frequencies for the ethane molecule is one which the authors are not prepared to discuss. If such an error has not been made, there would seem to be a flat contradiction between the thermodynamic data (including heat capacity measurements for gaseous ethane[15]) on the one hand, and on the other, the spectroscopic data as analyzed by Bartholomè and Karweil.[16] In addition, there is the difficulty in accounting theoretically for the high potential barrier apparently demanded by the thermodynamic data.[17]

However this contradiction may be resolved, the authors wish to emphasize that in dealing with the problem the experimental data on the ethane equilibrium cannot be ignored.

Summary

Additional experiments on the ethane–ethylene–hydrogen equilibrium have been carried out to determine whether the presence of volatile hydrocarbons higher than ethylene and ethane could have invalidated previous analytical work, as suggested by Kassel and Storch.[1] The evidence is that the error is certainly less than 10%, confirming the conclusion of Travers and Hockin.[2]

A comparison of all experimental values with values based on the Nernst Heat Theorem (and the Third Law) emphasizes the internal consistency of the data.

It is concluded that there is no good ground for ignoring the experimental data on the ethane equilibrium in dealing with the question of free rotation in the ethane molecule.

PRINCETON, N. J. RECEIVED JULY 14, 1938

---

[15] Kistiakowsky, *et al.*, *J. Chem. Phys.*, **6**, 407 (1938). See, however, Hunsman, *Z. physik. Chem.*, **39B**, 23 (1938).

[16] Bartholomè and Karweil, *ibid.*, **39B**, 1 (1938).

[17] Eyring, THIS JOURNAL, **54**, 3191 (1932).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Fluorinated Derivatives of Propane. II

BY ALBERT L. HENNE AND ELBERT C. LADD

Three chlorinated derivatives of propane (C_3Cl_8, $CHCl_2CCl_2CCl_3$ and $CCl_3CHClCCl_3$) have been synthesized and subjected to fluorination. Three monofluorides, three difluorides and two trifluorides have thus been made. These new compounds are described, their structural formulas established and the course of the fluorination thereby demonstrated.

Extending to the propane series the investigations which have covered methane and ethane compounds is not a mere expansion, because the propane molecule offers a new position on its center carbon atom, and because the increased distance between its ends affects the course of the fluorination. As the ultimate purpose is the synthesis of fluorinated derivatives of much greater length, it is essential to learn the effect that the position and the distance of the fluorinated groups exert upon the molecule as a whole.

Synthesis.—The heptachloropropanes were synthesized by condensing chloroform with tetrachloroethylene, or carbon tetrachloride with trichloroethylene, in the presence of aluminum chloride. From asymmetrical heptachloropropane, a treatment with potassium hydroxide gave hexachloropropylene, and the latter combined with chlorine to yield octachloropropane. This method, originated by Prins,[1] has been improved, as described in the experimental part, but it cannot be extended to the condensation of fluorinated molecules of methane and ethylene, for the reasons previously reported.[2]

The chlorinated propanes were thoroughly purified before subjecting them to fluorination. This precaution was taken because fluorination gives only one of the possible isomers at each stage, and the isolation of the fluorinated compounds in a pure state is much facilitated by starting from well-defined material. The fluorination was performed as indicated in the experimental part, but the isolation, purification, analysis and description of the new compounds followed the methods of preceding papers[3] and the results have been tabulated.

The reason for describing the fluorination procedures in detail is that chlorinated propanes may split into one molecule of chlorinated methane and one of chlorinated ethylene, which is merely the reverse of the condensation reaction by means of

---

[1] Prins, *J. prakt. Chem.*, [2], **89**, 416 (1914).

[2] I, Henne and Newman, THIS JOURNAL, **60**, 1697 (1938).

[3] *Ibid.*, **56**, 1726 (1934); **58**, 402, 404, 882, 884, 887, 889 (1936); **59**, 1200, 1400, 2434 (1937).

which they have been synthesized. Consequently, the fluorination products contain compounds resulting from the fluorination of the split products, which complicate the separation and affect the yields. The fluorinated methane derivatives are volatile and escape the field of reaction; the other by-products are $CCl_2{=}CCl_2$ and products derived therefrom, namely, CCl_3CCl_3, CCl_3CCl_2F, CCl_2FCCl_2F and CCl_2FCClF_2, on the one hand, and $CHCl{=}CCl_2$ and its derivatives, namely, $CHCl_2CCl_3$, $CHCl_2CCl_2F$ and $CHCl_2CClF_2$ on the other hand. It should be emphasized that this splitting is quite important with the chlorinated propanes, but vanishes rapidly with increasing fluorination of the molecules, as is evident from the fact that the by-products are related to the starting materials, and not to their fluorinated derivatives.

