product. Column chromatography over neutral alumina with pentane gave 4.0 g (73%) of pure **7**.

***o*-Benzoylbenzoic Acid.** To a stirred mixture of 2-methyl-3-phenylindene-d_x (686 mg, 3.3 mmol) and 25 mL of 0.04 M NaOH was added $KMnO_4$ (2.1 g, 13 mmol). The reaction mixture was stirred for 48 h at ambient temperature, after which excess permanganate was destroyed by addition of ethanol. Celite was added to facilitate the subsequent filtration. The filtrate was extracted once with ether to remove neutral organics, acidified, and further extracted with ether. Drying of the latter ethereal solution followed by removal of solvent afforded 129 mg (50% yield) of crude product. Recrystallization from CCl_4 gave 85 mg of pure acid, mp 125.0–125.5 °C (lit.[18] 127.5–128.5 °C), whose ^1H NMR spectrum matched that published.[19]

Thermal Rearrangements. A 10% solution of 2-(perdeuteriophenyl)-2-phenyl-1-methylenecyclopropane in CCl_4 or hexane was degassed, and the Pyrex ampule containing it was sealed. The ampule was heated at ~141 °C for 40–50 h. The solvent was then removed, and the desired indene was purified by elution from neutral alumina with pentane. The yield of pure indene was 65–80%.

Acknowledgment. The support of this research by the Robert A. Welch Foundation is gratefully noted.

Registry No.—**7**, 69795-95-5; benzophenone-d_5, 2694-78-2; benzene-d_6, 1076-43-3; benzoyl chloride, 98-88-4; diphenyldiazomethane-d_5, 69795-96-6; methyl α-bromoacrylate, 4519-46-4; 2-(perdeuteriophenyl)-2-phenyl-1-bromocyclopropanecarbinol, 69795-97-7; 2-(perdeuteriophenyl)-2-phenyl-1-bromocyclopropanecarbinol tosylate, 69795-98-8; 2-methyl-3-phenylindene-d_x, 69795-99-9; *o*-benzoylbenzoic-d_x acid, 69796-00-5; methyl 2-(perdeuteriophenyl)-2-phenyl-1-bromocyclopropanecarboxylate, 69796-01-6.

References and Notes

(1) M. Jones, Jr., M. E. Hendrick, J. C. Gilbert, and J. R. Butler, *Tetrahedron Lett.*, 845 (1970).
(2) The dispirooctanes **3** and **4** are presumably formed by initial isomerization of **1d** to benzylidenecyclopropane followed by its [2 + 2] dimerization, a process that is well precedented for methylenecyclopropanes.[3] The observation of **5**, whose structure is only tentative at present, is novel, but could be rationalized by way of a [2 + 4] cycloaddition of benzylidenecyclopropane. We thank B. Brock for these results.
(3) W. R. Dolbier, Jr., D. Lomas, T. Garza, C. Harmon, and P. Tarrant, *Tetrahedron*, **28**, 3185 (1972).
(4) J. R. Butler, Ph.D. Dissertation, The University of Texas at Austin, 1971.
(5) J. C. Gilbert and J. R. Butler, *J. Am. Chem. Soc.*, **92**, 2168 (1970); M. A. Alvarez-Rodriguez, M.A. Thesis, The University of Texas at Austin, 1972.
(6) C. W. Spangler, *Chem. Rev.*, **76**, 187 (1976), and references cited therein.
(7) E. N. Marvell, G. Caple, B. Schatz, and W. Pippin, *Tetrahedron*, **29**, 3781 (1973).
(8) W. R. Roth and J. Konig, *Justus Liebigs Ann. Chem.*, **699**, 24 (1966).
(9) R. Adams and D. S. Tarbell, *J. Am. Chem. Soc.*, **60**, 1260 (1938).
(10) An *inverse* deuterium isotope effect, k_H/k_D, of 0.963 ± 0.008 appears to operate in the cleavage of benzophenone cation radicals to the phenyl radicals and benzoyl carbocations in the mass spectrometer. This value was calculated on the basis of the reasonable assumptions (1) that the sum of the benzoyl-d_5 and benzoyl-d_4 peaks represented the rate constant, k_D, for cleavage of the cation radical to generate the deuterated carbocation, whereas the benzoyl-d_0 peak corresponded to the analogous rate constant, k_H, and (2) that the deuterium isotope effect was the same for cleavage of the d_4 and the d_5 cation radicals. The d_1–d_3 peaks, the sum total of which was 0.9% of the total peak area for benzoyl carbocations, were neglected in the calculation, and all peak heights were corrected for contributions from carbon-13. The observation of an inverse isotope effect is consistent with the greater anticipated stability of benzoyl-d_5 carbocations relative to the undeuterated species, an expectation that is based on the inverse isotope effect noted in the solvolysis of ring-deuterated benzhydryl chloride.[11]
(11) H. S. Klein and A. Streitweiser, Jr., *Chem. Ind. (London)*, 180 (1961); A. J. Kresge, K. N. Rao, and N. N. Lichtin, *ibid.*, 53 (1961).
(12) G. A. Olah et al., *J. Am. Chem. Soc.*, **86**, 1046 (1964); G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962).
(13) M. M. Bursey and F. W. McLafferty, *J. Am. Chem. Soc.*, **88**, 529 (1966).
(14) W. R. Dolbier, Jr., in "Isotopes in Organic Chemistry", Vol. 1, E. Buncel and C. C. Lee, Eds., Elsevier, Amsterdam, 1975, Chapter 2.
(15) L. I. Smith and K. L. Howard, "Organic Syntheses", Collect. Vol. 3, E. C. Horning, Ed., Wiley, New York, 1955, p 351.
(16) H. M. Walborsky, L. Barash, A. E. Young, and F. J. Impastato, *J. Am. Chem. Soc.*, **83**, 2517 (1961).
(17) H. M. Walborsky, F. J. Impastato, and A. E. Young, *J. Am. Chem. Soc.*, **86**, 3283 (1964).
(18) L. F. Lalley and C. J. Marvel, *J. Am. Chem. Soc.*, **54**, 4450 (1932).
(19) Sadtler Catalogue of Standard Spectra, Sadtler Research Laboratories, Inc., spectrum no. 6864.

