TABLE I

Compd	Bp, °C (mm)	$n^{20}\text{D}$	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Infrared absorption
III	70–72 (9)	1.4644	$C_{10}H_{16}O$	78.88	10.60	78.55	10.70	2900 (s), 2750 (s) 1725 (s), 1450 (s) 1380 (s), 875 (s), 835 (s)
VII	90–92 (10)	1.4534	$C_{11}H_{18}O_2$	72.48	9.95	72.41	10.08	2950 (s), 1735, 990 (s) 855 (s), 839 (s)
IV + V	88–89 (10)	1.4700	$C_{10}H_{16}O$	78.88	10.60	78.80	10.74	2925 (s), 1710 (s), 1460 (s) 1425 (s), 1360 (s), 980 (s) 750 (br)
XII	65–66 (0.3)	1.4740	$C_{10}H_{18}O$	77.86	11.76	77.93	11.59	3450 (br), 2950 (s) 1655 (s), 1385 (s)
XI	60–61 (1)	1.4458	$C_{11}H_{20}O_2$	71.64	10.95	71.31	10.70	2900 (s), 1710 (vs) 1155 (s)

1-methyl-3-isopropenylcyclopentylcarboxylate (X) by comparison with a known infrared spectrum.[10] The other three components are most likely the esters IX, X, and Xa.

Reduction of Isomerization Products.—Hydrogenation of 4.5 g of the product of acid-catalyzed isomerization of methyl 3,6,6-trimethylbicyclo[3.1.0]hexyl-3-carboxylate with HCl in 25 ml of methanol with 0.1 g of platinum oxide gave a quantitative yield of colorless oil (XI), bp 60–61 (1 mm), $n^{20}\text{D}$ 1.4458 (lit.[10] bp 60–61 (1 mm), $n^{20}\text{D}$ 1.4456). Gas–liquid partition chromatographic analysis of this material showed it to be composed principally of one major peak. Infrared spectral comparison of this material with that of an authentic sample[10] of methyl 1-methyl-3-isopropylcyclopentylcarboxylate showed them to be identical.

3,6,6-Trimethylbicyclo[3.1.0]hexyl-3-carbinol.—Acid VI (10 g) was placed in 50 ml of 50% alcohol. To this a mixture of 20 g of NaOH in 100 ml of H_2O was added with stirring. This mixture was allowed to stir overnight and then cooled. Extraction of the basic solution with ether followed by drying of the ethereal solution over anhydrous sodium sulfate and removal of solvent at reduced pressure yielded 4 g of crude 3,6,6-trimethylbicyclo-[3.1.0]hexyl-3-carbinol (XII). See Table I for properties. Acidification of the remaining aqueous solution gave, after extraction with ether and removal of solvent at reduced pressure, 4.5 g of 3,6,6-trimethylbicyclo[3.1.0]hexane-3-carboxylic acid (VI).

Registry No.—I, 2225-98-1; III, 13124-67-9; IV, 13124-68-0; V, 13124-69-1; VII, 13124-70-4; XI, 13124-71-5; XII, 13124-72-6; semicarbazone, 13124-59-9.

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Studies on Nitroso Compounds. III. The Effect of *ortho* Substituents on Dimerization. *o*-Bromine *vs.* *o*-Chlorine[1]

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It is known[3] that *ortho* substituents favor dimerization of aromatic nitroso compounds. For example, 2,6-dichloronitrosobenzene is strongly dimerized even in dilute solution,[1,3] whereas *p*- and *m*-chloronitrosobenzenes and 3,5-dichloronitrosobenzene[4,5] are not. If, as suggested in part I of this series,[3] steric inhibition of resonance in the monomers is the chief factor responsible for dimerization of *ortho*-substituted nitroso compounds, then it might be expected that increase in size of *ortho* group would increase dimerization. However, equilibrium constants for the dimer–monomer equilibria of 2,4,6-tribromo- and 2,4,6-trichloronitrosobenzenes[1,3–5] have been reported, and the tribromo compound appears to be considerably *less* dimerized than the trichloro. Since this result is not in harmony with the idea that bigger *ortho* groups should increase dimerization, a more extensive experimental investigation was undertaken. The present Note reports dimer dissociation constants for several 2,6-dibromonitrosobenzenes (including 2,4,6-tribromonitrosobenzene) and related 2,6-dichloro compounds, all in benzene solutions at 25°. The compounds were prepared by methods which have been described.[6] Physical constants of the samples used are given in the Experimental Section.

