Polyenes. IV. The Structure and Absorption Spectra of the Ethyl α- and β-Ionylideneacetates and Related Compounds[1]

BY WILLIAM G. YOUNG AND SEYMOUR L. LINDEN

The "β" structure originally proposed by Karrer, et al.,[2] for ethyl β-ionylideneacetate (Iβ), derived from β-ionone by the Reformatsky reaction, has been questioned recently by Sobotka and co-workers.[3] These workers believe that the ring double bond of β-ionone moves out of conjugation during the Reformatsky reaction and that the ester obtained is actually of the "α" configuration. Thus, the esters (Iα,β) obtained from both α- and β-ionone were considered to have the identical system of double bonds (i. e., "α") and the differences in physical properties between them were attributed to differences in stereochemical configuration. In view of the fact that ethyl β-ionylideneacetate has been an important intermediate and model compound for investigations aiming at the synthesis of vitamin A, it is important to establish the presence of a β-ionone ring in this substance. It is the purpose of this communication to present the evidence obtained in this Laboratory for a true "β" configuration in ethyl β-ionylideneacetate.[4]

$$R-COOEt \xrightarrow{KOH} R-COOH \xrightarrow{PCl_3}$$

$$I\alpha,\beta$$

IIα,β (R' = CH₃)
IIIα,β (R' = n-C₃H₇)
IVα,β (R' = i-C₃H₇)

α isomers, R =

β isomers, R =
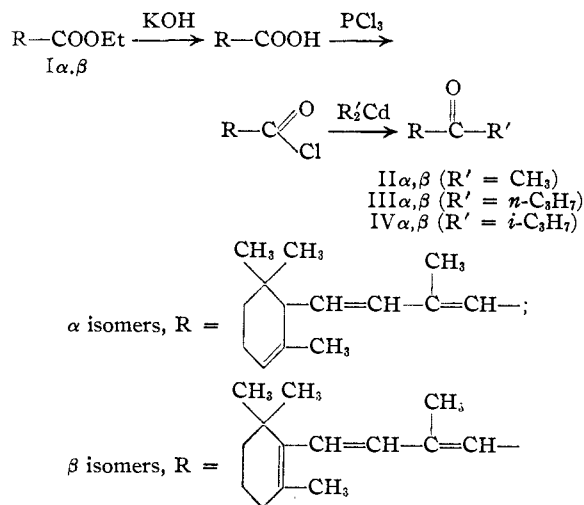
The evidence upon which Sobotka and co-workers base their conclusions is briefly as follows: (1) dry distillation of the barium salts of both the α- and β-ionylideneacetic acids yields the same cleavage product, viz., α-ionone; (2) the difference between the absorption spectra maxima of the α- and β-esters (ca. 12 mμ) is too small to be compatible with a difference of one conjugated double bond; (3) the absorption maximum of the β-ester is at a wave length about 15 mμ shorter than one would expect for a compound containing three double bonds conjugated with a carbethoxy group.

The dry distillation[3a,5] of the barium α- and β-ionylideneacetates was repeated in this Laboratory. The decomposition was found to proceed at a very high temperature—ca. 400°; no appreciable decomposition occurred at lower temperatures (150–200°). A small yield of a dark red liquid was obtained whose spectra, after redistillation, proved it to be mainly α-ionone.[6] The cleavage to α-ionone was accompanied by much deep-seated decomposition. Considerable quantities of low molecular weight fragments and water were were found in a trap cooled in a Dry Ice–acetone mixture. The α-ionone contained an impurity absorbing at 260 mμ (as yet uninvestigated) but no substance with a "broad inflection at 280–310 mμ" as reported by the English workers[5] was found. In view of the fact that the pyrolysis occurs at such a high temperature and is attended by such extreme decomposition, we do not believe that the isolation of a small yield of α-ionone is incompatible with a true "β" structure in the β-ionylideneacetic acid.

