anhydride was placed in the ultraviolet vessel.[3] Oxygen was bubbled continuously for 24 hr. through the solution at 50°. Fractional distillation under reduced pressure gave 2-oxa-3-cyclohexenyl acetate (II), 16.5 g. (4% yield), b.p. 47–49° (3 mm.), n^{20}_{D} 1.4532, d^{25}_{4} 1.107.

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.04. Found: C, 59.34; H, 6.90.

The compound II has been made by other workers[6] from vinyl acetate and acrolein; the physical constants given were: b.p. 77–78° (20 mm.), n^{20}_{D} 1.4596, d^{20}_{4} 1.1178.

Treatment of II with acidified 2,4-dinitrophenylhydrazine gave the yellow derivative of glutaraldehyde, m.p. 189–90° (nitrobenzene) (literature 186–187°[7]; 192°[6]).

2-Cyclopentene-1-one was identified in the lower boiling fractions by its 2,4-dinitrophenylhydrazone, m.p. 166.5–167.5° (literature[8] 166°).

Oxidation of 3-Methylcyclohexene.—The 3-methylcyclohexene was prepared from 3-bromocyclohexene and methylmagnesium iodide.[9]

Oxidation of 192 g. (2 moles) in 408 g. (4 moles) of acetic anhydride was carried out at 55–65° for 40 hr. Fractional distillation of this yellow solution under reduced pressure gave 65 g. of products and 185 g. of undistillable residue. Further fractional distillation of the 65 g. of products gave the ketonic product III, b.p. 45–47° (2 mm.), n^{20}_{D} 1.4646, and 19.75 g. (5.8% yield) of the hemi-acetal ester mixture boiling between 58–66° (2 mm.) and having a range of n^{20}_{D} of 1.4578 to 1.4589. Of this material 6.2 g., b.p. 61–62° (2 mm.), n^{20}_{D} 1.4583, comprised the product A.

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.53; H, 8.24. Found: C, 63.72; H, 7.96.

A 2,4-dinitrophenylhydrazone, m.p. 170–172°, was obtained from III. This was the derivative of either 3-methyl- or 4-methylcyclohex-2-en-1-one.[10]

Identification of A.—Addition of acidified 2,4-dinitrophenylhydrazine solution gave an orange deposit, m.p. 175–185°. Extraction with hot ethyl alcohol left the yellow derivative IX of a heptanedione; recrystallization from nitrobenzene gave m.p. 202–203°.

Anal. Calcd. for $C_{19}H_{20}N_8O_8$: C, 46.70; H, 4.12; N, 22.95. Found: C, 46.82; H, 3.88; N, 22.71.

The ethanol extract gave two red derivatives, m.p. 105–170° and m.p. 60–70°, which could not be purified.

A portion of A, 0.9 g., was shaken overnight with 1.5 g. of potassium permanganate in 50 ml. of water. The colorless solution was filtered, acidified with hydrochloric acid and distilled to dryness under reduced pressure. The dry residue was extracted with hot ethyl acetate. The ethyl acetate was removed at reduced pressure, leaving a sirupy residue.

A portion of the sirup gave a semicarbazone. Recrystallization from hot water gave m.p. 169.5° (literature[11] 168–169°).

Anal. Calcd. for $C_7H_{13}N_3O_3$: C, 44.95; H, 6.95; N, 22.45. Found: C, 44.68; H, 7.04; N, 22.44.

The remainder of the sirup was neutralized with sodium hydroxide and boiled for 1 hr. with alcoholic *p*-bromophenacyl bromide. Fractional recrystallization of the product gave the bis-ester of succinic acid, m.p. 206–208° (melting point undepressed by authentic specimen, m.p. 208–209°), and the bis-ester of 2-methylglutaric acid, m.p. 96–99°.

Anal. Calcd. for $C_{22}H_{20}O_6Br_2$: C, 48.00; H, 3.70; Br, 29.55. Found: C, 48.07; H, 3.97; Br, 29.93.

Repeated crystallization from absolute ethyl alcohol failed to change the melting point. The bis-ester prepared from authentic 2-methylglutaric acid[12] had the same range of melting point. The melting point of a mixture of the esters was 96–99°.

