

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 BF₃ 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-BF₃ 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]

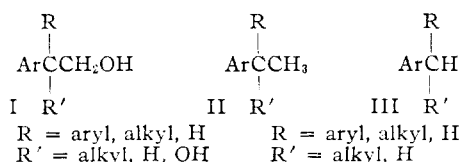
Raney Nickel Catalyzed C1-C2 Fission of 2-Arylethanols; the Single Carbon Fragment^{1,2}

BY WILLIAM A. BONNER AND THOMAS W. GREENLEE

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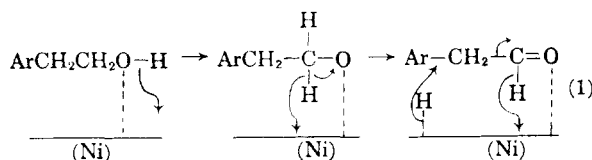
Experiments have been undertaken to establish the chemical identity of the single carbon by-product formed when 2-arylethanols of the type ArCRR'CH₂OH are cleaved to hydrocarbons of one less carbon atom (ArCHRR') by action of Raney nickel in refluxing ethanol. When 2-phenyl-1,2-propanediol-1-C¹⁴ (IV) was subjected to such reaction conditions the resulting ethylbenzene product was non-radioactive, indicating that only the -CH₂OH group at C1 in IV had been lost during the cleavage reaction. When the gases (chiefly H₂ and CH₄, with small amounts of CO₂) 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-C¹⁴ 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 reported³ 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 proposed³ 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 reported⁶ 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, CO₂, HCO₂H, CH₂O, CH₃OH or CH₄. 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).

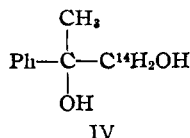
(4) R. Paul, *Bull. soc. chim.*, **8**, 507 (1941).

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

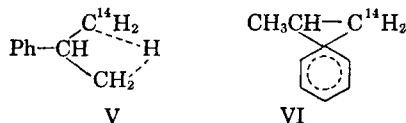
(6) M. Paty and J. Deschamps, *ibid.*, **208**, 1319 (1939).

of liquid products and application of mass spectrographic and/or radioactive tracer techniques to the various fractions so obtained.

At the outset it appeared desirable to establish whether the single carbon product, whatever its nature, in such cleavage processes arose exclusively from the hydroxymethyl group at C1 in I, or whether perhaps other carbon atoms in the aliphatic chain might be involved. To this end we have subjected 2-phenyl-1,2-propanediol-1-C¹⁴ (IV) to



cleavage reaction conditions, then separated the toluene (67%)³ and isopropylbenzene (33%) products quantitatively by vapor-liquid partition chromatography. The toluene product was completely void of radioactivity, indicating that the cleavage of IV involved exclusive removal of the hydroxymethyl group at C1. This observation is in accord with mechanism 1 and eliminates, of course, the possibility of the mechanistic intervention of any non-classical ionic (or equivalent radical) intermediates of the types V or VI.



When ethanol itself is heated with Raney nickel either under gentle^{4,5} or drastic⁶ conditions gaseous products are liberated. We have found that under our typical conditions for the cleavage reaction gases are evolved from a mixture of Raney nickel and refluxing ethanol at a steady rate of about 150 ml. per hour. When a cleavable substrate, 2-phenyl-1-propanol, was included in the reaction mixture the rate of gas evolution was decreased to about 90 ml. per hour under comparable conditions. Reactions of this type were then duplicated in the apparatus shown in Fig. 1, allowing the evolved gases to expand into the evacuated portion of the system at periodic intervals during the reaction. Columns 1 and 2 of Table I indicate the mass spectrometrically determined composition of the gases evolved when ethanol itself and ethanol containing 2-phenyl-1-propanol were heated with Raney nickel. The principal gaseous products in both experiments are seen to be hydrogen and methane, with only trivial quantities of such constituents as carbon monoxide or carbon dioxide. Furthermore, columns 1 and 2 indicate an essential identity of the compositions of the evolved gases, whether 2-phenyl-1-propanol was present or not, the small differences in percentage composition being not significantly larger than those encountered in duplicates of the individual experiments. These data are in sharp contrast to the report of Paul^{4,5} that considerable quantities of carbon monoxide are liberated by action of Raney nickel on saturated primary alcohols under such conditions.