The difference between the absorption maxima of the α- and β-esters is surprisingly small. Most α–β pairs of isomers exhibit a much larger difference (ca. 20–40 mμ) between their maxima.[7] However, we feel that this difference (12 mμ) is not too small to completely eliminate the possibility of a real difference of one conjugated double bond in the esters in question, particularly in view of the chemical evidence. On the other hand, it is unlikely that the difference of 12 mμ can be due merely to a difference in the stereochemical configurations of the double bonds in the unsaturated side-chains of these esters.

The ester derived from β-ionone has maximum absorption (283 mμ) at a considerably shorter wave length than would be expected. This is particularly noticeable when one compares the spectrum of the β ester with that of β-methyloctatrienic acid which has the same conjugated system and exhibits an absorption maximum at 296 mμ.[8]

(1) This work was made possible by a research grant from Sharp and Dohme, Inc.

(2) Karrer, Solomon, Morf and Walker, Helv. Chim. Acta, 15, 878 (1932).

(3) (a) Sobotka, Bloch and Glick, THIS JOURNAL, 65, 1961 (1943); (b) Sobotka and Bloch, Chem. Rev., 34, 435 (1944); (c) Sobotka, Darby, Glick and Bloch, THIS JOURNAL, 67, 403 (1945).

(4) The esters derived, respectively, from α- and β-ionone will hereafter be termed, for convenience, the α- and β-esters.

(5) Davies, Heilbron, Jones and Lowe, J. Chem. Soc., 584 (1935).

(6) It is interesting to note that Karrer and Ruegger, Helv. Chim. Acta, 28, 319 (1945), report obtaining pure β-ionone from the distillation of either barium salt. Karrer gives the melting point of the phenylsemicarbazone of β-ionone as 171–172° whereas Sobotka[3a] reports m. p. 160–162° for the same substance.

(7) Young, Andrews and Cristol, THIS JOURNAL, 66, 520 (1944).

(8) The absorption maximum of the ethyl ester of β-methyl-octatrienic acid would be expected to be within several mμ of 296 mμ; Smakula, Angew. Chem., 47, 657 (1934); Dimroth, ibid., 52, 545 (1939).

However, to conclude from this[3] that the β-ester contains one less conjugated double bond than β-methyloctatrienic acid is questionable for by a similar reasoning the α-ester (λ_{max}, 272 mμ) should contain one more conjugated double bond (and thereby become a "β" compound) than β-methyl hexadienic acid[8] (λ_{max}, 259 mμ) which absorbs 13 mμ lower. The use of absorption spectra as a method of determining the position of the ring double bond in this pair of esters is thus highly unsatisfactory. It should be noted, however, that saponification of the β-ester yields an acid which crystallizes on standing. The solid acid[2,7] obtained upon recrystallization exhibits a maximum at 294 mμ which is completely in accord with values predictable from the model compounds considered above.

The proposal that the α- and β-esters are both of the "α"-form is in direct conflict with extensive work already published from this Laboratory,[7] particularly the identity of the compounds prepared from the α- and β-ionylidenecyanoacetic acids with those obtainable from the α- and β-esters. The proposed α-configuration for the ester derived from β-ionone also conflicts with the vitamin A activity reported for synthetic products derived from the β-ester.[9] Vitamin A activity is only compatible with a β-configuration of the ring double bond.

Conclusive proof that the ester derived from β-ionone is a true "β"-isomer has been obtained by ozonolysis experiments.[10] Many samples of the β-ester, prepared at different times and from different samples of β-ionone, were ozonized under a variety of conditions. In every case only geronic acid (VI) could be isolated.[11] Very fortunately the markedly lower solubility of isogeronic acid semicarbazone in ethyl acetate[11b] permits the ready detection of as little as 5–10% in a mixture with the corresponding geronic acid derivative. In no case could any isogeronic acid (V) be isolated from ozonization of the β-ester. Ozonolysis of the α-ester yielded only isogeronic acid. In view of the fact that α-ionone and α-ionylideneacetone[7] also give only isogeronic acid, it is highly unlikely that the geronic acid isolated from the β-ester could have been formed from rearrangement of the "α" to the "β" form during ozonization. Ozonolysis of mixtures of the α- and β-esters gave readily separable (via the semicarbazones) mixtures of isogeronic and geronic acid. The only conclusion consistent with these facts is that no β to α rearrangement occurs during the Reformatsky reaction with β-ionone and that the α- and β-esters derived from α- and β-ionone, respectively, are genuine α-β isomers.

