butylphenyl)mercury and 3.45 g (0.015 g-atom) of sodium sand covered with 75 ml of nonane. After the mixture was stirred for 1 hr to ensure complete reaction, 6.7 g (0.05 mol) of *t*-butylbenzene containing 0.44 g (0.006 mol) of *t*-butyl alcohol was added to the flask. The reaction was carbonated, worked up, and esterified after 1 day to give a 10% yield of product which was composed of 34% methyl *m*-*t*-butylbenzoate and 66% methyl *p*-*t*-butylbenzoate.

Attempted Isomerization of *m*-*t*-Butylphenylsodium in the Presence of Sodium *t*-Butoxide but in the Absence of *t*-Butylbenzene. Essentially, method III was used as described above to prepare *m*-*t*-butylphenylsodium. To the nonane solution of this reagent was added 1.9 g (0.02 mol) of sodium *t*-butoxide but no *t*-butylbenzene. After 1 day, the mixture was carbonated and esterified. There was obtained a 76% yield of methyl *t*-butylbenzoates composed of 97% *meta* and 3% *para* isomer.

Examination of Supernatant Layers. a. *n*-Amylsodium in Nonane. *n*-Amylsodium was prepared from a 10.6-g (0.46 g-atom) sample of sodium sand in 175 ml of nonane and 21.3 g (0.20 mol) of *n*-amyl chloride in 25 ml of nonane. One hour after the *n*-amylsodium had been prepared, the *n*-amylsodium suspension was pipetted[30] into a centrifuge bottle and then centrifuged for 0.5 hr at 2500 rpm. A clear water white supernatant layer resulted. A 30-cc aliquot of this supernatant was removed with a hypodermic syringe and treated with 5 cc of trimethylchlorosilane. After 2 hr the resulting solution was analyzed by vpc.[31] Within the accuracy of the analytical method, it was shown that *n*-amylsodium was not present in the supernatant as adjudged by the absence of a peak corresponding in retention time to *n*-amyltrimethylsilane.[32]

b. *n*-Amylsodium–Sodium *t*-Butoxide in Nonane. *n*-Amylsodium was prepared in nonane exactly as described in a above. Sodium *t*-butoxide was prepared *in situ* by the addition of 5.92 g (0.08 mol) of *t*-butyl alcohol to the flask. The mixture was pipetted after 1 hr to a centrifuge bottle and centrifuged for 0.5 hr at 2500 rpm; a clear brown supernatant resulted. A 30-cc aliquot of the supernatant layer was treated with 5 cc of trimethylchlorosilane.[33] Analysis of this solution by vpc showed that the supernatant contained *n*-amylsodium and sodium *t*-butoxide as adjudged by the identification of *t*-butoxytrimethylsilane[34] and *n*-amyltrimethylsilane in the gas chromatogram by comparing the retention times with authentic samples.

A second 30-cc sample of the brown hydrocarbon layer was added to 10 ml of *t*-butylbenzene and after 6 hr trimethylchlorosilane was added to the solution. Vpc analysis showed that *t*-butylphenyltrimethylsilane (35% *meta* and 65% *para*) had formed as determined by comparing the gas chromatographic retention times with authentic samples.

Acknowledgment. This research was supported by the U. S. Army Research Office (Durham) to whom the authors are deeply indebted.

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[30] All transfer operations were carried out in glassware which had been dried at 120° and flushed with nitrogen.

[31] Silicone oil column at 100°. Helium flow of 40 cc/min.

[32] F. C. Whitmore, *et al.*, *J. Am. Chem. Soc.*, **68**, 475 (1946).

[33] The *n*-amylsodium was also characterized by carbonation and conversion to methyl caproate in the usual manner.

[34] W. Gerrard and K. D. Kilburn, *J. Chem. Soc.*, 1536 (1956).