To facilitate establishing the chemical identity of the single carbon cleavage reaction by-product,

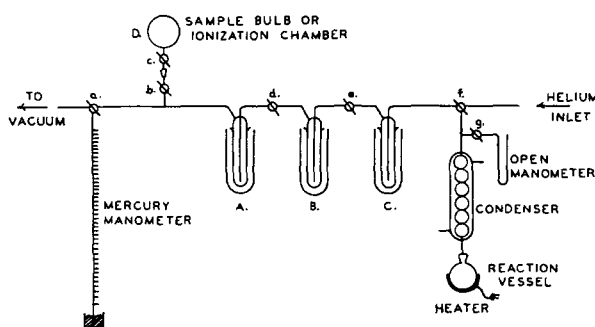


Fig. 1.—Vacuum line for cleavage reaction experiments.

attention was next turned to additional radioactive carbon tracer experiments. 2-Phenyl-1,2-propanediol-1-C¹⁴ (IV) and Raney nickel were heated in refluxing ethanol in the apparatus of Fig. 1, trap C being chilled by Dry Ice and trap B by pentane slush. As the reaction proceeded, gaseous products were again periodically bled into the evacuated portion of the system. The mass spectrometric analysis of the uncondensed gases in this experiment is given in column 3 of Table I, where the data appear qualitatively similar to those in columns 1 and 2. The mass spectrometer sample bulb at D in Fig. 1 was then replaced by an evacuated ionization chamber and a sample of the uncondensed gases was collected for radioactivity assay. Correction of the latter by appropriate volume and pressure data allowed calculation that the entire uncondensed gas sample contained only 0.11% of the initial radioactivity (no. 1, Table II), indicating that the methane fraction of the gas sample (no. 3, Table I) did not

TABLE I
PERCENTAGE COMPOSITION OF GASES SAMPLES IN VARIOUS
CLEAVAGE REACTION EXPERIMENTS

Gas	1	2	3	4	5	6	7
H ₂	63.0	60.7	62.2	94.4	56.6	71.1	7.7
CH ₄	33.8	36.1	24.3	0.1	20.1	16.0	0.1
CO	0.0	0.1	0.0	3.8	10.3	8.4	0.8
CO ₂	1.6	2.6	2.0	0.8	9.1	3.0	0.1
Other ^b	1.6	0.5	11.5 ^c	0.9	3.9 ^c	1.5	91.3 ^d

^a Legend: 1, gas from Raney nickel and refluxing ethanol; 2, gas from Raney nickel and refluxing ethanol containing 2-phenyl-1-propanol; 3, gas from Raney nickel and refluxing ethanol containing 2-phenyl-1,2-propanediol-1-C¹⁴; 4, gas from solution of residual catalyst from no. 3 in H₂SO₄; 5, gas from vacuum baking of residual catalyst from no. 3; 6, gas from vacuum baking of residual catalyst from no. 1; 7, gas from "hydrogen-free" Raney nickel and refluxing *n*-heptane containing 2-phenyl-1-propanol. ^b Including traces of oxygen, nitrogen, ethanol, acetaldehyde acetone, ethane and propane. ^c Principally residual air. ^d Residual sweep gas (helium) was 87.6%.

