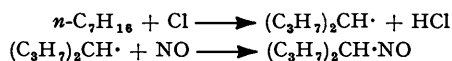


331. The Preparation of Nitrosoalkanes from Alkyl Nitrites.

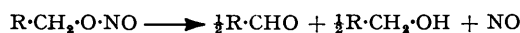
By B. G. GOWENLOCK and J. TROTMAN.

Every possible C₁—C₄ and one C₅ nitrosoalkane has been prepared pyrolytically from alkyl nitrites in a flow system, and the *cis*-dimers have been isolated except that of 2-methyl-2-nitrosopropane where sterically only the *trans*-dimer is possible. *trans*-Dimers have been detected in the products resulting when the *cis*-dimer is heated, and in two cases the *trans*-dimer has been isolated. Nitrosoalkane dimers have been detected in the products formed by photolyses of alkyl nitrites. The ultraviolet and infrared absorption spectra and other properties of the dimers are discussed, and possible mechanisms for the photolyses of alkyl nitrites are formulated.

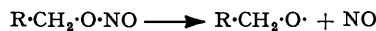
DIMERIC nitrosoalkanes have been either isolated^{1, 2} or detected² in the photolysis products of some alkyl nitrites. Dimeric 4-nitrosoheptane has been isolated from the photolysis products of *n*-heptane, nitric oxide, and chlorine mixtures, the reaction sequence being :



The chlorine atoms are produced photolytically from chlorine. A recent study of the pyrolysis and photolysis of *tert.*-butyl nitrite⁴ has shown that there are two different dimers of nitrosomethane, geometrical isomerism being the most probable explanation of the properties reported. Although photolysis of a number of alkyl nitrites yielded nitrosomethane or unidentified nitrosoalkanes,² it has been generally assumed⁵ that thermal decomposition of alkyl nitrites is best represented by the equation :



the initial reaction being :



subsequent reactions of the alkoxy-radicals producing the alcohol and aldehyde by a non-chain mechanism. The majority of the studies have been made by static methods with pressures of the order of 100 mm., reaction temperatures of about 200°, and reaction times of several minutes. With the possible exception of methyl nitrite,⁶ the equations quoted have little or no quantitative significance: in other cases,⁷ even qualitative identification of the aldehyde and/or alcohol is at best sketchy, and the amount of nitric oxide obtained was only 50—67% of that expected from the amount of nitrite decomposed. Rice and Rodowskas⁸ have suggested that the nitric oxide produced in the primary decomposition

¹ Coe and Doumani, *J. Amer. Chem. Soc.*, 1948, **70**, 1516.

² Tarte, *Bull. Soc. roy. Liège*, 1953, **22**, 26.

³ Müller and Metzger, *Chem. Ber.*, 1955, **88**, 165.

⁴ Gowenlock and Trotman, *J.*, 1955, 4190.

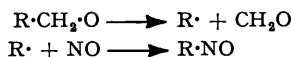
⁵ Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, 1954, p. 239.

⁶ Steacie and Shaw, *Proc. Roy. Soc.*, 1934, *A*, **146**, 388.

⁷ (a) Carter and Travers, *ibid.*, 1937, *A*, **156**, 495; (b) Gray, *ibid.*, 1954, *A*, **221**, 462; (c) Steacie and Shaw, *J. Chem. Phys.*, 1934, **2**, 345; 1935, **3**, 344; *Proc. Roy. Soc.*, 1935, *A*, **151**, 685; Steacie and Smith, *J. Chem. Phys.*, 1936, **4**, 504; Levy, *J. Amer. Chem. Soc.*, 1954, **76**, 3254.

⁸ Rice and Rodowskas, *J. Amer. Chem. Soc.*, 1935, **57**, 350.

can remove free alkyl radicals resulting from the decomposition of alkoxy-radicals, a nitrosoalkane being formed :