Carbon Monoxide Reactions. IV. The Mechanism of Cyclohexane Chlorocarbonylation

Warren A. Thaler

Contribution from the Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey. *Received February 20, 1968*

Abstract: The free-radical reaction of cyclohexane with carbon monoxide and carbon tetrachloride produces cyclohexanecarboxylic acid chloride and chloroform. The chlorination of cyclohexane by carbon tetrachloride is a competing process leading to chlorocyclohexane and chloroform. A quantitative relationship between these two processes and reaction variables such as CO pressure and CCl_4 concentration has been established and may be used to calculate the selectivity for the formation of acid chloride [RCOCl/(RCOCl + RCl)] under different reaction conditions. The relative concentration of cyclohexane-carbon tetrachloride exerts an unusual influence on both the reaction rate and conversion levels. This influence has been attributed to an autoinhibition of both chlorination and chlorocarbonylation by the acid chloride product. A competition between radical attack on cyclohexane and attack on acid chloride has been postulated wherein attack on acid chloride leads to stable free radicals incapable of propagating the reaction chain.

Paraffins are converted to acid chlorides by means of a free-radical "chlorocarbonylation" reaction with carbon tetrachloride and carbon monoxide utilizing either peroxide[1] or γ radiation[2] to initiate the radical chain. These reactions have been conducted in chrome–vanadium steel Aminco pressure reactors equipped with glass insert liners. Marked inhibition of both the chlorocarbonylation and the chlorination (in the absence of CO) of cyclohexane[1] was observed when traces of metal in combination with a small quantity of acid chloride contaminated the peroxide-initiated reactions. This difficulty, which was lessened by the use of glass liners, could be circumvented by using γ radiation from a cobalt-60 source instead of peroxide, and was subsequently attributed to a metal–acid chloride catalyzed destruction of the peroxide initiator.

The γ-initiated reaction was used successfully for the synthesis of a variety of primary and secondary acid chlorides, and product distributions were correlated with reaction conditions (temperature, CO pressure) and hydrocarbon structures. However, some inexplicable observations, such as the inability to prepare difunctional acid chlorides, as well as unusual decreases in rate, which limited the extent of conversion of reagents to products, prompted this more detailed examination of the influence of reaction variables.

Results and Discussion

Chlorocarbonylation of paraffins with carbon tetrachloride and carbon monoxide would be expected to

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[1] W. A. Thaler, *J. Am. Chem. Soc.*, **88**, 4278 (1966).

[2] W. A. Thaler, *ibid.*, **89**, 1902 (1967).

involve a series of chain propagation steps

$$RH + CCl_3 \xrightarrow{k_1} R\cdot + CHCl_3 \qquad (1)$$

$$R\cdot + CCl_4 \xrightarrow{k_2} RCl + \cdot CCl_3 \qquad (2)$$

$$R\cdot + CO \xrightleftharpoons[k_{-3}]{k_3} RCO\cdot \qquad (3)$$

$$RCO\cdot + CCl_4 \xrightarrow{k_4} RCOCl + \cdot CCl_3 \qquad (4)$$

in which the sequence of steps 1, 3, and 4 would produce acid chloride (eq 5) while the sequence of step 1 followed by step 2 would result in an undesired chlorination side reaction (eq 6). The proposed reaction

$$RH + CCl_4 + CO \longrightarrow RCOCl + CHCl_3 \qquad (5)$$

$$RH + CCl_4 \longrightarrow RCl + CHCl_3 \qquad (6)$$

steps appear reasonable since each of the individual steps have been observed in other reactions. Reaction steps 1 and 2 account for the chlorination of hydrocarbons by carbon tetrachloride[3] while 4 is important in the reaction of aldehydes with carbon tetrachloride.[4] Both the forward and reverse of step 3 are well-documented by several reactions, such as olefin–carbon monoxide copolymerizations,[5] aldehyde decarbonylations,[4,6] radical desulfurization of disulfides in the presence of CO,[7] etc.