contain the single carbon by-product of the cleavage reaction and that this methane must therefore have originated (*vide infra*) exclusively from the ethanol solvent. The pentane slush coolant was next removed from around trap B of the apparatus shown in Fig. 1, and the small amount (approximately 0.2 mmole) of condensed carbon dioxide therein was allowed to expand into the ionization chamber. This sample, however, contained (no. 2, Table II) only 0.29% of the original radioactivity, indicating that at best only a negligible trace of the cleavage reactant by-product could be carbon di-

oxide. The Dry Ice trap C of Fig. 1 contained a small quantity (60 mg.) of solid material whose radioactivity assay showed it to contain only 0.05% of the original label (no. 3, Table II). No attempt was made to characterize this material, though we suspect its identity as formaldehyde polymer. In any case, the lack of its origin from any significant amount of the Cl atom of IV is obvious. The total radioactivity accounted for among the gaseous products resulting on cleavage of IV was thus less than 0.5% of that in the original IV, indicating clearly that the single carbon by-product of the cleavage of IV must be sought either in the liquid or catalyst portions of reaction mixture.

TABLE II

RADIOCHEMICAL BALANCE DURING CLEAVAGE OF 2-PHENYL-1,2-PROPANEDIOL-1-C¹⁴ (IV)

Mole of IV reacted, 0.01163; specific radioactivity of IV, 0.157 mc./mole; total radioactivity present, 1.829 μ c.

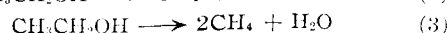
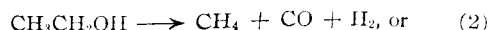
No.	Sample examined	Radioactivity found, μ c.	% of total
1	Uncondensed gases in col. 3, Table I	0.00206	0.11
2	Carbon dioxide from trap B, Fig. 1	.00527	.29
3	Solid material from trap c, Fig. 1	.00082	0.05
4	Reaction medium filtrate	.355	19.4
5	Recovered catalyst	1.37	75.0
Total		1.733	94.9

The catalyst was accordingly filtered from its supernatant and the filtrates and washings were diluted to a known volume. Radioactivity assay of an aliquot thereof indicated that the total liquid fraction of the reaction mixture contained (no. 4, Table II) only 19.4% of the original label. Another sample of the liquid fraction was placed on a vapor-liquid chromatographic column under conditions where the hydrocarbon components (ethylbenzene and isopropylbenzene- β -C¹⁴) were known to have greater retention times than other liquid components (ethanol and methanol, formaldehyde or formic acid). The entire ethanol fraction (which would contain such single carbon products) was recovered by chilling the effluent helium stream from the vapor chromatographic column during the appropriate time interval. The condensate was void of radioactivity, however, indicating that the radioactivity in the reaction medium filtrate (no. 4, Table II) must have been due solely to the presence therein of the simple dehydrogenation product (isopropylbenzene- β -C¹⁴) and possible unreacted IV, and not to any single carbon cleavage reaction by-product.

Since 80% of the original radioactivity in IV was still unaccounted for, the filtered catalyst from the cleavage reaction of IV was examined in some detail. When an aliquot of this recovered catalyst was assayed for radioactivity in the usual manner^{10,11} by digestion with Van Slyke solution it was found that 75% (no. 5, Table II) of the original radioactivity present in IV had remained associated with the catalyst during the cleavage reaction. A total of 95% of the original radioactivity having now been accounted for, we next undertook to establish the chemical state of the major fraction of the original label associated with the residual cata-

