

*Reaction of Nitric Oxide with Gaseous Hydrocarbon Free Radicals. Part II.\* Radicals produced by Pyrolysis of Di-n-butylmercury.*

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The products of pyrolysis of di-*n*-butylmercury in a flow system with nitrogen and nitric oxide as carrier gas have been studied. It is shown that a mixture of an oxime and a nitroso-compound is produced. The properties of this mixture are compared with those for the *isopropyl* radical reaction, and correlations with the monomeric and the dimeric state of aliphatic nitroso-compounds are drawn. The reaction products with nitrogen as carrier gas are also reported.

It has been established (*J.*, 1953, 3232) that *isopropyl* radicals react with nitric oxide to give a nitroso-compound and acetoxime. It has also been shown that perfluoroalkyl radicals and nitric oxide give deep blue perfluoroalkyl nitroso-compounds (Haszeldine, *ibid.*, p. 2075; Banus, *ibid.*, p. 3755). Gingras and Waters (*Chem. and Ind.*, 1953, 615) have established that nitric oxide reacts with 2-cyano-2-propyl radicals in benzene solution. It has also been established that alkoxy-radicals can react with nitric oxide (Mortlock and Style, *Nature*, 1952, 170, 706; Levy, *J. Amer. Chem. Soc.*, 1953, 75, 1801) to give the alkyl nitrite. It has been pointed out to us that Raley, Rust, and Vaughan (*ibid.*, 1948, 70, 88) isolated formaldoxime after thermal decomposition of di-*tert*-butyl peroxide in the presence of nitric oxide, probably from the reaction sequence  $\text{CH}_3\cdot + \text{NO} \longrightarrow \text{CH}_3\cdot\text{NO} \longrightarrow \text{H}_2\text{C}:\text{N}\cdot\text{OH}$ . It appears, therefore, that the simpler radicals react with nitric oxide to form an addition product.

Nitroso-compounds have been prepared by Tarte (*Bull. Soc. roy. Liège*, 1953, 22, 226) by the original photolytic method of Coe and Doumani (*J. Amer. Chem. Soc.*, 1948, 70, 1516). The preparation of nitrosomethane is described, and other nitroso-paraffins (probably nitrosoethane) which are liquid at room temperature are reported.

## EXPERIMENTAL

*Reaction in the Presence of Nitric Oxide.*—The experimental technique was essentially that used for the work with diisopropylmercury, pyrolyses being performed in the temperature range 376–410°. Di-*n*-butylmercury (B.D.H.) was purified by repeated bulb-to-bulb distillation under a high vacuum until a product of constant vapour pressure was obtained. The partial pressure of the di-*n*-butylmercury in the reaction vessel was about 0.016 mm. in all the runs; this is lower by a factor of about 8 than that for diisopropylmercury. The products of the pyrolysis were trapped in a U-tube at –78°, and two traps in series at –130° and –183° severally. Nitric oxide was consumed during pyrolysis at a rate varying from 0.03 to 0.1 mm./min. and was therefore added at intervals from the reservoir to keep the pressure in the reaction vessel constant to within  $\pm 0.2$  mm. On the completion of a run the U-tube contained mercury together with undecomposed di-*n*-butylmercury, the –130° trap contained a yellow solid and a colourless liquid (probably hydrocarbons), whereas the –183° trap contained a little yellow solid together with some hydrocarbon. The technique established in Part I was then used for determining the m. p. of the yellow solid; it melted in the range –60° to –55° to a yellow-brown liquid which speedily changed into a white solid. All other products were pumped off from the white solid under a vacuum and the solid was then examined. A small amount of a relatively involatile liquid remained and the ultra-violet absorption spectrum of this was obtained.

*Experiments with the white solid.* Chemical tests were made for nitroso- and oxime groups (Feigl, "Spot Tests," Elsevier, Amsterdam, 1939). Liebermann's nitroso-test (*op. cit.*, p. 267) gave a green colour, the product becoming green-yellow in sodium hydroxide solution. The oxime test (*op. cit.*, p. 291) gave a pink colour, and when the solid was fused with diphenylamine, and concentrated sulphuric acid was added, a blue colour resulted (Coe and Doumani, *loc. cit.*).

\* Part I, *J.*, 1953, 3232.

A sample of nitrosomethane prepared according to the method of Coe and Doumani also gave a green colour in the Liebermann test.

