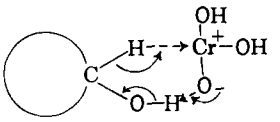
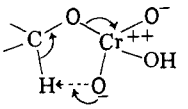


It is not as yet clear how this proposal[11] fits with our results since it requires the rate-determining abstraction of hydrogen by the approach of an external reagent in the transition state and it provides no sound basis for understanding the steric acceleration effects we and others[9] have observed for alicyclic and bicyclic alcohols.

A possible modification of the Westheimer mechanism, which can be reconciled with conclusions (1) and (2) above and with all the results we have considered thus far, specifies that the proton is removed in a cyclic transition state, the basic center of which resides on an electron dense oxygen on the chromate ester.[13a,b] In these circum-



stances, steric hindrance afforded by groups near the reaction center could result in rate acceleraton by restricting rotation about the C–O bond. Eliminating a number of (unstable, strained) conformations of the chromate ester the hindrance of the substituents increases the probability of attaining the five-membered cyclic transition state, pictured above, in which all the atoms involved are coplanar. Graham and Westheimer[12] have also considered an analogous cyclic transition state in the mechanism of benzaldehyde oxidation as a possible alternative to proton abstraction by water molecules acting as base.[14]

It is possible that the mere relief of steric strain in the chromate ester in going to the ketone may contribute to the rate as has been discussed for cyclohexanol and cyclopentanol derivatives[2,9,15] though this effect may not be of general importance. Furthermore, in the cyclic mechanism discussed here a good part of the diminished rate of 2-propanol (as compared to cyclohexanol and cyclopentanol oxidation) may be accounted for on the basis of reduced hindrance to rotational motion in the chromate ester.

(13) (a) Investigations currently in progress in these laboratories, bearing directly on the question of the position of this equilibrium as a function of the structure of the secondary alcohol and the acidity of the medium, do not as yet permit any specification of how extensively the alcohol has been converted to chromate ester prior to decomposition to ketonic product. (b) Similar cyclic transition states have often been suggested by R. T. Arnold and co-workers where the evidence seemed to indicate that proton transfer had *not* been effected through the direct intervention of an external base; see, for examples, R. T. Arnold, O. C. Elmer and R. M. Dodson, THIS JOURNAL, **72**, 4359 (1950), and R. T. Arnold and M. J. Danzig, *ibid.*, **79**, 892 (1957), as well as F. H. Westheimer and W. A. Jones, *ibid.*, **63**, 3283 (1941), and G. L. O'Connor and H. R. Nace, *ibid.*, **74**, 5454 (1952), **75**, 2118 (1953).

Experimental

Preparation of Alcohols.—All alcohols used were synthesized by standard techniques. Their physical constants agreed well with the literature in all cases.

Kinetic Runs.—The technique used for these runs is identical to that employed in aqueous acetic acid given by the authors in their previous publication.[4]

Acknowledgment.—We are grateful to the Hercules Powder Co. for supplying the pure samples of borneol and isoborneol.

(14) This is also consistent with the recent report of Westheimer to the 7th Reaction Mechanisms Conference, University of Chicago, Chicago, Ill., Sept. 6, 1958, indicating that the accelerating influence of added base on the rate of alcohol oxidation is sufficiently small to be a medium effect; see F. Holloway, M. Cohen and F. H. Westheimer, THIS JOURNAL, **73**, 65 (1951), as well as J. Roček and J. Krupička, *Coll. Czech. Chem. Comm.*, **23**, 2068 (1958).

(15) H. C. Brown, J. H. Brewster and H. Shechter, THIS JOURNAL, **76**, 467 (1954), and early articles cited therein.

NEWARK, DEL.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL CO. (INDIANA)]

Alkylation of *p*-Cresol: Effect of High Concentrations of Boron Trifluoride Catalyst

BY S. PAUL MALCHICK AND ROY B. HANNAN

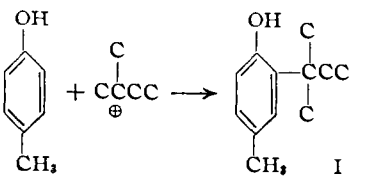
RECEIVED JUNE 27, 1958

Alkylation of *p*-cresol with tertiary alkylating agents (2-methylbutene-2 or *t*-amyl chloride) in the presence of 50 mole % boron trifluoride gave less than 20% of the expected 2-*t*-alkyl-4-methylphenol. The remainder of the phenolic materials was composed of 2-*sec*-alkyl-4-methylphenols, *p*-*t*-alkylphenols and 2,2'-bismethylenediphenols. Alkylation of *p*-$C^{14}H_3C_6H_4OH$ showed that the methylene carbon atom of the 2,2'-bismethylenediphenols was originally the methyl carbon of *p*-cresol. A hydride-ion transfer as an early step in the mechanism could explain the formation of saturated hydrocarbons and the suppression of the reaction by the presence of isopentane in the alkylation.

