Preparation and Reactions of N,N′-Diacyl-N,N′-dialkoxyhydrazines[1]

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Abstract: The oxidation of N-acyl-O-alkylhydroxylamines (I) with a number of oxidizing agents was found to give a previously unreported class of compounds, N,N′-diacyl-N,N′-dialkoxyhydrazines (II). The reactions of II can be initiated by nucleophylic attack on carbonyl carbon, electrophylic attack on alkoxy oxygen, or free-radical attack on either alkoxy oxygen or carbonyl carbon. A four-center mechanism for decomposition of II to ester and nitrogen appears to be important in the absence of strong nucleophiles, electrophiles, or free radicals.

During the course of studies on the decomposition of N-nitroso-N-acyl-O-alkylhydroxylamines[3] it became apparent that denitrosation and formation of the hydrazine II could explain some of the observed reactions. An alternate and more direct route to II would be direct oxidation of the N-acyl-O-alkylhydroxylamine I, and, in fact, an oxidative coupling of N-carbalkoxy-O-alkylhydroxylamines had already been reported by Crawford and Raap.[4] Compound II was prepared by the oxidation of I, and a study of the reactions of II was made.

Results and Discussion

Oxidation of I. The method of Crawford and Raap in which the hydrazine formed spontaneously from the silver salt of N-carbalkoxy-O-alkylhydroxylamine could not be applied to the synthesis of II where R was alkyl or aryl and R′ was alkyl. Treatment of I with silver oxide gave a relatively stable silver salt which decomposed on heating to metallic silver, nitrogen, and ester. It was presumed that the intermediate was II. Treatment of the silver salt of I with iodine gave nitrogen, the ester, and silver iodide, and an investigation of different oxidizing agents was started.

$RCONHOR'$

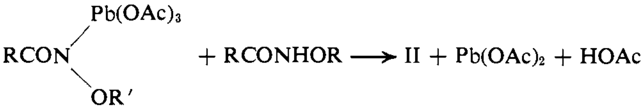
I

$$\begin{array}{c} RCONOR' \\ | \\ RCONOR' \end{array}$$

II

The hydrazines II where R was alkyl but not aryl and R′ was alkyl (Table I) were prepared successfully by the oxidation of I with lead(IV) acetate, ammonium hexachloroplumbate(IV), and lead(IV) oxide. Ester and nitrogen were obtained by treatment of I with *t*-butyl perbenzoate, benzoyl peroxide, cerium(IV) in acid, and by the photolysis of I in ether. I was recovered from treatment with iron(III) chloride, N-bromosuccinimide, mercury(II) oxide (red or yellow), potassium hexacyanoferrate(III), or azobisisobutyronitrile. Only the stronger oxidizing agents were effective in bringing about the oxidation of I.

The mechanism of oxidation could involve a transformation of I to the nitrogen free radical III and coupling, or it could involve an intermediate lead–hydroxylamine compound and a heterolytic process shown in eq 1.[5] Analogies for both processes can be found in the literature.[6,7] Electron spin resonance (esr) spectra were obtained from mixtures of I with various oxidizing agents, and indicate that nitrogen free radicals are formed in the reaction. Our spectra suggest the presence of III, related nitroxyl radicals, and other transients. The esr spectra are only consistent with free-radical intermediates, but such evidence is not conclusive.



(1)

$RCO\dot{N}OR'$

III

Attempts to obtain chemical evidence for III were not successful. No products from a back-biting hydrogen abstraction process[8] were detected, although high-dilution techniques were employed to retard the coupling process. Similarly attempted ring closure by free-radical addition to a double bond situated in the 5,6 position from the nitrogen was not successful. The oxidations were run under ultraviolet light to increase the chances of these free-radical reactions. Under these conditions the main part of the product was the ester (60%) (Table II), but many other minor constituents were observed in the gas chromatograms.

