Photochemical Initiation of Radical-Chain Addition of Phosphorus Trichloride to Olefins

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Abstract: The ultraviolet irradiation of phosphorus trichloride solutions of olefins has been found to be more efficient than benzoyl peroxide in initiating the radical-chain addition of phosphorus trichloride across the double bond of the olefins. Isobutylene and vinylcyclohexene which are not readily polymerized by the free-radical mechanism yield mainly the 1:1 product. Telomeric products are obtained with polymerizable olefins. Chain-transfer constants determined for vinylidene chloride, styrene, methyl acrylate, allyl acetate, and vinyl acetate are 0.0014, 0.025, 0.10, 1.0, and 1.5, respectively.

Addition of phosphorus trichloride across the double bond of octene-1 to form $C_6H_{13}CHClCH_2PCl_2$ by a free-radical-chain process initiated with acetyl peroxide has been reported by Kharasch, *et al.*[2] However, each mole of acetyl peroxide used as initiator yielded only 2.3 moles of product. An attempt by the authors to add phosphorus trichloride across the double bond of isobutylene or of ethylene with benzoyl peroxide as initiator also resulted in a low yield of olefin addition product. It seems likely that the low yield may be due to consumption of the peroxide initiator by a reaction with phosphorus trichloride which does not form active free radicals. The use of ultraviolet light as a more efficient initiator of the chain-addition reaction is reported here.

Phosphorus trichloride shows continuous absorption in the ultraviolet region and its photolysis into $Cl\cdot$ and $\cdot PCl_2$ radicals has been proposed.[3] Thus phosphorus trichloride under ultraviolet irradiation in the presence of an olefin should serve as free-radical source as well as the solvent and chain-carrying reagent in the free-radical-chain reaction.

Results

The ultraviolet irradiation of a phosphorus trichloride solution of isobutylene or of vinylcyclohexene yields mainly the 1:1 addition products $ClC_4H_8PCl_2$ and $ClC_8H_{12}PCl_2$, respectively. Small amounts of higher boiling material left as residue from distillation of the 1:1 addition products may contain telomers formed by the addition of phosphorus trichloride across two or more units of the monomer. Thus the olefins isobutylene, vinylcyclohexene,[4] and octene-1,[2] which do not readily polymerize by free-radical reactions, do react readily with phosphorus trichloride to yield the 1:1 addition product.

The ultraviolet irradiation of a solution of vinylidene chloride, styrene, or methyl acrylate in phosphorus trichloride yields mainly the telomeric products $Cl(C_2H_2Cl_2)_nPCl_2$, $Cl(C_8H_8)_nPCl_2$, and $Cl(C_5H_8O_2)_nPCl_2$, respectively. The phosphorus trichloride solution of allyl acetate or of vinyl acetate yields a mixture of 1:1 addition and telomeric products. Little or no product was obtained by ultraviolet irradiation of a phosphorus trichloride solution of allyl chloride, maleic anhydride, diethyl maleate, or 1,1,1-trichloropropene-2.

To determine what factors affect the yield of product from the isobutylene–phosphorus trichloride reaction, a series of reactions were run using an Hanovia H-3 high-pressure mercury arc lamp (100 w.) placed in a Corex glass well in the center of the reagent solution (see Figure 1). Little or no product was formed in the absence of the ultraviolet light (diffuse daylight part of the time). By irradiation for 20 hr. at 40°, 32 g. of crude product was obtained (see experiment 2, Table IA).

Table I

Expt. no.	Temp., °C.	Pressure, mm.	Time, hr.	Crude yield, g.	Average rate, g./hr.
A. Batch process: isobutylene/PCl_3 mole ratio = 0.17					
1	60	1430	19.3	43	2.2
2	40	1000	20	32	1.6
3	40	1000	20	39[a]	2.0[a]
4	40	1000	20	33[b]	1.7[b]
5	15	520	20	20	1.0
6	40	1000	7	26	3.7
7	40	1000	70	34	0.5
B. Continuous process: isobutylene/PCl_3 > 0.17					
8	10[c]	900	26.8	111	4.2
9	37[c]	1050	34	256	7.5

[a] Water added (0.2% on PCl_3). [b] Reactor evacuated and recharged after every 5 hr. with fresh isobutylene. [c] Temperature of well cooling water. Reaction temperature was probably between this and room temperature.