Introduction

The alkylation of *p*-cresol in acid-catalyzed systems generally produces 2-alkyl-4-methylphenols which are used commercially as oxidation inhibitors.[1] Reaction of *p*-cresol with 2-methylbutene-2 or *t*-amyl chloride would be expected to give 2-*t*-amyl-4-methylphenol (I).

With 1–25 mole % boron trifluoride as catalyst, I is obtained in good yield. However, with concentrations of BF_3 around 50 mole %, we have observed that the alkylation products include less than 20% of I.



The effect of BF_3 concentration on the alkylation does not appear to have been studied. Moreover, in view of the good yields of desired product

(1) W. Weinrich, *Ind. Eng. Chem.*, **35**, 264 (1948); L. J. Kitchen, THIS JOURNAL, **70**, 1290 (1948).

obtained at low catalyst concentrations, workers have had little occasion to be concerned with the minor amounts of by-products that are formed. In order to determine the effect of high concentrations of BF_3, we have attempted to identify the products of the alkylation and to establish the mechanism by which they are formed.

Accordingly, *p*-cresol was alkylated with 2-methylbutene-2 or *t*-amyl chloride. Volatile products were trapped out and analyzed by gas chromatography and mass spectrometry. The non-volatile reaction mixture was recovered, and the phenolic products were separated by two methods: elution chromatography, to separate the material into structural types, and distillation, to isolate individual components wherever possible.

Some insight into the mechanism of the reaction was gained both from the nature of the products and from the results of other experiments: alkylation was carried out in the presence of an added hydride-ion donor to establish an intermediate step; BF_3 was allowed to react with an alkylating agent, to tie down some side reactions, and with the expected product I, to examine part of the reaction path; C^{14}-labeled *p*-cresol was alkylated to determine the source of one of the products.

Experimental

p-Cresol (Eastman Kodak Co. practical grade) was distilled at atmospheric pressure, and a cut boiling within a one-degree range was taken; cryoscopic determination indicated a purity of 99.5 ± 0.2 mole %. Phillips pure grade 2-methylbutene-2 and Matheson, Coleman and Bell *t*-amyl chloride were used without further purification. Boron trifluoride gas was used directly from commercial cylinders.

The crude phenol products were distilled in spinning-band columns[2] at reduced pressure. Infrared spectra were recorded on a Perkin-Elmer model 21 spectrophotometer with NaCl optics. Beckman DU and Cary 11MS spectrophotometers were used for measurements in the ultraviolet region.

Alkylation of *p*-Cresol.—In a typical run, one mole (108 g.) of *p*-cresol was treated with boron trifluoride with stirring until the desired increase in weight was attained. Concentrations of BF_3 near 50 mole % could be obtained only by keeping the mixture below 50°. One mole of the alkylating agent (106.5 g. of *t*-amyl chloride or 70.0 g. of 2-methylbutene-2) was added to the *p*-cresol–BF_3 mixture at room temperature. The *t*-amyl chloride could be added all at once without causing a temperature rise, but HCl evolution required constant stirring to reduce foaming. The olefin had to be added slowly because of the temperature rise. The *p*-cresol–olefin reaction mixture was heterogeneous but gradually became homogeneous after 2 to 4 hours of stirring. A trap cooled by Dry Ice and acetone was connected to the outlet of the system to collect low-boiling materials.

After 4 hours, 150 ml. of water was added to take up the BF_3, the layers were separated and the organic layer was washed with two 100-ml. portions of water. Hydrocarbon solvent or ether was added to facilitate separation. The phenolic mixture was dried over Drierite and filtered, and the solvents were removed. The yield was 120–150 g. of crude product.

To investigate the effects of possible hydride-ion donors, several alkylations were carried out in the presence of 200 ml. of isopentane or *n*-hexane.