Oxidation of Tetralin.—A solution of 331 g. (2.5 moles) of redistilled tetralin in 383 g. (3.75 moles) of acetic anhydride was oxidized at 50–55° for 21 hr. and then at 70–73° for 17 hr. Fractional distillation of the amber solution under reduced pressure gave 42 g. of α-tetralone, 2,4-dinitrophenylhydrazone m.p. 256–257° (literature[13] 259–260°), and 81 g. (15.7% yield) of 2-oxa-3,4-benzcycloheptyl acetate (XI) as an oily solid. Several crystallizations from aqueous ethanol gave colorless plates, m.p. 60–61°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.90; H, 6.85. Found: C, 69.93; H, 7.17.

Treatment of XI with acidified 2,4-dinitrophenylhydrazine gave the golden yellow derivative of *o*-hydroxyphenylbutyraldehyde, m.p. 143–144° (literature[14] 149°).

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(6) C. W. Smith, D. G. Norton and S. A. Ballard, THIS JOURNAL, **73**, 5270 (1951).

(7) R. H. Hall and B. K. Howe, *J. Chem. Soc.*, 2480 (1951).

(8) G. N. Chelnokova and V. V. Korshak, *Sbornik, Statei Obshchei Khim.*, **2**, 1070 (1953); *C. A.*, **49**, 5297 (1955).

(9) R. T. Arnold, G. G. Smith and R. M. Dodson, *J. Org. Chem.*, **15**, 1256 (1950).

(10) (a) The following melting points are to be found for the 3-methyl-derivative: 172.5–173°, C. S. Marvel, THIS JOURNAL, **60**, 280 (1938); 173°, A. J. Birch, *J. Chem. Soc.*, 430 (1944); 173–174°, A. J. Birch, *J. Chem. Soc.*, 593 (1946); 170–171°, M. Mousseron, *Bull. soc. chim. France*, 462 (1952); 178–179°, M. S. Newman, *J. Org. Chem.*, **17**, 577(1952); 177–178°, G. F. Woods, THIS JOURNAL, **71**, 2028 (1949); 175–177°, M. W. Cronyn, THIS JOURNAL, **75**, 1247 (1953). (b) The 4-methyl-derivative is given as 173–174°, A. J. Birch, *J. Chem. Soc.*, 593 (1946); 172–173°, M. Mousseron, *Bull. soc. chim. France*, 1246 (1954).

(11) G. T. Tatevosyan, *et al.*, *Bull. Armenian branch Acad. Sci. USSR*, **5-6**, 37 (1944); *C. A.*, **40**, 3398 (1946).

(12) Kindly supplied by Prof. C. G. Overberger.

(13) F. Ramirez and A. F. Kirby, THIS JOURNAL, **74**, 4331 (1952).

(14) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1574 (1948).

WAYNE, N. J.

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

Concerning the Mechanism of the Reaction of Phosphorus Pentachloride with Ketones

BY MELVIN S. NEWMAN AND LOUIS L. WOOD, JR.

RECEIVED FEBRUARY 19, 1959

A mechanism for the reaction of phosphorus pentachloride with ketones is presented, the main feature of which involves the formation of a chlorocarbonium ion. The known reactions of ketones with phosphorus pentachloride are explained by the proposed mechanism.

Although phosphorus pentachloride has been used for a long time as a reagent which attacks the carbonyl group in aldehydes and ketones, there has been little discussion of possible mechanisms for these reactions. Because of an unexpected result in the reaction of 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone (I) with phosphorus pentachloride[1] we became interested in the mechanism of reaction of phosphorus pentachloride with carbonyl-containing compounds in general and with I and the analogous 4-methyl-4-trichloromethyl-2,5-cyclohexadienone[2] (II) in particular. Much work must be done before any mechanism can be considered to be established, but the scheme below accounts so well for a number of facts that it seems worthwhile to present at this time.