Hexakis[μ-(ethyl chlorocarbamato-*N,O*)]-μ_4-oxo-tetrazinc and Its Thermolysis in Simple Olefins

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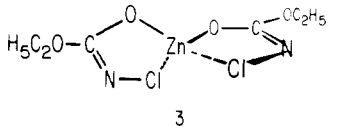
This report describes a new tetranuclear zinc compound, hexakis[μ-(ethyl chlorocarbamato-*N,O*)]-μ_4-oxo-tetrazinc, and its thermal decomposition in 2,3-dimethyl-2-butene and cyclohexene. Thermolysis in 2,3-dimethyl-2-butene gives mainly ethyl *N*(2,3-dimethyl-2-butenyl)carbamate, ethyl *N*-[3-(2,3-dimethyl-1-butenyl)]carbamate, five $C_{12}H_{22}$ isomers, and 2,3-dichloro-2,3-dimethylbutane. Studies with isotopically labeled reagents support the intermediacy of 2,3-dimethyl-2-butenyl cation. The cation partitions to products when captured by either olefin or a carbamate donor. Carbethoxynitrene is not an important intermediate. Thermolysis in cyclohexene gives very low yields of analogous products. This reaction does not appear to be general for olefins for reasons that are discussed.

Several well-characterized metal salts of *N*-chlorocarbamates (**1**) have been described.[1] Though they appear to be potential precursors for carboalkoxynitrenes (**2**) (eq 1), none have been reported to react this way.

$$\underset{\textbf{1, M = Na, K, Ag}}{M(ClNCO_2R)} \rightarrow MCl + \underset{\textbf{2}}{NCO_2R} \qquad (1)$$

However, Swern and Saika[2] obtained trace amounts of azabicyclo[4.1.0]heptane from the thermolysis of **1** (M = Ag, Na; R = C_2H_5) in cyclohexene, suggesting that some carbethoxynitrene might have formed in their experiments.

The original intent of our work was to examine those salts containing metals capable of intramolecular coordination with chlorine, such as the hypothetical ethyl *N*-chlorocarbamatozinc (**3**). Elimination of $ZnCl_2$ might be especially favorable



3

in this case since the zinc–chlorine bond would already be partially formed in the ground state. Moreover, **3** should be more soluble in olefins than the alkali metal and silver salts,

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Table I. Product Distribution from the Thermolysis of 4 in 2,3-Dimethyl-2-butene at 100 °C[a]

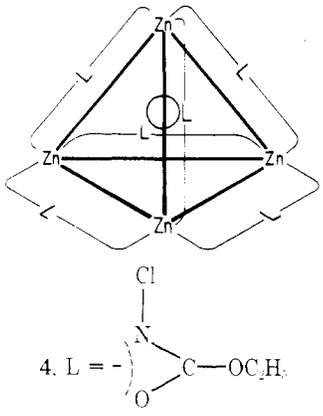
expt no.	$[N(C_2H_5)_3]$, M	reaction time, h	% yield[b] 5	6	7	8	9	10 + 11	12[c]	13	14
1	0	5	22	6.6	12	3.8	5.8	5.6	33	4.4	—
2	0	9	25	8.2	12	3.8	5.8	5.6	37	4.6	—
3	0.10	5	28	15	2.3	~0	0.6	0.4	57	~0	17
4	0.050	5	29	17	2.9	~0	0.5	0.5	59	~0	—

[a] 0.19 N **4**. [b] Calculated on the basis of 1 mol of product/equiv of **4**. [c] Calculated on basis of 1 mol of product/2 equiv of **4**.