Chromatographic Separation.—A chromatographic column 3 cm. in diameter and 70 cm. long was prepared with 350 g. of silica gel, Davison Grade 950, 60–200-mesh, in isoöctane.[3] A 3-g. sample of the crude phenol mixture dissolved in isoöctane was charged to the column, and elution was started with 3% anhydrous ether in isoöctane. Half-liter cuts were taken, and the ultraviolet absorption spectrum of each was recorded. After the *p*-cresol was completely removed from the column, the ether content of the eluent was increased to 15% to elute the more-polar phenols.

Cuts corresponding to peaks in the chromatogram were recombined into main fractions, and the products were recovered by removal of the solvent. Because of the high vapor pressure of some low-molecular-weight phenols, the solvent was removed by distillation through an Oldershaw column until the volume was reduced to 100–200 ml. The residue was then transferred to a tared 200-ml. flask, the solution was concentrated to 20–30 ml. through a small Vigreux-head column, and the remaining solvent was removed in a rotating evaporator under vacuum.

The chromatographic procedure gave four distinct fractions

Frac.	Wt. %	Significant infrared max., μ	Probable structure, phenol
1	15–20	2.81, 12.34	2-*t*-Alkyl-4-methyl-
2	10–15	2.92, 12.35	2-*sec*-Alkyl-4-alkyl-
3	30–50	3.06, 12.05, 12.37	*p*-Cresol and *p*-*t*-alkyl-
4	20–25	3.05, 12.35	2,2'-Bismethylenedi-

Each fraction was characterized by the wave length of the O–H stretching vibration[4] and by the wave lengths of the aromatic substitution bands in the infrared spectrum.

Identification of Individual Components.—The material collected in the cold trap was found to be 60–70% saturated hydrocarbon—about 75% isopentane and 25% isobutane and methylpentanes. The remainder consisted of olefins or alkyl chlorides, as governed by the alkylating agent used.

Careful fractional distillation of the crude phenol mixture gave many fractions that deposited crystals. Five crystalline materials were recovered: 2-*t*-butyl-4-methylphenol (IIa), m.p. 50–51.5°; *p*-*t*-butylphenol (IVa), m.p. 98–99°; *p*-*t*-amylphenol (IVb), m.p. 93–94°; 2,2'-methylenedi-*p*-cresol (Va), m.p. 120.5–121.5°; 2,2'-dihydroxy-5-methyldiphenylmethane[5] (Vb), m.p. 95–96°. Each was purified and characterized by melting point, mixed melting point with an authentic sample, and comparison of the infrared spectrum with that of the authentic material.

Reaction of 2-*t*-Amyl-4-methylphenol with BF_3.—*p*-Cresol was alkylated with 2-methylbutene-2 in the presence of 5% of an alkanesulfonic acid as catalyst; distillation gave a heart cut of 2-*t*-amyl-4-methylphenol, b.p. 121–122° (10 mm.), $n^{20}D$ 1.5210.

In a typical run, 0.25 mole (44.5 g.) of 2-*t*-amyl-4-methylphenol was treated with boron trifluoride at room temperature for one hour. The mixture gradually turned deep maroon. The boron trifluoride was not taken up as rapidly by the alkylphenol as it was by *p*-cresol; most of it passed out of the system. Although no further material condensed in the cold trap after about one hour, the reaction was allowed to proceed for four hours.

The product was worked up in the same way as in the alkylation procedure except that it was diluted to 500 ml. volumetrically and chromatographic analysis was run on a 50-ml. aliquot. The chromatogram gave the same four fractions as obtained from the alkylation and in about the same proportions. Elemental analysis of each fraction showed the presence of high-molecular-weight materials. The material in the cold trap was found by gas chromatography to be 67% isopentane, 17% isobutane and 16% hexanes.

Reaction of *t*-Amyl Chloride with BF_3.—A sample of *t*-amyl chloride was treated with BF_3 for 10 minutes and the cloudy mixture was allowed to stand for 4 hours. Water was added, and the organic layer was separated, washed twice with water, dried over Drierite, and filtered. Distillation yielded 50% *t*-amyl chloride, 30% material boiling up to 160° and 20% bottoms. Infrared spectra of the distillate and bottoms showed absorptions at 11.29 and 12.23 μ, indicative of $R_2C{=}CH_2$ and $R_2C{=}CHR$, respectively.