EXPERIMENTAL

With the exception of *isopentyl* nitrite, which was available commercially, all nitrites were prepared by the action of nitrous acid on the corresponding alcohol at 0°. The alcohols were commercial products apart from hexan-2-ol, 3-methylpentan-2-ol, and 3 : 3-dimethylbutan-2-ol which were prepared from acetaldehyde and the appropriate Grignard reagent. The nitrites were purified by bulb-to-bulb distillation *in vacuo* and pyrolyzed in the apparatus used for *tert.*-butyl nitrite⁴ with the reaction vessel at 320°. Nitrites that yielded nitrosomethane were decomposed in the presence of nitrogen (used as a carrier gas), whereas other nitrites were decomposed in the absence of a carrier gas by pumping the nitrite vapour through the reaction vessel; optimum yields were the criterion of technique employed. Decomposition products and undecomposed nitrites were trapped at either -78° or -183°. During every decomposition an increase in pressure was observed; admission of air to the apparatus gave brown vapours, indicating that this increase was due, in part or in whole, to nitric oxide which is not completely condensed in liquid oxygen. The cooled traps contained solids coloured from yellow-brown to blue-green. In addition, undecomposed nitrites and carbonyl compounds were also trapped as white solids. On warming to room temperature, the undecomposed nitrites and carbonyl compounds other than polymeric formaldehyde melted to faintly yellow liquids: the coloured solids melted to liquids of the same colour which rapidly changed to white solids (cf. refs 4, 9). The nitrosoalkane from *isohexyl* nitrite was of low vapour pressure and condensed to give a white solid above the level of the acetone in the -78° bath that surrounded the trap. When polymeric formaldehyde was deposited in the cooled trap, it was always separated from the nitrosoalkane deposit by a few cm., the (CH₂O)_n deposit being nearer to the bottom of the trap. The undecomposed nitrite and volatile carbonyl compound were pumped off from the solid nitrosoalkane dimer and trapped in a receiver cooled in liquid oxygen. Volatile carbonyl compounds proved to be either acetone or acetaldehyde and were identified as the semicarbazone or dimethone respectively. Polymeric formaldehyde was removed from the trap wall by a spatula; it had m. p. 170° and a dimethone derivative was prepared. M. p.s and mixed m. p.s were: acetone semicarbazone, 187°; acetaldehyde dimethone, 140°; formaldehyde dimethone, 189°. Dimeric nitrosoalkanes were purified from any isomeric oxime either by dissolution in ethanol, rapid cooling to -78°, and filtration of the white solid formed or, where high solubility in ethanol at -78° made this impossible, by shaking with ether at -30°, filtration, and washing with cold (-30°) ether. In both cases, white crystalline solids resulted; it was necessary to pump off all traces of solvent under a vacuum. The identified pyrolysis products are given in Table 1. The dimeric nitrosoalkanes prepared by the above techniques are, with one exception,

TABLE 1. *Pyrolysis products of alkyl nitrites.*

| Nitrite | CO compound | Nitrosoalkane | Nitrite | CO compound | Nitrosoalkane |
|----------------------------------|----------------------------------|---------------------|------------------------------------|----------------------------------|------------------------------------|
| Et | (CH ₂ O) _n | Me·NO | CHMePr ^a | Me·CHO | Pr ^a ·NO |
| Pr ^a * | (CH ₂ O) _n | Et·NO | CMe ₂ Et | COMe ₂ | Et·NO |
| Pr ⁱ * | Me·CHO | Me·NO | CHMeBu ^a | Me·CHO | Bu ^a ·NO |
| Bu ^a * | (CH ₂ O) _n | Pr ^a ·NO | CHMeBu ⁱ | " | Bu ⁱ ·NO |
| Bu ^s * | Me·CHO | Et·NO | CHMeBu ^s | " | Bu ^s ·NO |
| Bu ⁱ * | (CH ₂ O) _n | Pr ⁱ ·NO | CHMeBu ^t | " | Bu ^t ·NO |
| Bu ^t ⁴ | COMe ₂ | Me·NO | CHEt ₂ ·CH ₂ | (CH ₂ O) _n | C ₆ H ₁₁ ·NO |
| Bu ^a ·CH ₂ | (CH ₂ O) _n | Bu ^a ·NO | | | (probably |
| Bu ⁱ ·CH ₂ | (CH ₂ O) _n | Bu ⁱ ·NO | | | CHEt ₂ ·NO) |

* Adler, Pratt, and Gray (*Chem. and Ind.*, 1955, 1517) have recently isolated the same carbonyl compounds by pyrolysis of nitrites so marked.

cis-dimers, λ_{max.} (in H₂O) varying from 265 to 271 mμ; the exception is dimeric 2-methyl-2-nitrosopropane, λ_{max.} (in H₂O) 287 mμ. For a detailed summary of ultraviolet spectra see p. 1673. The detailed results for the *cis*-dimeric nitrosoalkanes are given in Table 2: apart from *cis*-dimeric nitrosomethane⁴ all are new compounds. Molecular weights were determined cryoscopically in benzophenone.