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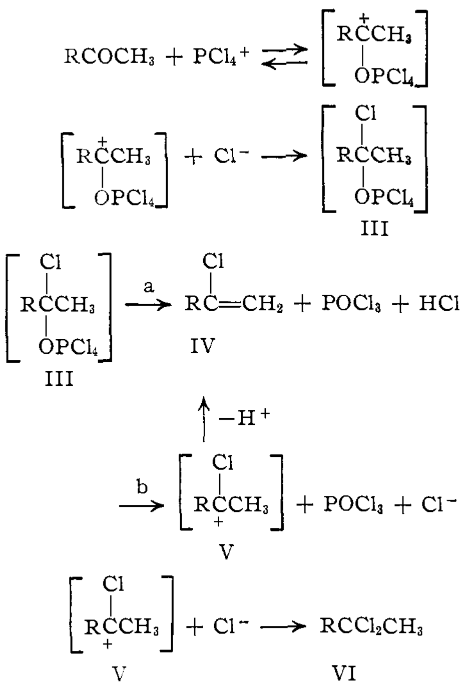
(1) M. S. Newman and L. L. Wood, Jr., *J. Org. Chem.*, **23**, 1236 (1958).

(2) K. von Auwers and W. Julicher, *Ber.*, **55**, 2167 (1922).

$$\mathrm{2PCl_5 \rightleftarrows PCl_4{}^+PCl_6{}^-} \qquad (1)$$



$$\mathrm{RCOCH_3 + PCl_4{}^+ \rightleftarrows \left[\begin{array}{c} R\overset{+}{C}CH_3 \\ | \\ OPCl_4 \end{array}\right]} \qquad (2)$$

$$\mathrm{\left[\begin{array}{c} R\overset{+}{C}CH_3 \\ | \\ OPCl_4 \end{array}\right] + Cl^- \longrightarrow \underset{III}{\left[\begin{array}{c} Cl \\ | \\ RCCH_3 \\ | \\ OPCl_4 \end{array}\right]}} \qquad (3)$$

$$\mathrm{\underset{III}{\left[\begin{array}{c} Cl \\ | \\ RCCH_3 \\ | \\ OPCl_4 \end{array}\right]} \xrightarrow{a} \underset{IV}{\overset{\displaystyle Cl}{\overset{|}{R C}}{=}CH_2} + POCl_3 + HCl} \qquad (4a)$$

$$\uparrow \mathrm{-H^+}$$

$$\mathrm{\xrightarrow{b} \underset{V}{\left[\begin{array}{c} Cl \\ | \\ RCCH_3 \\ + \end{array}\right]} + POCl_3 + Cl^-} \qquad (4b)$$

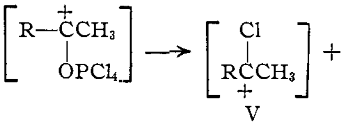
$$\mathrm{\underset{V}{\left[\begin{array}{c} Cl \\ | \\ RCCH_3 \\ + \end{array}\right]} + Cl^- \longrightarrow \underset{VI}{RCCl_2CH_3}} \qquad (5)$$

Equation 1.—The structure of solid phosphorus pentachloride has been established as $\mathrm{PCl_4{}^+}$ $\mathrm{PCl_6{}^-}$ by X-ray work,[3] the $\mathrm{PCl_4{}^+}$ ion being tetrahedral and the $\mathrm{PCl_6{}^-}$ ion being octahedral. In the vapor state, phosphorus pentachloride is monomeric and of a trigonal bipyramidal structure. Since certain solutions of phosphorus pentachloride are conducting[3] it is reasonable to propose that in the media usually involved in treating phosphorus pentachloride with ketones, the tetrachlorophosphonium ion, $\mathrm{PCl_4{}^+}$, is present and reactive.[4] The position of the equilibrium of equation 1 should be sensitive to solvent and to temperature.[5]

Equation 2.—This may be thought of as a nucleophilic attack of the carbonyl oxygen on phosphorus or as an electrophilic attack of the phosphorus on the carbonyl oxygen.[6] This step is probably an equilibrium, the position of which may be markedly affected by solvent.

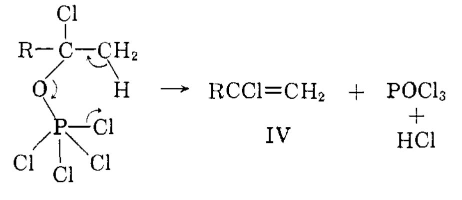
Equation 3.—The reaction of the electron-deficient ion formed in equation 2 with chloride ion (or some species capable of yielding a chloride ion, such as the $\mathrm{PCl_6{}^-}$ ion) yields the intermediate III whose stability depends on the usual variables such as structure of R, solvent, temperature, etc.

