N-Chloropiperidine.—A benzene solution of N-chloropiperidine was prepared by adding 400 ml of a 5% sodium hypochlorite solution to an ice-cooled stirred solution of 18 ml of piperidine (Matheson Coleman and Bell, bp 105–107°) in 100 ml of benzene. The ice bath was removed and the mixture was stirred for 20 hr. After separation, the organic phase was dried over magnesium sulfate and analyzed as 1.3 *M* in active chlorine. A 10.0-ml portion of the solution was exposed to nitric oxide. Nitric oxide was rapidly absorbed in an exothermic reaction yielding N-nitrosopiperidine and piperidine hydrochloride. Identification of N-nitrosopiperidine was based on gas chromatograph retention time and infrared absorption spectrum. Authentic N-nitrosopiperidine was prepared from *n*-butyl nitrite and piperidine. Piperidine emerged in 1.2 min and N-nitrosopiperidine in 4.2 min from a 0.25 in. × 3 ft column of 20% Dow Corning Hi-Vac Grease on 45/60 Chromosorb W at 150°, with a helium flow rate of 60 ml/min. An absorption at 1370 cm^{-1} appeared in the infrared absorption spectrum of N-nitrosopiperidine and was absent in the spectrum of piperidine. The absorption may be assigned to N—N=O.[17]

Piperidine hydrochloride melted at 243° and liberated vapors which smelled strongly of piperidine. The crystals did not depress the melting point of authentic piperidine hydrochloride on admixture.

N-Bromophthalimide.—A solution of 1.10 g (5.0 mmoles) of N-bromophthalimide (K & K Laboratories, Inc., minimum, 90% active bromine) in 10.0 ml of dry benzene was exposed to nitric oxide. Gas was absorbed and the solution became a deep red-brown color. Yellow crystals were filtered from the solution. Addition of piperidine to the filtrate yielded N-nitrosopiperidine and piperidine hydrobromide (mp 233°). The reaction products of piperidine with the filtrate were interpreted as evidence of the presence of nitrosyl bromide in the filtrate.

The yellow crystals decomposed in air, liberating nitrogen oxides and white phthalimide (mp 235–236°). A mixture melting point with authentic phthalimide was not depressed. The yellow precipitate thus appears to have been N-nitrosophthalimide which could be decomposed by atmospheric moisture to phthalimide and nitrous acid.

Registry No.—*m*-Chloroperbenzoic acid, 937-14-4; dibenzoyl peroxide, 94-36-0; *t*-butyl peracetate, 107-71-1; di-*t*-butyl peroxide, 110-05-4; *t*-butyl hypochlorite, 507-40-4; N-chloropiperidine, 2156-71-0; N-bromophthalimide, 2439-85-2.

[17] Reference in footnote *b*, Table I, p 306.

The Rearrangement of 3-Carene Oxide

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During our investigation of acid-catalyzed rearrangements of alicyclic epoxides to carbonyl compounds, the bicyclic terpene oxide 3-carene oxide (I) was found to yield an unusual bicyclic aldehyde on treatment with Lewis acid catalysts in inert solvent. Thus reaction of 3-carene oxide (I) with zinc bromide in refluxing benzene yielded three products, *p*-cymene (II, 10%), an aldehyde (III, 28%), and the *cis*- and *trans*-3-caranones (IV and V, 61%) (Scheme I). A similar mixture was observed when boron trifluoride etherate in benzene was used as the acid catalyst.

The formation of *p*-cymene and 3-caranones, respectively, as well as formation of an unsaturated aldehyde resulting from rearrangement, have been previously reported.[2–4] In each case, however, there has been no reference to the constitution of the aldehyde in question, except for reports of its unsaturation. Furthermore, there appeared to be some discrepency as to how, when, and with what rearrangement occurred.