Table II. Product Distribution from Authentic Carbethoxynitrene Generated in 2,3-Dimethyl-2-butene

reagent	% yield 5	6	7	8	9	10 + 11	13	15	16
17	7.9	3.9	0.2	0	0	0	1.4	60	~0
18	9.6	0.8	0.4	0	0	0	~0	55	1

which could improve nitrene trapping efficiency. However, instead of **3**, our synthesis gave hexakis[μ-(ethyl chlorocarbamato-N,O)]-μ_4-oxo-tetrazinc (**4**). This report describes the



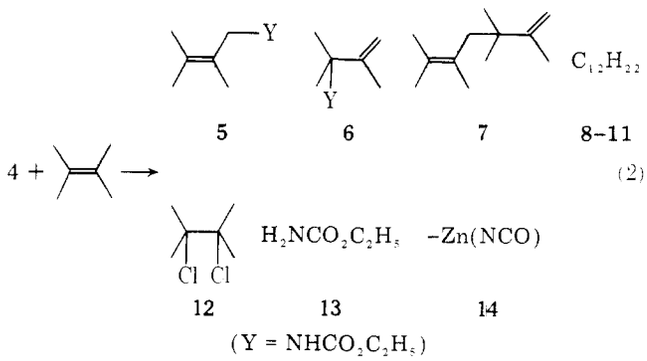
4, L = $^-O_2CNClCO_2C_2H_5$

characterization and some thermal chemistry of this new tetranuclear zinc compound.

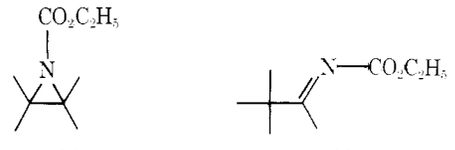
Results and Discussion

Diethylzinc reacts rapidly with a benzene solution of ethyl N-chlorocarbamate. A viscous oil remains after adding a trace of water and removing solvent. The oil is soluble in hexane and can be precipitated on cooling then dried to a colorless glass. The elemental analysis (C, H, N, Cl, Zn), molecular weight (FD mass spectrometry, vapor osmometry), iodometric equivalent weight, ^{13}C and ^1H spectra, IR spectrum, and its hydrolysis to ethyl N-chlorocarbamate are in excellent agreement with the composition $Zn_4O(ClNCO_2C_2H_5)_6$. The structural assignment is based on the analogous carboxylates, $Zn_4O(O_2CR)_6$, having structure **4** (L = ^-O_2CR),[3] although such compounds are rare. The amorphous nature of **4** seems to result from the presence of several stereoisomers differing in the relative orientation of the six bidentate ligands. The ^{13}C NMR spectrum supports this interpretation, having progressively more structure for those carbon atoms closest to the coordination sites (see paragraph at the end of paper regarding supplementary material). The carbonyl spectrum at δ 166.4 comprises an envelope of distinct but closely spaced signals over a range of about 1.5 Hz. However, the ^1H spectrum is insensitive to this subtle magnetic effect and shows only a single methylene quartet and triplet methyl pattern.

Thermolysis of 4 in 2,3-Dimethyl-2-butene. The thermolysis of **4** in 2,3-dimethyl-2-butene is essentially complete in about 5 h at 100 °C. The products are ethyl N-(2,3-dimethyl-2-butenyl)carbamate (**5**), ethyl N-[3-(2,3-dimethyl-1-butenyl)]carbamate (**6**), 2,3,3,5,6-pentamethyl-1,5-heptadiene (**7**), four uncharacterized $C_{12}H_{22}$ isomers (**8**–**11**), 2,3-dichloro-2,3-dimethylbutane (**12**), ethyl carbamate (**13**), and insoluble, zinc-bonded cyanate (**14**) (eq 2). Yields of products



5–**13** were determined by GLC with the reasonable assumption that the response factors for **7** and its isomers **8**–**11** are approximately equal. The $C_{12}H_{22}$ isomers **8**–**11** are numbered in order of their GLC retention times. The cyanate **14** was identified by converting it to AgNCO with $AgNO_3$ and comparing its IR spectrum with that of authentic material. Quantitative analysis was performed by infrared spectroscopy. The results are recorded in Table I, experiments 1 and 2. When small amounts of triethylamine are added to the reaction mixture, the carbamate yields increase while the yields of $C_{12}H_{22}$ dimers decrease (experiments 3 and 4). The amine was added to remove any HCl that might form during thermolysis, since HCl would likely decompose **4** by protonolysis and eventually produce chlorine and ethyl carbamate. Though not shown in Table I, ≤1% of N-carbethoxy-2,2,3,3-tetramethylaziridine (**15**) and ethyl N-(3,3,-dimethyl-2-butylidine)carbamate (**16**) are also formed.



The carbamates **5**, **6**, and **13** and olefin dimers are among the products expected from carbethoxynitrene. However, **15** should be the main product based upon results with authentic carbethoxynitrene generated from p-nitrobenzenesulfonoxyurethan (**17**) and the photolysis of ethyl azidoformate (**18**)[4] (Table II). Unfortunately, the comparison of Tables I and II is complicated somewhat by the instability of **15** under thermolysis conditions. When added to the reaction mixture, **15** is nearly completely converted with about one-third distributing between **6** and the imide **16**. Thus, it is the near absence of **16** in the thermolysis products and the marked differences

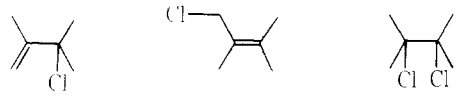
Table III. Thermolysis of 4 in 2,3-Dimethyl-2-butene with Added Deuterium-Labeled Reagents[a]

added reagent		5	6	7	8	9	10 + 11	12
19 + 20[b]	% yield	32	19	14	~0	4.5	4.5	50
	% d	54	53	64		66	58	
21[c]	% yield	25	14	2.8	~0	1	1	
	% d[d]	<1.4	<1.0	<3.5		<2.0	<2.0	71[e]

[a] 0.18 N **4**, 0.05 M $N(C_2H_5)_3$, 100 °C, 5 h. [b] 2.0 mmol of **19** + 8.4 mmol of **20** in 56 mL of reaction mixture. [c] 2.29 mmol of **21** in 47 mL of reaction mixture. [d] Quantitative limits of detection. [e] Only approximate, since the GLC peak is inhomogeneous due to a slight resolution of deuterated isomers.

between Tables I and II that exclude carbethoxynitrene as the important intermediate in the thermolysis of **4**.