Alkylation of C^{14}-Labeled *p*-Cresol.—To 0.4 mole (70 g.) of *p*-bromophenol in ether was added 0.8 mole of butyl-

(2) A. G. Nerheim and R. A. Dinerstein, *Anal. Chem.*, **28**, 1029 (1956).

(3) 2,2,4-Trimethylpentane, knock-test grade; this solvent did not contribute excessive amounts of residue or interfere with ultraviolet measurements.

(4) N. D. Coggeshall, THIS JOURNAL, **69**, 1620 (1947); W. C. Sears and L. J. Kitchen, *ibid.*, **71**, 4110 (1949); R. A. Friedel, *ibid.*, **73**, 2881 (1951).

(5) Prepared according to British Patent 672,820, May 28, 1952.

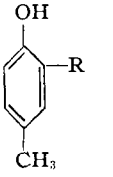
lithium in ether.[6] The mixture was refluxed 1.5 hours, and 0.4 mole (57 g.) of $C^{14}H_3I$ (spec. activity = 0.2 μc. per millimole) was added. The organic layer was separated and dried, and the ether was evaporated. Distillation at 1–2 mm. gave 16 g. (30% yield) of *p*-cresol.

The labeled *p*-cresol was alkylated with 2-methylbutene-2 in the presence of 50 mole % BF_3. Fractional distillation gave several fractions, b.p. 160–180° (0.5 mm.), which were chromatographically separated over silica gel with 10% ether in isoöctane as the eluent. The last fractions were concentrated, and the crystalline 2,2′-methylendi-*p*-cresol was filtered off directly; m.p. 119–120.5°.

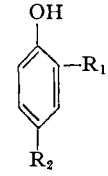
The radioactivity of the starting *p*-cresol and that of the bisphenol were compared by liquid scintillation counting.[7] Samples were prepared by dissolving 1 g. of the radioactive material in 20 ml. of a solution containing 6.9 g. per liter of diphenyloxazole in C.P. toluene and diluting to 50 ml. with toluene. The total counts per minute were then determined on both materials. After correcting for quenching, the ratio of bisphenol counts to *p*-cresol counts per mole was found to be 3.2. The theoretical ratio for the case in which the methylene carbon atom is radioactive is 3.0; that for its being inactive is 2.0.

Discussion

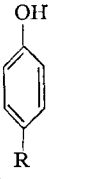
Alkylation of *p*-cresol with 2-methylbutene-2 or *t*-amyl chloride at 25 mole % BF_3 gave a high yield of I, as expected. With 50 mole % BF_3 present, the alkylation resulted in a mixture of phenolic products, which was separated by chromatography into four general classes of compounds: 2-*t*-alkyl-4-methylphenols (II), 2-*sec*-alkyl-4-alkylphenols (III), *p*-*t*-alkylphenols (IV) and 2,2′-bismethylenediphenols (V)



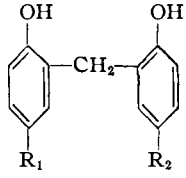
IIa, R = *t*-butyl



III, R_1 = *s*-alkyl



IVa, R = *t*-butyl
IVb, R = *t*-amyl

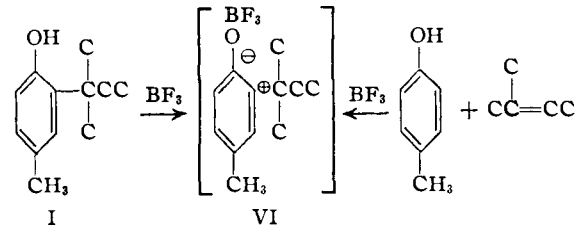


Va, R_1 and R_2 = CH_3
Vb, R_1 = CH_3, R_2 = H

In addition, isopentane and other volatile saturated hydrocarbons were isolated during the alkylation.

Attempts to trace the course of the reaction by quantitative determination of the products were hampered by formation of high-molecular-weight materials. Reaction of *t*-amyl chloride alone with BF_3 showed that these materials are formed by side reactions of the alkylating agents with the catalyst.

When 2-*t*-amyl-4-methylphenol (I) was treated with BF_3, the rapid absorption usually exhibited by phenols did not occur. Only after continued addition of BF_3 did much reaction take place. The same sort of products were obtained as in the alkylation of *p*-cresol at high concentrations of BF_3. An $-OBF_3$ group apparently cannot exist in a position *ortho* to a tertiary alkyl group, probably because of steric effects. An intermediate ion-pair (VI) is produced which is probably the same as that formed in the alkylation.