Reactions of II. The N,N′-diacyl-N,N′-dialkoxyhydrazines appear to be less stable than the N,N′-dicarbalkoxy-N,N′-dialkoxyhydrazines already reported.[4] Only those hydrazines (see Table I) with an aliphatic group on the acyl part of the molecule were able to withstand shipment to a microanalytical laboratory. In every case in which the acyl group R was aromatic, decomposition commenced during the preparation as evidenced by the evolution of nitrogen gas. An indication of the rate of decomposition is shown in the molecular weight determinations of II in bromoform by freezing point depression (Figure 1). The initial

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[1] Presented in part before the Northwest Regional Meeting of the American Chemical Society, Richland, Wash., June 1967, Abstracts, p 27.

[2] Taken from the Ph.D. theses of M. W. Mosher, University of Idaho, 1967, and M. A. Khan, University of Idaho, 1965.

[3] J. H. Cooley, P. T. Jacobs, M. A. Khan, L. Heasley, and W. D. Goodman, *J. Org. Chem.*, 30, 3062 (1965).

[4] R. J. Crawford and R. Raap, *ibid.*, 28, 2419 (1963).

[5] A coordination compound of I with calcium chloride has been isolated: J. D. McCown, M.S. Thesis, University of Idaho, 1964.

[6] J. Kalvoda, G. Anner, and A. Wettstein, *Helv. Chem. Acta*, 46, 352 (1965).

[7] R. Criegee in "Oxidation in Organic Chemistry," K. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, p 277.

[8] L. P. Kuhn, G. G. Kleinspehn, and Alan C. Duckworth, *J. Am. Chem. Soc.*, 89, 3858 (1967).

Table I. N,N′-Diacyl-N,N′-dialkoxyhydrazines Prepared by Lead Tetraacetate Oxidation

Acyl group	Alkoxy group	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	$Ir_{C=O}$, cm^{-1}
CH_3CO	C_2H_5	72	47.05	7.84	13.72	46.96	7.67	13.66	1730
CH_3CO	C_3H_7	66	51.80	8.35	11.84	51.95	8.83	11.93	1730
CH_3CO	C_4H_9	79	55.40	9.23	10.74	54.87	10.00	10.01	1725
CH_3CO	C_5H_{11}	76	58.31	9.74	9.71	59.43	9.96	9.16	1730
C_2H_5CO	C_3H_7	68	55.38	9.23	10.77	55.57	9.36	10.69	1730
C_2H_5CO	$CH_3CH{=}CHCH_2$	87	59.13	8.35	9.87	60.09	8.83		1740
C_2H_5CO	C_4H_9	79	59.41	9.75	9.71	59.60	9.59	9.49	1730

Table II. Yield[a] of Ester Obtained by Oxidation of RCONHOR′

R	R′	Oxidizing agent	Solvent	Ester, %
CH_3	C_4H_9	Benzoyl peroxide	Benzene	61
		Photolysis	Ether	61
CH_3	C_5H_{11}	LTA[b]-photolysis	Benzene	74
		ACP[b]	Ether-heptane	37
		Photolysis	Ether	69
CH_3	$CH_2{=}CH(CH_2)_3$	LTA	Benzene	80
CH_3	$CH_2{=}CH(CH_2)_2$	LTA	Benzene	76
		ACP	Benzene	80
p-$CH_3C_6H_4$	C_8H_{17}	Silver oxide	Ether	93
p-$CH_3C_6H_4$	C_4H_9	LTA	Benzene	96
C_6H_5	p-$NO_2C_6H_4CH_2$	Cerric sulfate	Water	10
p-$CH_3OC_6H_4$	$CH{\equiv}CCH_2$	LTA	Benzene	76
$(CH_3)_2CH$	C_5H_{11}	LTA	Benzene	89
$(CH_3)_2CH$	C_3H_7	ACP	Benzene	97
		Silver oxide	Ether	91
		Lead dioxide	Benzene	97
		Benzoyl peroxide	Benzene	85
		t-Butyl perbenzoate	Benzene	91

[a] No attempt was made to isolate the hydrazine which was allowed to decompose to the ester. Analysis for the ester was carried out by gas chromatography using the internal standard technique described by Keulemans (A. I. M. Keuelemans, "Gas Chromatography," Reinhold Publishing Corp., New York, N. Y., 1957, p 32). [b] ACP is ammonium hexachloroplumbate(IV). LTA is lead tetraacetate.