⁴ Chilton and Gowenlock, *J.*, 1953, 3232; 1954, 3174.

TABLE 2. *cis*-Dimeric nitrosoalkanes.

| Compound | M. p. | Found | | | | Required | | | |
|---|-------|-------|-------|-------|----------|----------|-------|-------|----------|
| | | C (%) | H (%) | N (%) | <i>M</i> | C (%) | H (%) | N (%) | <i>M</i> |
| (CH ₃ ·NO) ₂ | 97·5° | 27·0 | 6·5 | 29·4 | 92 | 26·7 | 6·7 | 31·1 | 90 |
| (C ₂ H ₅ ·NO) ₂ | 84 | 40·6 | 8·5 | 22·8 | 118 | 40·7 | 8·5 | 23·7 | 118 |
| (<i>n</i> -C ₃ H ₇ ·NO) ₂ | 76 | 49·4 | 9·7 | 18·9 | 147 | 49·3 | 9·7 | 19·2 | 146 |
| (<i>iso</i> -C ₃ H ₇ ·NO) ₂ | 60 | 49·0 | 9·7 | 19·0 | 148 | 49·3 | 9·7 | 19·2 | 146 |
| (<i>n</i> -C ₄ H ₉ ·NO) ₂ | 72 | 55·3 | 10·3 | 16·1 | 166* | 55·2 | 10·4 | 16·1 | 174 |
| (<i>iso</i> -C ₄ H ₉ ·NO) ₂ | 80 | 54·9 | 10·7 | 15·8 | 171 | 55·2 | 10·4 | 16·1 | 174 |
| (<i>sec</i> -C ₄ H ₉ ·NO) ₂ | 61 | 54·9 | 10·3 | 15·9 | 162* | 55·2 | 10·4 | 16·1 | 174 |
| (C ₅ H ₁₁ ·NO) ₂ | 42 | 59·2 | 10·9 | 13·5 | 192* | 59·4 | 11·0 | 13·9 | 202 |

* Faint blue colour appeared during determination.

Conversion of cis-Dimers into trans-Dimers.—The method established for nitrosomethane⁴ (dissolution of the *cis*-dimer in chloroform, warming, and recrystallisation) was inapplicable to other nitrosoalkanes owing to the production of monomer (blue colour) in chloroform, with subsequent production of the oxime; in addition, the *trans*-dimers were very soluble in chloroform. The following method was therefore employed. The *cis*-dimer was rapidly heated to a few degrees above the m. p. and then cooled rapidly to room temperature. This process was then repeated two or three times. The resultant white solid was dissolved in a few ml. of ether and cooled to -78° , whereupon a white solid was deposited. This was rapidly filtered off in the cold and washed with cold (-78°) ether. The white solid was then allowed to warm to room temperature, whereupon in most cases it changed to a liquid (either melting or dissolving in traces of ether) below room temperature. Stable white solids were formed in two cases, *viz.*, *trans*-dimeric 2-nitrosopropane, m. p. 52° [Found: C, 48·8; H, 9·5; N, 19·0%; *M* (cryoscopic in benzophenone), 143. C₃H₇ON requires C, 49·3; H, 9·7; N, 19·2%; *M* 146]. and *trans*-dimeric 2-methyl-1-nitrosopropane, m. p. 40° [Found: C, 54·4; H, 10·1; N, 15·9%; *M* (cryoscopic in benzophenone), 176. C₄H₉ON requires C, 55·2; H, 10·4; N, 16·1%; *M* 174]. The liquid products were not analysed. *trans*-Dimeric 2-methyl-2-nitrosopropane was isolated by the purification technique used for *cis*-dimers; it had m. p. 70° (lit.,¹¹ disappears at 76°).

Ultraviolet Absorption Spectra.—Absorption spectra were measured as for nitrosomethane;⁴ the solvents were water, ethanol, ether, and carbon tetrachloride. Organic solvents produce the *trans*-dimer from the *cis*-dimer,⁴ this reaction being so rapid in carbon tetrachloride and ether that only λ_{\max} of the *trans*-dimer could be observed. In ethanolic solution, the λ_{\max} value for *cis*-dimers increased with time and consequently speedy measurement was essential. The rate of isomerisation varied; isomerisation was complete in 1 hr. for the 1-nitrosobutane dimer and in 36 hr. for the nitrosomethane dimer (*cis*-dimeric nitrosoethane and 2-methyl-1-nitrosopropane were of the same degree of stability as *cis*-dimeric nitrosomethane). Absorption maxima are given in Table 3. In each case where the pure *trans*-dimer has not been prepared, λ_{\max} was determined for the product obtained on heating the *cis*-dimer to the m.p., cooling, re-heating to the m. p., and cooling, the process being repeated until λ_{\max} reached a maximum. (Usually three repetitions were necessary.)