According to the proposed mechanism the relative amounts of alkyl chloride and acid chloride are described by eq 7. (Since these reactions involve long

$$\frac{d(RCl)}{d(RCOCl)} = \frac{k_2(R\cdot)(CCl_4)}{k_4(RCO\cdot)(CCl_4)} \qquad (7)$$

kinetic chains,[2] the initiation and termination steps do not contribute significantly to the quantity of products.) If one makes the customary steady-state assumption that within a very short time radicals are being generated at the same rate at which they are consumed (eq 8) then

$$\frac{d(RCO\cdot)}{dt} = k_3(R\cdot)(CO) - k_{-3}(RCO\cdot) - k_4(RCO\cdot)(CCl_4) = 0 \qquad (8)$$

the steady-state concentration of acyl radicals is governed by eq 9. Substituting this expression into eq 7 in

$$(RCO\cdot) = \frac{k_3(R\cdot)(CO)}{k_{-3} + k_4(CCl_4)} \qquad (9)$$

the place of (RCO·) gives an expression for the relative rates of formation of alkyl chloride and acid chloride which is free from radical concentration terms which are difficult to measure.

$$\frac{d(RCl)}{d(RCOCl)} = \frac{k_2k_{-3}}{k_3k_4(CO)} + \frac{k_2}{k_3(CO)}(CCl_4) \qquad (10)$$

Since chlorocarbonylations have been run at constant carbon monoxide pressure, then under conditions where the difference in initial and final carbon tetrachloride concentrations is not large, the ratio of alkyl chloride to acid chloride is closely approximated by eq 11 where $\overline{(CCl_4)}$ is the mean carbon tetrachloride concentration.

$$\frac{(RCl)}{(RCOCl)} = \frac{k_2k_{-3}}{k_3k_4(CO)} + \frac{k_2}{k_3(CO)}\overline{(CCl_4)} \qquad (11)$$

The obvious implications of eq 11 are that the selectivity for acid chloride formation [(RCOCl)/(ROCCl + RCl)] will increase with increasing carbon monoxide and decreasing carbon tetrachloride concentrations, and the maximum selectivity to acid chloride (as CCl_4 concentration approaches zero) is limited only by the carbon monoxide concentration. The chlorocarbonylation (130°) of cyclohexane with initial carbon tetrachloride concentrations ranging from 8.6 to 0.10 *M* at several fixed carbon monoxide pressures was examined in order to test the validity of eq 11. A plot of (RCl)/(RCOCl) *vs.* (CCl_4) should give a straight line with a slope of $k_2/k_3(CO)$ and a *Y* intercept of $k_2k_{-3}/k_3k_4(CO)$. The data in Figure 1 indicate a good linear dependence of (RCl)/(RCOCl) with (CCl_4) at each of five different CO pressures (measured at 25°) ranging from 600 to 5300 psi. The intercept/slope ratio should represent k_{-3}/k_4, the specific reaction rate at which the acyl radical loses carbon monoxide relative to its rate of reaction with CCl_4 (130°). The value calculated from Figure 1 is 2.9 ± 0.6 l. mol^{-1} for the cyclohexyl acyl radical ($C_6H_{11}CO\cdot$). This number appears reasonable when compared with the independently measured value of 1.14 (135°) for the isopropylacyl radical (($(CH_3)_2CHCO\cdot$) which is also a secondary radical, and contrasts markedly with the values for primary (0.14) and tertiary (12.3) acyl radicals.[4b] Determination of k_2/k_3 from each of the slopes of plots in Figure 1 would require independent measurements of the concentration of CO in solution at 130° for each of the reaction pressures. Unfortunately such data is not available. The fact that the slope multiplied by the CO pressure is not a constant but decreases with increasing CO pressure is consistent with an earlier observation[1] and suggests that CO solubilities have a nonlinear dependence on pressure. It is significant for synthetic purposes that at high CO pressures the slope is small, and the selectivity to acid chloride shows only a small dependence on carbon tetrachloride (72–88% for 8.6–1.0 *M* CCl_4 at 5300 psi) while selectivities at lower pressures become quite sensitive to CCl_4 concentrations (37–72% for 8.6–0.1 *M* CCl_4 at 2400 psi).

The data in Figure 1 are useful for predicting the selectivity to acid chloride for a given set of reaction conditions; however, additional data was required to optimize reaction rates and acid chloride yields (yield = conversion × selectivity). Although higher concentrations of CCl_4 could be expected to give faster reaction rates, it was observed that at higher CCl_4 concentrations rates began to slow down to the point where it was not possible to achieve complete conversion of CCl_4 to products even when cyclohexane was present in excess. In contrast, at low CCl_4 concentrations reactions went to completion quickly (Table I).