value of approximately 230 (calcd for $C_{10}H_{20}N_2O_4$, 232) was observed to decrease to a final reading of approximately 116 (calcd for $C_5H_{10}O_2$, 116). The mechanism considered most reasonable for the decomposition is a series of two first-order reactions (eq 2 and 3), and a plot of volume nitrogen evolved *vs.* time (Figure 2) gives the expected "s" shaped curve.[9] The presence of intermediate VI was not observed directly although infrared, ultraviolet, and nmr measurements were attempted. From the molecular weight data plotted in Figure 3 the value of k_1 was estimated as 6×10^{-3} min^{-1}. All of the change in molecular weight would occur in step one since the nitrogen is evolved and does not contribute to the freezing point depression. The

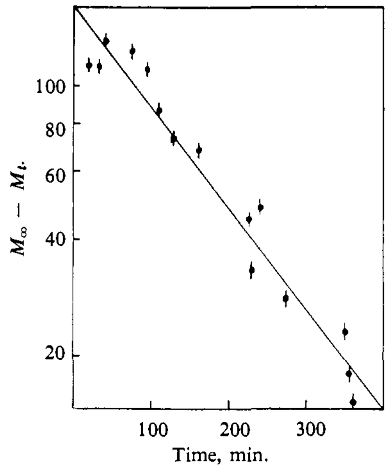

Figure 1. Log $M_\infty - M_t$ *vs.* time for N,N′-diacetyl-N,N′-dipropoxyhydrazine in bromoform at 31.9 ± 0.1°.

$$II \xrightarrow{k_1} \underset{VI}{CH_3CON{=}NOC_3H_7} + CH_3COOC_3H_7 \quad (2)$$

$$VI \xrightarrow{k_2} CH_3COOC_3H_7 + N_2 \quad (3)$$

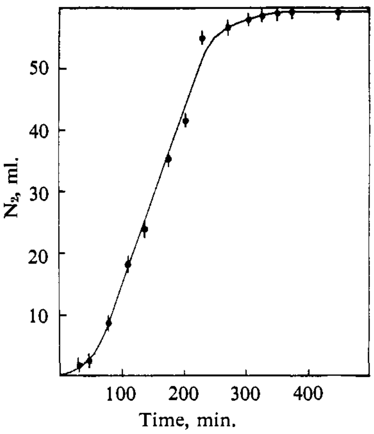

Figure 2. Volume of nitrogen *vs.* time for N,N′-diacetyl-N,N′-dipropoxyhydrazine in bromoform at 31.9 ± 0.1°.

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(9) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 167–171.

Table III. Decomposition of II in Alcohols and Amino Solvents

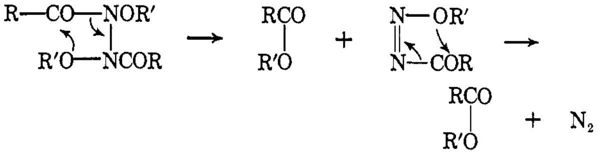
R	R′	Solvent, SH	Catalyst	Temp, °C	R′OH, %	$R{-}\overset{O}{\overset{\|}{C}}{-}OR'$, %	$R\overset{O}{\overset{\|}{C}}{-}S$, %	Others, %
CH_3	C_4H_9	CH_3OH	. . .	68	0	97	0	
CH_3	C_2H_5	CH_3OH	. . .	68	0	88	0	
CH_3	C_3H_7	$C_6H_5CH_2OH$	. . .	25	38	63	0	
CH_3	C_3H_7	$C_6H_5CH_2OH$	. . .	204	39	51	15	22[a]
CH_3	C_3H_7	$C_6H_5NH_2$	. . .	26	48	50	0	
CH_3	C_3H_7	$C_6H_5NH_2$	. . .	184	53	41	38	
CH_3	C_2H_5	NH_3	. . .	−33	. .	. .	70	
C_2H_5	C_4H_7	NH_3	. . .	−33	84	10	85	
C_2H_5	C_4H_7	C_3H_7OH	$NaOC_3H_7$	25	62	2	69	
CH_3	C_3H_7	C_5H_9OH	I_2	25	61	38	50	3[b]
CH_3	C_3H_7	CCl_4	I_2[c]	25	. .	15	. .	71,[d] 3[e]
C_2H_5	C_4H_7	C_3H_7OH	I_2	25	49	29	53	

