7. *The Preparation of Some Isotopically Labelled Nitrosoalkanes.*

By L. Batt, J. K. Brown, B. G. Gowenlock, and K. E. Thomas.

cis- and *trans*-Dimers of deuterated nitrosomethane are prepared by the pyrolysis of deuterated isopropyl nitrite, and *cis*- and *trans*-dimers of [^{15}N]-nitrosomethane and -nitrosoethane by the reaction of pyrolytically generated methyl and ethyl radicals with [^{15}N]nitric oxide. The infrared absorption frequencies of the compounds are listed.

Dimeric nitrosoalkanes can be prepared by a variety of methods.[1] Two simple methods of preparation of the gaseous monomer are available, namely the pyrolysis of alkyl nitrites [2,3] and the direct reaction of free radicals with nitric oxide.[4] It is probable that

---

[1] Gowenlock and Lüttke, *Quart. Rev.*, 1958, **12**, 321.
[2] Gowenlock and Trotman, *J.*, 1955, 4190.
[3] Gowenlock and Trotman, *J.*, 1956, 1670.
[4] Chilton and Gowenlock, *J.*, 1953, 3232; 1954, 3174.

both preparative methods involve this direct combination and that in the pyrolysis (as distinct from the photolysis) of nitrites the mechanism can be represented by

$$\begin{aligned} R^1R^2R^3C{-}O{-}NO &\longrightarrow R^1R^2R^3C{-}O\cdot + NO \\ R^1R^2R^3C{-}O\cdot &\longrightarrow R^1R^2C{=}O + R^3\cdot \\ R^3\cdot + NO &\longrightarrow R^3NO \end{aligned}$$

Thus it should be possible to make isotopically labelled nitrosoalkanes by labelling either the alkyl nitrite or the nitric oxide. The production of such isotopically labelled molecules should assist in a detailed assignment of the vibration frequencies in the dimeric nitrosoalkanes. We already possess some information concerning the infrared absorption spectra of nitrosoalkane dimers,[2,3,5,6,7] and the effects of deuterium [8] and ^{15}N substitution [9] on the infrared absorption of a variety of molecules have been studied. Direct synthesis is necessary because it has been shown that neither dimer of nitrosomethane will undergo any exchange reaction with heavy water.[10]

EXPERIMENTAL

Deuterated Nitrosomethane Dimers.—The preparative route was

$$(CD_3)_2CO \xrightarrow{NaBH_4} [(CD_3)_2C{\cdot}OH]_4BNa \xrightarrow{D_2O} (CD_3)_2CD{\cdot}OH \xrightarrow{HNO_2} (CD_3)_2CD{\cdot}ONO$$
$$\xrightarrow{heat} CD_3{\cdot}NO + CD_3{\cdot}CDO.$$