Failure to produce difunctional acid chlorides from either the chlorocarbonylation of cyclohexane with excess CCl_4 and CO (eq 12), or from the reaction of CO

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[3] (a) J. P. West and L. Schmerling, *J. Am. Chem. Soc.*, **72**, 3525 (1950); (b) J. P. West and L. Schmerling, U. S. Patents 2,553,799; 2,553,800 (1951).

[4] (a) S. Winstein and F. H. Seubold, *J. Am. Chem. Soc.*, **69**, 2916 (1947); (b) D. E. Applequist and L. Kaplan, *ibid.*, **87**, 2194 (1965).

[5] M. M. Brubaker, D. D. Coffman, and H. H. Hoehn, *ibid.*, **74**, 1509 (1952).

[6] (a) J. B. Conant, C. N. Webb, and W. C. Mendum, *ibid.*, **51**, 1246 (1929); (b) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, pp 205–214, 275–317.

[7] C. Walling, O. H. Basedow, and E. S. Savas, *J. Am. Chem. Soc.*, **82**, 2181 (1960).

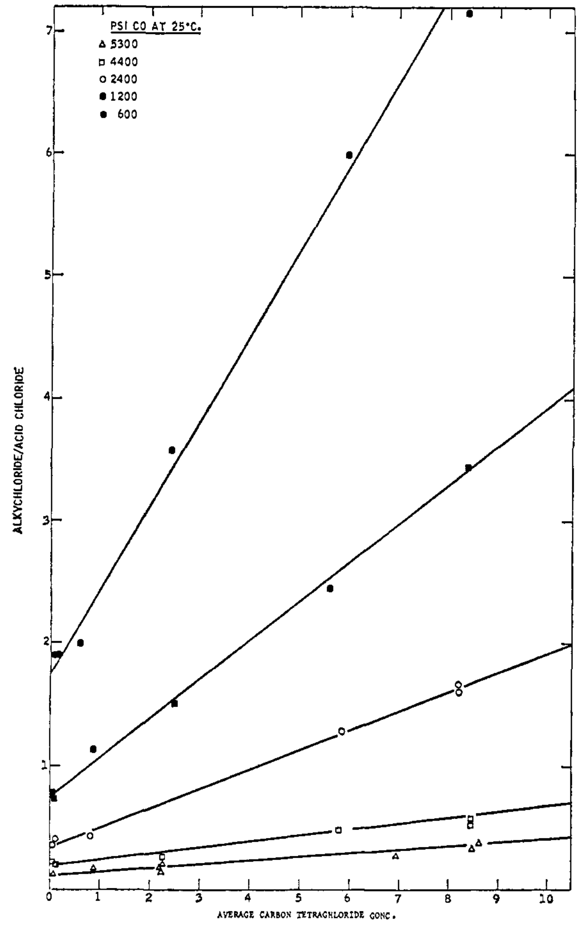
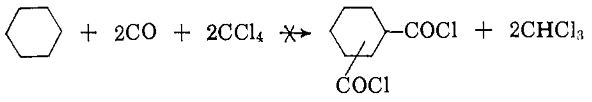
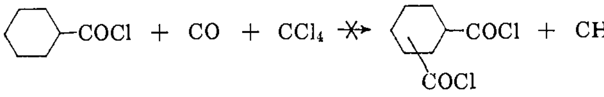


Figure 1. Effect of CCl_4 concentration on selectivity, 130°.

and CCl_4 with cyclohexanecarbonyl chloride (eq 13) was consistent with the observed inability to achieve complete conversions with high initial CCl_4 concentrations, and implicated the acid chloride product as a possible source of difficulty.