Conversion of trans-Dimers into cis-Dimers.—Ultraviolet irradiation of aqueous or ethanol solutions of pure *trans*-dimers altered the λ_{\max} to that characteristic of the corresponding *cis*-dimer except in the case of *trans*-dimeric 2-methyl-2-nitrosopropane where λ_{\max} was unaltered. The same behaviour was observed for solutions of the *cis*-dimer which had been heated to give a limiting λ_{\max} value, which we claim to be that for the *trans*-dimer. Irradiation was by a Hanovia S500 lamp placed 6 in. from Unicam silica cell containing the solution, irradiation being for 1 min. Conditions were such as to give a lower limit for λ_{\max} and only small amounts of oxime. Pyrolysis of the pure *trans*-dimers under conditions similar to those used for *trans*-dimeric nitrosomethane⁴ gave coloured (yellow-brown to blue) solids in the liquid-oxygen trap. On warming to room temperature these became white solids, whose absorption spectra (in H₂O) were characteristic of the pure *cis*-dimer (Bu¹) or of the *cis*-dimer slightly contaminated with the oxime (Pr¹).

Spot Tests.—Every nitroso-dimer gave the diphenylamine-concentrated sulphuric acid test.¹

Photolysis of Alkyl Nitrites.—Photolysis was effected in a 250-ml. transparent silica bulb which contained about 1 ml. of the nitrite. The liquid was shielded from ultraviolet light, and the vapour was irradiated by the Hanovia lamp with either an unfocused or a focused beam. In the former case, the lamp was placed 6 in. from the bulb; in the second, the focusing agent was a silica bulb containing water. Irradiation times for the unfocused beam were 10 min.,

and the product was either an oil or crystals. The bulb temperature increased slightly during the unfocused runs. Product analysis was confined to the measurement of the ultraviolet absorption spectra in ether and water. The λ_{\max} value in ether indicates the formation of nitrosoalkanes and the λ_{\max} value in water was regularly 1—2 $m\mu$ higher than the value for the pure

TABLE 3. Ultraviolet absorption (wavelengths in $m\mu$).

| Nitroso-compound | In H ₂ O | | In EtOH | | In Et ₂ O † | | In CCl ₄ | |
|--|---------------------|----------------|--------------------|----------------|------------------------|----------------|---------------------|----------------|
| | λ_{\max} . | log ϵ | λ_{\max} . | log ϵ | λ_{\max} . | log ϵ | λ_{\max} . | log ϵ |
| <i>cis</i> -Me | 265 | 4.00 | 269 | 4.00 | 286 | — | 291 | — |
| <i>trans</i> -Me | 276 | 4.03 | 282.5 | 4.01 | 286 | 4.01 | 291 | 4.06 |
| <i>cis</i> -Et | 266 | 4.02 | 272 | 3.94 | 288 | 3.87 | 292 | 4.00 |
| <i>trans</i> -Et | 277 | — | 285 | — | 288 | — | 292 | — |
| <i>cis</i> -Pr ^a | 268 | 4.04 | 273 | 3.98 | 291 | 3.96 | 295 | 4.03 |
| <i>trans</i> -Pr ^a | 280 | — | 287 | — | 291 | — | 295 | — |
| <i>cis</i> -Pr ^b | 267 | 4.02 | 273 | 3.87 | 290 | 3.90 | 295 | 4.00 |
| <i>trans</i> -Pr ^b | 280 | 4.01 | 286 | 3.98 | 290 | 3.95 | 295 | 4.00 |
| <i>cis</i> -Bu ^a | 268 | 4.06 | 273 | 3.87 | 291 | 3.94 | 296 | 4.00 |
| <i>trans</i> -Bu ^a | 282 | — | 289 | — | 291 | — | 296 | — |
| <i>cis</i> -Bu ^b | 270 | 4.04 | 276 | 4.00 | 294 | 3.96 | 298 | 4.02 |
| <i>trans</i> -Bu ^b | 285 | 4.01 | 291 | 3.98 | 294 | 3.96 | 298 | 4.02 |
| <i>cis</i> -Bu ^c | 269 | 4.02 | 275 | 3.95 | 293 | 3.89 | 297 | 4.01 |
| <i>trans</i> -Bu ^c | 284 | — | 290 | — | 293 | — | 297 | — |
| <i>trans</i> -Bu ^d | 287 | — | — | — | { 295 * | — | — | — |
| | | | | | { 675 * | — | — | — |
| <i>cis</i> -C ₆ H ₁₁ | 271 | 3.98 | 278 † | 3.86 | 297 | 3.91 | 300 | 4.01 |
| <i>trans</i> -C ₆ H ₁₁ | 287 | — | 294 | — | 297 | — | 300 | — |