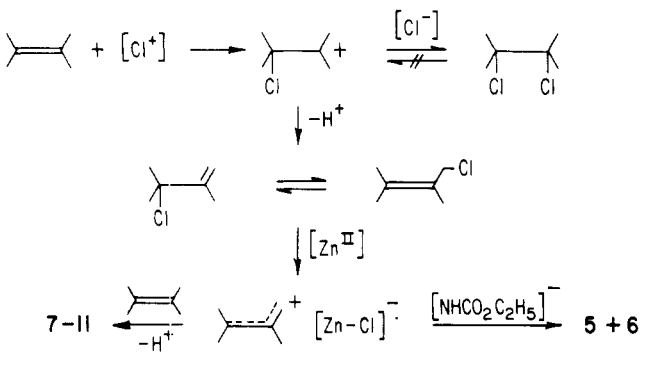
Isotope Labeling Experiments. Isotope labeling experiments confirm the above conclusion and also support the intermediacy of 2,3-dimethyl-2-butenyl cation in the thermolysis of **4**. When 3-chloro-2,3-dimethyl-1-butene-d_1 (**19**), 1-



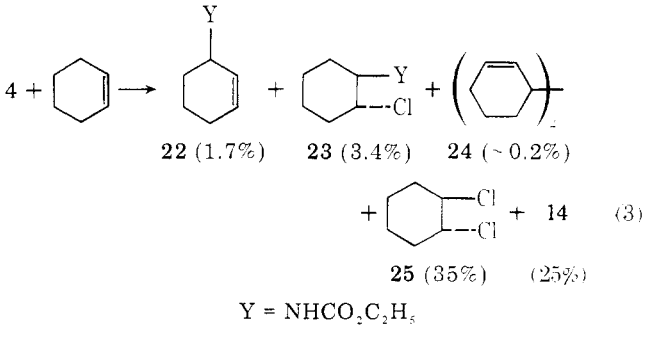
19-d_1 **20**-d_1 **21**-d_{12}

chloro-2,3-dimethyl-2-butene-d_1 (**20**), and 2,3-dichloro-2,3-dimethylbutane-d_{12} (**21**) are added during thermolysis, the label distributes as shown in Table III. The four most important features of these data are: (1) the addition of **19** and **20** causes substantial label to appear in the carbamates **5** and **6** and in the dimers **7**–**11**, (2) the percent label in the two carbamates is equal (similarly, the percent label in the dimers is nearly equal), (3) the ratio of **5** to **6** is unchanged on adding **19** and **20**, and (4) negligible label appears in the reaction products on the addition of **21**. Scheme I describes an abbreviated mechanism most consistent with these data. The reactants in brackets are described in this way because their complete structures are unknown. The intermediate, 2,3-dimethyl-2-butenyl cation, partitions to products when captured by either olefin or a carbamate donor. Interconversion of allylic chlorides is likely under these conditions, with the equilibrium strongly favoring 1-chloro-2,3-dimethyl-2-butene.[5] According to this scheme, the addition of **19** and **20** should not alter the ratio among the dimers. It is difficult to establish this accurately because, except for **7**, dimer concentrations in the control experiments are near the lower limits of our analysis. Nevertheless, the dimer ratios in the two experiments of Table III are in good agreement. This scheme further requires that substitutive chlorination of the olefin be a favorable step, and we indeed find that the chlorination of 2,3-dimethyl-2-butene gives mainly allylic chlorides with smaller amounts of the addition product **12**. If **4** is a source of [Cl^+], then the cyanate **14** may originate from concerted or step-wise elimination of ethoxide.

Scheme I



Thermolysis of 4 in Cyclohexene. Unlike 2,3-dimethyl-2-butene, the thermolysis of **4** in cyclohexene gives very low yields of carbamates (eq 3). However, with the exception of



22 (1.7%) **23** (3.4%) **24** (~0.2%)

25 (35%) (25%)

Y = $NHCO_2C_2H_5$

trans-ethyl *N*-(2-chlorocyclohexyl)carbamate (**23**), the products are analogous to those obtained in 2,3-dimethyl-2-butene. Thus, carbamylation of olefins by **4** does not appear to be a general reaction, probably because preferential substitutive chlorination is a required step. This may be the important criterion for carbamylation by this method.

Experimental Section

Reagents. Cyclohexene and 2,3-dimethyl-2-butene were purchased and distilled from Na/K under nitrogen through a 3-ft column packed with glass helices. Ethyl carbamate and the benzene solution of diethylzinc were also purchased and used without further purification. Ethyl *N*-chlorocarbamate,[2] *N*-*p*-nitrobenzenesulfonoxyurethan (**17**),[6] ethyl azidoformate (**18**),[7] and the chlorobutenes **19** and **20**[4] were prepared according to earlier reports. *trans*-1,2-Dichlorocyclohexane (**25**) was purchased from Chem Samples, Columbus, Ohio.