(12)



(13)

The resistance of cyclohexanecarbonyl chloride to chlorocarbonylation suggested that the acid chloride product may itself be an inhibitor of the chlorocarbonylation of cyclohexane. If radicals were reacting with acid chloride to produce a species incapable of propagating the reaction chain, then the effectiveness of cyclohexanecarbonyl chloride as an inhibitor would depend upon the ratio of paraffin to acid chloride since this ratio controls the relative amount of attack on paraffin compared to acid chloride. The ratio of cyclohexane to acid chloride at any given conversion level is determined by the initial cyclohexane to CCl_4 ratio down to the 1:1 level; beyond this point the hydrocarbon/acid chloride ratio is not affected by additional CCl_4. Thus, more retardation and consequently poorer conversions would be observed as the initial CCl_4 concentration is increased until equimolar concentrations are reached (Table I). This competitive autoinhibition theory predicts that the ratio of reactive hydrocarbon to carbon tetrachloride is more important than the actual concentration of CCl_4. This was confirmed using benzene as an inert diluent and demonstrating that in a reaction mixture which contained 8:1 total hydrocarbon to CCl_4, but had a 2:1 ratio of cyclohexane to CCl_4, only a 29.6% conversion was obtained in 16 hr (5300 psi, 130°). A similar reaction utilizing 8:1 cyclohexane to CCl_4 went to *completion* within this period while a 2:1 cyclohexane to CCl_4 reaction mixture not containing any inert diluent gave 37.9% conversion (Table II). Thus, a decrease in the actual carbon tetrachloride concentration decreased the conversion while a similar decrease in the carbon tetrachloride relative to cyclohexane resulted in a marked increase in conversion, indicating that (substrate)/(CCl_4) rather than CCl_4 concentration is the dominant factor influencing conversions.

Table I. Effect of Hydrocarbon/CCl_4 Ratio on Conversion Rates[a]

C_6H_{12}/CCl_4	Initial concn of CCl_4, *M*	Conversion,[b] %
0.116	8.62	34.8
0.200	7.20	31.4
1.00	3.85	26.7
2.00	2.71	37.9
4.00	1.66	71.9
6.00	1.23	79.5
8.00	0.962	103[c]
16.0	0.528	103[c]
90.5	0.100	100[d]

[a] 5300 psi CO at 25°; 130° reaction temperature. [b] 16-hr runs. [c] Less than 11 hr. [d] Less than 3 hr.

Table II. Conversion Rate Dominated by C_6H_{12}/CCl_4 Rather Than CCl_4 Concentration[a]

Total hydrocarbon/CCl_4	Cyclohexane/CCl_4	Concn of CCl_4, *M*	Conversion, %
2	2	2.71	37.9
8[b]	2	1.04	29.6
8	8	1.00	103

[a] 5300 psi CO at 25°; 130°; 16 hr. [b] 6:2:1, benzene–cyclohexane–carbon tetrachloride.

The inhibiting influence of acid chloride on a radical chain reaction involving trichloromethyl radical could also be demonstrated by examining the effect of adding acid chloride to simple chlorinations of cyclohexane by CCl_4 (eq 6). The extent of conversion of cyclohexane and carbon tetrachloride to chlorocyclohexane and chloroform in both peroxide and γ-initiated reactions was strongly influenced by the amount of acid chloride added to the system (Table III). It is significant that the acid chloride undergoes very little reaction compared to cyclohexane at acid chloride levels as high as 2:1 cyclohexane to acid chloride, and explains the good material balances[2] observed in chlorocarbonylations of various hydrocarbons. Apparently none of the possible radical reactions of acid chlorides[8] are involved in the destruction of any sizable quantity of the product; however, it is evident that very small amounts of reaction with acid chloride significantly influence the yield of product by effecting conversion rates and limiting the degree of conversions which can be attained.

(8) U. Schmidt, *Angew. Chem.*, 77, 216 (1965).

Table III. The Effect of Added Cyclohexanecarboxylic Acid Chloride on the Chlorination of Cyclohexane by Carbon Tetrachloride[a]

$$C_6H_{12} + CCl_4 \xrightarrow[\gamma\ \text{radiation}]{C_6H_{11}COCl} C_6H_{11}Cl + CHCl_3$$

% conversion		Acid chloride/initial cyclohexane, mol	
$CHCl_3$	$C_6H_{11}Cl$	Initial	Final
81.0	79.0	0	0
48.5	49.0	0.125	0.125
37.2	36.9	0.250	0.248
25.8	25.0	0.500	0.495

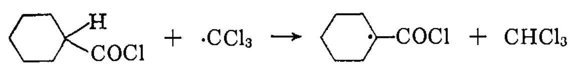
[a] 2:1 cyclohexane to CCl_4; γ initiation; 130°; 16 hr.