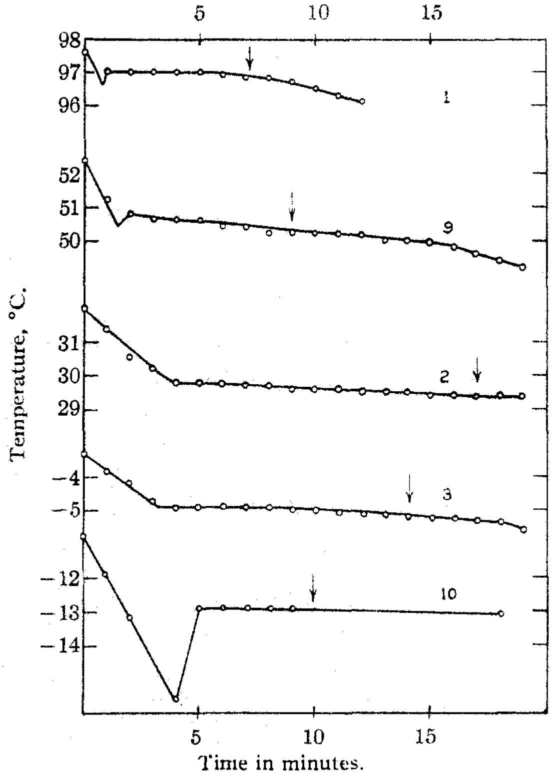


Fig. 1.—Freezing curves. Numbers refer to compounds in Table I. Arrows denote end of stirring.

Determination of Structure.—In the determination of the structural formulas advantage was taken of the fact that fully halogenated compounds are crystalline, in contrast with compounds which have hydrogen in the molecule. Even with only one hydrogen atom present, the compounds are liquids, and become glassy at very low temperatures only. It was, therefore, practical to substitute the hydrogen by chlorine and isolate the resulting fully halogenated compound in a state of high purity by alternating fractional distillation and fractional crystallization. A second step of the determination consisted in synthesizing three derivatives, $CCl_3CCl_2CCl_2F$, $CCl_3CCl_2CClF_2$ and $CCl_3CF_2CCl_3$, as described elsewhere.[4] The third step was the reaction with zinc in alcohol. This, however, requires qualification.

In general, when a polyhalogenated compound is treated with zinc in alcohol, two atoms of halogen are removed and a derivative of ethylene is formed. It has, so far, been an inflexible rule that the heavier halogens are removed preferentially, and an analysis of the zinc salts produced is then sufficient to establish the nature of the removed halogens. However, in the present case, the situation was complicated by the fact that all the resulting ethylenic compounds proved unstable, some of them exceedingly so; therefore, the procedure had to be modified in order to retain its significance. When the zinc reactions were performed, the tests for chloride and fluoride ions were made at repeated intervals, as soon as the reaction started, and it was found that at that stage zinc chloride only was produced. Conversely, when the reaction was allowed to proceed to completion, it was always found that some fluorine had been removed from the organic molecules, and also that much less fluorine than chlorine had combined with the zinc; therefore, it was held that significance would be attached only to the tests performed in the early stages of the zinc reaction, when the concentration of reaction products in the alcohol was still small, and the decomposition of the ethylenic compounds minimized.

Results of the Structure Determination.—Synthetic $CCl_3CCl_2CCl_2F$ melts at 97° and is identical with the product obtained by fluorinating C_3Cl_8 (No. 1 in table).

The monofluoride (No. 7) formed from *s*-C_3HCl_7 yields zinc chloride only in a treatment with zinc in alcohol, and by chlorination in sunlight it gives the compound melting at 97°. Moreover, it gives a mixture of ethylenic compounds boiling over a 3° range, after treatment with alcoholic potassium hydroxide, and this mixture treated with chlorine yields the compound melting at 97°, exclusively. Its formula is therefore $CCl_3CHClCCl_2F$.