It is also possible that the ion formed in equation 2 may collapse directly to the chlorocarbonium ion V with loss of phosphorus oxychloride.



$$\mathrm{\left[\begin{array}{c} R{-}\overset{+}{C}CH_3 \\ | \\ OPCl_4 \end{array}\right] \longrightarrow \underset{V}{\left[\begin{array}{c} Cl \\ | \\ RCCH_3 \\ + \end{array}\right]} + POCl_3} \qquad (3a)$$

Equation 4a.—The formation of a chloroolefin IV, a product often found in significant amount on the reaction of phosphorus pentachloride with ketones, may be the result of the collapse of III, possibly by a cyclic mechanism involving a six-atom ring, *e.g.*

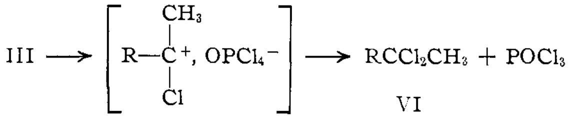


$$\mathrm{\longrightarrow \underset{IV}{RCCl{=}CH_2} + \begin{array}{c} POCl_3 \\ + \\ HCl \end{array}} \qquad (4a)$$

Equation 4b.—The intermediate III may undergo ionic decomposition to yield the chlorocarbonium ion V which would be stabilized by resonance involving the π-electrons of the chlorine atom.[7] We believe that the chlorocarbonium ion V is the most significant species involved in the general case of the reaction of aldehydes and ketones with phosphorus pentachloride. This ion V may be formed by more than one route, but the reactions of aldehydes and ketones can readily be accounted for by the assumption that V is the species involved in going to products.

The chloroölefin IV may result from the loss of a proton from V. The dissociation of III may involve steps and species similar to those involved in the case of the analogous chlorosulfites of alcohols.[8]

Equation 5.—The final step in the formation of dichloride VI is the reaction of the chlorocarbonium ion V with some species capable of providing a chloride ion, such as the $\mathrm{PCl_6{}^-}$ ion. It is also possible that III may dissociate into an ion pair, which then collapses to products, as[8]



$$\mathrm{III \longrightarrow \left[\begin{array}{c} CH_3 \\ | \\ R{-}C^+,\ OPCl_4{}^- \\ | \\ Cl \end{array}\right] \longrightarrow \underset{VI}{RCCl_2CH_3} + POCl_3} \qquad (5a)$$

We do not believe that the product $\mathrm{RCCl_2CH_3}$ is formed by an SN2 type attack by chloride ion on III because of the fact that pinacolone (R = *t*-butyl) reacts so readily with phosphorus pentachloride in the cold to form about equal amounts of dichloride and chloroölefin.[9] Such an SN2 mechanism would involve the neopentyl type of steric hindrance in this case.

Discussion

In surveying the products formed by the reaction of ketones of varying structure with phos-

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(3) D. Clark, H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 642 (1942). In this paper other references to $\mathrm{PCl_5}$ are given.

(4) See A. V. Kirsanov and V. P. Molosnova, *Zhur. Obshchei Khim.*, **28**, 30 (1958); *C. A.*, **52**, 12760^b (1958), for mention of addition of $\mathrm{PCl_4{}^+}$ ion to the carbonyl group of an ester.

(5) On heating $\mathrm{PCl_5}$ a different equilibrium becomes important, namely, $\mathrm{PCl_5 \rightleftarrows PCl_3 + Cl_2}$ (1a). For this reason chlorinated side products are often obtained if the temperature of a reaction involving phosphorus pentachloride is not controlled, preferably in the 0–20° range.

(6) Interestingly evidence for existence of the compounds $\mathrm{PCl_4{}^+AlCl_4{}^-}$ and $\mathrm{PCl_4{}^+FeCl_4{}^-}$ has been obtained. See Y. A. Fialkov and Y. B. Buryanov, *Doklady Akad. Nauk S.S.S.R.*, **92**, 585 (1953); *C. A.*, **48**, 5708^c (1954); *Zhur. Obshchei Khim.*, **25**, 2391 (1955); *C. A.*, **50**, 9197^i (1956). It should be of interest to see what effect the use of aluminum chloride and ferric chloride would have on reactions involving phosphorus pentachloride.