The isomerization or rearrangement of epoxides to carbonyl compounds is a general reaction.[5–10] The structures of the rearranged products, however, can depend on a variety of factors, *i.e.*, the direction of oxide ring opening, the relative migratory aptitudes of the different substituent groups,[11] and the stereochemistry of the molecule itself[7,10] with respect to the approach of a bulky catalyst.[7,12]

The correlation between rearrangement course and stereochemistry of the ring system can be shown by the difference in the aldehyde products arising from rearrangement of bicyclic terpene oxides[7–9] when compared to those from chair-form cyclohexane oxides.[5,6,10] In order to determine the nature of this rearrangement in the carane series, a study was undertaken to determine the structure of the aldehydic rearrangement product of 3-carene oxide. Aldehyde III gave a positive silver mirror test with Tollins reagent. Attempted catalytic hydrogenation of III with platinum on charcoal catalyst or platinum oxide (Adams catalyst) at room temperature yielded at times a small absorption of hydrogen; however, unsaturation appeared unlikely. The infrared spectrum of III did not indicate the presence of an olefinic system. The nuclear magnetic resonance spectrum[13] of III exhibited an eleven-proton singlet at τ 9.02 assigned to three equivalent tertiary methyl groups and two methine bridgehead protons, a two-proton multiplet centered at τ 8.8, and a two-proton multiplet centered at τ 7.8 assigned to the four ring protons. Lastly, there was a singlet aldehydic proton at 0.6. From this data it can be seen that there are no hydrogens α to the aldehydic group; there are three tertiary methyl, two methine protons at high field,[14] and no vinyl protons.

Oxidation of aldehyde III with silver oxide yielded the corresponding acid VI. This acid, along with the corresponding alcohol XII, was also formed *via* the Cannizzaro reaction with aldehyde III. Esterification of III with diazomethane gave bicyclic ester VII which was ring opened with saturated HCl(g) in ether to yield

[1] To whom communications regarding this work should be sent.

[2] B. A. Arbuzov, *Zh. Obshch. Khim.*, **9**, 255 (1939).

[3] Z. G. Isaeva and B. A. Arbuzov, *ibid.*, **19**, 884 (1949).

[4] Z. G. Isaeva and B. A. Arbuzov, *ibid.*, **24**, 1250 (1954).

[5] S. M. Naqui, J. F. Horwitz, and R. Filler, *J. Am. Chem. Soc.*, **79**, 6283 (1957).

[6] E. A. Braude, A. A. Webb, and M. U. S. Sultanbawa, *J. Chem. Soc.*, 3328 (1958).

[7] B. A. Arbuzov, *Ber.*, *68*, 1430 (1935).

[8] L. C. King and H. Farber, *J. Org. Chem.*, **26**, 326 (1961).

[9] R. Dulou, Y. Chritien-Bessiere, and J. P. Montheard, *Compt. Rend.*, **254**, 3374 (1962).

[10] R. L. Settine, G. L. Parks, and G. P. K. Hunter, *J. Org. Chem.*, **29**, 616 (1964).

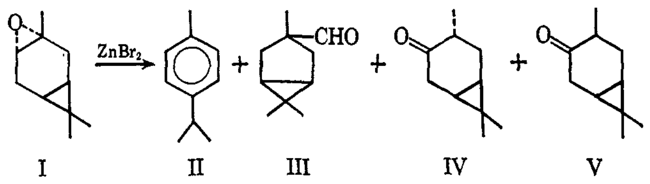
[11] S. Winstein and R. B. Henderson, "Heterocyclic Compounds," R. Elderfield, Ed., Vol. I, John Wiley and Sons, Inc., N. Y., 1950, p 1.

[12] M. P. Harshorn, D. N. Krik, and A. F. A. Wallis, *J. Chem. Soc.*, 5494 (1964).

[13] Proton nmr spectra were obtained in carbon tetrachloride solution at 60 Mc (spinning) on a Varian A-60A spectrometer.