---

[4] THIS JOURNAL, 59, 2434 (1937), and paper now presented for publication

TABLE I

No.	Compounds	M. p., °C.	B. p., °C.	t	d^t_4	n^t_α	n^t_D	n^t_β	MR_D	AR_F	Cl/F Obsd.	Cl/F Calcd.	Mol. wt. Obsd.	Mol. wt. Calcd.
1	$CCl_3CCl_2CCl_2F$	97.0	236.8								6.76	7.00	300	303
2	$CCl_2FCCl_2CCl_2F$	29.8	194.2	35.0	1.79151	1.47191	1.47418	1.48052	45.02	0.98	2.96	3.00	289	287
3	$C_3Cl_5F_3$	− 4.9	152.3	20.0	1.77023	1.43738	1.43959	1.44510	40.21	1.04	1.65	1.67	268	270
4	$CHCl_2CCl_2CCl_2F$	Glass	210.0	20.0	1.77384	1.50024	1.50311	1.51012	44.80	0.64	5.78	6.00	272	269
5	$CHCl_2CCl_2CClF_2$	Glass	168.4	20.0	1.73162	1.45995	1.46241	1.46853	40.09	.95	2.54	2.50	256	252
6	a-$C_3HCl_4F_3$	Glass	129.8	20.0	1.69124	1.41767	1.41967	1.42466	35.27	1.10	1.30	1.33	233	236
7	$CCl_3CHClCCl_2F$	Glass	207 dec.	20.0	1.76188	1.49836	1.50105	1.50814	44.94	0.78	6.1	6.0	265	269
8	$CCl_2FCHClCCl_2F$	Glass	167.4	20.0	1.71720	1.45745	1.45972	1.46585	40.22	1.02	2.50	2.50	252	252
9	$CCl_3CCl_2CClF_2$	50.8	193.4								3.05	3.00	285	287
10	$CCl_3CF_2CCl_3$	−12.9	194.2	20.0	1.8105		1.47996		45.00	0.98	3.00	3.00	287	287
11	$CCl_3CF_2CCl_2F$	<−80	154.5	20.0	1.7590		1.43939		40.46	1.12	1.67	1.67	267	270

The monofluoride (No. 4) obtained from asymmetrical C_3HCl_7, treated in the same ways, yields $ZnCl_2$ only, is transformed into the compound melting at 97° by chlorination, gives, with potassium hydroxide, a single ethylenic derivative boiling over a 0.2° range, the chlorination of which yields again the derivative melting at 97°. Therefore its formula can only be $CHFClCCl_2CCl_3$ or $CHCl_2CCl_2CCl_2F$ and a choice can be based only on analogy with preceding cases. In view of the fact that CCl_3 groups have always been much more easily fluorinated than $CHCl_2$ groups, and of the fact that the experimental conditions used are regarded as inadequate to attack the $CHCl_2$ group, the second formula is adopted.

The difluorides are, without exception, identical whether obtained directly, or from the monofluorides. Therefore, one of their fluorine atoms is located on an end carbon. By chlorination in sunlight, the difluoride (No. 5) from a-C_3HCl_7 gives a compound melting at 51°, identical with synthetic $CCl_3CCl_2CClF_2$. Its formula is therefore either $CHF_2CCl_2CCl_3$ or $CHCl_2CCl_2CClF_2$, and the latter is chosen for the reasons given in discussing the monofluoride. These reasons become even more convincing when comparing the plausibility of a $CClF_2$ group in contrast to a CHF_2 group.

The difluoride (No. 8) obtained from s-C_3HCl_7 must be $CCl_2FCHClCCl_2F$, because it yields zinc chloride only, in a zinc treatment, and because its chlorination yields a compound melting at 30°, identical with the difluoride (No. 2) obtained from C_3Cl_8. The latter must therefore be $CCl_2FCCl_2CCl_2F$.

The structure of the trifluorides (Nos. 3 and 6) is not demonstrated, but can be predicted with plausibility. From C_3Cl_8, the trifluoride (No. 3) should be written $CCl_2FCCl_2CClF_2$, mostly because it has a relatively high melting point (−4°) and the only other possible formula, $CCl_2FCClFCCl_2F$ would call for a much lower melting point. From s-C_3HCl_7, the trifluoride should be $CCl_2FCHClCClF_2$, mostly because the fluorination of a —CHCl— group has never been performed with antimony fluoride. It is expected that by chlorination in sunlight this trifluoride will yield the compound melting at −4°, and thereby prove the structure proposed for the trifluoride obtained from C_3Cl_8. Finally, from a-C_3HCl_7, the trifluoride (No. 6) could be either $CHCl_2CClFCClF_2$ or $CHClFCCl_2CClF_2$ though the ease with which it is obtained miligates somewhat against the latter formula. By chlorination in sunlight, a compound should be obtained with a melting point somewhere between −10 and −15°, as would befit a compound written $CCl_3CClFCClF_2$. This is confirmed by a preliminary experiment which gave a melting point of −13 to −12°.

