A.-1 $(3.0 \text{ g}, 8.2 \times 10^{-3} \text{ mol})$ dissolved in 100 ml of dried benzene in a sealed tube was heated in an oil bath at 90°. After a few minutes the color of the benzene solution disappeared with evolution of nitrogen. The colorless solution was cooled and concentrated under reduced pressure, and then a chromatographic separation was performed on a silica gel column using benzene as eluent. Diphenylacetylene was obtained in 85-90% yield, mp $59-60^{\circ}$ (lit.¹⁵ mp $60-61^{\circ}$); spectroscopic data are in agreement with those recorded on a sample independently prepared.¹⁵ Anal. Caled for C14H10: C, 94.34; H, 5.66. Found: C, 94.25; H, 5.68.

Route B.-1 (3.0 g, 8.2×10^{-3} mol) was dissolved in 100 ml of chloroform and the solution was allowed to stand at 25° until the color disappeared (3-4 days); by evaporation of solvent under reduced pressure and chromatographic separation on a silica gel column using benzene as eluent, diphenylacetylene in 85-90% yield was obtained.

Registry No. -1, 34220-14-9; 2, 501-65-5.

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The Effects of Group IVA Organometallics on the Reaction of Ethoxycarbonylnitrene with Cyclohexene^{1a}

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It has recently been reported that C-H bonds involving the carbon atom directly linked to a group IV metal (silicon and tin) are inert to dichlorocarbene generated by the thermal decomposition of phenyl-(bromodichloromethyl)mercury. However, secondary or tertiary β C–H bonds underwent insertion readily.² Furthermore, the activating effect of a metal β to a C–H bond is in the order $Sn > Ge > Si.^3$

We wish to report that tetramethyltin (α C-H bonds), as well as trimethylisobutyltin (β C-H bond), is inert to insertion by ethoxycarbonylnitrene generated under a variety of reaction conditions.

Ethoxycarbonylnitrene can be generated by the thermal or photolytic decomposition of ethoxycarbonyl azide⁴ (eq 1) or by base-induced α elimination from N-pnitrobenzenesulfonyloxy $urethane (eq 2)^5$ and gives addition and insertion reactions similar to carbenes.

However, we have found that thermal decomposition of ethoxycarbonyl azide in pure tetramethyltin or solutions of tetramethyltin in carbon tetrachloride or methylene chloride as inert solvents gave only recovered organotin starting compound, a few per cent yield of urethane, $CH_3CH_2OC(=O)NH_2$, from hydrogen ab-

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straction by the nitrene, and small amounts of viscous, polymeric orange-red oils as products. A polymeric gum was also observed when pivaloylnitrene was generated in unreactive solvents such as methylene chloride.7

The α elimination reaction (eq 2) with 33 mol %tetramethyltin in methylene chloride gave a 97% yield of triethylammonium *p*-nitrobenzenesulfonate and, upon work-up, yielded only recovered tetramethyltin and a small amount of urethane. Since a tertiary, β C-H bond is the most reactive toward dichlorocarbene for tetraalkyltin, -germanium, or -silicon compounds, trimethylisobutyltin was prepared and allowed to react in acetonitrile solution with thermally generated ethoxycarbonvlnitrene. However, gas chromatography after concentration of the reaction mixture showed peaks only for solvent, starting organotin compound, and urethane.

Since insertion into C-H bonds is attributed to the carbonylnitrene principally in the singlet electronic state,⁸ the effect of organometallic group IVA compounds on the singlet-triplet character of this nitrene was evaluated. The major products obtained upon thermal decomposition of ethoxycarbonylazide in cyclohexene are given in eq 3.4 The insertion products



(2, 3, and 4) are mainly due to reaction of cyclohexene with singlet nitrene, products 5 and 6 are from triplet nitrene, and product 1 is from either singlet or triplet.⁸

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⁽⁸⁾ W. Lwowski, editor, "Nitrenes," Interscience Publishers, New York, N. Y., 1970, pp 200-207.

TABLE I							
THERMAL	DECOMPOSITION	OF	ETHYL	AZIDOFORMATE	τN	CYCLOHEXENE	

Reaction ^a		Concentration					
	Solvent	Vol %	Mol %	1	2, 3, 4	5	б
1°	None	0	0	3.5	3.0	1.00	0.68
2	None	0	0	6.8	12.0	1,00	Trace
34	None	0	0	8.6	8.9	1.00	0.68
4 ^d	None	0	0	8.6	8.2	1.00	0.58
				(18.6)	(17.7)	(2.16)	(1.25)
5°	None	0	0	11.7	23.6	1.00	0.17
				(20.2)	(40.8)	(1.73)	(0.29)
6	CH_2Br_2	50.0	59.5	6.8	6.3	1.00	3.5
7	CH_2Br_2	70.7	78.2	18.7	7.21	1.00	0.30
				(63.2)	(24.4)	(3.38)	(1.00)
8	CH_2Br_2	90.0	92.8	15.8	3.6	1.00	0.42
9ª	CH_2Br_2	90.0	92.8	19.3	4.4	1.00	0.95
101	$\rm CH_2 Cl_2$	90.0	93.4	9.2	2.3	1.00	Trace
11	$(CH_3)_4Sn$	10.0	9.7	7.5	10.1	1.00	0.68
12	$(CH_3)_4Sn$	90.0	86.9	2.6	0.18	1.00	0.15
137	(CH ₃) ₄ Si	90.0	87.0	17.0	1.19	1.00	0.75