Equilibrium constants were determined spectrophotometrically by following the characteristic[4,5,7] monomer absorption at 750–800 mμ. It can be shown[1] that, if Beer's law applies, if light absorption is due to monomer only, and if a simple monomer–dimer equilibrium is involved, then a plot of D/CL *vs.* D^2/CL^2 should be linear where D is optical density, C is concentration in moles/liter of total nitroso compound (all figured as monomer), and L is length of cell in centimeters. The intercept on the D/CL axis gives ϵ (the molar extinction coefficient per centimeter of cell length), and a set of values of K_c can then be calculated. K_c (in moles/liter) is the equilibrium constant for the following process.

$$ArN_2O_2Ar \rightleftarrows 2ArNO$$

Plots of D/CL *vs.* D^2/CL^2 were linear for all compounds. "Best" values (by least squares) of equilibrium constants are recorded in Table I.

Two comments on the data in Table I are required. First, it is clear that the 2,6-dibromo compounds are less dimerized than corresponding 2,6-dichloro ones by a factor of 20–30 in K_c sec.; the precision with which equilibrium constants were determined was much lower

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Table I

Equilibrium Constants for Dissociation of 2,6-Dibromo-4-X- and 2,6-Dichloro-4-X-Nitrosobenzene Dimers in Benzene

para substituent X	2,6-Dibromo K_c, moles/l.[d]	2,6-Dibromo K/K_0[a] ratio	K_{Br}/K_{Cl}[b] ratio	2,6-Dichloro $K_c \times 10^{-2}$, moles/l.[d]	2,6-Dichloro K/K_0[c] ratio
H	0.39 ± 0.02	1.0	26	1.5 ± 0.15[e]	1.0
CH_3	0.95 ± 0.02	2.4	24	3.9 ± 0.4[e]	2.6
Cl	1.40 ± 0.40	3.5	28	4.9 ± 0.5[e]	3.3
Br	1.20 ± 0.20[f]	3.1	21	5.7 ± 0.6[e]	3.8

[a] Ratio of K_c for 2,6-dibromo-4-X- to K_c 2,6-dibromonitrosobenzene. [b] Ratio of K_c for 2,6-dibromo-4-X-nitrosobenzene to K_c for the corresponding 2,6-dichloro-4-X-nitrosobenzene. [c] Ratio of K_c for 2,6-dichloro-4-X- to K_c for 2,6-dichloronitrosobenzene. [d] The error limits given represent standard deviations for the mean K_c. [e] From ref 1. [f] Data reported in ref 4 lead to K_c = 0.92 for 2,4,6-tribromonitrosobenzene, also in benzene solution at 25°.

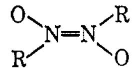
for the 2,6-dibromo series, particularly the last three (column 2, Table I). The apparent difference in K_c values for 2,6-dibromo-4-chloro- and 2,4,6-tribromonitrosobenzenes, for example, is well within experimental error and not statistically significant.

Since the Hammett[8,9] σ constants for chlorine and bromine are nearly the same, and also their resonance substituent constants, $\sigma_R{}^0$,[10] and polar substituent constants,[11] σ^*, derived from aliphatic reactivities *and* from *ortho*-substituted benzoate reactivities, whereas there steric substituent constants[11] differ considerably, it seemed probable to the present authors that the 20–30-fold increase in dissociation constant on exchanging *o*-chlorine for -bromine is a steric effect. A referee has suggested, however, that the relative importance of electronic effects of bromine and chlorine in monomer and dimer may be different from *ortho* and *para* positions. Simple MO calculations indicate that resonance effects from the two positions should be about the same. Since Taft's treatment[10,11] shows that dipolar and resonance effects differ little for chlorine and bromine, but their steric effects do, the most straightforward interpretation of the data in Table I appears to be in terms of a steric effect.

It was also suggested that an even larger *ortho* substituent than bromine may favor dimerization to a greater extent than bromine, and *o*-nitronitrosobenzene[12] was quoted as a possible example of such a case. However, *o*-nitro, -carbethoxy,[13] and probably -phenyl[5] are special cases in that they are conjugated with the benzene ring and so themselves subject to steric inhibition of resonance by the nitroso group. This "double-acting" or "mutual" steric inhibition of resonance is likely to produce anomalous steric effects.[14]

A second referee has suggested that two opposed types of steric hindrance are operating. The first is steric inhibition of resonance in the monomers, which has been dealt with in previous papers.[1,3] The second is the steric barrier to N–N approach and bond formation in the dimers. This latter type of steric hindrance is then perhaps responsible for the large K_{Br}/K_{Cl} ratio (Table I, column 4). If this explanation is correct, the decreased dimerization of 2,6-dibromo compounds means that there is an optimum size of *ortho* group for promoting dimerization, and this optimum has been exceeded in passing from 2,6-dichloro- to 2,6-dibromonitrosobenzenes.