[a] Acetic acid. [b] Propanal. [c] 4 mol of I_2/mol of hydrazine. [d] Propanal. [e] Propyl propionate.

value of k_2 was estimated to be 1×10^{-2} min^{-1} using the equation

$$C - C_\infty = \frac{A_0}{k_1 - k_2}(k_2 e^{-k_1 t} - k_1 e^{-k_2 t})$$

Either acid (Figure 3) or iodine accelerate the rate of decomposition of II. From Crawford and Raap's work an electrophylic attack of the proton on the alkoxy oxygen, and elimination of alcohol and acylium ion was anticipated. With acid catalysis and in cyclohexanol both the ester containing the alkoxy group of the hydrazine and the ester with the cyclohexyl group of solvent were obtained. A similar result (Table III) was obtained by the decomposition of N,N′-diacetyl-N,N′-dipropoxyhydrazine in boiling benzyl alcohol without acid catalysis. On the other hand, when II was allowed to decompose in refluxing methanol or in benzyl alcohol at room temperature neither the methyl nor benzyl esters were formed. A four-center mechanism, eq 4, would best explain these latter results, while the results with acid catalysis or heat suggest an acylium ion intermediate.



(4)

When iodine was added to II, decomposition was quite vigorous. Halogen was observed to be consumed in these reactions by iodimetric titration. An acylium ion or acid iodide intermediate was suggested by the fact that N,N′-diacetyl-N,N′-dipropoxyhydrazine in cyclopentanol gave propyl acetate, propyl alcohol, propanal, and cyclopentyl acetate (Table III). From this same hydrazine in carbon tetrachloride with excess iodine a high yield of propanal with some propyl acetate, propyl propionate, and hydrogen iodide was obtained. The propanal, propyl propionate, and hydrogen iodide would be explained as arising from propyl hypoiodite which in turn came from a primary decomposition of the hydrazine with iodine. Propyl hypochlorite has been reported to decompose quite rapidly to propionaldehyde and hydrogen chloride,[10] while alkoxy radicals have been shown to give esters.[11] Acetyl chloride was identified in the decomposition of N,N′-diacetyl-N,N′-di-*p*-nitrobenzylhydrazine with chlorine in carbon tetrachloride. Other products include *p*-nitrobenzyl acetate and α,α-di-*p*-nitrobenzyloxy-*p*-nitrotoluene, a product previously reported from a free-radical decomposition of *p*-nitrobenzyl nitrite[12] or from the thermal decomposition of *p*-nitrobenzyl perchlorate.[13] Direct evidence for the hypophalite intermediate came from the ultraviolet spectral measurements which show absorption maxima at 290 and 360 mμ. The absorption maxima of hypoiodites was estimated from reported values of hypochlorites[14,15] to be 290 and 360 mμ. The peak at 290 mμ was observed to be stronger as expected for the hypophalite. The catalysis of decomposition of II by iodine could involve either homolytic or heterolytic mechanisms and could involve a primary attack on either alkoxy oxygen or acyl carbon.

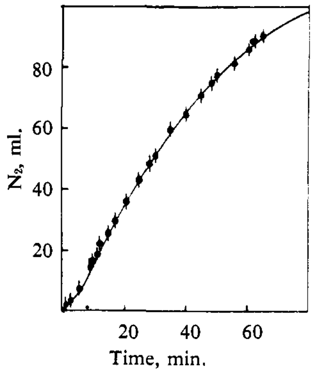


Figure 3. Volume of nitrogen *vs.* time for N,N′-diacetyl-N,N′-dipropoxyhydrazine in 11.5 *M* acetic acid.

Small molecular weight amines such as ammonia, methylamine, and ethylamine reacted violently with II to give the corresponding amide, alcohol, some ester, and nitrogen. On the other hand, with larger amines

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[10] F. D. Chattaway and O. G. Blackberg, *J. Chem. Soc.*, 2999 (1923).