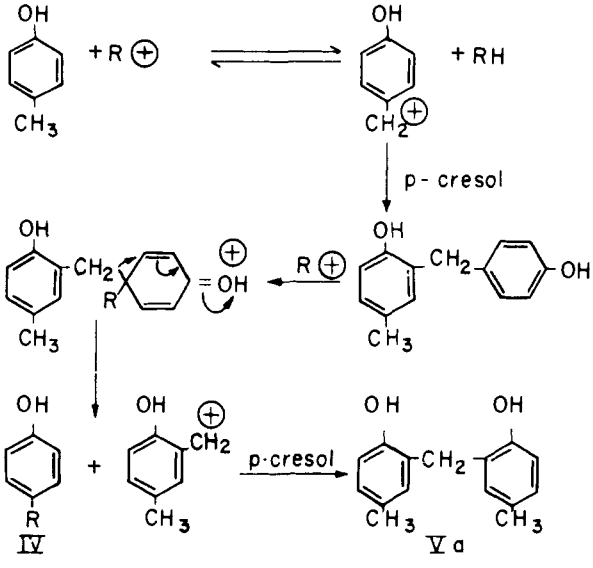


I VI

An early step in the reaction must be transfer of a hydride ion to a tertiary carbonium ion, with the formation of a benzyl cation.[8] Evidence for such a transfer was the isolation of saturated hydrocarbons. Added isopentane, a good hydride-ion donor, suppressed the formation of the unexpected products and gave a good yield of I; *n*-hexane did not do so.

The loss of a methyl group by *p*-cresol in the formation of the *p*-*t*-alkylphenols plus the appearance of a methylene group in the bisphenols suggests that an interdependent mechanism is involved. The alkylation of p-$C^{14}H_3C_6H_4OH$ and recovery of the 2,2′-bismethylenedi-*p*-cresol showed that the methylene carbon was radioactive and therefore derived from the methyl group in *p*-cresol.

In the over-all mechanism, high concentrations of boron trifluoride must inhibit the normal alkylation reaction by forming a complex with most of the *p*-cresol. The complexed *p*-cresol may then undergo the reaction sequence



IV Va

For simplicity, the BF_3 portions of the structures have been omitted.

The material represented as III is probably 2-*sec*-alky-4-alkylphenol, which arises from a hydride shift within a *t*-alkyl carbonium ion and is analogous to examples reported in the alkylation

(6) R. G. Jones and H. Gilman, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 351–353.

(7) I. A. Berstein, *Tracerlog*, **59**, 5 (1954).

(8) A similar process has been proposed to account for analogous products obtained in the alkylation of *p*-xylene: L. Schmerling, J. P. Luvisi and R. W. Welch, paper presented at one-day Symposium of the Chicago Catalysis Club, May 17, 1958.

of benzene.[9] The formation of *t*-butylated products during the alkylation must result from a side reaction of the *t*-amyl ion similar to that described by Friedman and Morritz.[10]

Conclusion.—In the presence of boron trifluoride, alkylation of *p*-cresol by tertiary alkylating agents can proceed by two mechanisms. At low BF_3 concentrations, normal alkylation results in *ortho* substitution by reaction of the *t*-alkyl carbonium ion with an uncomplexed *p*-cresol molecule. At high concentrations, the availability of uncomplexed *p*-cresol is reduced; hydride transfer then occurs and leads to the formation of *p*-*t*-alkylphenols, bismethylenediphenols and saturated hydrocarbons.

The effect of the structure of the alkylating agent remains to be studied. Further investigation into the properties of the *p*-cresol–BF_3 complex may shed further light on the mechanism of aromatic substitution.

WHITING, IND.

(9) B. S. Friedman and F. L. Morritz, THIS JOURNAL, **78**, 2000 (1956), and references cited there.

(10) B. S. Friedman and F. L. Morritz, *ibid.*, **78**, 3430 (1956).