Addition of 0.2% water to the phosphorus trichloride did not inhibit the reaction but surprisingly increased the yield to 39 g. (experiment 3). That the product obtained here was mainly the same 1:1 addition compound was determined by distilling and isolating 33 g. of this material. Raising the temperature to 60° increased the yield to 43 g. (experiment 1) and lowering the temperature to 15° dropped the yield to 20 g. (experiment 5). Extending the irradiation time to 70 hr. did not increase the yield (experiment 7) while 25.5 g. of crude product was obtained after only 7 hr. (experiment 6). Apparently the reaction was gradually stopped by some autoinhibiting effect. This effect was not produced by a gaseous product which gradually replaced the isobutylene. This was shown by evacuating the gases and re-

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[1] W. R. Grace Co., Polymer Chemicals Division, Clifton, N. J.

[2] M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Am. Chem. Soc.*, 67, 1864 (1945); U. S. Patent 2,489,091 (1949).

[3] H. Trivedi, *Chem. Abstr.*, 28, 1272 (1934).

[4] E. C. Ladd and J. R. Little, U. S. Patent 2,510,699 (1950).

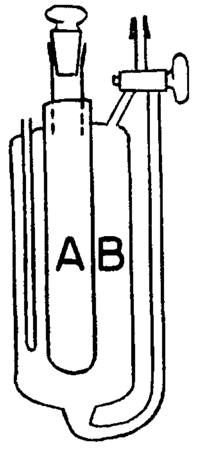


Figure 1. Batch reactor: A, Corex D glass well; B, Pyrex glass irradiation vessel.

charging with fresh isobutylene at approximately 5-hr. intervals during a 20-hr. run which yielded 33 g. of crude product (experiment 4). The cause or a contributor to the autoinhibition effect may have been a brown film which was deposited on the walls of the Corex glass well containing the mercury lamp.

In an attempt to eliminate the autoinhibiting effect and the formation of a film on the well, the reaction was run in a semicontinuous process in which isobutylene and phosphorus trichloride were continuously passed over an irradiation well which was cooled with a water jacket. The product was accumulated in a pot from which the reagents were distilled, condensed, and passed back over the irradiation well (see Figure 2). In a 26.8-hr. run with the well jacket water at 10° the crude yield was 111 g. (experiment 8, Table IB). In a 34-hr. run with the well at 37° the crude yield was 255 g. (experiment 9). Thus the increased yield at higher temperature is again demonstrated. At the lower temperature a white film was deposited on the well, but at the higher temperature no film was observed.

In addition to the high-boiling crude product obtained as a residue after distilling off phosphorus trichloride, experiment 9 also yielded 16 g. of *t*-butyl chloride which was isolated by redistilling the phosphorus trichloride forerun.

Distillation of the crude high-boiling product from experiment 9 showed that approximately 85% consisted of the 1:1 addition product. Analysis of the 1:1 addition product fractions by proton magnetic resonance showed that they consist of both possible addition isomers, 2-chloro-2-methylpropyldichlorophosphine (III) and 1-chloro-2-methylisopropyldichlorophosphine (IV). Also present in the first fractions of the distillate were the two isobutenyl isomers, methallylphosphine dichloride (VII) and 2-methylpropenylphosphine dichloride (VIII). The estimated composition of the 1:1 product is 37% III, 50% IV, 3% VII, and 10% VIII.

Discussion

The quantity of light absorbed by phosphorus trichloride (the portion of Hanovia H-3 light transmitted by Corex D glass up through the 2967-Å. line) is estimated at 0.003 einstein/hr. Yields of the phosphorus trichloride–isobutylene addition product approaching 13 moles/einstein absorbed have been obtained by photochemical initiation at a temperature somewhat below 37°. There are indications that a higher yield may be obtained at higher temperatures. The effect of reagent ratio was not investigated. The autoinhibiting effect observed in the batch process is at least reduced by means of a continuous process in which the high-boiling products of the reaction are removed from the irradiated zone.