Investigations of the ultra-violet absorption spectra of solutions of the solid were made with a Unicam SP. 500 photoelectric quartz spectrophotometer. As the composition of the substance was unknown, only the data for  $\lambda_{\max}$  in dilute solutions are presented, no determination of  $\epsilon$  values being made. The values obtained are given in Tables 1 (aqueous solutions) and 2 (ethereal solutions). It is noteworthy that the  $\lambda_{\max}$  values were unaltered by the substitution

TABLE 1.

Substance	$\lambda_{\max}$ (m $\mu$ )	Substance	$\lambda_{\max}$ (m $\mu$ )
Solid .....	<200, 267	Acetaldoxime <sup>a</sup> .....	203
Solid + HCl .....	<200, 267	Butyraldoxime <sup>b</sup> .....	<200
Nitrosomethane .....	266—267	isoPropyl solid <sup>c</sup> .....	<200, 266

<sup>a</sup> Prepared by usual methods.      <sup>b</sup> Product from L. Light & Co.      <sup>c</sup> Part I.

of a silica trap at  $-130^\circ$  for the Pyrex trap. A specimen of the solid, kept under a vacuum in a small Pyrex tube and in the dark, soon became moist and within a day completely melted. After 8 weeks the presence of a small quantity of crystals on the walls of the tube was noticed. In ether the crystals showed peaks at 208 and 289 m $\mu$ , and the liquid at 207 and 288—289 m $\mu$ . Thus any separation achieved by this method was slight and this contrasts with the isopropyl case.

Other specimens of the solid were sealed off under a vacuum and submitted to microanalysis (Weiler and Strauss): low values for nitrogen were obtained unless the method of analysis was modified by using Friederich's micro-Kjeldahl method with hydriodic acid as noted by Coe and

TABLE 2.

Substance	$\lambda_{\max}$ (m $\mu$ )	Substance	$\lambda_{\max}$ (m $\mu$ )
Solid (Pyrex trap) .....	209, 289—290	Acetaldoxime .....	211—212
Solid (silica trap) .....	210, 289	Butyraldoxime .....	212
Nitrosomethane .....	287	U-Tube washings .....	209, 211, 290 (Inf. 250—255)
isoPropyl solid <sup>a</sup> .....	209—211, 289—292, 665	Di-n-butylmercury .....	211—212, (Inf. 250—255)
Liquid in $-130^\circ$ trap ...	210—212, 289—290	2-Methyl-2-nitrosopropane ...	300, <sup>b</sup> 665, <sup>b</sup> 296, <sup>c</sup> 675 <sup>c</sup>

<sup>a</sup> Part I.    <sup>b</sup> Baly and Desch, *J.*, 1908, **93**, 1752.    <sup>c</sup> Jander and Haszeldine, *J.*, 1954, 912.

Doumani (*loc. cit.*) (Found: C, 39.1; H, 8.4; N, 21.7. Calc. for  $C_2H_5ON$ : C, 40.7; H, 8.5; N, 23.7. Calc. for  $C_4H_9ON$ : C, 55.2; H, 10.1; N, 16.1%). The solid, when freshly prepared, was a white waxy substance with a sweet penetrating smell. It melted over the range  $58-62^\circ$  to a blue liquid which became a pale blue green as the temperature rose. The liquid charred at about  $138^\circ$ .

The behaviour of the solid in various solvents was investigated and the appearance of colours on dissolving, on gentle warming, and on boiling, was noted. The colour that appeared on dissolution faded completely, the rate of disappearance varying with the solvent. Benzene, ethyl acetate, acetic acid, and ethanol solutions all gave a colour on boiling that could not be regenerated by further heating. In all other cases, reheating reproduced the colour, albeit very faintly in some cases. The results are given in Table 3.

*Reaction in the Absence of Nitric Oxide.*—A number of experiments were performed in which nitrogen was used as the carrier gas, the experimental method being similar to that used by us for diisopropylmercury (*Trans. Faraday Soc.*, 1953, **49**, 1451), the trap temperatures being  $-50^\circ$ ,  $-130^\circ$ , and  $-196^\circ$ . The velocity constant,  $k$ , was determined from the mercury produced (trapped out at  $-50^\circ$ ), the relation being  $d[Hg]/dt = k[Bu_2Hg]$ . The velocity constant was unaltered in the presence of nitric oxide, suggesting the absence of a chain reaction, and the temperature dependence was given by the expression  $\log_{10} k$  (sec.<sup>-1</sup>) =  $15.02 - 45,600/2.303RT$ , all experiments being carried out at a total pressure of about 4.4 mm. The hydrocarbons condensed in the  $-130^\circ$  and  $-196^\circ$  traps were estimated by expansion into spaces of known volumes and fractional volatilisation by use of baths at different temperatures; where possible, samples were analysed for unsaturated compounds by Melville and Robb's method (*Proc. Roy. Soc.*, 1949, *A*, **196**, 445), and in the case of  $C_6$  and  $C_8$  hydrocarbons the samples were weighed.