Fully deuterated acetone (5 g.) (Merck and Co., Canada) was added to deuterium oxide (25 ml.) and cooled to 0°. Sodium borohydride (1 g.), dissolved in deuterium oxide (25 ml.), was added dropwise (30 min.), the solution being stirred magnetically. The solution was allowed to warm to room temperature, aqueous sodium nitrite (10 ml.) was added, and the solution was then recooled to 0°. Concentrated sulphuric acid (2·5 ml.) in water (10 ml.) was added dropwise (10 min.) and the resultant alkyl nitrite was separated, washed with water, sodium hydrogen carbonate solution, and water, and dried (Na_2SO_4). The yield was 3 g. (32%). The nitrite was pyrolysed in a flow system [3] (vessel temperature 325—330°; initial pressure of nitrogen carrier gas, 4 mm.; pressure of nitrite about 0·1 mm.; contact time about 0·8 sec.). Under these conditions about 20% of the nitrite decomposed. The unchanged nitrite and deuteroacetaldehyde were distilled from the *cis*-dimer of deuteronitrosomethane formed in the trap system [3] and re-pyrolysed. Under these conditions the aldehyde does not decompose. The *cis*-dimer formed was evacuated at 10^{-4} mm. pressure for several hours and purified by rapid recrystallisation from methanol. 0·4 g. of the deuterated *cis*-dimer of nitrosomethane was thus prepared (40% yield based on the nitrite, 12% yield based on the acetone). The *cis*-dimer had m. p. 98° 97·5°, unlabelled [2]); $\lambda_{max.}$ (in water) 265 mμ, (265 mμ, unlabelled [2]). The corresponding *trans*-dimer was prepared by heating the *cis*-dimer slowly to 120° in a sealed melting point tube, and purified by vacuum sublimation; the sample had m. p. 123° (122°, unlabelled [2]), $\lambda_{max.}$ (in water) 275 mμ (276 mμ, unlabelled [2]). Infrared absorption spectra of potassium chloride discs were measured on a Perkin-Elmer 21 double-beam spectrometer and on a Grubb-Parsons single-beam spectrometer. The major bands are as follows (full spectra will be offered for the D.M.S. series): *cis*-dimer 2900w, 2280w, 1650w, 1432m, 1395s, 1257w, 1133m, 1035m, 870m, 845m, 680m, 675w, 570w; *trans*-dimer 2860w, 2400w, 2180w, 2100w, 1640w, 1455w, 1290s, 1220s, 1010m, 970m, 810s, 800s, 675w, 570w.

[^{15}N]-*Dimers.*—Only 0·25 g. of a 5—9M-solution of >95% [^{15}N]nitric acid was available (20th Century Electronics Ltd.) and this was reduced to nitric oxide by mercury and sulphuric acid; 1·1 l. of [^{15}N]nitric oxide at 35 mm. Hg were thus prepared. Commercial di-t-butyl peroxide and diethylmercury were purified by bulb-to-bulb distillation, middle fractions only

---

[5] Lüttke, *Z. Elektrochem.*, 1957, **61**, 976.

[6] Gowenlock, Spedding, Trotman, and Whiffen, *J.*, 1957, 3927.

[7] Tarte, *Bull. Soc. chim. belges*, 1954, **63**, 525.

[8] Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen, London, 1958, p. 248 and elsewhere.

[9] Kübler, Lüttke, and Weckherlin, *Z. Elektrochem.*, 1960, **64**, 650.

[10] Lüttke, private communication.

being retained. Pyrolysis was carried out in a flow system,[4,11,12] with reaction times of about 0·5—1 sec., a carrier gas of about 2 mm. Hg of nitrogen and about 2 mm. Hg of nitric oxide (initial pressures), reactant pressures of 0·5 mm. Hg (for di-t-butyl peroxide) and 0·3 mm. Hg (for diethylmercury), and vessel temperatures of 320° and 340°. During a pyrolysis nitric oxide was added at suitable intervals to maintain the total pressure approximately constant. When unlabelled nitric oxide was used samples of the *cis*-dimers of nitrosomethane and nitrosoethane were prepared which had the same infrared absorption spectra as the nitroso-compounds prepared from pyrolysis of alkyl nitrites.[2,3,6] The yields of the [^{15}N]-dimers were *cis*-dimer of [^{15}N]nitrosomethane (m. p. 90°), 20 mg; *cis*-dimer of [^{15}N]nitrosoethane, 4 mg. *trans*-Dimer of [^{15}N]nitrosomethane was prepared from the *cis*-dimer by the same technique of melting and sublimation as the deutero-*trans*-dimer. *trans*-Dimer of [^{15}N]nitrosoethane was prepared by shaking a small quantity of the *cis*-dimer with carbon tetrachloride, and identified by the infrared absorption spectrum. The main absorption bands of [^{15}N]-dimers were as follows: *cis*-dimer of [^{15}N]nitrosomethane 3050w, ~1420m sh, 1374s, 1337s, ~1100w sh, ~1056w sh, 1017s, 737m; *trans*-dimer of [^{15}N]nitrosomethane 3050w, 1273s, 1125s, 924m; *cis*-dimer of [^{15}N]nitrosoethane 2940w, 1420s, 1370s, 1328m, 1290m, 1265m, 1215w, 1075m, 1035s, 955m; *trans*-dimer of [^{15}N]nitrosoethane * 2940w, 1214s, 1140—1120 broad m, 885s. In all of these cases the spectra were measured in potassium chloride or bromide discs, with the exception of the final example which was measured in carbon tetrachloride solution.