lyst. When a sample of this catalyst was dissolved in dilute sulfuric acid, mass spectrometric analysis of the radioactive gas sample evolved gave the data in no. 4, Table I. Of the non-hydrogen components of this gas sample, carbon monoxide makes up the bulk (67.8%), while carbon dioxide (14.3%) and methane (1.8%) are present in markedly smaller amount. These facts indicate clearly that the principal single carbon by-product formed on cleavage of IV with Raney nickel is carbon monoxide, which remains strongly adsorbed on the catalyst surface. To confirm this conclusion we have attempted to liberate the adsorbed gases from the above residual cleavage catalyst alternatively by baking an aliquot of the latter at 200° (1 mm.) in the evacuated apparatus of Fig. 1. The composition of the radioactive gas which was desorbed in this experiment is shown in no. 5 of Table I. Of the non-hydrogen components of this mixture methane (46.5%) now makes up the bulk, whereas carbon monoxide (23.8%) and carbon dioxide (21%) are present in smaller quantity. The trivial percentage of methane in no. 4 compared to the relatively high percentage of methane in no. 5 of Table I, as well as the inverse with respect to carbon monoxide quantities in these two cases, indicate clearly that the adsorbed carbon monoxide produced from such cleavage reactions was reduced to methane during the subsequent vacuum baking of, and resulting gas desorption from, the residual catalyst. This thermal desorption phenomenon, which occurs quite abruptly at about 200° (1 mm.), appears to be an irreversible exothermic process accompanied by weak chemiluminescence. It has been noted with Raney nickel samples whether or not they have been used as cleavage reaction catalysts and involves, we believe, the recombination of adsorbed hydrogen atoms to molecular hydrogen. In the present instance this process appears to provide a vigorous reducing environment for the adsorbed carbon monoxide from the cleavage reaction, yielding methane. These interesting phenomena are under further investigation at the present time.

In the light of our above radiochemical and analytical data it is apparent that the high percentages of methane in gas samples no. 1 and 2 of Table I must have arisen from a competing Raney nickel-catalyzed cleavage reaction involving the ethanol solvent itself, *i.e.*



In view of the essential absence of carbon monoxide in gas samples no. 1 and 2 it is obvious that the carbon monoxide required by Equation 2, if operative, must likewise have been adsorbed on the catalyst surface. This conclusion is confirmed and equation 3 is discountable as a source of methane by the data of no. 6, Table I. In this experiment the residual catalyst remaining after refluxing ethanol with Raney nickel (no. 1, Table I) was subjected to similar thermal gas desorption at 200° (1 mm.), producing a gas sample comparatively slightly richer in carbon monoxide than that of no. 5, Table I.

Finally, we have undertaken to duplicate several of our previous³ cleavage experiments using as cata-

lyst "hydrogen free" Raney nickel, prepared by the above baking of ordinary Raney nickel at 200° *in vacuo*.⁷ When 2-phenyl-1-propanol and hydrogen-free Raney nickel were heated in heptane solvent for several hours, ethylbenzene, but no isopropylbenzene, was formed. The gases liberated during this reaction were collected and analyzed mass spectrometrically in the usual way to provide the data in no. 7 of Table I, where it is seen again that carbon monoxide is the principal single carbon cleavage reaction by-product. A material balance calculation showed, however, that most of the carbon monoxide produced by the cleavage of 2-phenyl-1-propanol with hydrogen free Raney nickel once again remained adsorbed on the catalyst surface. The fact that only ethylbenzene and no isopropylbenzene resulted from this reaction suggests that while surface adsorbed hydrogen on the nickel is unnecessary for the occurrence of the cleavage reaction, such adsorbed hydrogen is necessary for the ordinarily competing simple dehydroxylation reaction.

The analytical and radiochemical data in our various experiments, as summarized in Tables I and II, are, we believe, adequately explained in terms of mechanism (1) for the Raney nickel-catalyzed cleavage of 2-arylethanols, where the carbon monoxide by-product remains strongly adsorbed as such to the catalyst surface. Confirmation of these conclusions has come from stereochemical studies, to be reported presently, involving cleavage of optically active 2-arylethanols having an asymmetric center at C2.

Experimental

2-Phenyl-1,2-propanediol-1-C¹⁴ (IV).—Acetophenone (29 g.) and sodium cyanide (29.5 g.) containing 0.2 mc. of KC¹⁴N, were allowed to react in ether (22 ml.) and water (36 ml.) on gradual addition of hydrochloric acid (51 ml.) at 5–10° after the procedure of Eliel and Freeman.⁸ The resulting acetophenone cyanohydrin was hydrolyzed by action of concentrated hydrochloric acid and the 2-hydroxy-2-phenylpropanoic-1-C¹⁴ acid thereby produced was isolated and purified as described.⁸ The yield of purified acid having a specific radioactivity of 0.157 mc./mole was 14.5 g. (14% based on NaCN). A variety of attempts to increase the yield, based on NaCN, by modifying Eliel and Freeman's procedure was unsuccessful.