[11] P. Gray, P. Rathbone, and A. Williams, *ibid.*, 3932 (1960).

[12] N. Kornblum and W. M. Weaver, *J. Org. Chem.*, **23**, 1213 (1958).

[13] P. F. G. Praill, *J. Chem. Soc.*, 3162 (1957).

[14] H. E. Ungnada, Ed., "Organic Electronic Spectral Data," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960.

[15] J. J. Custer and S. Natelson, *Anal. Chem.*, **21**, 1005 (1949).

such as dibutylamine or aniline (II) decomposed slowly to the ester and nitrogen. When II was heated to refluxing with aniline, the anilide, alcohol, and ester were obtained. These results would be explained by a nucleophilic attack of the small amines on the acyl carbon atom. Steric factors would appear to be important.

The decomposition of N,N′-dipropionyl-N,N′dibutoxyhydrazine with sodium propoxide occurred with vigor. Butyl propionate, propyl propionate, and butyl alcohol were obtained. As with the amines a nucleophilic attack on the acyl carbon is reasonable.

Reaction of II with oxides of nitrogen or stable free radicals indicated a free-radical mode of decomposition for II. Dinitrogen tetroxide has been found to react as NO^+ and NO_3^- in a heterolytic reaction or as NO_2 in a free-radical reaction. The alkyl nitrite and no alkyl nitrate were observed by reaction of dinitrogen tetroxide with alkoxide ion, while the alkyl nitrate and no alkyl nitrite were observed with the alkoxy radical.[3] Alkyl nitrate and no alkyl nitrite were observed in the reaction of II with dinitrogen tetroxide. The alkyl nitrite was obtained with II and nitrogen monoxide. Triphenylmethyl ethyl ether was obtained from N,N′-diacetyl-N,N-diethoxyhydrazine with triphenylmethyl free radical. These reactions are explained by a free-radical attack of the reagents on the alkoxy oxygen.

Two attempts were made to cleave the N–N bond of II by hydrogenolysis. Reduction of the acyl group occurred from treatment of II with lithium aluminum hydride, and a mixture of alcohols and the normal ester product were obtained. With sodium hydrosulfite, II decomposed in the usual way to the ester and nitrogen. No trace of I was observed in either reaction, and cleavage of the N–N bond did not occur.

Experimental Section

Melting points are all corrected. Microanalyse are due to Dr. A. Bernhardt (Mühlheim, Germany) and Galbraith Laboratories (Knoxville, Tenn.). Infrared spectra were determined with a Perkin-Elmer 137 spectrometer. Ultraviolet and visible spectra were determined with a Beckman DB spectrometer, while nmr spectra were determined with a Varian A-60 spectrometer.

N,N′-Diacetyl-N,N′-diallyloxyhydrazine. General Method for Preparation of II. To a solution of 1.15 g (0.01 mol) of N-acetyl-O-allylhydroxylamine[16] in 15 ml of anhydrous benzene 1.18 g (0.005 mol) of lead tetraacetate was added. The reaction mixture was cooled to room temperature and stirred for 0.5 hr. The inorganic material was removed by filtration, and the organic solution was washed with water and dried. When the solvent was removed by evaporation under reduced pressure, 1.05 g (94%) of a colorless liquid remained. The nmr and infrared spectra were as expected for II. *Anal.* Calcd for $C_{10}H_{16}N_2O_4$: C, 52.63; H, 7.04; N, 12.28. Found: C, 52.39; H, 7.34; N, 12.54.

Molecular Weight of N,N′-Diacetyl-N,N′-dipropoxyhydrazine. The freezing point of freshly distilled bromoform (bp 146° (692 mm)) was determined as 6.90°. To 89.94 g of bromoform was added 0.5384 g of N,N′-diacetyl-N,N′-dipropoxyhydrazine. The freeqing point of 6.51° was determined, and using the equation

$$M = K_f \frac{(\text{grams of solute})(1000)}{\Delta T(\text{grams of solvent})}$$