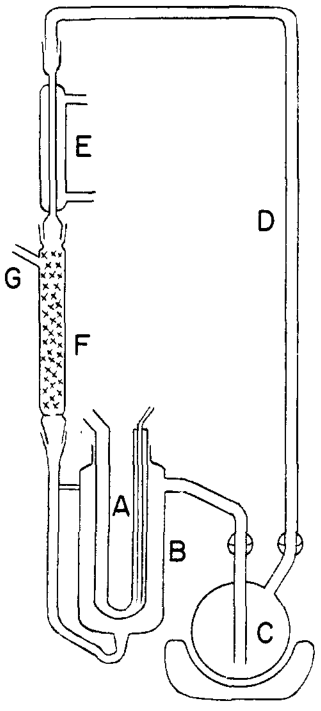
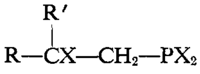
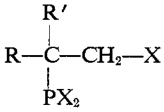


Figure 2. Continuous reactor: A, Corex D glass well with water cooling jacket; B, Pyrex glass irradiation vessel; C, distillation pot; D, fractionating column; E, condenser; F, gas absorption vessel; G, gas inlet.

Kharasch[2] assumed that the chain-carrying radical in the transfer step was the ·PCl_2 radical and that the product from octene and phosphorus trichloride had the structure I (where R is C_6H_{13}, R′ is H, and X is Cl).


$$\mathrm{R{-}\overset{R'}{C}X{-}CH_2{-}PX_2}$$
I


$$\mathrm{R{-}\underset{PX_2}{\overset{R'}{C}}{-}CH_2{-}X}$$
II

Recently Fontal and Goldwhite[5] have reported that in the free-radical-chain addition of phosphorus tribromide to propylene, both products I and II are formed (where R is CH_3, R′ is H, and X is Br) and have proposed that both Br· and ·PBr_2 are chain-carrying radicals.

Analysis of the proton magnetic resonance spectrum of the 1:1 addition product of phosphorus trichloride to isobutylene from experiment 9, fraction 2 indicates that both products III and IV are present. The products obtained by Kharasch, *et al.*,[2] with octene and by Ladd and Little[4] with vinylcyclohexene may also be mixtures of the two isomeric products of type I and II.

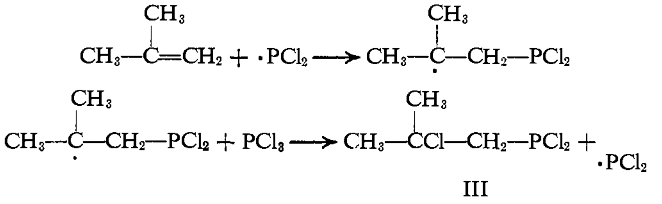
(5) B. Fontal and H. Goldwhite, *Chem. Commun.* (London), [6], 111 (1965).

The nuclear magnetic resonance spectrum of fraction 1 from the distillation of the 1:1 addition products from experiment 9 shows that, in addition to the isomeric products III and IV, there are also present two olefinic products. The n.m.r. spectrum and the low chlorine analysis for this fraction are consistent with the structures VII and VIII for these olefinic products. Isobutenylphosphorus dichloride (or possibly a mixture of the above isomers) has previously been prepared by Walsh, *et al.*,[6] from the reaction of phosphorus pentachloride on isobutylene followed by reduction with yellow phosphorus.

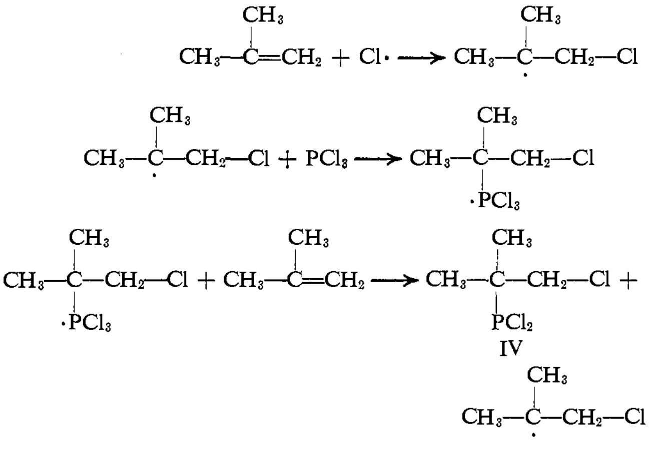
If both Cl· and ·PCl_2 radicals are chain carriers as per the Fontal and Goldwhite[5] proposal, the following reactions would account for the observed products.