A final answer to the question of why there should be an optimum size of *ortho* group (and if indeed there is one) must await further experimental work. One obvious possibility was considered: namely, that there may be a big change in dimer structure on proceeding from the 2,6-dichloro to the 2,6-dibromo series. This seems unlikely, however, because not only is the effect of *para* substituents on dimerization (see columns 3 and 6 of Table I) nearly the same in the two series, but also the ultraviolet spectra of the corresponding 2,6-dichloro and 2,6-dibromo dimers were virtually identical. The same was true of the ultraviolet and visible spectra of the monomers. A very strong band at 1250–1290 cm^{-1} occurs in the infrared spectra of all dimers in both series, a band known[15] to be characteristic[16] of the following *trans*-azodioxide structure. This



band, the asymmetric stretch of the *trans*-N_2O_2 group, is observed at 1289–1290 cm^{-1} in the spectrum of the dimer of 2,4,6-tribromonitrosobenzene and at 1258–1259 cm^{-1} in the spectrum of the dimer of *p*-bromonitrosobenzene. Both of these compounds are known from X-ray work[17,18] to have the *trans*-azodioxide structure. The band is also observed in the infrared spectra of dimers of *trans* structure in the aliphatic series,[16] but does not occur in the spectra of *cis*-azodioxide structures.[15,16] The positions of these bands for compounds of interest in the present investigation are given in Table II.

Table II

Position of Characteristic, Strong Infrared Band (in Reciprocal Centimeters) of Nitrosobenzene Dimers

para substituent X	2,6-Dibromo-4-X	2,6-Dichloro-4-X	4-X
H	1283[a]	1285[a]	(1409, 1397)[b-d]
Cl	1290[a]	1287[a]	1252[b]
Br	1290[a] (1289)[b]	1284[a]	1258[a] (1259)[b]
CH_3	1275[a]	1286[a]	1252[b]

[a] Present work, solid in Nujol mill. [b] Luttke,[15] solid in KBr disk. [c] Present work, solid in KBr disk. [d] This dimer was assigned the *cis*-azodioxide structure in ref 15.

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(14) It was also pointed out by the referee that *o*-methyl and -bromo substituents have quite different K_c values;[4] yet their steric substituent constants[11] for *o*-benzoate substitution are identical. This is true, and the effect of *o*-methyl *vs.* *o*-bromine is being investigated in these laboratories. However, we chose to investigate the difference between *o*-bromine and -chlorine first because they do have almost identical resonance and polar substituent constants (Taft) but different sizes. The methyl group does not have the same resonance or polar substituent constants as bromine (or chlorine), and comparing methyl with bromine involves changing too many variables at once to allow straightforward interpretation of any difference.

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Experimental Section

The compounds were prepared and purified by methods which have been described.[6] The nitrosobenzenes used in the present investigation had the following physical properties: 2,6-dibromo-, mp 134–135° (lit.[6] mp 135–136°), ϵ_0 40.54 (763 mμ); 2,6-dibromo-4-methyl-, mp 136–138° (lit.[6] mp 136.5–138°), ϵ_0 42.57 (758 mμ); 2,6-di-bromo-4-chloro-, mp 110–111° (lit.[6] mp 110–111°), ϵ_0 42.75 (773 mμ); 2,4,6-tribromo-, mp 122–124° (lit.[6] mp 122–123°), ϵ_0 43.48 (772 mμ) [lit.[4] ϵ_0 43.5 (775 mμ)].

Infrared spectra of the crystalline dimers were run as Nujol mulls and KBr or KI pellets. The spectrometer was a grating instrument with resolution of about 1–2 cm^{-1} (Perkin-Elmer 337 G). Peak positions were reproducible to within ± 1 cm^{-1} and were the same in Nujol mull or pressed disk.

Spectrophotometric measurements were carried out and temperatures were controlled to within $\pm 0.05°$ of 25° as described previously.[1] Stock solutions were made up at 25° and dilutions were made (also at 25°) by means of calibrated pipets and volumetric flasks. Practice runs on nitrosobenzene itself (which does not dimerize in dilute solution) showed that Beer's law was obeyed closely on diluting stock solutions in this way, so that solvent losses due to evaporation and other dilution errors were not serious.