Hexakis[μ-(ethyl chlorocarbamato-*N*,*O*)]-μ_4-oxo-tetrazinc (4). A dry 16-oz screw-cap glass bottle containing a magnetic stirring bar was charged with 12.68 g (0.103 mol) of ethyl *N*-chlorocarbamate and 220 mL of dry benzene. A solution containing 0.0514 mol of diethylzinc in 35 mL of benzene was then slowly added under N_2 at 5–10 °C with rapid stirring. There was a rapid evolution of gas. The clear, colorless, viscous solution was then stirred for an additional 30 min, and 235 μL of water was added. The mixture was stirred for 1 h as it warmed to room temperature. Benzene was then removed under reduced pressure, and the residue was placed in a vacuum oven overnight at room temperature to give 15.70 g of crude product. This product was then stirred with 75 mL of a hexane mixture (Fisher) for 1 h. Approximately 13.8 g or 88% dissolved. This solution was decanted and placed in a freezer at −18 °C. An oil separated. The solution was decanted, and the oil was placed in a vacuum oven at room temperature overnight. Hexane evaporation caused the oil to foam into a rigid glass: 9.18 g (9.06 mmol); 71% yield of **4**; NMR (cyclohexane-d_{12}) δ 1.28 (t, 3, J = 7 Hz), 4.22 (q, 2, J = 7 Hz); mol wt calcd for $^{64}Zn_4O(^{35}ClNCO_2C_2H_5)_6^-$ 1003.72 amu, found (field desorption mass spectrum) 1004.0 ± 0.5 amu and (vapor osmometry) 1.04×10^3; IR (8% in cyclohexane-d_{12}) no NH, 1578, 1525, 1485, 1381, 1342, 1100 cm^{-1}; calcd equiv wt 84.7, found (iodometry) 84.2.

Anal. Calcd for $C_{18}H_{30}Cl_6O_{13}N_6Zn_4$: C, 21.35; H, 2.99; Cl, 21.01; N, 8.30; Zn, 25.82. Found: C, 21.91; H, 3.33; Cl, 20.88; N, 8.38; Zn, 25.02.

Hydrolysis of 4. A dry 4-oz screw-cap bottle charged with 1.88 g (1.85 mequiv) of **4**, 25 mL of ether, and 0.80 mL (0.044 mol) of water was agitated for 18 h at room temperature during which time a white precipitate formed. The mixture was centrifuged and the ether phase decanted. The precipitate was then extracted twice with 25-mL ali-

quots of ether. The ether phases were combined, and the ether was removed under reduced pressure giving ethyl *N*-chlorocarbamate (1.14 g, 9.23 mmol) 83%.

Thermolysis of 4. A dry 7-oz glass beverage bottle containing a magnetic stirring bar was charged under nitrogen with 1.73 g (0.0102 equiv) of **4**. The equivalent weight for thermolysis experiments is defined as the molecular weight divided by 6. The bottle was capped and olefin was added volumetrically with a dry syringe. The contents were then stirred and purged with 1.5 L of nitrogen through a needle at 9 L/h. A second cap was then placed on the bottle and the bottle was placed in a stirred oil bath at 100 °C. At the appropriate time, the contents were cooled to room temperature and transferred to a bottle containing naphthalene, the internal GLC standard. The residue remaining in the bottle was rinsed with a few milliliters of olefin, and the rinse was combined with the reaction solution. Analyses of products from 2,3-dimethyl-2-butene were performed on a 60-μl sample using a 5 ft × 0.25 in. column packed with 20% Ucon 50 HB 5100 on 70/80 mesh Anakrom type U. A glass-lined injection port heated at 195 °C was used in all experiments. The order of increasing retention times for the reaction products is **12** < **8** < **9** < **10** < **11** < **7** < **15** < ethyl carbamate < **16** < **6** < naphthalene < **5**. These products are not produced in the gas chromatograph. Analysis before thermal decomposition shows only a small amount of ethyl carbamate. GLC analyses of reaction mixtures in cyclohexene were performed on a 3 ft × $^3/_{16}$ in. column containing 3% OV17 on Chromosorb G.

Ethyl *N*-(2,3-Dimethyl-2-butenyl)carbamate (5). The reaction products from several thermal decomposition experiments were combined, and the 2,3-dimethyl-2-butene was removed by distillation. The remaining residue was further distilled using a 13-cm Vigreux column. A fraction boiling mainly at 63 °C (0.16 mm) was collected. GLC showed this crude distillate to comprise about 65% of the carbamate **5**. This was further purified by preparative GLC using a 5 ft × 0.25 in. column packed with 20% Ucon 50 HB5100 on 40/60 mesh Chromosorb W operating at 160 °C: IR (neat) 3340, 1695 cm^{-1}; NMR ($CDCl_3$) δ 1.23 (t, 3, J = 7 Hz), 1.68 (broad s, 9), 3.78 (d, 2, J = 6 Hz), 4.12 (q, 2, J = 7 Hz), 4.7 (broad, 1); mass sepctrum, parent ion m/e 171.