Initiation: $PCl_3 \xrightarrow{h\nu} Cl\cdot + \cdot PCl_2$

Transfer by ·PCl_2:

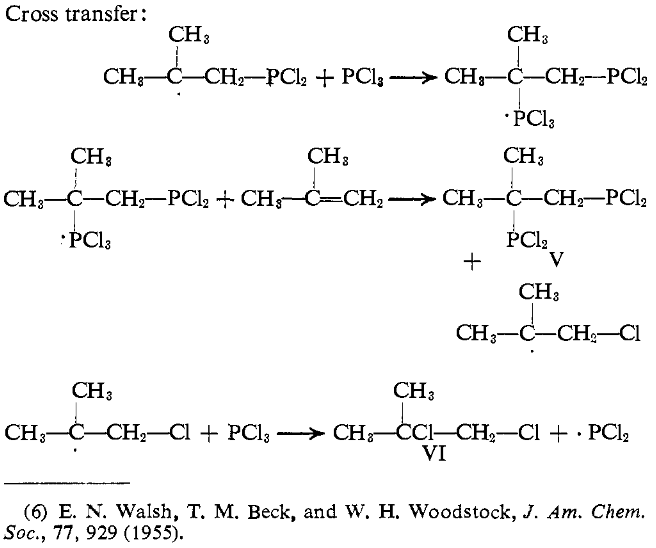


Transfer by Cl·:



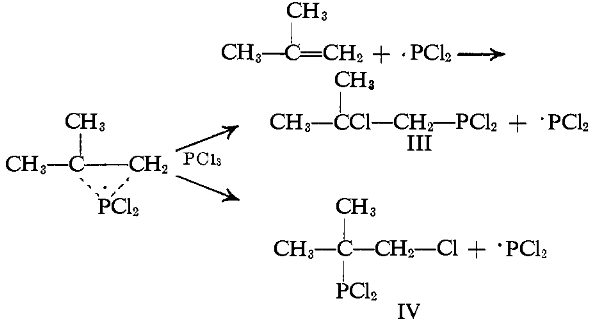
However, if these reactions occur, then one should expect that cross-transfer reactions should also occur to form products V and VI. These cross-transfer products were not isolated from the reaction. However, it is possible that the diphosphine V could have been present in the high-boiling residue along with telomeric products and the dichloride VI could have been in the phosphorus trichloride fraction or in the forerun of the 1:1 product fraction. The presence of small amounts of these cross-transfer products would not have been observed.

Cross transfer:

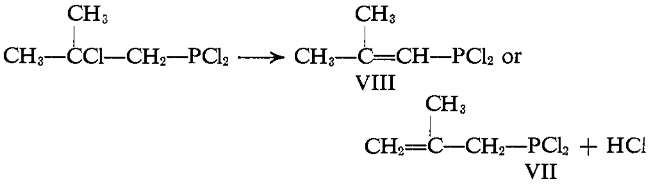


The formation of the two possible 1:1 addition products of phosphorus trichloride and olefin and the absence of cross-transfer products can be accounted for by a bridged radical intermediate which could react with phosphorus trichloride to form either product III or IV.

Transfer by bridged radical:



The olefinic products VII and VIII could be formed by thermal decomposition of compound III to split out hydrogen chloride. Hydrogen chloride has been shown to react readily with isobutylene to form *t*-butyl chloride.[7] The moles of *t*-butyl chloride isolated is approximately equal to the sum of the moles of products VII and VIII isolated.



The relative rate of combination of monomer and solvent dM/dS was determined for the reactions producing telomeric products from the analysis of the total product for chlorine or phosphorus. From this and from the ratio of monomer and solvent in the reaction mixture, M/S, transfer constants, C_s, have been calculated for these monomers in phosphorus trichloride using the equation according to Walling.[8] These

$$dM/dS = 1/(C_s) + 1$$

transfer constants, arranged in Table II in the order of increasing values, are given with the reservation that the last four have been calculated from products in the low molecular weight range where chain transfer has been observed to vary appreciably with radical chain length.[9] These transfer constants with phosphorus trichloride are in the general range and in the approximate order of transfer constants with carbon tetrachloride.[10]

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(6) E. N. Walsh, T. M. Beck, and W. H. Woodstock, *J. Am. Chem. Soc.*, 77, 929 (1955).

