

ADDITION OF TETRACHLOROMETHANE TO 1,5-HEXADIENE

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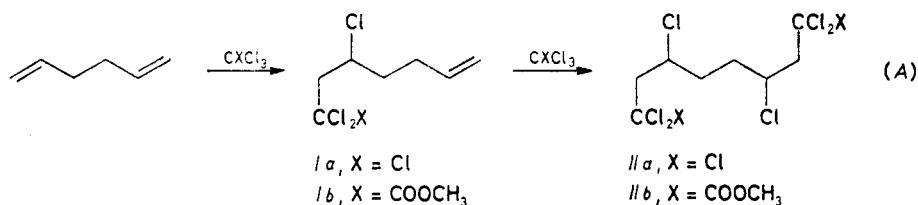
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The 2 : 1 adduct as the final product of the addition of tetrachloromethane to 1,5-hexadiene catalyzed by copper(I)-butylamine complex was obtained in high yield (96%) under mild reaction conditions. Predominant 1 : 1 adduct formation was observed in the presence of a palladium catalyst or dibenzoyl peroxide initiator.

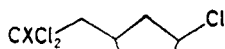
Addition reactions of 1,5-hexadiene with different polyhalogenated compounds including CCl_4 (refs¹⁻⁸), CBr_4 (ref.⁶), $\text{CCl}_3\text{COOCH}_3$ (ref.⁹), $\text{P}(\text{O})\text{Cl}_2\text{CCl}_3$, $\text{P}(\text{S})\text{Cl}_2$, CCl_3 , $\text{P}(\text{O})(\text{OC}_6\text{H}_5)\text{ClCCl}_3$ (all ref.²) and perfluoroalkyl iodides^{10,11} have been reported. The course of the additions catalyzed by CuCl (refs^{1,2,9}), CuCl_2 (ref.⁹), CuO (ref.⁸), $\text{Cr}(\text{CO})_3(\text{C}_{10}\text{H}_8)$ (ref.⁴), $\text{RuCl}_2(\text{PPh}_3)_3$ (ref.³), $\text{Pd}(\text{PPh}_3)_4$ (refs^{7,11}), Me_3Al (ref.⁷), FeCl_3 (ref.⁹), $\text{Fe}(\text{CO})_5$ (refs^{5,6}), Ra-Nickel (ref.¹⁰) or initiated by azo bis-isobutyronitrile⁶ indicates formation of different reaction products. In general, the reaction may proceed as the monoaddition or diaddition, providing the 1 : 1 (*I*) and 2 : 1 (*II*) adducts (Eq. (A)), respectively.



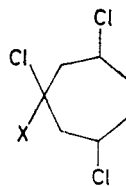
In some cases 1 : 1 (refs^{4-6,8,10,11}) or 2 : 1 adducts⁷ were reported as the final products, while formation of a mixture of 1 : 1 and 2 : 1 adducts was reported by other authors^{1-3,5,9}. Moreover, the formation of cyclic products *III* and *IV* was also sometimes observed^{2,9}, indicating the tendency of some intermediates to undergo intramolecular cyclization.

Previously, we reported the exclusive formation of 1 : 1 adduct *Ia* using CuO-diethylamine catalytic system⁸. The present work is concerned with the diaddition

reaction with respect to the preferential formation of 2 : 1 adduct *Ila* achieved by modification of the catalyst.



III



IV

EXPERIMENTAL

Materials. Tetrachloromethane (Lachema, Brno), 1,5-hexadiene and butylamine (Fluka, Buchs) were distilled prior to use. (Tetrakisacetone)nitrile)copper(I) perchlorate was prepared according to the known procedure¹². The other chemicals were used as obtained.

Analytical methods. GC analysis of the products and reaction mixtures was carried out on HP-4890A instrument equipped with HP Ultra-1 capillary column. Product yields were calculated from GC data using undecane as an internal standard. ¹H and ¹³C NMR spectra of the products were recorded on Varian XL 200 spectrometer. Mass spectra were recorded on Shimadzu QP-100 mass spectrometer.

The addition catalyzed by copper(I)-butylamine complex. The mixture of 32.7 mg (0.1 mmol) of Cu(CH₃CN)₄ClO₄, 820 mg (10 mmol) of 1,5-hexadiene, 156 mg (1 mmol) of undecane and 20 ml of tetrachloromethane was placed in 30 ml glass ampoule equipped with the septum and a magnetic stirrer. The stirred reaction mixture was heated to 80°C under nitrogen and 29.2 mg (0.4 mmol) of butylamine were injected through the septum. Then butylamine was continuously added during 5 h in a total amount of 160 mg (2.2 mmol). The samples of the reaction mixture were analyzed by GC in 30 minute-intervals after treatment with dilute hydrochloric acid (10%). GC analysis of the final reaction mixture showed 96.1% yield of adduct *Ila* and the total conversion of 1,5-hexadiene. Only a small amount (1.7%) of compound *Ia* was detected.

A similar procedure was used for preparation of a mixture of adducts *Ia* and *Ila*. Column chromatography was used for their separation and purification.

5,7,7,7-Tetrachloro-1-heptene (Ia). ¹H NMR (δ): 5.03–5.07 m, 2 H (CH₂=); 5.7–5.9 m, 1 H (—CH=); 2.2–2.4 m, 2 H (H-3); 1.8–2.1 m, 2 H (H-4); 4.25–4.32 m, 1 H (—CHCl—); 3.08–3.29 m, 2 H (H-6). ¹³C NMR (δ): 116.15 (CH₂=); 136.35 (—CH=); 30.13 (C-3); 38.05 (C-4); 56.94 (—CHCl—); 62.26 (C-6); 96.79 (CCl₃). MS (*m/e*, %): 199 (C₇H₁₀Cl₃, 10); 163 (C₇H₉Cl₂, 15); 127 (C₇H₈Cl, 33); 109 (C₃H₃Cl₂, 22); 67 (C₅H₇, 80); 55 (C₄H₇, 100); 41 (C₃H₅, 83).