* 295 absorption peak decreases with time, 675 peak increases with time.

† Changes very rapidly to give λ_{\max} 294 $m\mu$. ‡ When the ether was pumped off from the ethereal solution of *cis*-dimer, λ_{\max} determinations on aqueous solutions of the residue always gave values characteristic of the corresponding *trans*-dimer.

cis-dimer (except in the case of the focused photolysis of ethyl nitrite, when pure crystals of *trans*-dimeric nitrosomethane, m. p. 122°, were formed). Brief irradiation of the aqueous solution altered the λ_{\max} value to that characteristic of the pure *cis*-dimer; subsequent heating of this solution altered it to that characteristic of the *trans*-dimer. The λ_{\max} values obtained indicate that the same nitrosoalkane was formed in both the pyrolytic and photolytic decomposition of the alkyl nitrites investigated. (Photolysis of *isopropyl* and 1 : 2 : 2-trimethylpropyl nitrite was not attempted.) Photolysis was not further investigated as the yields of nitrosoalkane were always small, and there was always considerable production of oxime.

Production of Blue Colours in Solvents.—No dimer gave a blue colour in aqueous solution, and *trans*-dimeric 2-methyl-2-nitrosopropane was different from the other dimeric nitrosoalkanes in that it gave blue solutions in organic solvents owing to production of the monomer. Neither *trans*-dimeric 2-nitrosopropane nor *trans*-dimeric 2-methyl-1-nitrosopropane gave blue colours on dissolution in organic solvents: momentary blue colorations were observed when the solutions were heated. The *cis*-dimers, with the exception of *cis*-dimeric 2-methyl-1-nitrosopropane and nitrosomethane,⁴ gave blue colours on dissolution in benzene, toluene, and ether, which colour rapidly faded leaving a colourless solution. Very faint blue colours were observed on dissolution in carbon tetrachloride. Each of these solutions became blue on heating, as did chloroform, ethanol, and acetone solutions of these *cis*-dimers. *cis*-Dimeric 2-methyl-1-nitrosopropane gave blue colours in the above solvents when the solution was heated. In every case, the blue solution faded on cooling, leaving a colourless solution.

Infrared Absorption Spectra [carried out by M. St.C. FLETT].—The following infrared absorption bands (cm.⁻¹) were measured on a Grubb-Parson S4 Double Beam Spectrophotometer (w = weak, m = medium, s = strong, vs = very strong), the potassium bromide disc technique being used.

trans-Dimeric 2-methyl-1-nitrosopropane: 3004 s, 2907 m, 1475 m, 1422 m, 1395 m, 1381 m, 1357 s, 1321 s, 1302 s, 1225 vs, 1174 m, 1147 s, 1126 m, 990 w, 957 w, 940 w, 887 m, 865 w, 821 m.

cis-Dimeric 2-methyl-1-nitrosopropane: 3068 m, 2968 s, 2882 s, 1600 w, 1464 s, 1431 s, 1393 vs, 1346 s, 1302 m, 1256 s, 1215 s, 1177 m, 1151 w, 1128 w, 1098 s, 1042 s, 963 w, 951 m, 904 m, 889 w, 822 w, 780 s, 683 s.

cis-Dimeric 1-nitrosopropane: 3004 s, 2907 s, 1437 s, 1413 s, 1391 m, 1339 m, 1311 w, 1271 w, 1247 w, 1212 w, 1086 w, 1042 m, 1026 w, 905 w, 808 w.

is too insoluble to allow $\log \epsilon$ to be measured; for the latter, the $\log \epsilon$ values are identical for the two dimers. Where monomer production occurs, isomerisation to the oxime would then be possible, leading to some loss of *trans*-dimer and a low $\log \epsilon$ value for the *cis*-dimer. Examination of Table 3 suggests that some oxime is formed after monomer production when *cis*-dimeric 2-nitrosopropane is dissolved in ether, as the $\log \epsilon$ value is lower than for the pure *trans*-dimer. It is probable that oxime is also produced from the other *cis*-dimers.