(7) See A. Streitwieser, Jr., *Chem. Rev.*, **56**, 674 (1956), for a discussion of the effect of halogen atoms attached to an electron-deficient carbon.

(8) See ref. 7, p. 730 ff.

(9) P. D. Bartlett and L. J. Rosen, THIS JOURNAL, **64**, 544 (1942).

phorus pentachloride one can account for most of the products by application of the equations listed above and by taking into account special features introduced by varying the nature of R. Specific examples are cited below.

Simple aliphatic ketones such as 2-butanone[10] and pinacolone[9] react to give about equal amounts of dichloride and chloroölefin if the temperature is held low. The ready tendency of phosphorus pentachloride to act as a chlorinating agent[5] at moderate temperatures (*e.g.*, 70°) is illustrated by the conversion of 2,2-dimethyl-3-pentanone into 2,2-dimethyl-4-chloro-3-pentanone[11] as compared to the ready conversion[9] of pinacolone into dichloride (2,2-dimethyl-3,3-dichlorobutane) and chloroolefin (2-chloro-3,3-dimethyl-1-butene) at 0–5°.

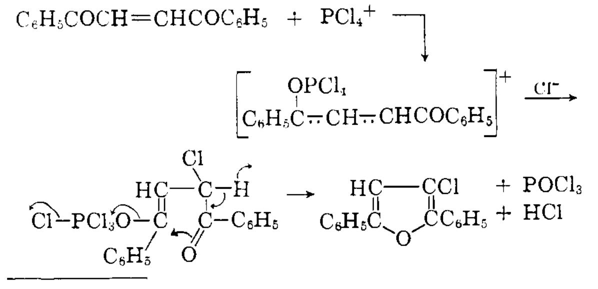
The fact that pinacolone yields unrearranged products may be interpreted as evidence either that the chlorocarbonium ion has a lesser tendency toward rearrangement than the corresponding hydrocarbon carbonium ion or that the intermediate III collapses directly to dichloride and chloroölefin.

That steric hindrance of reaction of ketones with phosphorus pentachloride may be an important factor is indicated by the fact that 2-methyl-5-isopropylacetophenone is chlorinated at the tertiary hydrogen of the isopropyl group to yield 2-methyl-5-(2-chloro-2-propyl)-acetophenone,[12] whereas acetophenone readily yields the expected dichloride and chloroölefin.[13]

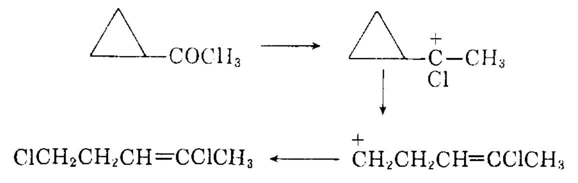
In accounting for the reaction products of simple ketones the chlorocarbonium ion V is not necessary, as the collapse of III, or of an intimate ion-pair, could readily lead to dichloride VI. However, in more complicated cases the involvement of V seems indicated, although other possibilities are not ruled out. For the sake of simplicity in the following examples, ions of type V will be used.

Crotonaldehyde yields a mixture of 1,1-dichloro-2-butene and 1,3-dichloro-1-butene[14] (*ca.* 90%). The chlorocarbonium ion $(CH_3CH \cdots CH \cdots CHCl)^+$ reacts preferentially at the 3-position.

The formation of 2,5-diphenyl-3-chlorofuran in high yield (90%) from both *cis*- and *trans*-dibenzoylethylene[15] at moderate temperatures (25–40°) is explained as

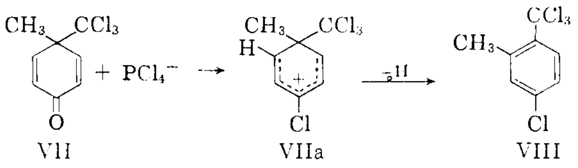


The conversion of methyl cyclopropyl ketone in 92% yield to 2,5-dichloro-2-pentene[16] may be explained as