The above experiments, which are slow and depend on intense sunlight, are under way and will be reported together with the preparation of the tetrafluorides, which is also under way. It is not intended to fluorinate further, as this would merely make new compounds, but shed no additional light on the fluorination course.

Discussion.—The criterion for purity was the freezing curve, whenever possible. These curves are given and speak for themselves. When the compounds formed glasses instead of crystals, the Engler distilling range was used, and found to be 0.2° or less, except in the case of No. 7, which decomposed when distilled at normal pressure and gave a 3° range.

The analyses gave rise to the difficulties reported before, which forced the use of the chlorine/fluorine ratio, instead of the customary percentages. The use of this ratio has the disadvantage that it is much more affected by small experimental errors than are the percentages. Nevertheless, the results leave no doubt as to the identity of the compounds.

The molecular weights, taken by freezing point depression in benzene, gave particularly good values. The molecular refraction was computed by means of the Lorentz–Lorenz formula. The atomic refraction *AR*F was obtained by subtracting from the molecular refraction the required number of carbon increments (2.418), chlorine increments (5.967) and hydrogen increments (1.100), and dividing by the number of fluorine atoms in the compound considered. The atomic refraction increases always with the degree of fluorination; it is much more steady in fully halogenated compounds than in hydrogen bearing derivatives.

Experimental

Preparation of $CHCl_2CCl_2CCl_3$.—Ten gram molecules of tetrachloroethylene, 20 gram molecules of chloroform and 50 g. of aluminum chloride were placed in a 5-liter round-bottomed flask equipped with a reflux condenser and heated to gentle boiling during twenty hours. The reaction mixture was cooled and poured into water, washed, decanted and dried. A fractional distillation yielded, besides the unreacted material recovered, 6.8 gram molecules of α-heptachloropropane, boiling at 163–166° at 90 mm.

Fluorination of $CHCl_2CCl_2CCl_3$.—Two procedures were used, the first to obtain a mixture rich in mono- and difluorides, the second a product rich in di- and trifluorides.

First Procedure.—In a one-liter flask 1160 g. of α-C_3HCl_7 and 740 g. of SbF_3Cl_2 were placed and vigorously stirred so that the temperature of the mixture would never exceed 50°. After the mixture had cooled to 30°, it was heated slowly to 130–140° and held there for five hours. It was then cooled, poured into water, washed with hydrochloric acid to remove the antimony salts, then with water and dried. These operations gave 907 g. of reaction products containing approximately 60 g. of trifluoride, 315 g. of difluoride and 435 g. of monofluoride.

Second Procedure.—In a 3-liter flask 1970 g. of heptachloride mixed with 1245 g. of SbF_3Cl_2 was heated to 140–150° and held at this temperature for eight hours. The subsequent operations were identical with those of the first procedure and yielded 1740 g. of crude product which separated into 400 g. of trifluoride, and 1000 g. of difluoride, approximately. The remainder of the material was composed of ethylenic derivatives, and of fluorinated compounds of ethane, resulting from the splitting of the propane molecule. The more abundant by-products were $CCl_2{=}CCl_2$, CCl_3CCl_2F, CCl_2FCCl_2F and C_2Cl_6.

Preparation of C_3Cl_8.—Ten gram molecules of $CHCl_2CCl_2CCl_3$ was placed in a 5-liter flask, equipped with an efficient stirrer, and a solution of 600 g. of potassium hydroxide in methanol was added dropwise. The heat evolved is considerable, and the addition of the hydroxide should be slow to avoid splitting the propane molecule. After completion of the addition the mixture was stirred during an additional hour and then washed with water. The hexachloropropylene thus obtained (2300 g.) was treated with a slow current of chlorine, in sunlight, and with the temperature constantly kept below 50°. When crystals of octachloropropane prevented further passage of the chlorine, the mixture was allowed to stand in sunlight until it became snow white. It could then be separated by filtration under suction, but this was not done, on account of the high vapor tension of C_3Cl_8. Fractional distillation was used instead. The unchlorinated product was then returned for a further treatment with chlorine. When the operations were conducted with care, and without localized heating, the yields were quantitative.