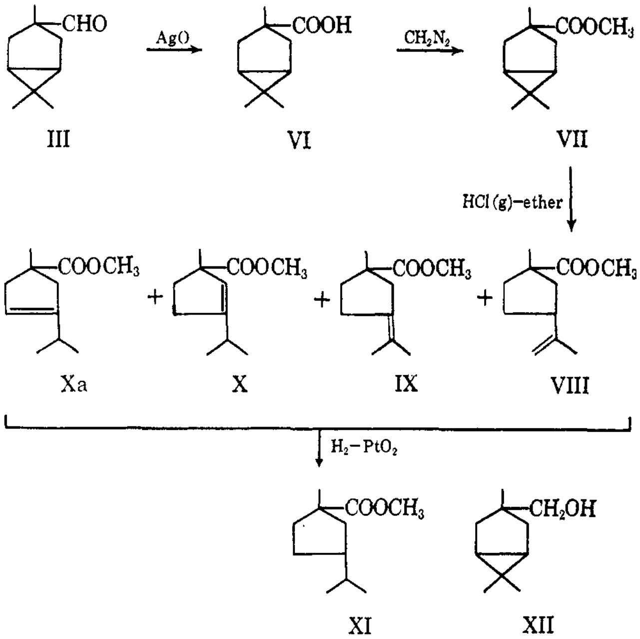
[14] The lack of a high-field absorption owing to tertiary protons on the cyclopropane ring is at first disturbing, since these appear on the original 3-carene oxide at τ 9.55; however, recently the bicyclo[3.1.0]hexyl system has been shown to have the cyclopropyl bridgehead protons shifted downfield to τ 9.02. That this is not a magnetic anisotropic effect owing to the carbonyl moiety is suggested by the fact that these signals are still at τ 8.9 in the corresponding alcohol XII: P. G. Gassman and F. V. Zalar, *J. Am. Chem. Soc.*, **88**, 3070 (1966); P. Story, private communication.

SCHEME I

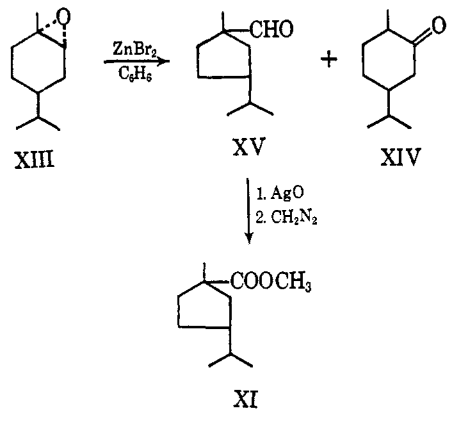


a mixture of VIII, IX, X, and Xa. Hydrogenation of this mixture gave complete conversion to ester XI which was identified as methyl 1-methyl-3-isopropylcyclopentylcarboxylate (Scheme II) by comparison of its infrared spectrum with that of an authentic sample prepared as shown in Scheme III.[10]

SCHEME II



SCHEME III



A comparison of the gas chromatographic retention time infrared and nmr spectra of the methyl ester XI derived from aldehydes III and XV showed them to be identical. Thus aldehyde III must be 3,6,6-trimethylbicyclo [3.1.0]hexanecarboxaldehyde which with mineral acid is converted to a mixture of aldehydes of which 1-methyl-3-isopropenylcyclopentylcarboxaldehyde is most prevalent.

Since cyclopentyl alcohol derivatives have been of particular interest in perfumery,[15] further evaluation of derivatives of these materials, such as XII, is indicated by the linalool-type fragrance of the various esters mentioned above.

Experimental Section

Epoxidation of 3-Carene.—To a solution of 135 g (1.0 mole) of 3-carene in 2000 ml of benzene was added slowly a solution containing 214.3 g (1.0 mole) of 80% *m*-chloroperbenzoic acid in 2000 ml of benzene. Heat was evolved in this process and an ice bath was used to maintain the temperature from 40 to 42°. The mixture was then allowed to stir overnight. The excess *m*-chloroperbenzoic acid was washed out with sodium bicarbonate and water, after which the excess benzene was removed under reduced pressure. The crude 3-carene oxide was then distilled on a spinning-band column, giving 126 g (82%) of a colorless liquid: bp 52–53° (0.3 mm); infrared absorption at 2950 (s), 1450 (db), 1060 (s), 839 (s) cm^{-1}.