The *trans*- are more volatile than the corresponding *cis*-dimers, and *trans*-dimeric 2-methyl-2-nitrosopropane is very volatile. The *cis*- are more soluble in polar solvents than the *trans*-dimers; as the size of the alkyl group increases, the solubility of the *cis*-dimer in solvents of low dielectric constant increases.

Tarte's results² for the photolysis of alkyl nitrites differ slightly from ours, mainly for nitrites containing *n*- and *iso*-alkyl groups. The differences, which are probably due to Tarte's inadequate analytical technique for nitrosoalkanes, are summarised in Table 4.

TABLE 4. Nitrite photolyses.

| R in RO·NO | Our product | Tarte's product | R in RO·NO | Our product | Tarte's product |
|-----------------|---------------------|---------------------|---------------------------------|---------------------|--------------------|
| Pr ⁿ | Et·NO | No nitroso-compound | Bu ⁿ | Et·NO | A nitroso-compound |
| Bu ⁿ | Pr ⁿ ·NO | " " | CH ₂ Bu ^t | Pr ⁿ ·NO | " " |
| Bu ^t | Pr ^t ·NO | Me·NO | Bu ^t | Me·NO | Me·NO |
| | | | CMe ₂ Et | Et·NO | A nitroso-compound |

There is as yet no satisfactory explanation for the differences in the properties of *trans*-dimeric nitroso-compounds. With halogenated nitroso-compounds, either the dimer is non-existent or it readily depolymerises in organic solvents. The dimer does not exist when three halogen atoms are bonded to the α -carbon atom (*e.g.*, CF₃·NO¹²), when two halogen atoms are bonded to the α -carbon atom (*e.g.*, CH₃·CCl₂·NO¹³), or when one halogen atom is bonded to an α -carbon atom that has no hydrogen atom (*e.g.*, Me₂CBr·NO¹⁴). The dimers exist when one halogen is bonded to an α -C atom that carries an α -hydrogen atom [*e.g.*, (CHMeCl·NO)₂¹⁵] or when the halogen is bonded to a β -carbon atom [*e.g.*, (Cl·CH₂·CMe₂·NO)₂¹³]. Such effects are attributable to alteration of the inductive effect, which when operating to its full extent can produce repulsion between the two positively charged nitrogen atoms sufficient to overcome the N-N bonding forces. It is however difficult to apply such ideas to the case of dimers containing *tert.*-alkyl groups, all of which produce the monomer when dissolved in organic solvents, without predicting similar behaviour for dimers containing primary and secondary alkyl groups. The effect of other substituents, *e.g.*, NO₂, Ac, CH₂Ac, is also difficult to explain. Energies and entropies of activation for monomer production are needed before an adequate theory of the dissociation process can be formulated.

The infrared absorption data follow the pattern of previous measurements. The *trans*-dimer investigated has its strongest absorption at 1225 cm.⁻¹ and is thus similar to the *trans*-dimers previously measured,^{3, 4, 13} the absorption being due to the N-O stretching. The *cis*-dimers investigated have their strongest absorption bands at 1393 and 1437 cm.⁻¹ which are close to the 1399 cm.⁻¹ band which we have tentatively identified with one of the two N-O frequencies in *cis*-dimeric nitrosomethane.⁴ Further studies of the infrared absorption spectra of other *cis*-dimers are required; a detailed assignment of the spectra is therefore postponed.

One of us (J.T.) thanks the Department of Scientific and Industrial Research for a Maintenance Grant. We thank Imperial Chemical Industries Limited for the loan of a Unicam Spectrophotometer, Mr. M. St.C. Flett for the infrared determinations, and Dr. D. H. Whiffen for discussions of the interpretation of the infrared spectra.

UNIVERSITY OF WALES, UNIVERSITY COLLEGE, SWANSEA.
UNIVERSITY OF BIRMINGHAM.

[Received, November 21st, 1955.]

¹² Haszeldine, *J.*, 1953, 2075; Banus, *ibid.*, p. 3755.

¹³ Tarte, *Bull. Soc. chim. belges*, 1954, **63**, 525.

¹⁴ Piloty, *Ber.*, 1898, **31**, 452.

¹⁵ Steinkopf and Jürgens, *J. prakt. Chem.*, 1911, **84**, 686.