Although strong evidence has been obtained for autoinhibition of chlorocarbonylation due to subsequent reaction(s) of the acid chloride product, the small extent to which such reactions are occurring obscures the nature of this process. It suggests the formation of a very small quantity of an effective species such as relatively stable free radical which is incapable of propagating the chain and instead brings about termination. Two such mechanisms can be envisaged involving either abstraction of the α-hydrogen or addition to the carbonyl group. The α-C–H has the lowest bond energy, and from this consideration should be most reactive toward the highly selective trichloromethyl radical. On the other hand, the α position is deactivated toward electronegative radicals by the electron-withdrawing carbonyl group. In any event it does not seem likely that abstraction of a secondary hydrogen from cyclohexanecarboxylic acid chloride would produce a stable radical, and only the α radical would be expected to be sufficiently stable to inhibit the reaction. The effectiveness of several acid chlorides in retarding the chlorination of cyclohexane is shown in Table IV. If α radicals were responsible, both acetyl chloride which would give a more reactive primary α radical, and pivalyl chloride, which is incapable of producing an α radical, should be ineffective inhibitors. To the contrary, the data indicate that these two acid chlorides are the most effective inhibitors and would appear to preclude the participation of eq 14 as a significant route to a stable free-radical inhibitor of cyclohexane chlorocarbonylation.

Table IV. The Effect of Acid Chlorides on the CCl_4 Chlorination of Cyclohexane[a]

	% conversion		Acid chloride/initial cyclohexane, mol	
Acid chloride	$CHCl_3$	$C_6H_{11}Cl$	Initial	Final
None	81.5	79.5	0	0
n-$C_{11}H_{23}COCl$	67.5	68.3	0.50	...
CH_3COCl	9.8	10.6	0.50	0.52
$(CH_3)_3CCOCl$	0	0	0.50	0.51

[a] 2:1 cyclohexane-CCl_4; γ initiation; 130°; 16 hr.



(14)

The greater effectiveness of the acid chlorides containing fewer C–H bonds is consistent with a competition between a noninhibiting hydrogen abstraction from both cyclohexane and acid chloride, and an inhibiting reaction involving the acid chloride group. Although the nature of such an interaction is uncertain, radical addition to a carbonyl group is not without precedent,[9] and it is possible that addition to the carbonyl group could produce a species which is incapable of either abstracting a hydrogen from cyclohexane or a chlorine from carbon tetrachloride to continue propagation of the radical chain.

In summary, the yields of acid chloride obtained in a fixed time interval from the reaction of a hydrocarbon such as cyclohexane with CCl_4 and CO are maximized by the use of high CO/CCl_4 and high cyclohexane/CCl_4 ratios. The ratio of CO/CCl_4 determines the relative amounts of cyclohexane–carboxylic acid chloride and chlorocyclohexane which are formed (selectivity), while the cyclohexane/CCl_4 ratio influences the conversion rate. The selectivity to acid chloride can be calculated utilizing eq 11 and has a limiting value (as $(CCl_4) \rightarrow 0$) which is fixed by the carbon monoxide pressure. The

Table V. Chlorocarbonylation of Cyclohexane (130°)