Anal. Calcd for $C_9H_{17}NO_2$: C, 63.12; H, 10.01; N, 8.18. Found: C, 63.21; H, 10.02; N, 8.20.

Ethyl *N*-[3-(2,3-Dimethyl-1-butenyl)]carbamate (6). A fraction boiling at 53–57 °C (0.3 mm) was collected and found to comprise about 66% of carbamate **6**. This solution was further purified by preparative GLC using a 10 × 0.25 in. column packed with 20% SE-30 on Chromosorb W operating at 150 °C: IR (neat) 3440, 3090, 1705, 1640, 890 cm^{-1}; NMR ($CDCl_3$) δ 1.21 (t, 3, J = 7 Hz), 1.41 (s, 6), 1.75 (q, 3, $J \approx 1$ Hz), 4.06 (q, 2, J = 7 Hz), 4.87 (m, 3).

This product is identical with that obtained by rearrangement of *N*-carbethoxy-2,2,3,3-tetramethylaziridine (**15**) in a sealed tube at 150 °C for 210 h. Distillation of this product gave carbamate **6**: bp 74–76 °C (1.5 mm); 78% yield.

Anal. Calcd for $C_9H_{17}NO_2$: C, 63.12; H, 10.01; N, 8.18. Found: C, 63.16; H, 10.04; N, 8.20.

2,3,3,5,6-Pentamethyl-1,5-heptadiene (7). The residue remaining after removal of 2,3-dimethyl-2-butene was distilled using a 13-cm Vigreux column and a fraction was collected boiling up to 68 °C (2.7 mm). This solution was redistilled, and the distillation was followed by gas chromatography until the heptadiene **7** was concentrated in the pot to about 54%. The solution was then further purified by preparative GLC using a 5 ft × 0.25 in. column packed with 20% Ucon 50 HB 5100 on 40/60 mesh Chromosorb W operating at 100 °C: IR (neat) 3090, 1635, 892 cm^{-1}; mass spectrum, parent ion m/e 166; NMR ($CDCl_3$) δ 1.02 (s, 6), 1.63 (s, 9), 1.79 (m, 3, $J \approx 1$ Hz), 2.08 (s, 2), 4.70 (m, 2, $J \approx 1$ Hz).

Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.99; H, 13.33.

Hydrocarbons (8–11). A typical reaction mixture was concentrated by distilling off 2,3-dimethyl-2-butene at atmospheric pressure. Components **8** through **11** were than analyzed using a PE 270 gas chromatograph-coupled mass spectrometer containing a 10 ft × $^1/_8$ in. column packed with 10% Ucon 5100 on 60/80 mesh Chromosorb W. Components **10** and **11** are very poorly resolved and appear as a single, skewed peak. All four components were shown to be hydrocarbons, $C_{12}H_{22}$, with parent ions m/e 166.

2,3-Dichloro-2,3-dimethylbutane (12). A 50-mL, three-neck flask fitted with a magnetic stirring bar, a dry ice condenser, and a chlorine gas inlet was charged with 35 mL of 2,3-dimethyl-2-butene. The stirred butene was then cooled to −80 °C with dry ice, and 0.144 mol of chlorine was passed over the solution at 0.134 mol/h. The reaction mixture was allowed to warm to room temperature and then placed on a rotary evaporator at 35–40 °C until a slightly wet solid remained. This was crystallized from ethanol–water and dried for 4 min (0.2 mm) at room temperature to give 1.5 g (9.7 mmol), 6.7% yield, of **12**, mp 151–153 °C (sealed tube) [lit.[8] mp 158 °C]. Anticipating that these crystals were still wet, the solid was dissolved in 5 mL of ether, and the ether phase was separated from the small amount of water present. Evaporation of the ether, first in the atmosphere and finally under vacuum for 10 min, gave white crystals: mp 158.5–160 °C; NMR ($CDCl_3$) single resonance at 1.77 ppm. The dichloride **12** is highly volatile and prolonged exposure under vacuum or to the atmosphere results in substantial losses.

Authentic dichloride **12** and the component designated **12** from the thermal decomposition of **4** have identical GLC retention times and mass spectra. The mass spectra do not show the parent ion, but rather the $C_6H_{12}Cl^+$ and $C_5H_9Cl_2^+$ fragment ions.

Zinc-Bonded Cyanate (14). A preparative scale thermolysis of **4** was carried out with a reaction mixture comprising 7.19 g (0.0425 equiv) of **4** and 1.24 g (0.0122 mol) of triethylamine in 230 mL of 2,3-dimethyl-2-butene. The residue from this experiment was dried overnight in a vacuum oven at room temperature and extracted with 50 mL of dry CCl_4. The extract was decanted, and the residue was rinsed with CCl_4 and dried again. A 1-g aliquot was dissolved in 35 mL of 2% aqueous HNO_3 to give a homogeneous solution. The stirred solution was then treated with 20% aqueous $AgNO_3$ until no further precipitation occurred. The mixture was stirred in the dark for several minutes, filtered through a sintered glass funnel, washed several times with water and once with ethanol, and then dried in a vacuum oven at room temperature. The infrared spectrum was determined in AgCl. The spectrum was in excellent agreement with that of AgOCN.[9] This reaction was used for the quantitative analysis of OCN by infrared. The reference band chosen for AgOCN was 590 cm^{-1}, while that of the internal reference, $Ba(NO_3)_2$, was 815 cm^{-1}. An excellent calibration curve was obtained from standard mixtures of the authentic salts in AgCl.