Fluorination of C_3Cl_8.—Three procedures have been used, to obtain mixtures rich in mono-, di- and trifluoride, respectively.

First Procedure.—In a round-bottomed flask equipped with an air-cooled reflux condenser, 960 g. of C_3Cl_8, 180 g. of SbF_3 and 40 g. of $SbCl_5$ were heated for eight hours at 140°. The following day 30 g. of SbF_3Cl_2 was added and the heating was continued at 140° for another six hours. During this treatment, the lower layer containing most of the SbF_3 gradually liquefied and dissolved in the upper layer of organic material. The liquid reaction mixture was poured into commercial hydrochloric acid while still hot, and washed free of antimony salt. The crude product, amounting to 910 g., solidified at room temperature. By fractional distillation at 90 mm. it was separated into one-half of monofluoride and one-half of unreacted C_3Cl_8.

Second Procedure.—In a round-bottomed flask equipped with an air-cooled reflux condenser 1500 g. of C_3Cl_8, 560 g. of SbF_3 and 75 g. of $SbCl_5$ were mixed and heated for five hours on a steam-bath. A further quantity of 100 g. of $SbCl_5$ was then added in small portions, and the heating continued for twenty hours. The reaction mixture, which had become progressively homogeneous, was allowed to cool before it was poured into aqueous acid, then washed and dried. The crude product amounted to 1092 g., from which about 750 g. of difluoride was obtained by fractional distillation at 90 mm.

Third Procedure.—In a round-bottomed flask equipped with an air-cooled reflux condenser 1220 g. of C_3Cl_8, 500 g. of SbF_3 and 75 g. of $SbCl_5$ were heated on a steam-bath for twelve hours. A further portion of 80 g. of $SbCl_5$ was added and heating continued on the steam-bath for two hours. The mixture was then cooled, and the liquid layer decanted from the crystalline antimony salts into a flask equipped with a water-cooled reflux condenser, and 400 g. of SbF_3Cl_2 was added. The reaction was then heated to 140° without haste, because the fluorination reaction is quite active at the start. It is advisable to have a pan of ice water ready to chill the mixture if it threatens to escape control. After the temperature of 140° had been reached, the heating was continued for two hours. Then, after complete cooling, the washing, drying and distillation were performed as in the preceding cases. The crude product amounted to 700 g., and contained about 300 g. of trifluoride.

Preparation of $CCl_3CHClCCl_3$.—Trichloroethylene (520 g.), carbon tetrachloride (1220 g.) and aluminum chloride (50 g.) were stirred in a 2-liter flask at 20–30° for forty-eight hours. Access of moisture was prevented by thorough drying at the start, by using a mercury seal on the stirrer, and by protecting the vent with a calcium chloride tube. The reaction mixture was poured cautiously into ice water, vigorously shaken, decanted, washed with water, dried over calcium chloride and subjected to distillation at atmospheric pressure to recover the unreacted materials. As soon as this nears completion, the distillation is pursued at reduced pressure, with a carbon dioxide trap to stop the light boiling compounds. The distillation at 20 mm. gave 551 g. of chlorinated propane, boiling from 126 to 132°; this was a 49% conversion yield. The tar formation amounted to 5%, and the remainder of the ingredients was recovered unreacted. The reaction did not take place at lower temperatures, and resinification increased rapidly at higher temperatures. At 70°, resinification was complete. Consequently, the lower conversion yield was accepted, and the recovered materials were repeatedly re-treated.

Fluorination of $CCl_3CHClCCl_3$.—Two procedures were employed, to obtain products rich in mono- and in difluoride, respectively.

First Procedure.—In a 1-liter round-bottomed flask 500 g. of *s*-heptachloropropane, 120 g. of SbF_3 and 20 g. of $SbCl_5$ were placed, stirred vigorously for three hours and then heated to 70–80° for one hour, with stirring continued. The mixture was cooled, and its liquid layer, after pouring into hydrochloric acid, was washed, dried and distilled at 90 mm. The crude product amounted to 427 g., of which a little more than one-third was monofluoride.