Mole ratio C_6H_{12}/CCl_4 (initial)	CCl_4 concn (average, $\bar{M}$)	Reaction time, hr	Conversion, %	Mole ratio $C_6H_{11}Cl/C_6H_{11}COCl$	Selectivity, %
		5300 psi of CO at 25°			
0.116	8.57	4	10.0	0.383	72.3
0.116	8.44	16	36.1	0.379	72.5
0.116	8.45	16	33.6	0.334	75.7
0.250	6.91	16	31.4	0.284	77.9
1.00	3.34	16	36.7	0.316	76.0
2.00	2.19	16	38.7	0.181	84.7
2.00	2.18	16	39.4	0.163	86.0
2.00	2.20	16	37.9	0.163	86.0
2.00	2.23	16	35.6	0.216	82.2
8.65	0.84	3	25.2	0.179	84.0
90.5	0.07	1.5	52.9	0.134	88.2
		4400 psi of CO at 25°			
0.116	8.54	8	16.6	0.495	66.9
0.116	8.43	16	37.7	0.540	64.9
0.116	8.43	16	37.6	0.572	63.6
0.408	5.94	6	16.5	0.513	66.1
0.408	5.82	17	25.9	0.490	67.1
2.00	2.26	8	33.4	0.271	78.7
90.5	0.05	3	95.8	0.221	81.9
90.5	0.06	1.5	70.3	0.211	82.6
		2400 psi of CO at 25°			
0.116	8.41	16	43.2	1.62	3.75
0.116	8.40	16	44.3	1.64	37.9
0.408	5.85	6	23.5	1.29	43.7
2.00	2.55	3	13.0	0.751	57.1
8.65	0.80	3	34.4	0.422	70.3
90.5	0.05	3	100	0.379	72.5
90.5	0.06	1.5	74.4	0.395	71.7
		1200 psi of CO at 25°			
0.116	8.38	16	48.4	3.45	22.5
0.408	5.58	16.5	44.9	2.46	28.9
2.00	2.50	3	15.7	1.51	39.8
8.65	0.85	1.5	23.9	1.13	46.9
90.5	0.05	3.3	100+	0.76	56.9
90.5	0.06	1.5	67.7	0.75	57.3
		600 psi of CO at 25°			
0.116	8.36	16	50.5	7.16	12.0
0.408	5.95	16	44.7	5.99	14.3
2.00	2.42	3	21.4	4.21	21.8
8.65	0.62	5	70.8	1.99	33.5
90.5	0.05	2.2	93.7	1.90	34.4

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(9) E. I. Helba and L. C. Anderson, *J. Am. Chem. Soc.*, **81**, 1117 (1959).

cyclohexane/CCl_4 ratio indirectly reflects the cyclohexane/acid chloride ratio which appears to determine the relative amount of inhibitor producing reaction with the acid chloride, the nature of which is obscure.

Experimental Section

Chlorocarbonylations were conducted in the previously described manner.[2] Volumetric solutions were prepared which contained the desired concentrations of cyclohexane and carbon tetrachloride as well as 1-chloro-3-fluorobenzene (50 mol % of CCl_4) used as an inert internal standard for vapor phase chromatographic (vpc) analysis. In each run 20 ml of reaction mixture in a glass-lined bomb was pressurized with CO at 25° and then heated to 130°. The rocked bomb was then irradiated with a cobalt-60 source of approximately 6000 Ci.

Selectivities and conversions were determined by treating reaction mixtures with excess ethanol and analyzing for cyclohexane consumption and chloroform, chlorocyclohexane, and ethyl cyclohexanecarboxylate production, using an F & M 810 gas chromatograph equipped with a 2-ft D.C. 200 silicone oil column in series with a 7-ft Ucon LB550X, 20% on 60–80 mesh, acid-washed Chromosorb W. The unit was programmed at 6°/min from 75 to 176° with a 10-min upper limit hold. Area ratios of the product peaks to the internal standard (1-chloro-3-fluorobenzene) were measured and multiplied by the appropriate correction factor determined by calibration with weighed mixtures of authentic samples.

Conversions were measured from both $CHCl_3$ formation and ($C_6H_{11}Cl$ + $C_6H_{11}COCl$) formation, and when practical from cyclohexane consumption. The selectivity to acid chloride was determined from the relative ratio of $C_6H_{11}Cl$ to $C_6H_{11}COCl$. Examples of data obtained at several pressures are presented in Table V.

Chlorinations of cyclohexane and acid chloride mixtures with CCl_4 in the absence of carbon monoxide were conducted in glass tubes fitted with Fischer & Porter Teflon valves. The tubes were maintained at 130° by means of a thermostated cyclindrical aluminum block drilled to accommodate the 1-in. o.d. glass tubes. The reaction tubes were arranged so that each received an equal dose of radiation. The chlorinations were analyzed in the same fashion as the chlorocarbonylations.