The above 2-hydroxy-2-phenylpropanoic-1-C¹⁴ acid was reduced to 2-phenyl-1,2-propanediol-1-C¹⁴ (IV) using lithium aluminum hydride in ether solution after the procedure of Eliel and Freeman.⁹ The crude product was purified by distillation (b.p. 115° (7 mm.)). The distillate, which crystallized slowly on standing, was used as such in the experiments below.

Raney Nickel-catalyzed Cleavage of 2-Phenyl-1,2-propanediol-1-C¹⁴ (IV).—This reaction was conducted by treating the above diol IV with excess Raney nickel in refluxing ethanol in the manner described previously.³ The hydrocarbon products of the reaction were isolated in the previous fashion and the ethylbenzene and isopropylbenzene- β -C¹⁴ components were separated quantitatively using the vapor-liquid partition chromatographic column previously described.³ Examination of the ethylbenzene fraction by wet combustion¹⁰ to carbon dioxide followed by counting¹¹ of the latter in an ionization chamber with the aid of a Cary model 31 vibrating reed electrometer indicated the ethylbenzene fraction to be void of radioactivity.

The Single Carbon By-product on Cleavage of 2-Phenyl-1,2-propanediol-1-C¹⁴.—The above diol IV (1.77 g., 1.829

mc.), Raney nickel (*ca.* 15 g.) and absolute ethanol (25 ml.) were placed in the reaction vessel of the vacuum line shown in Fig. 1, trap A being replaced by a 2-liter flask. The entire system was evacuated and flushed with helium several times, with the open manometer shut off. Trap C was then surrounded by a Dry Ice-acetone mixture and trap B by pentane slush made by chilling pentane with liquid nitrogen. The entire system to stopcock f was evacuated and the sample bulb at D was flamed and cooled. Stopcocks a, b and c were closed, a being arranged so as to include the mercury manometer. The reaction vessel and condenser below f contained helium at atmospheric pressure. Reflux of the reaction mixture was commenced and stopcock g was opened. Whenever the evolved gases caused a pressure increase in the reaction vessel, as shown by the open manometer, the excess pressure was cautiously bled into the evacuated line by manipulation of stopcock f. After a 4.5-hour reflux period the pressure in the entire system was about 0.5 atmosphere and heating was stopped and stopcock f was closed. At this point stopcocks b and c were opened allowing collection in D of a sample of the uncondensed gases for mass spectrometric analysis.¹² The above is the general procedure by which the data in experiments 1, 2, 3 and 7 in Table I were obtained. The sample bulb at D was next replaced by an evacuated ionization chamber which was then opened to the system to collect a second gas sample for radioactivity assay. The partially filled ionization chamber was filled to atmospheric pressure with carbon dioxide prior to its installation on the vibrating reed electrometer. After counting, the ionization chamber was replaced at D and the entire system to stopcock c was again evacuated. Stopcock a was closed to the vacuum pump and the pentane slush bath was removed from trap B, allowing the carbon dioxide therein condensed to evaporate into the system. The ionization chamber was removed, filled with tank CO₂ and counting was conducted as before. The known volumes of the components of the vacuum line in Fig. 1 and the observed pressure changes on the mercury manometer during the above manipulations permitted correction of the observed radioactivities in the ionization chamber to the entire gas samples. In this way the data in nos. 1 and 2 of Table II were collected. The 60 mg. of solid material in trap C was assayed as usual,^{10,11} no attempt being made at its characterization.