Reaction of 3-Carene Oxide with Zinc Bromide.—To a refluxing solution of zinc bromide in 500 ml of dry benzene was slowly added a solution containing 108.5 g (0.71 mole) of 3-carene oxide in 500 ml of dry benzene. The exothermic reaction that followed was easily controlled with a water bath. After addition was completed, the mixture was refluxed for 2 hr, cooled, and 500 ml of water was added. The benzene solution was washed three times with water to remove zinc salts and dried over sodium sulfate, and then the solvent was removed at reduced pressure. There was obtained 10.5 g (98%) of a pleasant-smelling yellow oil. Gas–liquid partition chromatographic analysis[16] showed this oil to be composed of four major components. Distillation of the product at reduced pressure using a Nester–Faust spinning-band column yielded three fractions: fraction I, 14.4 g, bp <50° (10 mm), was a hydrocarbon whose infrared spectrum indicated an aromatic absorption. The nuclear magnetic resonance spectrum, when compared with that of an authentic sample, showed this to be *p*-cymene. Fraction II, 20.9 g, bp 70–72° (10 mm), was an aldehyde which did not appear to contain unsaturation. Gas–liquid partition chromatographic analysis[16] has shown this to be pure 3,6,6-trimethylbicyclo[3.1.0]-hexane-3-carboxaldehyde, semicarbazone mp 189–190° (*Anal.* Calcd for $C_{11}H_{19}N_3O$: C, 63.07; H, 9.14; N, 20.15. Found: C, 63.11; H, 9.30; N, 20.10). Fraction III, 64 g, bp 80–82° (10 mm), contained only the isomeric ketonic materials *cis*- and *trans*-3-caranone (lit.[17] bp 98–99 (19 mm) $n^{20}D$ 1.4703), identified by comparing infrared absorption curves with those of authentic samples. No other volatile materials were present and a pot residue of 6 g remained.

3,6,6-Trimethyl-3-carboxylbicyclo[3.1.0]hexane (VI).—3,3,6-Trimethylbicyclo[3.1.0]hexylcarboxaldehyde (11 g, 0.07 mole) was dissolved in a solution containing 100 ml of alcohol, 20 g (0.12 mole) of $AgNO_3$, and 100 ml of water. To this a solution of 10 g (0.25 mole) of sodium hydroxide in 125 ml of water was added with stirring. The silver precipitate was filtered off and the water removed at reduced pressure. The residue was extracted with ether, acidified, and again extracted with ether. Evaporation of the solvent yielded 10 g of crude acid which crystallized on standing. This material was shown to be pure by the gas chromatographic analysis of its methyl ester VII prepared using diazomethane. See Table I for properties.

Acid-Catalyzed Rearrangement of Methyl 3,6,6-Trimethylbicyclo[3.1.0]hexyl-3-carboxylate (VII).—Methyl 3,6,6-trimethylbicyclo[3.1.0]hexyl-3-carboxylate, 5 g (0.028 mole), was dissolved in 50 ml of anhydrous ether and dry hydrogen chloride was passed into the well-cooled solution until it was saturated. After standing overnight, the acid was removed by extraction with bicarbonate solution and the ethereal solution was dried over anhydrous sodium sulfate. Removal of the ether solvent at reduced pressure yielded 4.6 g of a brown oil. An infrared spectrum of this crude material showed no chlorine absorption but did show terminal olefin absorption at 1625 and 885 cm^{-1}. Gas–liquid partition chromatographic analysis indicated at least four components with the major component identified as methyl

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[15] H. E. Eschinazi, *Chem. Eng. News*, **37** [39], 53 (1959).

[16] Gas chromatographic column data: length, 25 ft × 1/8 in.; packing, neopentyl glycol succinate 10% on Chromosorb W, 60–80 mesh.

[17] H. Kuczynski and Z. Chadbusinski, *Roczniki Chem.*, **29**, 437 (1955).

TABLE I

Compd	Bp, °C (mm)	n^{20}_{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}_{D} 1.4458 (lit.[10] bp 60–61 (1 mm), n^{20}_{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.

Acknowledgment.—This study was supported by a grant from the Mississippi Heart Association.

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.

$$\mathrm{ArN_2O_2Ar} \rightleftarrows \mathrm{2ArNO}$$

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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(1) Part II: R. R. Holmes, R. P. Bayer, L. A. Errede, H. R. Davis, A. W. Wiesenfeld, P. M. Bergman, and D. L. Nicholas, *J. Org. Chem.*, **30**, 3837 (1965).

(2) To whom correspondence should be sent.

(3) R. R. Holmes, *ibid.*, **29**, 3076 (1964), and references therein.

(4) V. Keussler and W. Luttke, *Z. Elektrochem.*, **63**, 614 (1959).

(5) W. J. Mijs, S. E. Hoekstra, R. M. Ulmann, and E. Havinga, *Rec. Trav. Chim.*, **77**, 746 (1958).

(6) R. R. Holmes and R. P. Bayer, *J. Am. Chem. Soc.*, **82**, 3454 (1960).

(7) K. Nakamoto and R. E. Rundle, *ibid.*, **78**, 1113 (1956).