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α-Silyl-*cis*-stilbenes from Silylcarbonium Ions and from the Platinum-Catalyzed Addition of Silanes to Diphenylacetylene

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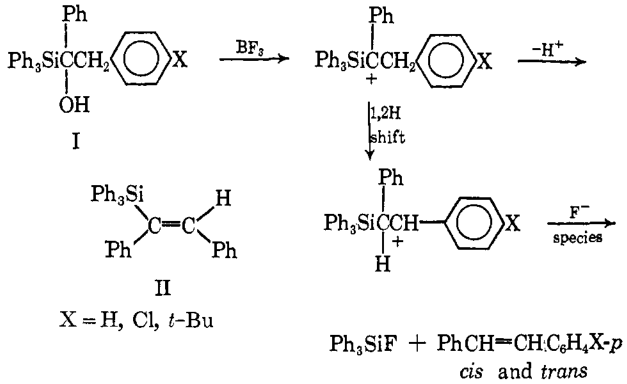
Contribution from the Lash Miller Laboratories, Department of Chemistry, University of Toronto, Toronto, Ontario, Canada. *Received February 16, 1968*

Abstract: Treatment of triphenylsilylbenzylphenylcarbinols with BF_3 gives rise to α-triphenylsilyl-*cis*-stilbenes. These same compounds are produced by platinum-catalyzed addition of silanes to diphenylacetylene, and it is shown that the α-silyl-*cis*-stilbenes are readily converted photochemically into 9-silylphenanthrenes. With the asymmetric silane R_3Si^*H the configuration of the asymmetric center is retained during the formation and photolysis of α-R_3Si^*-*cis*-stilbene.

Considerable interest has developed in recent years in the stereochemistry of platinum-catalyzed additions of silanes to unsaturated carbon–carbon systems. Benkeser[1] has shown that chloroplatinic acid or platinum on carbon-catalyzed additions of trichlorosilane to 1-alkynes occur with *cis* stereochemistry. More recently, Sommer[2] has shown that when optically active 1-naphthylphenylmethylsilane adds to 1-octene using platinum catalysts, the addition occurs with complete retention of configuration at the asymmetric silicon atom, optically active adducts being obtained in good yield.

In connection with our work on the behavior of silylcarbonium ions,[3] we found that treatment of a variety of silylbenzylphenylcarbinols (I) with boron trifluoride gave rise, in 30–40% yield, to compounds which appeared to be α-silyl-*cis*-stilbenes (II), as well as to other fragments such as triphenylfluorosilane, and *cis*- and *trans*-stilbenes derived from decomposition of the original silylcarbonium ion.



A possible alternative synthesis which would establish the identity of these compounds was the platinum-catalyzed addition of triphenylsilane to diphenylacetylene. Although little study has been made of additions to disubstituted alkynes, Speier has stated that trichlorosilane-*d* adds in a *cis* manner to diphenylacetylene,[4] and Polyakova, *et al.*,[5] have examined the polymers formed in silane additions to diphenylacetylene using chloroplatinic acid as catalyst.

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[1] R. A. Benkeser and R. A. Hickner, *J. Amer. Chem. Soc.*, **80**, 5298 (1958).

[2] L. H. Sommer, K. W. Michael, and H. Fugimoto, *ibid.*, **89**, 1519 (1967).

[3] A preliminary report of some of this work has appeared. See A. G. Brook, K. H. Pannell, G. E. LeGrow, and J. J. Sheeto, *J. Organometal. Chem.* (Amsterdam), **2**, 491 (1964).

[4] J. W. Ryan and J. Speier, *J. Amer. Chem. Soc.*, **86**, 895 (1964).

[5] A. M. Polyakova, V. V. Korshak, M. D. Suchkova, V. M. Vdovin, and N. A. Chumaevskii, *Vysokomolekul. Soedin.*, **2**, 1360 (1960); *Chem. Abstr.*, **55**, 21643 (1961).