About 0.6 g of the dry residue from a thermolysis experiment was stirred in the dark for 2 h with 42 mL of 10% aqueous $AgNO_3$. The mixture was filtered, and the solid was washed several times with water, followed by an ethanol wash. The solid was then vacuum dried at room temperature for about 2 h and intimately mixed with about 0.3 g of $Ba(NO_3)_2$, and the infrared spectrum was determined in AgCl. The NCO content was then determined from the calibration curve.

***N*-Carbethoxyl-2,2,3,3-tetramethylaziridine (15) and Ethyl *N*-(3,3-Dimethyl-2-butylidine)carbamate (16).** These carbamates were reported earlier[4] and were identified as reaction products by their GLC retention times and mass spectra.

Carbethoxynitrene from 17 and 18. These experiments were described earlier.[4]

Thermolysis of 4 in 2,3-Dimethyl-2-butene with Added 19 and 20. The thermolysis of **4** in 2,3-dimethyl-2-butene was carried out in the usual way using 1.74 g (10.3 mequiv) of **4** and 0.30 g of triethylamine in 56 mL of 2,3-dimethyl-2-butene. A mixture of 0.24 g (2.0 mmol) of **19** and 0.99 g (8.4 mmol) of **20** was added through a syringe in three approximately equal increments at 0.5, 1.5, and 2.0 h. The deuterium assay was performed by GLC–MS using an undeuterated reaction mixture as a reference. Added **19** and **20** were not considered in calculating the yields described in Table III.

1,2-Dichloro-1,2-dimethylbutane-d_{12} (21). Pinacol-d_{12} hexahydrate was prepared from acetone-d_6 in 34.4% yield using the procedure described by Adams and Adams.[10] A 7-oz beverage bottle was then charged with 5.0 g (0.021 mol) of pinacol-d_{12}·$6H_2O$ and 50 mL of water which had been saturated with HCl gas at −20 °C. The bottle was capped and allowed to stand at room temperature for 13 days.[8] The mixture was filtered and the crude product crystallized from ethanol/water. The crystals were then dissolved in ether, and the ether solution was dried over $CaCl_2$. Ether was then removed by distillation and the solid residue dried in a vacuum oven at room temperature for 4–5 min. Longer drying time can result in losses since **21** is highly volatile. The dry product was then sublimed in a cold-finger sublimer. Sublimation was carried out at 75 °C (1 atm) by connecting the sublimer to a shallow Hg well. After sublimation was complete (~2 h), the crystals were washed off the cold finger with ether. Removing ether in the usual way gave 1.2 g (7.2 mmol), 34%, of **21**: mass spectrum, d_{12} (58%), d_{11} (23%), d_{10} (7%), d_9 (4%), d_8 (2%), d_7–d_4 (1%), for a total of 92 atom % d.

Thermolysis of 4 in 2,3-Dimethyl-2-butene with Added 21. The thermolysis of **4** in 2,3-dimethyl-2-butene was carried out in the usual way using 1.49 g (8.71 mequiv) of **4**, 0.25 g of triethylamine, 47 mL of 2,3-dimethyl-2-butene, and 0.3869 g (2.29 mmol) of **21**. The yield of dichloride expected in this experiment is 2.48 mmol. GLC analysis shows a total of 4.68 mmol. Assuming that 2.48 mmol was produced from the reaction, there remains 2.20 mmol, 96% of added **21**.

Ethyl *N*-(3-Cyclohexenyl)carbamate (22). The carbamate **22** was prepared according to the procedure described by Lwowski and Mattingly:[7] bp 81 °C (0.45 mm); IR (CCl_4) 3460, 3352, 1726, 1653 cm^{-1}, reported IR 3454, 3348, 1720, 1653 cm^{-1}.

***trans*-Ethyl *N*-(2-Chlorocyclohexyl)carbamate (23).** The carbamate **23** was prepared according to the procedure described by Swern and Foglia:[11] mp 94–95 °C (lit. mp 96–97 °C).

3,3′-Bicyclohexenyl (24). This was prepared according to the procedure described by Lwowski and Mattingly:[7] bp 90 °C (4.3 mm) (lit. bp 85–89 °C (3.7–4.0 mm)).

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Supplementary Material Available: ^{13}C NMR spectrum of compound 4 (1 page). Ordering information is given on any current masthead page.

Registry No.—**4**, 69705-71-1; **5**, 1611-51-4; **6**, 64227-21-0; **7**, 53256-17-0; **12**, 594-85-4; **13**, 51-79-6; **15**, 56488-02-9; **16**, 56488-01-8; **17**, 2955-74-0; **18**, 817-87-8; **19**, 56488-05-2; **20**, 56488-04-1; **21**, 69653-42-5; **22**, 1541-28-2; **23**, 18296-24-7; **24**, 1541-20-4; **25**, 822-86-6; 2,3-dimethyl-2-butene, 563-79-1; cyclohexene, 110-83-8.