The results were only approximate, the molar ratios of the hydrocarbons produced being of the order  $C_2 : C_4 : C_6 : C_8 = 6 : 1 : 1 : 0.1$ . The quantities of  $C_3$  compound produced were always very small; any  $C_5$  or  $C_7$  hydrocarbons produced were included with the  $C_6$  and  $C_8$  respectively.

TABLE 3.

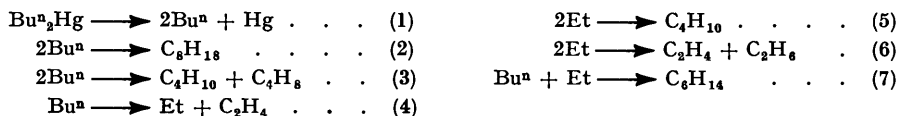
Solvent	B. p.	$\epsilon$	Colour * of solution on :		
			dissolving	gentle heating	boiling
$n-C_5H_{12}$ .....	36°	1.85		(Insoluble)	
$n-C_6H_{14}$ .....	69	1.91		(Insoluble)	
$CCl_4$ .....	77	2.22	—	—	—
Dioxan .....	101	2.24	—	B—G	B—G
$C_2H_6$ .....	80	2.30	B—G	B—G	B—G
PhMe .....	111	2.38	B	—	B
$Et_2O$ .....	35	4.36	B	—	—
$CHCl_3$ .....	61	4.64	B	B	B
$CHBr_3$ .....	150	4.73	—	—	—
$EtOAc$ .....	77	6.11	B	—	B
$AcOH$ .....	118	6.13	—	—	B—G
$CH_2Cl_2$ .....	40	9.14	B	—	B—G
$COMe_3$ .....	56	21.45	—	B	B
$EtOH$ .....	78	25.8	—	—	B
$Pr^iNO_2$ .....	131	~30	—	B—G	B—G
$CH_3CN$ .....	82	37.5	—	B—G	B—G
$H_2O$ .....	100	80	—	—	—

\* B = Blue, B—G = Blue-green.

The percentage unsaturation of the  $C_2$  fraction was between 80 and 100% and of the  $C_4$  fraction between 10 and 23%. Frey and Hepp (*J. Amer. Chem. Soc.*, 1933, 55, 3357) give ethylene and *n*-butane as the principal gaseous products of the pyrolysis of di-*n*-butylmercury in a flow system. Our hydrocarbon balance was within 5% of the theoretical value.

## DISCUSSION

The solid product formed on pyrolysis of di-*n*-butylmercury in nitric oxide at 376—410° is evidently a mixture of an oxime and a nitroso-compound. The pyrolysis reactions in the absence of nitric oxide are probably :



Such a reaction scheme would account for the products observed. The first step may involve the production of the radical  $Bu^aHg$  which then decomposes, though the similarity of the frequency factor to those for diisopropylmercury (Chilton and Gowenlock, *loc. cit.*) and di-*n*-propylmercury (*idem*, to be published) suggests that the two-bond fission is more likely. In the presence of nitric oxide the reactions



with subsequent partial isomerization to the oxime are suggested. Our analytical results suggest that mainly nitrosoethane and acetaldoxime are obtained, and this conclusion is that expected from consideration of the hydrocarbon products in the absence of nitric oxide. It may also be noted that the penetrating odour of butyraldoxime was absent from our product.

Many of the detailed results are analogous to those for the isopropyl case and similar interpretation of the results can thus be made. The melting of the yellow solid at  $-60^\circ$  to  $-55^\circ$  and its subsequent transition to a white solid we ascribe to the sequence: nitrosoalkane monomer (solid)  $\longrightarrow$  nitrosoalkane monomer (liquid)  $\longrightarrow$  nitrosoalkane dimer (solid). The oxime transition suggested by us in Part I has since been disproved experimentally, since no yellow colours were observed in the traps when acetoxime was passed through the reaction vessel under normal reaction conditions.