(7) F. R. Mayo and J. J. Katz, *ibid.*, **69**, 1339 (1947).

(8) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 153.

(9) F. R. Mayo, *J. Am. Chem. Soc.*, 70 3689 (1948); J. R. Little, C. H. Stiteler, F. O. Guenther, and F. R. Mayo, unpublished work from this laboratory.

(10) J. R. Little, unpublished information from this laboratory.

Table II[a]

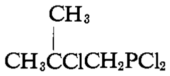
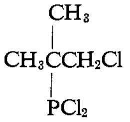
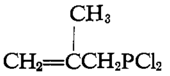
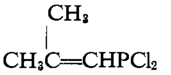
Monomer	Monomer charge, g.	M/S	Temp., °C.	Time, hr.	Product, g.	Anal., %	dM/dS	C_s
Vinylidene chloride	51.5	0.25[b]	60	17.5	35	0.29 (P)	109	0.0014
Styrene	36.4	0.10[c]	57	20	10	17.2 (Cl)	4.6	0.025
Methyl acrylate	26.0	0.10	40	17.5	6	34.1 (Cl)	2.0	0.10
Allyl acetate	100	0.50	40	64	31	37.4 (Cl)	1.5	1.0
Vinyl acetate	100	0.50	60	64	25	42.5 (Cl)	1.3	1.5

[a] M/S is initial monomer solvent ratio in feed. dM/dS is monomer solvent ratio in product. C_s is transfer constant. Reaction was initiated by ultraviolet irradiation except with vinylidene chloride where 2.0 g. of azobisisobutyronitrile was used. [b] Average value 0.15 used in calculation of transfer constant. [c] Average value 0.09 used in calculation of transfer constant.

Table III

Expt. no.	% Cl found	n^{20}D	B.p., °C. (mm.)
1	54.9	1.5075	80–81 (19)
3		1.5095	67–68 (9)
6	54.7	1.5109	63–66 (8)
7		1.5078	57–58 (5)
9(1)	48.9	1.5159	
(2)	53.4	1.5133	83 (20)

Table IV. N.m.r. Spectra[a]

Compd.	Structure	Group	δ	J_{MeP} (or J_{CH_2P})	Compn., %
III	 $CH_3\overset{CH_3}{\overset{\vert}{C}}ClCH_2PCl_2$	CH_3	1.76	1.5	36
		CH_2	3.06	7.2	
IV	 $CH_3\underset{PCl_2}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}CH_2Cl$	CH_3	1.33	15.7	51
		CH_2	3.77	5.0	
VII	 $CH_2{=}\overset{CH_3}{\overset{\vert}{C}}CH_2PCl_2$	CH_3	1.9	3	3
		CH_2—P	3.14	13.3	
		CH_2=C	4.98		
VIII	 $CH_3\overset{CH_3}{\overset{\vert}{C}}{=}CHPCl_2$	CH_3	1.97	1.4	10
		CH_3	2.07	1.6	
		CH	6.25		

[a] 56.4 Mc./sec.; p.p.m. downfield from Me_4Si = 0.

Experimental Section

Phosphorus trichloride–isobutylene batch process experiments were run in a cylindrical Pyrex glass vessel of 4 cm. o.d. equipped with a Corex D glass well of 2.0 cm. o.d., a thermometer well, an inlet at either top or bottom for gases, and an opening for charging and removing liquids (Figure 1). An Hanovia H-3 high-pressure mercury 100-w. lamp with the outer glass covering removed was used for irradiation. Temperature of the reaction was regulated by immersing the reactor in a constant temperature water bath and measured in the reactor thermometer well. The reactor was charged with about 500 g. of redistilled phosphorus trichloride, evacuated until the liquid charge began to boil, and then pressured from the bottom with isobutylene (Matheson Co.). The pressure–temperature relationship found for a charge of 35.2 g. of isobutylene and 517 g. of phosphorus trichloride (0.17 mole ratio) was 1430 at 60°, 1000 mm. at 40°, and 650 mm. at 22°. Pressure was kept approximately constant during the reaction by admitting more isobutylene at intervals. After the specified irradiation time, the excess phosphorus trichloride was removed by atmospheric pressure distillation through a 2-ft. Vigreux column. Then the product was transferred to a small flask equipped with a 1-ft. Vigreux column of small bore, and the remaining phosphorus trichloride was removed by vacuum distillation. The residue was taken as the crude yield. Subsequent distillation of product from several of the experiments showed that the crude product was essentially free of phosphorus trichloride.