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

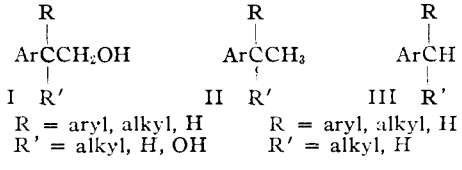
Raney Nickel Catalyzed C1–C2 Fission of 2-Arylethanols; the Single Carbon Fragment[1,2]

BY WILLIAM A. BONNER AND THOMAS W. GREENLEE

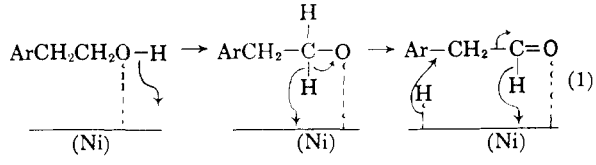
RECEIVED NOVEMBER 7, 1958

Experiments have been undertaken to establish the chemical identity of the single carbon by-product formed when 2-arylethanols of the type $ArCRR'CH_2OH$ are cleaved to hydrocarbons of one less carbon atom ($ArCHRR'$) by action of Raney nickel in refluxing ethanol. When 2-phenyl-1,2-propanediol-1-C^{14} (IV) was subjected to such reaction conditions the resulting ethylbenzene product was non-radioactive, indicating that only the $-CH_2OH$ group at C1 in IV had been lost during the cleavage reaction. When the gases (chiefly H_2 and CH_4, with small amounts of CO_2) evolved during such cleavage reactions were examined for radioactivity in the case of IV they were found to contain less than 0.5% of the label. The liquid fraction obtained on filtering the catalyst after cleavage of IV was found to be void of radioactivity except for that (19%) which could be accounted for by the isopropylbenzene-β-C^{14} present among the products therein. Examination of the residual catalyst after cleavage of IV showed it to contain over 75% of the original label. Solution of this residual catalyst in sulfuric acid provided a gas sample containing radioactive carbon monoxide as its major single carbon constituent. These observations are in accord with the conclusion that carbon monoxide, strongly adsorbed to the catalyst surface, is the major single carbon by-product of the Raney nickel-catalyzed cleavage of 2-arylethanols.

In 1957, we reported[3] our observations that 2-aryl primary alcohols (I) and their corresponding aldehydes undergo simultaneous deoxygenation to



alkylaromatic hydrocarbons (II) of similar carbon skeleton as well as C1–C2 carbon–carbon bond cleavage to alkylaromatics of one less carbon (III) under the influence of Raney nickel catalyst in refluxing ethanol solvent. The relative quantities of simple deoxygenation product II and cleavage product III varied over rather wide ranges depending upon the nature of R and R' in I, and no significant amounts of cleavage products at all were noted when a 2-aryl substituent or a primary alcohol function were absent in the starting reactant. A tentative mechanism (1), involving initial dehydrogenation of the 2-arylethanol to an intermediate aldehyde, was proposed[3] to rationalize the known facts of such C1–C2 cleavage processes. A mechanism such as (1) would predict the formation of carbon monoxide as the single carbon by-product of the cleavage reaction, and indeed Paul has reported[4,5] without analytical details the production of carbon monoxide by action of Raney nickel on several primary alcohols under roughly comparable conditions. Paty and Deschamps, on the other hand, have reported[6] methane (80%) and carbon dioxide (10–15%) as the principal gaseous products along with only small quantities (4%) of carbon monoxide by action of Raney nickel on ethanol at 225–280° and 1430–3420 p.s.i. In view of the experimental sketchiness of Paul's reports and the possibly conflicting data of Paty and Deschamps, we have undertaken an experimental evaluation of mechanism 1 by seeking to isolate and characterize the single carbon by-product in C1–C2 cleavage reactions of the above type. Such a by-product might consist of one or more of any of the stable single carbon compounds containing H and/or O, *i.e.*, C, CO, CO_2, HCO_2H, CH_2O, CH_3OH or CH_4. Our principal experimental tools in this study have involved fractional freezing of the gaseous reaction products, vapor–liquid partition chromatographic separation



(1) This constitutes Communication XI in the series "The Stereochemistry of Raney Nickel Action"; for X see THIS JOURNAL, **81**, 1448 (1959).

(2) This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

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

(4) R. Paul, *Bull. soc. chim.*, **8**, 507 (1941).

(5) R. Paul, *Compt. rend.*, **208**, 1319 (1939).

(6) M. Paty and J. Deschamps, *ibid.*, **208**, 1319 (1939).