^a Reaction mixture bubbled with N_2 and then refluxed under N_2 atmosphere, except where noted, for 72 hr at 80°. ^b Absolute yields (%) in parentheses. ^c Oxygen present, air atmosphere. ^d Duplicate run used to establish the limits of reproducibility of the system. ^e Carefully degassed, reaction under N_2 . ^f Degassed, evacuated sealed-tube reaction.

The reaction was studied under a variety of conditions with the results outlined in Table I.

Discussion

The transition from the initially formed singlet nitrene to a lower energy triplet state due to collisional deactivation by inert solvent has been observed for ethoxycarbonylnitrene⁹ and cyanonitrene.¹⁰ In addition, a "heavy-atom" effect¹¹ was noted for cyanonitrene¹⁰ but not for ethoxycarbonylnitrene.⁹ Using the product ratios from cyclohexene to judge the singlet-triplet character of the carbonylnitrene, we find that the presence of oxygen greatly increases the triplet character of the reaction as reported earlier by Lwowski.⁴ Reaction 5 gives relative ratios and absolute yields very similar to those reported by Lwowski⁴ and shows the dramatic increase in singlet character obtained when the system has been thoroughly degassed of oxygen. Changing the concentration of cyclohexene from 100 to 50 to 30 to 10 mol % by dilution with methylene bromide (reactions 4, 6-8) gives an overall reduction in singlet character as expected from collisional deactivation of the nitrene.¹² This dilution effect is also evident from reactions 11 and 12. In general, the absolute yields of addition and insertion products decrease with increasing triplet character of the nitrene^{4,7,10} probably owing to radical side reactions. Reaction 5 in Table I was the only instance of those which we studied in which the reaction mixture was colorless after the reaction was completed; the others were either orange solutions or, in cases where triplet character was very high, orange-red oils or gums were produced. We have no explanation at this time for the unusually high yields observed in reaction 7.

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(10) A. G. Anastassiou, *ibid.*, **89**, 3184 (1967).

(11) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 29.

The most significant entries in Table I are reactions 12 and 13 which show a decrease in singlet character greater than can be rationalized on the basis of collisional deactivation when tetramethyltin or -silicon is used as an inert solvent. Since 12 gave much less singlet products than 13, it is tempting to invoke a heavy-atom effect to explain the results. However, methylene bromide gave more singlet product than a comparable concentration of tetramethyltin even though bromine has a higher spin-orbit coupling constant than tin,¹¹ there are two bromines per molecule, and the bromine atoms are less shielded than the tin atom. Furthermore, methylene chloride (reaction 10) gave less singlet products than methylene bromide (reaction 9) even though the former reaction mixture was degassed and the latter was not.

We would propose that the observed inertness to nitrene insertion of the C-H bonds of the group IV organometallic compounds studies is attributable to greatly enhanced triplet character of the carbonylnitrene partly due to collisional deactivation and partly due to an effect of the metal which we cannot explain at this time but which does not seem to be a heavyatom effect. The inertness of even a tertiary β C-H bond, as in trimethylisobutyltin, is not unexpected given the general higher selectivity and lower reactivity of nitrenes compared to those of carbenes.

Experimental Section

Reagents.—Ethoxycarbonylazide, bp 40-41° (30 mm), was prepared from potassium azide and ethyl chloroformate.⁴ Cyclohexene, bp 83°, was distilled through a 2-ft glass helices packed column and stored under nitrogen over potassium hydroxide pellets. *N-p*-Nitrobenzenesulfonyloxyurethane was prepared by the method previously described,⁵ mp 115-116°. Tetramethylsilane, J. T. Baker, bp 26-27°, was used without purification. Tetramethyltin, bp 76-77°, and trimethylisobutyltin, bp 70° (60 mm), were prepared by the usual Grignard procedure.¹³

Product Composition.—Cyclohexene-nitrene reaction mixtures were concentrated by distillation and the relative ratios and, in a few select cases, absolute yields were determined by vpc analysis (Aerograph A-700) in which peak areas were obtained by the "cut

⁽¹²⁾ Since collisional deactivation and the heavy-atom effect are molecular phenomena, reporting concentrations as volume per cent¹⁰ seems inappropriate. However, the mole per cent concentrations are not significantly different for these solvents to affect the basic arguments.