Phosphorus trichloride–isobutylene continuous process experiments were run in a cylindrical Pyrex glass reactor of 5.3 cm. o.d. equipped with a 4.4-mm. o.d. well and water-cooling jacket both of Corex D glass, an inlet at the bottom, and an overflow outlet at the top (Figure 2). The mercury lamp used for the batch experiments was also used here. The reactor overflow extended to the bottom of a distillation flask. An open column above the flask carried isobutylene and phosphorus trichloride distillate to the top of a water-cooled condenser and the condensate flowed through a gas absorption column filled with glass beads to the bottom of the reactor. A gas inlet at the top of the gas absorption column was used to introduce isobutylene. Temperature was controlled by the water flowing through the irradiation well jacket. The apparatus was charged with 250 to 350 ml. of redistilled phosphorus trichloride, about 100 ml. being required to fill the reactor and the remainder overflowing into the distilling flask. After evacuating and flushing the system twice with isobutylene gas, the distilling flask was heated to distill phosphorus trichloride through the reactor, isobutylene was introduced to the desired pressure, and the lamp was turned on. The crude yield was determined as in batch experiments above.

Distillation of the crude product from various experiments yielded 5–10% of a forerun, 5–10% of a residue, and 80–90% of the 1:1 addition product $ClC_4H_8PCl_2$. The product from experiment 9 appeared to contain in addition appreciable amounts of $C_4H_7PCl_2$ (see Table III). *Anal.* Calcd. for $C_4H_8PCl_3$: Cl, 55.1. Calcd. for $C_4H_7PCl_2$: Cl, 45.2.

The isomeric products in fractions 1 and 2 of experiment 9 were identified and their approximate amounts were established from their proton magnetic resonance spectra at 56.4 Mc./sec. (see Table IV). Essentially only the saturated products appeared in the spectrum for fraction 2 and both showed doublets for methyl and for methylene groups. The isomers were distinguished by assigning the smaller constant J_{MeP} = 1.5 c.p.s. to the compound with methyl most remote from phosphorus. Both unsaturated isomers appeared in the spectrum from fraction 1 along with both saturated isomers. The unsaturated isomers were distinguished by assigning the multiplet at δ = 6.25 p.p.m. to CH. The intensity of the two equal methyl doublets at δ = 1.97 and 2.07 p.p.m. corresponded to the intensity of this multiplet. Also the lower intensity of the methyl and methylene doublets for compound VII corresponded to the low intensity of the multiplet at $\delta = 4.98$ p.p.m. for $CH_2{=}C$.

There was also obtained 16 g. of *t*-butyl chloride, b.p. 50–54°, from experiment 9 in which 255 g. of crude, high-boiling product was obtained.

The phosphorus trichloride–vinylcyclohexene experiment was run in the batch process apparatus described above. A charge of 51.5 g. of vinylcyclohexene, freshly washed with ferrous sulfate solution and distilled over sodium and 385 g. of redistilled phosphorus trichloride, was flushed with nitrogen and then irradiated for 16 hr. at 55°. Unreacted reagents were removed by distillation at atmospheric pressure. Vacuum distillation yielded 20 g. of 1:1 product, b.p. 104–120° (4 mm.), $n^{20}\text{D}$ 1.5475. *Anal.* Calcd. for $C_8H_{12}Cl_3P$: Cl, 43.4; P, 12.6. Found: Cl, 42.5; P, 12.7. The higher boiling product left as a residue amounted to 4 g.

Phosphorus trichloride reactions with the olefins listed in Table II and with those reported above to yield little or no product were run in the batch apparatus in a manner similar to the experiments with isobutylene and vinylcyclohexene above except that product residues after removal of unreacted reagents were not distilled. An attempt to distill a portion of the phosphorus trichloride–vinyl acetate product under vacuum resulted in decomposition.