1,1,1,3,6,8,8-Octachlorooctane (IIa). ¹H NMR (δ): 3.1–3.4 m, 2 H (H-2 and H-7); 4.0 to 4.5 m, 1 H (H-3 and H-6); 1.8–2.5 m, 2 H (H-4 and H-5). ¹³C NMR (δ): 96.46 (CCl₃); 62.10 and 62.28 (C-2 and C-7); 56.47 and 57.03 (—CHCl—); 35.19 and 35.68 (C-4 and C-5). MS (*m/e*, %): 351 (C₈H₁₀Cl₇, 1); 315 (C₈H₉Cl₆, 22); 279 (C₈H₈Cl₅, 18); 243 (C₈H₇Cl₄, 29); 219 (C₇H₇Cl₄, 23); 183 (C₆H₆Cl₃, 24); 143 (C₃H₂Cl₃, 55); 117 (CCl₃, 16); 109 (C₃H₃Cl₂, 160).

The addition initiated by dibenzoylperoxide. The mixture of 121 mg (0.5 mmol) of dibenzoyl peroxide, 820 mg (10 mmol) of 1,5-hexadiene, 156 mg (1 mmol) of undecane and 20 ml of tetra-

chloromethane was heated to 80°C in 30 ml glass ampoule under nitrogen for 5 h with stirring and then analyzed by GC; the mixture contained products *Ia* in 55.4% and *Ila* in 14.1% yield, respectively.

The addition catalyzed by palladium acetate-triphenylphosphine system. The mixture of 4.5 mg (0.02 mmol) Pd(OAc)₂, 10.5 mg (0.04 mmol) PPh₃, 5.5 mg (0.04 mmol) K₂CO₃, 82 mg (1 mmol) 1,5-hexadiene, 62.5 mg (0.4 mmol) undecane and 4 ml tetrachloromethane was heated to 80°C in 5 ml glass ampoule under nitrogen with stirring. Composition of reaction mixture was analyzed by GC after treatment with silica gel. The reaction ended after 2.5 h when no changes in the composition of the reaction mixture were observed. Products *Ia* and *Ila* were obtained in 35.7% and 5.0% yield, respectively.

RESULTS AND DISCUSSION

The addition of tetrachloromethane to 1,5-hexadiene was studied from the point of view of the formation of 1 : 1 and 2 : 1 adducts (*Ia*, *Ila*) in dependence on the

TABLE I
Product yields in the addition of tetrachloromethane to 1,5-hexadiene at 80°C

Catalyst	Reaction time, h	Yield, % ^a	
		<i>Ia</i>	<i>Ila</i>
Cu(CH ₃ CN) ₄ ClO ₄ -BuNH ₂	5	1.7	96.1
Pd(OAc) ₂ -PPh ₃ -K ₂ CO ₃	2.5	35.7	5.0
Bz ₂ O ₂	5	55.4	14.1

^a Determined by GC analysis.

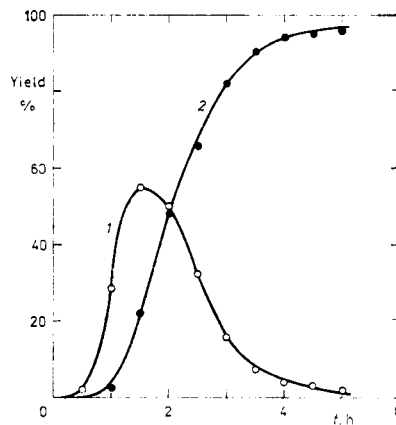


FIG. 1

The course of the addition of tetrachloromethane to 1,5-hexadiene catalyzed by copper(I) complex. 1 adduct *Ia*, 2 adduct *Ila*

type of the catalyst. The course of the addition was examined in detail in the presence of the copper(I)-butylamine complex ($\text{Cu}(\text{BuNH}_2)_2\text{ClO}_4$), which was the very efficient and selective catalyst. The catalyst was generated in situ from (tetrakisacetonitrile)copper(I) perchlorate by adding butylamine in excess.

The results obtained are presented in Fig. 1 which shows typical course of consecutive reactions, 1 : 1 adduct *Ia* being the intermediate. Thus, at the end of the reaction the 2 : 1 adduct *Iia* was formed in high yield (96.1%) as the final product. For comparison, additional experiments with palladium catalyst¹³ and dibenzoyl peroxide were carried out. In the presence of palladium catalyst or dibenzoyl peroxide initiator the predominant formation of 1 : 1 adduct *Ia* was observed, up to 35.7% and 55.4% yields, respectively, evidently due to their lower activity (Table I). The 2 : 1 adduct *Iia* was a minor product (5% and 14.1% yield, respectively).

The attention was also paid to the possibility of intramolecular cyclization of intermediates. The formation of cyclic products *IIIa* and *IVa* in the presence of copper catalysts (CuCl or $\text{CuCl}_2\text{-Et}_3\text{N.HCl}$) was reported in the addition of tetrachloromethane to 1,5-hexadiene¹ (120°C, 20 h). In our case cyclic products have not been found in any final reaction mixture (including the use of palladium or dibenzoyl peroxide systems). This result was confirmed by an independent experiment in which 5,7,7-tetrachloro-1-heptene (*Ia*) was heated with copper(I)-butylamine complex at 80°C for 5 h. GC analysis did not show formation of cyclic products even in traces. Therefore, one can conclude that copper(I)-butylamine catalyst is very active and selective and thus suitable for facile carrying out the diaddition additions of nonconjugated dienes.

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