Using experimental optical densities and concentrations, plots of D/CL *vs.* D^2/CL^2 were constructed and "best" straight lines were determined by least squares. The intercepts on the D/CL axes gave ϵ_0, and, from this, individual values of α, the fraction of nitroso compound actually present in solution as monomer, could be calculated from experimental optical densities. Knowing α, equilibrium constants were computed from the following relationship where C is the concentration of total nitroso compound, all figured as monomer.

$$K_c = 2C(\alpha^2/1 - \alpha)$$

Registry No.—2,6-Dibromonitrosobenzene dimer, 13084-82-7; 2,6-dichloronitrosobenzene dimer, 31084-83-8; 2,6-dibromo-4-methylnitrosobenzene dimer, 13084-84-9; 2,6-dichloro-4-methylnitrosobenzene dimer, 13084-85-0; 2,6-dibromo-4-chloronitrosobenzene dimer, 13115-02-1; 2,4,6-trichloronitrosobenzene dimer, 13084-86-1; 2,4,6-tribromonitrosobenzene dimer, 13084-87-2; 2,6-dichloro-4-bromonitrosobenzene dimer, 13084-88-3.

Decomposition of Nitrate Esters to Alcohols

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In connection with the synthesis of 3-nitraza-1,5-pentanediol from the corresponding dinitrate, we have developed a simple, high-yield procedure for the conversion of primary nitrates to alcohols. This transformation can be effected first in the presence of secondary nitramines and second without the formation of the undesirable side-reaction products which accompany hydrolytic decomposition.

Baker and co-worker[1] have carried out a systematic study of the hydrolytic decomposition of organic nitrates. The results of their investigation clearly demonstrated that the hydrolytic decomposition of organic nitrates involves the simultaneous occurrence of reactions 1–3. The formation of aldehydes and olefins under neutral, acidic, or basic conditions makes the hydrolytic decomposition of nitrate esters to alcohols of little preparative value. Other methods have been reported for the decomposition of nitrate esters to alcohols. Hydrazine hydrate is an excellent reagent for reducing sugar nitrates[2] but gives only fair yields with primary aliphatic nitrates.[3] Alkaline hydrosulfides have been reported[4] to decompose nitrates to alcohols in excellent yields if the nitrate ester does not contain functional groups such as secondary nitramines that are unstable under basic conditions.

$$Y + CH_2(CH_2R)ONO_2 \longrightarrow CH_2RCH_2Y + NO_3^- \quad (1)$$

$$Y + HCHRCH_2ONO_2 \longrightarrow YH + CHR{=}CH_2 + NO_3^- \quad (2)$$

$$Y + HCH(CH_2R)ONO_2 \longrightarrow YH + CH_2RCHO + NO_2^- \quad (3)$$

The literature reveals two potential methods for the preparation of 3-nitraza-1,5-pentanediol from the corresponding dinitrate. Acetolysis of the dinitrate followed by acid hydrolysis of the diacetate with methanolic hydrochloric acid as described by Feuer and Swarts[5] gave only a trace of the desired diol. Apparently, the diol forms and then cyclizes under the acidic conditions of the hydrolysis to a morpholine derivative.[6] The alternative procedure involves the room-temperature decomposition of nitrate esters by trifluoroacetic acid to a mixture of the corresponding trifluoroacetate, carboxylic acid, and nitric oxide.[7] We speculated that under refluxing conditions, evolution of the nitric oxide would occur, facilitating formation of high yields of the trifluoroacetate, which, on subsequent methanolysis, would result in the attainment of the desired diol. Decomposition of the dinitrate of 3-nitraza-1,5-pentanediol in refluxing trifluoroacetic acid does, indeed, eliminate oxidation to the carboxylic acid by the nitric oxide; however, the trifluoroacetolysis is exceedingly slow, requiring a reaction time of 1 week. Substitution of formic acid for trifluoroacetic acid gives the diformate after refluxing overnight. Subsequent methanolysis yields the desired diol in almost quantitative yield.

The generality of the formolysis reaction is further demonstrated by the conversion of pentaerythritol trinitrate to pentaerythritol. The absence of any molecular rearrangement in this neopentyl system is obtained from the H^1 nmr spectrum of the methanolysis product. The spectrum is identical with that obtained for pentaerythritol. The decomposition of nitrate esters to alcohols *via* an intermediate formate ester enjoys several advantages over previously described procedures. The yields are high, the reaction can be carried out in the presence of a nitramine, and product isolation is simplified.

Experimental Section

CAUTION! Nitrate esters should be handled with care.

3-Nitraza-1,5-pentanediol.—The dinitrate of 3-nitraza-1,5-pentanediol,[8] 13 g (0.054 mole), was dissolved in 150 ml of 97%

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