DISCUSSION

Tentative assignments of some of the vibration frequencies have already been made [1,2,3,5,6,7] for some of the dimeric nitrosoalkanes and it is of interest whether the infrared spectra of the isotopically labelled dimers are consistent with these assignments. With the dimers containing nitrogen-15, we expect that the shifts will be small (of the order of 10 cm.$^{-1}$) and that they will be observed in the infrared-active skeletal stretching and deformation vibrations of the C–N, N–N, and N–O system. In the *trans*-dimer of nitrosomethane (symmetry C_{2h}) the shifts from 1284 to 1273, from 1132 to 1125 and from 935 to 924 cm.$^{-1}$ (in all cases figures for the unlabelled compound being given first) are compatible with the respective assignments of antisymmetric stretching of N–O and C–N and infrared-active CNO bending vibrations. The first two of these assignments have been made previously, the third is tentative. In the case of deuterium substitution we note that, as expected, the N–O asymmetrical stretching vibration is virtually unaltered at 1290 cm.$^{-1}$. The 1132 cm.$^{-1}$ vibration of the hydrogen compound is absent from the deutero-compound possibly owing to a mixing of the C–N vibration with a methyl umbrella vibration that has been displaced by deuterium substitution.

In the *cis*-dimer of nitrosomethane (symmetry C_{2v}) two N–O stretching frequencies, two C–N stretching frequencies, and the N=N stretching frequency could be affected by the nitrogen-15 substitution. We suggest that the observed shifts from 1399 to 1374, and from 1343 to 1337 cm.$^{-1}$ are compatible with the assignment to the two N–O stretching modes. Similarly, the C–N stretching modes may well be associated with the shifts from 1061 to 1056, and from 1021 to 1017 cm.$^{-1}$. In the deuterium-substituted *cis*-dimer the N–O frequencies may be associated with the bands at 1432 and 1395 cm.$^{-1}$. It is necessary to add that all such assignments need further substantiation and, in particular, the N=N frequency must be located.

The shifts in the frequencies of the *trans*-dimer of nitrosoethane on being labelled with nitrogen-15 are from 1225 to 1214, and from 1145 to 1140—1120 cm.$^{-1}$. Both these shifts are not incompatible with the previous assignments of N–O and C–N stretching vibrations. The corresponding shifts in the *cis*-dimer of nitrosoethane are from 1426 to 1420, from 1299 to 1290, from 1078 to 1075, from 1043 to 1035, and from 963 to 955 cm.$^{-1}$. These provide

---

* Only the strongest bands are listed as only a very small sample was available. Weak bands arising from a small quantity of *cis*-dimer present are ignored.

[11] Gowenlock, Polanyi, and Warhurst, *Proc. Roy. Soc.*, 1953, *A*, **218**, 269.

[12] Gowenlock, *Chem. Soc. Special Publ.*, No. 9, 1958, 62.

some confirmation of previous assignments which were 1426 (N–O stretching), 1299 (either N=N or N–O stretching), 1078, and 1043 cm.$^{-1}$ (C–N stretching vibrations). The success of the synthetical methods given here suggests that the same general routes could be employed for the preparation of other isotopically labelled nitrosoalkanes.

We thank Professor W. Lüttke and Dr. D. H. Whiffen for discussion of the spectra, Dr. P. Pritchard Jones for assistance in early attempts to synthesise the deutero-dimers, the University of Birmingham for an Appeals Fund Scholarship (to L. B.), and the D.S.I.R. for a maintenance grant (to K. E. T.).

DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY, BIRMINGHAM, 15.

[*Received, June 23rd,* 1961.]