The ultra-violet absorption spectra are noteworthy. The good correlation with nitroso-methane strengthens the case for identification of the 266—267  $m\mu$  peak (aqueous solution) and 287—292  $m\mu$  peak (ethereal solution) with a dimeric nitroso-compound. The values of 300 and 665  $m\mu$  given by Baly and Desch (*loc. cit.*) and 296 and 675  $m\mu$  given by Jander and Haszeldine (*loc. cit.*) for 2-methyl-2-nitrosopropane and of 650—710  $m\mu$  for unimolecular halogenated nitrosoalkanes (Hammick and Lister, *J.*, 1937, 489; Lewis and Kasha, *J. Amer. Chem. Soc.*, 1945, **67**, 994) provide no argument against such an identification. No value for the absorption peak in the visible region was taken for ethereal solutions because fading was too rapid, but as the solution was blue the absorption was probably in the 650—710  $m\mu$  range. It is noteworthy that nitrosomethane dimer, which does not give a blue colour on dissolution in ether, gives an absorption maximum almost identical with those for compounds isolated in this (and the previous) investigations.

It might be argued that the failure to give the Liebermann colours is a reason for discounting the formation of a nitroso-compound; however, although tertiary aliphatic nitroso-compounds give this test (Bamberger and Seligman, *Ber.*, 1903, **36**, 685), yet nitrosomethane fails to give it. We suggest that Coe and Doumani's diphenylamine test (*loc. cit.*) is a better general test for primary and secondary aliphatic nitroso-compounds than the Liebermann test.

The behaviour of the solid when dissolved in various solvents is similar to that in the *isopropyl* case. The simplest feature is that of colour production on boiling, which is probably a temperature effect, being given by all solvents boiling above 40° with the exception of carbon tetrachloride, bromoform, and water. The last two solvents showed the same exceptional behaviour in the *isopropyl* case. It is worthy of note that no nitroso-compound gives a blue colour in aqueous solution. The colour change on dissolution occurs only in the solvents of low dielectric constant, the range being somewhat similar to those reported in Part I.

TABLE 4.

Compound	Colours on dissolution	Colours on heating solid	Colours on heating soln.	$\lambda_{max.}$ ( $m\mu$ )		Colour at —130°
				Ether	Water*	
Me·NO .....	Colourless	Transient blue (>122°) few degrees above m. p.	Blue in toluene (110°)	287	266—267	Not yet investigated
Et·NO .....	Either colourless or immediate blue becoming colourless	Blue (>58—62°)	Blue (>40°) in certain solvents	289—290	267	Yellow : transition —60° to —55°
Pr <sup>1</sup> ·NO ...	Either colourless or immediate blue becoming colourless	Blue-green (>85—95°)	Blue (>80°) in certain solvents	290	266	Yellow : transition —85° to —78°
Bu <sup>4</sup> ·NO ...	Colourless, slowly becoming blue	Blue (>76°)	Immediate blue colour, blue on cooling	300, 296 665, 675	—	Not yet investigated

\* Aqueous solutions are all colourless.

There is now sufficient evidence to show that simple nitrosoalkanes exist and that isomerization to oximes is not instantaneous. The evidence for this misunderstanding is based upon some papers published fifty years ago which expressed the *opinion* that speedy isomerization occurred at room temperature (cf. Schmidt, *Ber.*, 1902, **35**, 2323; Bamberger and Seligman, *Ber.*, 1903, **36**, 685, 701). This opinion has been treated as fact for many years and should now be abandoned in the light of the work by Coe and Doumani (*loc. cit.*), Tarte (*loc. cit.*), and the present authors (*loc. cit.*). In this connection it is necessary to point out that nitroso-compounds are reasonably stable in the gas phase at 230—280° (*isopropyl*) and 376—410° (present investigation). The misconception concerning isomerization (the nitroso-hydroxyimino-system) is probably based on an analogy with the behaviour of nitrolic acids and nitrosoacetone, which isomerize rapidly. It should be noted that halogenonitrosoparaffins containing secondary hydrogen atoms and  $\alpha$ -nitroso-

esters only isomerise slowly, and phenylnitrosomethane isomerises extremely slowly (cf. Sidgwick, "The Organic Chemistry of Nitrogen," Oxford, 1945, pp. 204—226).

The general properties of simple nitrosoalkanes are summarised in Table 4. The evidence available suggests an increasing stability of the monomeric state  $R\cdot NO$  in the series  $R = Me < Et \sim Pr^i < Bu^t$ , a blue-green colour being associated with nitroso-monomer, the dimer being colourless.

Studies of the reaction products of other free radicals with nitric oxide are in progress, and we are also investigating the preparation, properties, and structure of pure nitrosoalkanes. These will be reported later.

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