⁽¹³⁾ J. G. A. Luijten and G. J. M. Van Der Kerk, "Investigations in the Field of Organotin Chemistry," Tin Research Institute, Middlesex, England, 1955.

Notes

and weigh'' technique. A $5 \text{ ft} \times 0.25 \text{ in}$. 15% XF-1150 on 60/80Chromosorb W column gave overall satisfactory separation of the major products except for the insertion products (2, 3, and 4) which gave a broad, long-retention peak. However, a 5 ft \times 0.25 in. 10% QF-1 on 60/80 Chromosorb W was needed to achieve good separation of 5 from 6.

Products 5 and 6 were identified by comparison of retention times with those of and coinjection with authentic samples. Products 1, 2, 3, and 4 were identified by collection from the gas chromatograph and comparison of nmr and ir spectra with published data.⁴ To obtain calibration factors to correct for differences in detector sensitivity, it was assumed that products 1, 2, 3, and 4 (isomers) have the same sensitivity. The relative ratios given are therefore corrected for the differences in detector sensitivity for 6 and 5 and 1, 2, 3, and 4.

Registry No.—Ethoxycarbonylnitrene, 2655-26-7; cyclohexene, 110-83-8; (Me)₄Sn, 594-27-4; (Me)₄Si, 75-76-3; ethyl azidoformate, 817-87-8.

Radiation and Ultraviolet Induced Addition of Alcohols to Ethyl Crotonate

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Radical addition reactions of alcohols to double bonds have been reported to be carried out using radical initiators,^{2a-c} ultraviolet light,^{2a,d-g} and radiation techniques.³

Although the radiation-induced addition of alcohol to ordinary olefins has been described to give both telomeric products and 1:1 adduct,^{3a} the reaction with a relatively stable substrate such as halogeno olefin is known to produce mainly 1:1 adduct^{3b-e} in good yield. The photochemical addition of alcohols to α,β -unsaturated acid derivatives in the presence of a sensitizer was reported to yield γ -butyrolactones by Schenck^{2d} and Pfau,^{2e-g} but the analogous radiation-induced reaction has not been known. Consequently, as a part of our studies on organic synthesis by means of radiation-induced reactions, γ -ray and ultraviolet-induced addition reactions to α,β -unsaturated acids and esters,⁴ which seem to be considerably stable to γ radiation,^{4b} were studied.

Irradiation of ethyl crotonate (1a) or crotonic acid (1b) in an excess of alcohol with ⁶⁰Co γ rays gave the corresponding 3-methyl-4-alkyl substituted γ -butyrolactones (4), small amounts of telomeric products of crotonate (5, 6) and polymeric products.



The yield of lactones and conversion of ethyl crotonate in the radiation-induced addition reactions are summarized in Table I. The formation of γ -butyro-

	TABL	εI		
RADIA	ATION-INDUCED AI	DITION	of Alcohoi	4
	to Ethyl Cr	OTONATI	$\mathbf{E}^{\boldsymbol{a}}$	
	$Conversion^{b,c}$		-Yield, ^{b,c} %	
Alcohol	of 1a , %	4 .	5	6
Methanol	68	1	Trace	Trace
Ethanol	96	16^{d}	1	0.5
2-Propanol	97	54	4	2

1-Propanol 9496 3 $\mathbf{2}$ 2-Butanol 95 18^{f} 3 1 3-Pentanol 9510 $\mathbf{2}$ 3 239 0 Benzyl alcohol 450 ^a Irradiation time, 72 hr; dose rate, $0.9-1.0 \times 10^6$ r/hr; molar tio of alcohol to ethyl crotonate, 15. ^b Based on ethyl crotonate

ratio of alcohol to ethyl crotonate, 15. ^b Based on ethyl crotonate employed. ^c By glpc analysis. ^d Trans: cis, 4:5. ^e Trans: cis, 2:3. ^f Trans and cis isomers were not separated in glpc analysis. ^e Trans: cis, 2:1.

lactone (4) seems to proceed through a radical chain mechanism initiated by an α -hydroxyalkyl radical. This is supported by the fact that the reaction was retarded by the addition of a radical scavenger.

It is of interest that a considerable amount of cis lactone was obtained from the reaction of crotonate with ethanol, 1-propanol, and benzyl alcohol. 2-Butanol also produced trans- and cis lactones, but their relative ratio could not be determined by glpc analysis. The formation of two isomeric lactones may well be the result of alternate approaches of the hydroxyalkyl radical to the double bond of ethyl crotonate. For example, if the hydroxyalkyl radical attacks the carboncarbon double bond as shown in A, and the resulting intermediate radical abstracts hydrogen from alcohol, the cis isomer would be obtained. The attack of hydroxyalkyl radical as depicted in B would give rise to the trans isomer. Although the predominance of cis isomer in ethanol and 1-propanol, and trans isomer in benzyl alcohol, has not been adequately explained, it may well be due to the relative degree of steric interaction in pathways A and B. Similar isomeric ratios

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