The reaction vessel was next removed and the contents were filtered (sintered glass funnel), the damp dry catalyst being rinsed several times by slurring with ethanol and again sucking damp dry. The catalyst was bottled and stored at 0° and the filtrate and rinsings were diluted to 40.0 ml. A 0.10-ml. aliquot of the filtrate was assayed in the usual way,^{10,11} and the radioactivity found in the aliquot was multiplied by 400, providing the data in no. 4 of Table II. In another experiment a portion of the above filtrate was placed on the usual vapor-liquid partition chromatographic column³ and the initial fraction containing all oxygenated constituents was collected prior to efflux of the hydrocarbon products. This initial fraction was void of radioactivity, indicating that the radioactivity in the reaction medium filtrate must have been due exclusively to its isopropylbenzene- β -C¹⁴ constituent (plus possibly some unreacted starting material).

An aliquot of the above residual catalyst was assayed in the usual way,^{10,11} and the radioactivity found was corrected to the entire sample by multiplication by the reciprocal aliquot factor, providing the data in no. 5 of Table II. In another experiment an aliquot of the residual catalyst was placed in a small 2-necked flask equipped with a dropping funnel. This was placed under the condenser in the apparatus of Fig. 1, the system was evacuated and dilute sulfuric acid was added through the dropping funnel. After the catalyst had dissolved a sample of the evolved gases was collected and assayed as before, providing the analytical data of no. 4, Table I. A sample of this gas was collected in the ionization chamber and assayed for radioactivity as before. The total radioactivity calculated as associated with the catalyst by this criterion, however, did not check well with no. 5 in Table II, presumably because of the non-typical composition of the gases (mainly H₂ rather than CO₂) in the ionization chamber under these conditions. Finally, an aliquot of the above residual catalyst was placed in a flask under the condenser of Fig. 1, a Dry Ice-acetone

(7) F. H. Hauptmann and B. Wladislaw, *THIS JOURNAL*, **72**, 707, 711 (1950).

(8) E. L. Eliel and J. P. Freeman, *Org. Syntheses*, **33**, 7 (1953).

(9) E. L. Eliel and J. P. Freeman, *THIS JOURNAL*, **74**, 925 (1952).

(10) O. K. Neville, *ibid.*, **70**, 3501 (1948).

(11) V. A. Raaen and G. A. Ropp, *Anal. Chem.*, **25**, 174 (1953).

(12) These were performed by Stanford Research Institute.

mixture was placed around trap C and the system was evacuated. The catalyst was warmed cautiously with a free flame, evaporating residual ethanol. As heating was continued (to ca. 200° as determined by separate experiments employing a heating bath) gases desorbed abruptly from the catalyst, a process accompanied by evolution of heat and light, and samples of these gases were collected in the usual manner for mass spectrographic and radioactivity assays. The data in nos. 5 and 6 of Table I were obtained on gas samples collected in this manner. Radioactivity assay of the gas sample in question followed by appropriate pressure and volume corrections indicated that the sample contained only about 36% of the radioactivity known (no. 5, Table II) to be associated with the residual catalyst. Accordingly, the catalyst remaining after the above vacuum

baking was analyzed for additional radioactivity by the usual wet combustion procedure, and found to contain radioactivity to an extent accounting for an additional 24% of that known to be present. A solid residue remaining after the above wet combustion was filtered and re-assayed in the same way, accounting for an additional 11% of the radioactivity in no. 5, Table II. These results suggest that the thermal desorption process for Raney nickel samples containing adsorbed hydrogen and carbon monoxide not only involves conversion of the latter to methane, as discussed above, but also conversion to some quite refractory form of carbon, possibly a carbon-nickel alloy. This question is under further investigation.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Pyrolysis of Esters. XVII. Effect of Configuration on the Direction of Elimination¹