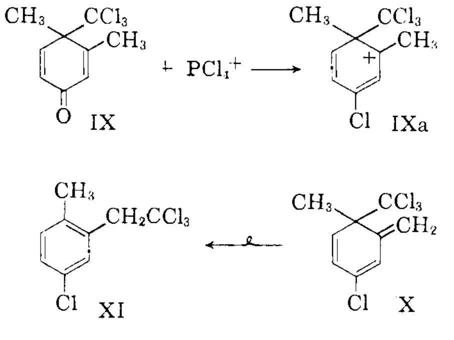
Similar rearrangements involving the cyclopropylmethyl cation are known.[17]

The reaction of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (VII) to yield 2-methyl-4-chlorobenzotrichloride[2] (VIII) is explained as



In this case the chlorocarbonium ion of general formula V is pictured as in VIIa. The rearrangement of the methyl group occurs when sufficient positive charge is built up on a carbon adjacent to the quaternary carbon atom containing the methyl and trichloromethyl groups.

The rearrangement of the analogous 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone (IX) to 3-(β,β,β-trichloroethyl)-4-methylchlorobenzene (XI) follows a different course[1] because the methyl in the 3-position of IX stabilizes the carbonium ion IXa essentially as shown in IXa. There is no tendency for the 4-methyl group in IXa to migrate to the carbon containing the methyl group since an aromatic ring would not result. Therefore the ion IXa loses a proton to yield the triene X which undergoes a 1:3 rearrangement of the trichloromethyl group to yield XI.[18]



In both examples cited above, collapse of a species such as III or an intimate ion pair does not seem to offer as attractive a path as the dissociation of III to an ion such as V (eq. 4b) which then undergoes the changes indicated to yield the products found.

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(10) B. Charpentier, *Bull. soc. chim.*, [5] **1**, 1407 (1934).

(11) V. Vasselier, *ibid.*, [4] **43**, 563 (1928); the reaction mixture was heated to 70°.

(12) M. S. Malinovskii and N. M. Medyantseva, *Zhur. Obshchei Khim.*, **19**, 324 (1949); *C. A.*, **43**, 6595^f (1949). The reaction mixture was held at low temperature first and then was warmed.

(13) W. Taylor, *J. Chem. Soc.*, 304 (1937). He believed that chloroolefin and dichloride were formed "simultaneously" from some intermediate.

(14) L. J. Andrews, THIS JOURNAL, **68**, 2584 (1946).

(15) R. E. Lutz and F. N. Wilder, *ibid.*, **56**, 2145 (1934).

(16) I. A. Diyakonov, *J. Gen. Chem.* (*USSR*), **10**, 414 (1940); *C. A.*, **34**, 7861^3 (1940).

(17) Reference 7, p. 710.

(18) The formation of a semibenzene analogous to X is described by K. von Auwers, *Ann.*, **352**, 219 (1907); see also K. von Auwers, *Ber.*, **44**, 788 (1911), and K. von Auwers and K. Ziegler, *Ann.*, **425**, 217 (1921), for other studies of semibenzenes.

In conclusion, we might point out that all of the products obtained by treating ketones and aldehydes at low temperature with phosphorus pentachloride may be logically accounted for by assuming that a chlorocarbonium ion such as V is formed. The formation of the multiplicity of products above outlined from V involves steps which appear logical in the light of our present concepts of carbonium ion behavior.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

The Effects of Chain and Ring Substitution on the Raney Nickel-catalyzed Cleavage of 2-Arylethanols[1,2]

BY THOMAS W. GREENLEE AND WILLIAM A. BONNER

RECEIVED MARCH 2, 1959

A representative array of 2-phenylethanols containing alkyl or aryl substituents at C2 or containing *meta-* or *ortho–para* directing groups in the *para* nuclear position has been prepared. Each substance has been subjected to the prolonged action of Raney nickel in refluxing ethanol, and the crude reaction products resulting therefrom have been examined for their relative quantities of C1 dehydroxylation and C1–C2 cleavage products by means of vapor–liquid partition chromatography. The introduction of alkyl or aryl substituents on C2 of 2-phenylethanol progressively increased the cleavage/dehydroxylation ratio. No gross differences in the cleavage/dehydroxylation ratio was noted for 2-phenylethanols containing a *meta* directing substituent (COOMe) or an *ortho–para* directing substituent (OMe) in the *p*-position, although the over-all reaction rate was markedly slower in the latter case. When 2-(*p*-nitrophenyl)-ethanol was treated with Raney nickel, preliminary rapid reduction of the nitro group appeared to occur. The reaction products, corresponding almost exclusively to those of C1–C2 cleavage, showed the occurrence of both N,N-dialkylation of the amino group and nuclear reduction, *i.e.*, they were mainly N,N-diethyl-*p*-toluidine and 1-methyl-4-(N,N-diethylamino)-cyclohexane.

