 4-H), 3.45 (1, m, 5-H), 4.71 (1, br.s, 2-H), 7.0–7.5 (10, m, Ph); IR (KBr) $\nu_{C=O}$ 1780 and 1775 cm^{-1}. (Found: C, 73.5; H, 5.7; N, 4.6. $C_{19}H_{17}NO_3$ requires: C, 74.3; H, 5.6; N, 4.6%). Compound **9** was treated with excess of diazomethane solution (ether, 0°) for seven days obtaining diester **5**.

3-*Methyl-r* − 2, *c* − 4, *t* − 5-*triphenyloxazolidine* (*r* − 2, *c* − 4, *t* − 5-**6a**), yield 516 mg (82%). Product identical with the compound obtained in the reaction of phenyldiazomethane with N-benzylidenemethylamine and benzaldehyde in the presence of cuprous bromide.

*An attempt of thermal isomerization of cis-*1-*methyl-*2, 3-*diphenylaziridine* (**3a**). 210 mg (1 mmole) of **3a** soln in 5 ml mesitylene were placed in a flask equipped with condenser. The contents were heated for 40 hr under argon to b.p. A sample was taken every 10 hr and, following removal of the solvent, a ^{1}H NMR spectrum was recorded ($CDCl_3$). As the reaction proceeded, aziridine decomposed, but no *trans*-isomer formation was observed.

Syntheses of imidazolidines **2a-b**

General procedure. A mixture of 10 mmole *meso* or *dl*-7[30] and benzaldehyde (1.1 g) in 10 ml of xylene was refluxed for 8 hr (**7a**) or for 15 hr (**7b**). Following evaporation of the solvent, the remainder was distilled and product obtained was additionally crystallized. Using *meso*-diamines **7a-b** we obtained a mixture of imidazolidine isomers *r* − 2, *t* − 4, *t* − 5 and *r* − 2, *c* − 4, *c* − 5 in the ratio of 2:5 (^{1}H NMR). In the course of distillation on an oil pump, the isomer *r* − 2, *t* − 4, *t* − 5 underwent conversion into stable isomer *r* − 2, *c* − 4, *c* − 5.

1,3-*Dimethyl-r* − 2, *t* − 4, *t* − 5-*triphenylimidazolidine* (*r* − 2, *t* − 4, *t* − 5-**2a**), (observed in mixture ^{1}H NMR spectrum), compound identical with the product of catalytic decomposition of phenyldiazomethane in imine **1a**.

1,3-*Dimethyl-r* − 2, *c* − 4, *c* − 5-*triphenylimidazolidine* (*r* − 2, *c* − 4, *c* − 5-**2a**), yield 2.05 g (62%), colourless plates, m.p. 64–66° (from EtOH), b.p. 158–60°/0.06 mm (lit.[31] m.p. 66–68°, b.p. 176–80°/1 mm); ^{1}H NMR ($CDCl_3$) 2.1 (6, s, CH_3), 3.7 (1, s, 2-H), 4.0 (2, s, 4-H + 5-H), 6.9–7.8 (15, m, Ph).

1,3-*Dimethyl-r* − 2, *c* − 4, *t* − 5-*triphenylimidazolidine* (*r* − 2, *c* − 4, *t* − 5-**2a**), yields 2.75 g (80%), colourless crystals, m.p. 78–79° (from MeOH); ^{1}H NMR ($CDCl_3$) 1.83 (3, s, CH_3), 2.13 (3, s, CH_3), 3.6 (1, d, J = 8 Hz, 5-H), 3.9 (1, d, J = 8 Hz, 4-H), 4.76 (1, s, 2-H), 7.0–7.6 (15, m, Ph). (Found: C, 84.0; H, 7.3; N, 8.5. $C_{23}H_{24}N_2$ requires: C, 84.1; H, 7.4; N, 8.5%).

1,3-*Diethyl-r* − 2, *t* − 4, *t* − 5-*triphenylimidazolidine* (*r* − 2, *t* − 4, *t* − 5-**2b**), (observed in the reaction mixture ^{1}H NMR spectrum), compound identical to the unstable isomer obtained in the catalytic decomposition of phenyldiazomethane in imine **1b**.

1,3-*Diethyl-r* − 2, *c* − 4, *c* − 5-*triphenylimidazolidine* (*r* − 2, *c* − 4, *c* − 5-**2b**), yield 2.43 g (71%), m.p. 51–52° (from EtOH), b.p. 160–63°/0.2 mm. Compound identical to the stable isomer obtained in the catalytic decomposition of phenyldiazomethane in imine **1b**.

1,3-*Diethyl-r* − 2, *c* − 4, *t* − 5-*triphenylimidazolidine* (*r* − 2, *c* − 4, *t* − 5-**2b**), yield 2.77 g (81%), colourless oil, b.p. 168–72°/0.2 mm; ^{1}H NMR ($CDCl_3$) 0.61 (3, t, CH_3), 0.66 (3, t, CH_3), 2.0 (2, q, CH_2), 2.6 (2, q, CH_2), 3.66 (1, d, J = 8 Hz, 5-H), 3.91 (1, d, J = 8 Hz, 4-H), 4.95 (1, s, 2-H), 7.0–7.6 (15, m, Ph). (Found: C, 84.5; H, 7.7; N, 7.5. $C_{25}H_{28}N_2$ requires: C, 84.2; H, 7.9; N, 7.8%).

Syntheses of oxazolidines **6**

General procedure. A mixture of 10 mmole *threo* or *erythro*-**8**[32] and benzaldehyde (1.1 g) in 10 ml of benzene was refluxed for 10 hr. Following evaporation of the solvent, the remainder was crystallized from MeOH.

3-*Methyl-r* − 2, *c* − 4, *t* − 5-*triphenyloxazolidine* (*r* − 2, *c* − 4, *t* − 5-**6a**), yield 2.61 g (83%), compound identical to the product of catalytic decomposition of phenyldiazomethane in imine **1a** in the presence of benzaldehyde.

3-*Methyl-r* − 2, *c* − 4, *c* − 5-*triphenyloxazolidine* (*r* − 2, *c* − 4, *c* − 5-**6a**), yield 2.70 g (85%), colourless crystals, m.p. 94–95° (from MeOH); ^{1}H NMR ($CDCl_3$) 2.1 (3, s, CH_3), 3.97 (1, d, J = 8 Hz, 4-H), 4.83 (1, s, 2-H), 5.27 (1, d, J = 8 Hz, 5-H), 6.8–7.7 (15, m, Ph). (Found: C, 83.2; H, 7.0; N, 4.3. $C_{22}H_{21}NO$ requires: C, 83.8; H, 6.7; N, 4.4%).

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