References and Notes

(1) M. M. Campbell and G. Johnson, *Chem. Rev.*, **78**, 65 (1978), and references cited therein.
(2) D. Saika and D. Swern, *J. Org. Chem.*, **33**, 4548 (1968).
(3) H. Koyama and Y. Saito, *Bull. Chem. Soc. Jpn.*, **27**, 112 (1954); P. J. Durrant and B. Durrant, "Introduction to Advanced Inorganic Chemistry", Wiley, New York, 1962, p 809.
(4) P. P. Nicholas, *J. Org. Chem.*, **40**, 3396 (1975).
(5) L. F. Hatch and G. E. Journey, *J. Am. Chem. Soc.*, **75**, 3712 (1953).
(6) W. Lwowski and T. J. Maricich, *J. Am. Chem. Soc.*, **87**, 3630 (1965).
(7) W. Lwowski and T. Mattingly, Jr., *J. Am. Chem. Soc.*, **87**, 1947 (1965).
(8) T. Koida and T. Oda, *Bull. Chem. Soc. Jpn.*, **41**, 307 (1968).
(9) R. A. Nuquist and R. O. Kagel, "Infrared Spectra of Inorganic Compounds (3800–45 cm^{-1})", Academic Press, New York, 1971, p 71.
(10) R. Adams and E. W. Adams, "Organic Synthesis", Collect. Vol. I, Wiley, New York, 1941, p 459.
(11) T. A. Foglia and D. Swern, *J. Org. Chem.*, **31**, 3625 (1966).

Regiospecific Formation of Azoxyaralkanes (Diazene *N*-Oxides) from *N,N*-Dibromo Compounds and Nitrosobenzene[1]

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An improved directed synthesis of azoxyaralkanes from *N,N*-dibromo compounds and nitrosobenzene is described. Unlike the prior related method, yields of azoxy compounds are not sensitive to the nature of the *N,N*-dihalo compound; i.e., high yields were obtained from all types (primary, secondary, and tertiary) of alkyl groups in $RNBr_2$. Several aspects of the mechanistic features are discussed.

Previously, we reported that a wide variety of azoxy compounds can be regiospecifically synthesized through the reaction of *N,N*-dichloroamines with nitroso compounds.[3,4] Although the method enjoys wide scope, yields of azoxy compounds are usually not outstanding for reactions involving primary or secondary alkyl-*N,N*-dichloroamines.

The aim of this study was to make the method more attractive by substantially increasing the yields for various types of *N,N*-dihalo substrates and to furnish additional mechanistic insight.

Results and Discussion

Synthesis. In this synthesis of azoxy compounds, the promoting effect of certain transition metal salts does not appear to involve the metal atom.[5] For example, in the case of cobaltous bromide or cupric bromide, we have shown that bromide ions are rapidly oxidized by the *N,N*-dichloroamines through a halogen exchange reaction in which the more reactive *N,N*-dibromoamines are generated (eq 1). The overall transformation resembles the conversion of hypochlorite to hypobromite by means of bromide ion.[6]

$$RNCl_2 + MBr_2 \xrightarrow{\text{fast}} RNBr_2 + MCl_2 \qquad (1)$$

In the present study, pure *N,N*-dibromo compounds, such as *N,N*-dibromo-α-aminoisobutyronitrile or *N,N*-dibromo-*tert*-butylamine, were found to react with nitrosobenzene in acetonitrile or methylene chloride to afford the corresponding *N*-alkyl-*N*′-phenyldiazene *N*′-oxides in excellent yields. At room temperature the reaction is complete within a few minutes (eq 2). Under similar conditions, the corresponding

$$RNBr_2 + C_6H_5NO \rightarrow RN{=}N(O)C_6H_5 + Br_2 \qquad (2)$$

N,N-dichloroamines do not react.[3] The progress of the transformation can be followed by observing the dramatic color change which occurs as the initial dark green mixture turns red upon liberation of free bromine. Fortunately, similar high yields of azoxy compounds can be more conveniently obtained by treatment of the readily available *N,N*-dichloroamines with 1 molar equiv each of bromide salt and nitrosobenzene in acetonitrile solution under mild conditions. High yields (70–92%) of azoxy compounds were obtained.

The results are summarized in Table I. Although the reaction does not require exclusive use of arylnitroso substrates, this study mostly involved nitrosobenzene since it gave higher yields, can be easily purified, and is more stable in solution than most alkylnitroso compounds.[7] Product yield with $(CH_3)_3CNO$ was somewhat lower. With the bromide-promoted synthesis, there appear to be no great differences in yields of azoxy compounds with tertiary, secondary, or primary alkyl-*N,N*-dichloroamines. In addition, high yields were obtained from *N,N*-dichloroneopentylamine and *N,N*-dichloro-*tert*-octylamine, even though the corresponding *N,N*-dibromoamines are too unstable for isolation via the halogen exchange reaction.[5] Although our main attention was focused on *N,N*-dihaloamines, good results were also realized with analogous derivatives of urethane and arylsulfonamide. The products from $RNCl_2$ exhibited various degrees of instability on standing, as evidenced by a darkening in color. As a result, some difficulties were experienced in obtaining high purity samples for microanalyses, e.g., the product from **4**. All azoxy materials gave satisfactory IR and NMR spectra. Those containing primary or secondary alkyl groups showed no molecular ion in the mass spectrum.

The low yield from primary and secondary alkyl groups

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