where $K_f = 14.4$, the molecular weight of 240 (calcd for $C_{10}H_{20}N_2O_4$, 232) was determined. The sample was placed in a constant-temperature bath at 31.9°, and the molecular weight was redetermined at intervals from 1 to 3 hr. The data from four such runs are plotted in Figure 1, and a rate constant at 31.9° was determined to be 6.0×10^{-3} min^{-1} from the slope. Rate constants at 40 and 48° of 7.8×10^{-3} and 8.6×10^{-3} were also observed, and an activation energy of 5 kcal/mol for the reaction was calculated using the equation

$$\log \frac{k_{T_2}}{k_{T_1}} = \frac{H_a(T_2 - T_1)}{2.3RT_2T_1}$$

Gas Evolution from N,N′-Diacetyl-N,N′-dipropoxyhydrazine. The sample was dissolved in a suitable solvent, placed in a constant temperature bath, and connected to a gas buret. The nitrogen was collected over water or 50% potassium hydroxide. In a typical run 1.035 g (0.00446 mol) of the hydrazine evolved 97 ml of gas, and the calculated volume was 100 ml. Data from two runs are plotted in Figures 2 and 3.

Decomposition of N,N′-Diacetyl-N,N′-dibenzylhydrazine in Cyclohexanol with Added Acid. General Method for Reactions in Table III. To a rapidly stirred solution of 1.524 g (0.00461 mol) of the hydrazine in 25 ml of cyclohexanol was added two drops of concentrated sulfuric acid. After 1 hr cyclopentyl acetate was added as an internal standard, and the mixture was analyzed on a 9-ft polypropylene glycol glpc column and found to contain 0.54 g (41%) of cyclohexyl acetate, 0.41 g (41%) of benzyl alcohol, and 0.48 g (35%) of benzyl acetate.

In a control reaction, 1.0 g (0.0067 mol) of benzyl acetate with 15 ml of cyclohexanol and two drops of sulfuric acid was stirred for 1 hr and analyzed as above. The control was found to contain 0.095 g (8%) of cyclohexyl acetate, 0.053 g (7%) of benzyl alcohol, and 0.85 g (85%) of benzyl acetate.

Reaction of N,N′-Diacetyl-N,N′-dipropoxyhydrazine with Nitrogen Monoxide. In 40 ml of chlorobenzene that was purged with nitrogen was placed 1.00 g (0.0043 mol) of the hydrazine. The solution was purged again, and nitrogen monoxide, that had been passed through a Dry Ice trap to remove dinitrogen trioxide, was bubbled in for 5 min. The reaction solution was degassed, and about 0.5 ml of the material was distilled under high vacuum into a Dry Ice trap. The distillate showed infrared, ultraviolet, and nmr spectra identical with propyl nitrite. Analysis of the mixture by glpc showed 0.11 g (15%) of propyl nitrite, 0.038 g (7%) of propyl alcohol, and 0.58 g (67%) of propyl acetate.

Reaction of N,N′-Diacetyl-N,N′-di-*p*-nitrobenzyloxyhydrazine with Nitrogen Dioxide. To 2 g (0.0095 mol) of N-aceto-O-benzylhydroxylamine (C=O at 1670 cm^{-1}) dissolved in 300 ml of boiling chloroform was added 2.25 g (0.005 mol) of lead tetraacetate and a small amount of calcium carbonate. After the mixture had been stirred for 30 min, it was filtered, washed with water, and dried with magnesium sulfate, and the solvent was removed under reduced pressure. A yellow, effervescent oil remained (C=O at 1730 cm^{-1}). The oil was dissolved in 50 ml of chloroform–carbon tetrachloride mixture, and nitrogen dioxide was bubbled into the flask for 10 min. The infrared spectrum of the reaction mixture showed strong absorptions at 1610 and 1370 cm^{-1}. The solvent was removed and fractional crystallization from petroleum ether (bp 30–60°)–ether (1:1) mixture afforded 0.16 g (8.5%) of *p*-nitrobenzyl nitrite, mp 66–71°, and 1.11 g (60%) of *p*-nitrobenzyl acetate, mp 78–79.5°

Reaction of N,N′-Dipropionyl-N,N′-diethoxyhydrazine with Nitrogen Dioxide. Nitrogen dioxide was bubbled into a solution of 1.046 g (0.00488 mol) of the hydrazine in dry xylene for 10 min. The solution was distilled under reduced pressure into a Dry Ice trap. The infrared, ultraviolet, and nmr spectra of the distillate were as expected for ethyl nitrate, and the yield of ethyl nitrate was estimated as 0.069 g (8%) from the nmr spectrum. Analysis by glpc showed 0.018 g (4%) of ethanol, 0.328 g (36%) of ethyl propionate, and a trace of acetaldehyde.