Amination of Alkylbenzenes with Trichloramine–Aluminum Chloride. Synthetic Utility and Theoretical Aspects[1,2]

Peter Kovacic, Joseph A. Levisky, and Christian T. Goralski[3]

Contribution from the Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106. *Received August 17, 1965*

Abstract: Direct amination of monoalkylbenzenes with trichloramine in the presence of aluminum chloride provided *m*-alkylanilines as the predominant basic product. Yields varied from <5% for diphenylmethane to 53% for isopropylbenzene. *o*-Xylene gave a basic mixture consisting of 2,3-xylidine (57%) and 3,4-xylidine (43%). 3,5-Xylidine was obtained from *m*-xylene, and 2,5-xylidine from *p*-xylene. Pseudocumene provided a mixture of amines containing mainly 2,3,5-trimethylaniline. Only small amounts of mesidine were formed from mesitylene, in addition to 2,3,5-trimethylaniline. The amination reaction proves to be synthetically useful for the preparation of certain *m*-alkylanilines. Further mechanistic information, particularly in relation to steric factors, is provided for this novel reaction which is believed to proceed by σ-substitution.

The literature dealing with aromatic amination by halamines is quite sparse. Minisci and Galli[4] reported that amination of anisole with N-chloropiperidine and ferrous salt produces *p*-piperidinoanisole. Benzimidazoles are obtained from N-arylamidines by treatment with sodium hypochlorite and base.[5] The N-chloroamidine is presumed to be the intermediate involved in cyclization. Other pertinent references have been discussed previously.[6]

Recent reports from this laboratory revealed that direct amination of aromatic compounds with halamines in the presence of a Lewis acid catalyst represents a new method of aromatic substitution (σ-substitution) resulting in unusual orientation.[6,7] For example, toluene–trichloramine–aluminum chloride produced *m*-toluidine. The present study involves the alkylbenzene series with emphasis on synthetic utility and mechanistic aspects.

Results and Discussion

Reactions of trichloramine with alkylbenzenes were generally carried out in the presence of large amounts of aluminum chloride ($AlCl_3/NCl_3$ molar ratio of 2). A solution of trichloramine in *o*-dichlorobenzene was added slowly to a heterogeneous mixture of the catalyst and aromatic hydrocarbon at 10° (Table I). Benzene afforded aniline in 20% yield.

In the case of the monoalkylbenzenes, the corresponding *m*-alkylaniline constituted the principal basic product. This is in accord with the previous studies involving toluene.[6] The isolated amines are shown in the order of decreasing yield: *m*-isopropylaniline (*m*-cumidine) (53%), *m*-toluidine (36%), *m*-ethylaniline (31%), *m-sec*-butylaniline (29%), *m-n*-propylaniline (28%), *m-n*-butylaniline (18%), *m-t*-butylaniline (8%), *m*-cyclohexylaniline (<5%), 3-aminodiphenylmethane (<5%), and 3-aminobibenzyl (<5%).

With higher alkylbenzenes, the indicated results were obtained: 3,5-dimethylaniline (23%) from *m*-xylene; 2,5-dimethylaniline (22%) from *p*-xylene; 2,3-dimethylaniline (16%) and 3,4-dimethylaniline (12%) from *o*-xylene. Pseudocumene provided a mixture of bases containing mainly 2,3,5-trimethylaniline (13%). Amination of mesitylene led to formation of mesidine (2%) and 2,3,5-trimethylaniline (6%).

We have been unable to formulate a reasonable, over-all correlation between aromatic structure and yield. Various factors should be taken into account: resonance, induction, dielectric constant, solvation, polarity, etc. An important consideration may be the speed of the competing chlorination reaction which can destroy N-halamines.

$$3C_6H_5R + NCl_3 \xrightarrow{AlCl_3} 3ClC_6H_4R + 3HCl + NH_3 \qquad (1)$$

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(1) Paper II, Aromatic Amination with Halamines: presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

(2) Taken largely from the M.S. Thesis (1965) of J. A. L.

(3) National Science Foundation Undergraduate Summer Fellow, 1964.

(4) F. Minisci and R. Galli, *Tetrahedron Letters*, No. 8, 433 (1965).

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