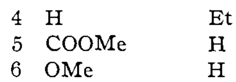
In an earlier paper[3] we have reported that the action of Raney nickel in refluxing ethanol (reductive desulfuration conditions) on 2-arylethanols leads both to simple C1 dehydroxylation producing alkylaromatics, as well as to C1–C2 carbon bond fission yielding alkylaromatics one homolog lower. More recently it has been reported that the single carbon cleavage fragment in the fission process is carbon monoxide strongly adsorbed to the nickel catalyst surface,[4] and that such C1–C2 fission is accompanied by predominant inversion of configuration[5] when the carbon atom adjacent to the aromatic nucleus is asymmetric. These observations have been qualitatively correlated by a tentative mechanism[3-5] involving concerted S$_N$2 attack by hydrogen adsorbed on the Raney nickel surface on C2 of those 2-arylethanols undergoing C1–C2 fission. At an intermediate stage in our investigations it appeared to us that research into the cleavage/dehydroxylation ratios of substituted 2-arylethanols, particularly those bearing *p*-substituents, might afford mechanistic insight. A brief report of the results of these studies is given in the present paper.

2-Phenylethanols containing electron-withdrawing groups (NO_2, COOMe) and electron-releasing groups (OMe, Br) in the *p*-position were prepared by standard methods, then subjected to the action of Raney nickel in refluxing ethanol under previously employed conditions.[3-5] The mixed reaction products were isolated as usual[3] and separated into individual components by vapor–liquid partition chromatography. The latter were finally characterized by their infrared absorption spectra and/or VLPC retention times.

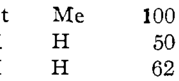
In Table I are recorded the results of these experiments. The approximate composition of each crude reaction mixture with respect to cleavage and dehydroxylation products is given. Included for comparison purposes are similar data[3,5] obtained with 2-arylethanols substituted at C2 with additional alkyl or aryl substituents.

TABLE I

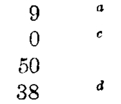
EFFECTS OF CHAIN AND NUCLEAR SUBSTITUTION IN 2-ARYLETHANOLS ON THE RELATIVE EXTENTS OF C1–C2 CLEAVAGE AND C1 DEHYDROXYLATION



I



II



III

No.	Starting material, I X	R	R′	Cleavage product, II, %	Dehydroxylation product, III, %	Note
1	H	H	H	33	67	[a]
2	H	H	Ph	67	33	[a,b]
3	H	H	Me	91	9	[a]
4	H	Et	Me	100	0	[c]
5	COOMe	H	H	50	50	
6	OMe	H	H	62	38	[d]
7	$NO_2 \rightarrow NH_2$	H	H	97	3	[e]
8	Br	H	H	0	0	[f]

[a] Data taken from ref. 3. [b] One Ph ring reduced to cyclohexyl in the cleavage product. [c] Data taken from ref. 5. [d] Very little reaction occurred; 90% of I recovered unchanged; *cf*. Experimental. [e] Introduced as 2-(*p*-nitrophenyl)-ethanol, but apparently reduced almost immediately by Raney nickel. The cleavage products were *p*-$MeC_6H_4NEt_2$ and 1,4-$MeC_6H_{10}NEt_2$. The dehydroxylation product was *p*-$EtC_6H_4NEt_2$. [f] Reaction product was exclusively 2-phenylethanol resulting from nuclear debromination. No cleavage or dehydroxylation products were noted.

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[1] This constitutes Communication XIII in the series "The Stereochemistry of Raney Nickel Action"; for XII see ref. 5.

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[3] J. A. Zderic, W. A. Bonner and T. W. Greenlee, THIS JOURNAL, **79**, 1696 (1957).

[4] W. A. Bonner and T. W. Greenlee, *ibid.*, **81**, 2122 (1959).

[5] W. A. Bonner and T. W. Greenlee, *ibid.*, **81**, 3336 (1959).