N,N′-Diacetyl-N,N′-diethoxyhydrazine with Triphenylmethyl Free Radical. A benzene solution of triphenylmethyl free radical was prepared from zinc dust and 0.4 g (0.015 mol) of triphenylmethyl chloride in a vacuum line. The triphenylmethyl free radical solution was transferred into an evacuated vessel containing 0.277 g (0.00137 mol) of the hydrazine in 10 ml of benzene, and the mixture was allowed to react for 2 hr at room temperature. Triphenylmethyl ethyl ether (0.038 g, 5%) was isolated by fractional crystallization, and 0.073 g (30%) of ethyl acetate was found using glpc. Upon evaporation, triphenylmethyl peroxide contaminated with a carbonyl compound (C=O at 1750 cm^{-1} in Nujol) remained. The carbon compound could not be separated.

N,N′-Dipropionyl-N,N′-diallyloxyhydrazine with Lithium Aluminum Hydride. A vigorous reaction occurred when 0.90 g (0.0035 mol) of the hydrazine was combined with 0.14 g (0.0035 mol) of lithium aluminum hydride in dry ether. Unreacted lithium aluminum hydride was destroyed, and the ether solution was found

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[16] J. H. Cooley, W. D. Bills, and J. R. Throckmorton, *J. Org. Chem.*, 25, 1734 (1960).

to contain 0.138 g (33%) of 1-propanol, 0.187 g (46%) of allyl alcohol, and 0.185 g (23%) of allyl propionate.

N,N′-Dipropionyl-N,N′-diallyloxyhydrazine with Sodium Hydrosulfite. A solution of 0.50 g (0.00193 mol) of the hydrazine and 1.0 g (0.0048 mol) of sodium hydrosulfite in 15 ml of methanol and 10 ml of water was stirred for 25 min. The reaction mixture was found to contain 0.08 g (26%) of allyl alcohol and 0.28 g (63%) of allyl propionate by glpc.

N,N′-Diacetyl-N,N′-di-*p*-nitrobenzyloxyhydrazine with Chlorine. Chlorine was bubbled into 1.82 g (0.00435 mol) of the hydrazine in 75 ml of 1:1 carbon tetrachloride–chloroform mixture for 30 min. The solution was distilled, and the first 4 ml showed an infrared spectrum identical with acetyl chloride. From the distillate acetamide was prepared by addition of concentrated ammonia. From the residue 0.40 g (31%) of a solid, mp 211.5–213°, shown to be *p*-nitrobenzaldehyde di-*p*-nitrobenzyl acetal[12] and 1.02 g (61%) of *p*-nitrobenzyl acetate were separated.

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The Addition of Trichlorosilane to Cyclic Olefins

Robert A. Benkeser, Stanley Dunny, George S. Li, P. G. Nerlekar,[1] and Stewart D. Work

Contribution from the Chemical Laboratories of Purdue University, West Lafayette, Indiana 47907. *Received September 28, 1967*

Abstract: The addition of trichlorosilane, in the presence of chloroplatinic acid, to 1-, 3-, and 4-ethylcyclohexenes as well as to ethylidene- and vinylcyclohexanes was studied in detail. In every case, the major product was 2-cyclohexylethyltrichlorosilane. In the reaction with the ethylcyclohexenes, the recovered olefin fraction was found to contain all the possible monoolefin isomers except vinylcyclohexane. Contrary to reports, 1-*n*-propylcyclohexene also adds trichlorosilane in the presence of chloroplatinic acid to form 3-cyclohexylpropyltrichlorosilane. The unchanged olefins recovered from this reaction are composed again of a mixture of the various isomers. The above findings now eliminate the necessity for invoking anything but a smooth, consecutive double-bond shift along the chain in these cyclic systems as suggested by the mechanism of Harrod and Chalk. Platinum complexes, like dichlorobis(ethylene)-μ,μ'-dichloro-diplatinum(II) and dichlorobis(ethylcyclohexene)-μ,μ'-dichloro-diplatinum(II), were also effective catalysts in producing terminal adducts in the reaction of 1-ethylcyclohexene with trichlorosilane, while platinum on charcoal was not. This, in conjunction with other qualitative observations which were made, suggests that a soluble platinum complex, rather than platinum metal itself, is the active catalyst in such systems.