Second Procedure.—Heptachloropropane (916 g.), SbF_3 (520 g.) and $SbCl_5$ (100 g.) were placed in a 1-liter round-bottomed flask and stirred overnight at room temperature. The mixture was then heated for ten hours on a steam-bath, cooled to separate most of the antimony chloride, decanted into acid, washed, dried and distilled at 90 mm. The crude product amounted to 630 g., of which a little more than one-half was the difluoride.

Summary

The syntheses of C_3Cl_8, $CHCl_2CCl_2CCl_3$ and $CCl_3CHClCCl_3$ have been improved. From these compounds, the mono-, di- and trifluorides have been obtained by replacement of chlorine atoms by fluorine. The formulas of the new derivatives have been established experimentally for the mono- and difluorides, and reasoned out for the trifluorides. The properties have been tabulated, together with those of three additional fluorochloropropanes which were synthesized independently for identification purposes. The course of the fluorination has thus been established.

THE MIDGLEY FOUNDATION
OHIO STATE UNIVERSITY
COLUMBUS, OHIO

RECEIVED JULY 9, 1938

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Reaction of Isobutene and Diisobutene with Phenol, with and without Scission of C–C Linkages

BY V. N. IPATIEFF, HERMAN PINES AND B. S. FRIEDMAN

In previous papers[1] it was shown that when diisobutene reacts with benzene in the presence of sulfuric acid, *t*-butyl-, *p*-di-*t*-butyl-, and tri-*t*-butylbenzene are formed. In view of the fact that Niederl and Natelson and co-workers[2,3] failed to notice analogous products observed by others[4] when phenol was treated with diisobutene in the presence of sulfuric acid, it was decided to investigate this reaction.

When Natelson's[3] directions were followed closely, the product contained no butylphenol. A compound not previously reported, which appears to be 2,4-di-*t*-octylphenol [2,4-di-($\alpha,\alpha,\gamma,\gamma,$-tetramethobutyl)-phenol], was isolated in addition to the expected *p*-*t*-octylphenol [*p*-($\alpha,\alpha,$-$\gamma,\gamma,$-tetramethobutyl)-phenol].

When, however, phenol and diisobutene were treated with a large excess of sulfuric acid and the temperature allowed to rise to 85%, the product was found to contain some *p*-*t*-butylphenol.

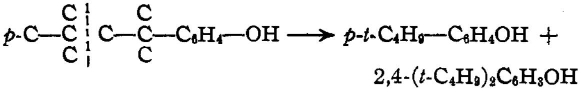
The alkylation of phenol with diisobutene in the presence of phosphoric acid required a temperature of 150°; and the yield of *p*-*t*-octylphenol was quite low. *p*-*t*-Butylphenol was isolated and identified.

The production of the *p*-*t*-butylphenol could have taken place by either of two series of reactions

$$\text{Diisobutene} \longrightarrow 2\ i\text{-}C_4H_8 \qquad \text{(A)}$$

$$i\text{-}C_4H_8 + C_6H_5OH \longrightarrow t\text{-}C_4H_9\text{-}C_6H_4OH$$

$$\text{Diisobutene} + C_6H_5OH \longrightarrow t\text{-}C_8H_{17}\text{-}C_6H_4OH \qquad \text{(B)}$$



$$p\text{-}C{-}\underset{C}{\overset{C}{C}}\ \vdots\ C{-}\underset{C}{\overset{C}{C}}{-}C_6H_4{-}OH \longrightarrow p\text{-}t\text{-}C_4H_9{-}C_6H_4OH + 2,4\text{-}(t\text{-}C_4H_9)_2C_6H_3OH$$

The possibility that reaction could take place by (B) is evidenced by the fact that *p*-*t*-octylphenol heated under pressure to 140° in the presence of 90% phosphoric acid was cleaved to pro-

---

[1] (a) Ipatieff and Pines, THIS JOURNAL, **58**, 1056 (1936); (b) Ipatieff and Pines, *J. Org. Chem.*, **1**, 464 (1936).

[2] (a) Niederl and Natelson, THIS JOURNAL, **55**, 2571 (1933); (b) Niederl, Natelson and Beekman, *ibid.*, **53**, 272 (1931).

[3] Natelson, *ibid.*, **56**, 1584 (1934).

[4] British Patent, 453,335, Aug. 20, 1936; *C. A.*, **31**, 485 (1937). *Cf.* Smith and Rodden, THIS JOURNAL, **59**, 2353 (1937), who used aluminum chloride.