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RECEIVED JULY 25, 1958

Vapor-phase chromatography showed that the pyrolysate from methyl *cis*-2-acetoxycyclohexanecarboxylate contained only methyl 2-cyclohexenecarboxylate and no methyl 1-cyclohexenecarboxylate. Similarly, the pyrolysate from the methyl *trans*-2-acetoxycyclohexanecarboxylate contained 97% of the conjugated ester and only 3% of the unconjugated isomer. Thus it appears that no *trans* elimination occurred in this cyclic system. Additional evidence that no rearrangement occurs during pyrolysis was obtained from the fact that pyrolysis of methyl 3-acetoxycyclohexanecarboxylate gave a mixture of methyl 2- and 3-cyclohexenecarboxylates but no conjugated ester.

Since Hurd and Blunck³ proposed that esters pyrolyze by a unimolecular cyclic mechanism, evidence that supports this proposal has accumulated. One of the most convincing pieces of evidence is the demonstration that γ -lactones that can not sterically form an intermediate six-membered ring are stable at 600°, while larger lactones that can form a transient six-membered ring pyrolyze normally at 500°.⁴ Alexander and Mudrak⁵ showed also that in five- or six-membered cyclic systems *cis* elimination occurred more readily than did *trans* elimination. While both the *cis*- and *trans*-2-methylindanyl acetates gave the same product, 2-methylindene, a temperature approximately 200° higher was required for decomposition of the *trans* isomer. Similarly, pyrolysis of *cis*-2-phenylcyclohexyl acetate gave by a normal *cis* elimination 93% of 3-phenylcyclohexene but by an apparent *trans* elimination 7% of 1-phenylcyclohexene. The mechanism of this *trans* elimination is still a matter of speculation. Of course, Blomquist and Goldstein⁶ showed that, if the ring was large enough, a so-called *trans*-hydrogen could be eliminated by a normal cyclic process.

Bordwell, *et al.*,⁷ recently have shown that, if the activation of the hydrogen atom is great enough,

ionic elimination reactions that normally proceed by way of a *trans* mechanism can be made to proceed through a *cis* mechanism. More recently, Bordwell and Landis⁸ have shown that, if the *trans* hydrogen is sufficiently activated, the Chugaev elimination proceeds in a *trans* manner. It, therefore, seemed possible that, if the activation of the hydrogen atom was great enough, a *trans* elimination might take place during vapor-phase ester pyrolysis. In fact, a study of models showed that a transient six-membered ring was possible in a *trans* arrangement of the ester group and the hydrogen atom if the two groups were both equatorial and impossible if the two groups were both axial. Earlier work had shown that a carboxy group has a strong directional influence on the elimination so that pyrolysis of a β -acetoxycyclohexyl ester produced almost exclusively the conjugated olefin.⁹ It seemed possible, therefore, that pyrolysis of methyl *cis*-2-acetoxycyclohexanecarboxylate (I) might give rise to some *trans* elimination.

Mousseron and Canet¹⁰ pyrolyzed both ethyl *cis*- and *trans*-2-acetoxycyclohexanecarboxylates (as well as the corresponding xanthates) and reported, as the only product, the conjugated olefin, ethyl 2-cyclohexenecarboxylate. Although the product suggests a *trans* elimination, the authors pointed out the possibility that the elimination might have proceeded by a normal *cis* elimination to produce the unconjugated olefin IV which then isomerized to the more stable conjugated olefin III.

- (1) Previous paper in this series, *THIS JOURNAL*, **81**, 651 (1959).
- (2) Office of Naval Research Fellow, 1955-1957; Goodyear Tire and Rubber Co. Fellow, 1957-1958.
- (3) C. D. Hurd and F. H. Blunck, *THIS JOURNAL*, **60**, 2419 (1938).
- (4) W. J. Bailey and C. N. Bird, Abstracts of the 132nd National Meeting of the American Chemical Society, Miami, Fla., April, 1957.
- (5) E. R. Alexander and A. Mudrak, *THIS JOURNAL*, **72**, 1810, 3194 (1950); **73**, 59 (1951).
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