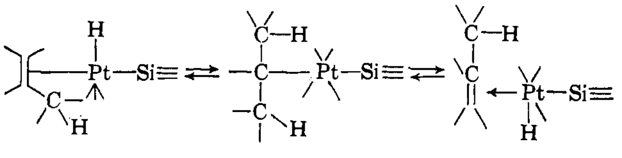
In 1957, Speier and coworkers[2] made the important discovery that certain silicon hydrides, like trichlorosilane, added to 2-pentene in the presence of catalysts like chloroplatinic acid to form the same terminal adduct as that obtained from 1-pentene.

$$\text{1- or 2-pentene} \xrightarrow[\text{H}_2\text{PtCl}_6]{\text{SiHCl}_3} \text{CH}_3(\text{CH}_2)_4\text{SiCl}_3$$

Since the advent of this discovery, numerous papers[3] have appeared relating to the scope of this transformation and the possible mechanism involved.

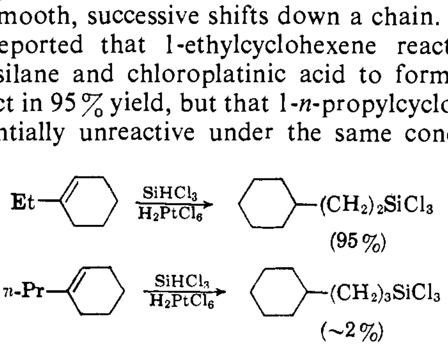
Recently a mechanism was proposed[4] for these reactions which in essence involved the reversible formation of a π complex between the transition metal and the double bond of the olefin, followed by another reversible interconversion between the π complex and a σ complex. The latter would involve a direct bond between the metal atom and one of the carbon atoms composing the original olefin linkage. This mechanism would predict a stepwise migration of the double bond down an alkyl chain by progressive hydrogen shifts *via* the intermediacy of the platinum atom.

The similarity between this mechanism and that proposed for the "oxo" reaction has been pointed out.[5]



Recently it has also been shown that silane additions can be catalyzed by iron pentacarbonyl[6] and a dicobalt octacarbonyl[7] which supports the analogy drawn with the "oxo" process.

It came to our attention that there was at least one report[8] in the literature which suggested that the double-bond migration in such silane additions was not occurring by smooth, successive shifts down a chain. Thus, it was reported that 1-ethylcyclohexene reacts with trichlorosilane and chloroplatinic acid to form terminal adduct in 95% yield, but that 1-*n*-propylcyclohexene was essentially unreactive under the same conditions.



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(1) National Chemical Laboratory, Poona, India.

(2) J. L. Speier, J. A. Webster, and G. H. Barnes, *J. Am. Chem. Soc.*, 79, 974 (1957).

(3) For example, see M. R. Stober, M. C. Musolf, and J. L. Speier. *J. Org. Chem.*, 30, 1651 (1965), and previous papers in this excellent series.

(4) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, 87, 16 (1965).

(5) J. F. Harrod and A. J. Chalk, *ibid.*, 87, 1133 (1965).

(6) A. N. Nesmeyanov, R. Kh. Freidlina, E. C. Chukovskaya, R. G. Petrova, and A. B. Belyavsky, *Tetrahedron*, 17, 61 (1962).

(7) A. J. Chalk and J. F. Harrod, *J. Am. Chem. Soc.*, 87, 1133 (1965).

(8) T. G. Selin and R. West, *ibid.*, 84, 1863 (1962).