(9) Kuhn and Morris, *Ber.*, **70B**, 853 (1937); Karrer and Rüegger, *Helv. Chim. Acta*, **23**, 284 (1940); Vul'fson, *C. A.*, **37**, 6657 (1943); Milas, U. S. Patent 2,369,158, Feb. 13, 1945; *C. A.*, **39**, 5044 (1945).

(10) Lindenbaum, Andrews and Young, THIS JOURNAL, **66**, 2130 (1944).

(11) (a) Karrer, Helfenstein, Wehrli and Wettstein, *Helv. Chim. Acta*, **13**, 1094 (1930); (b) Karrer, Morf and Walker, *ibid.*, **16**, 975 (1933).
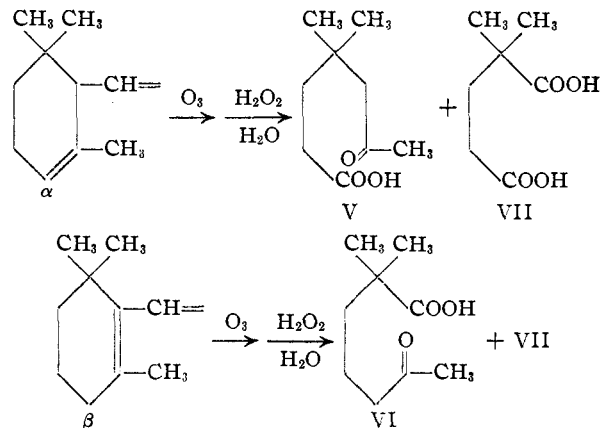
The highest yield of geronic acid obtained, by us, from ozonization of the β-ester was 20%. The procedure used to isolate the geronic acid from the ozonolysis mixture is necessarily involved and there is ample opportunity for mechanical and chemical losses (due to possible decomposition of the geronic acid by the hydrogen peroxide and sulfuric acid used to decompose the ozonide). Experiments were devised to determine the actual per cent. recovery of geronic acid under the conditions used in its isolation from an actual ozonization. Pure geronic acid was prepared by ozonization of β-cyclocitral.[12,13] Accurately weighed samples, designed to give approximately the same concentrations as obtained during the handling of the reaction mixture from an actual ozonization, were dissolved in acetic acid. The resulting solution was then treated as if it were a solution of the β-ester ozonide. In three such experiments the per cent. recovery was 46, 36 and 50%. Since it is highly improbable that isogeronic acid would be lost in preference to geronic acid, these results indicate that the yield of geronic acid semicarbazone actually isolated (20%) undoubtedly represents the original formation of about a 40% yield of geronic acid.

The α- and β-esters, like other conjugated systems, absorb ozone very slowly[14,15] necessitating the use of a large excess of ozone which causes considerable "over-ozonization" of the ozonide once formed. It is well known[16] that exposure of an ozonide to excess ozone markedly decreases the yield of identifiable fragments. Thus, the yield of recognizable degradation products to be expected from such a conjugated system as is contained in the β-ester is necessarily low, at best. By extracting the dicarboxylic acid fraction from the ozonization mixture, after removal of geronic or isogeronic acid, we were able to obtain a 15% yield of α,α-dimethylglutaric acid (VII). The same acid was obtained from both the α- and β-esters.

(12) Strain, *J. Biol. Chem.*, **102**, 137 (1933).

(13) Young and Linden, in process of publication.

(14) Noller, Carson, Martin and Hawkins, THIS JOURNAL, **58**, 24 (1936).

(15) Henne and Hill, *ibid.*, **65**, 752 (1943).

(16) Long, *Chem. Rev.*, **27**, 437 (1940).

The dicarboxylic acid is undoubtedly derived from degradation of the ozonide by the excess ozone.[17]

The most interesting spectral anomaly exhibited by the series of compounds derived from α- and β-ionone is the absorption spectra of the α- and β-ionylideneacetones[7] (IIα,β) obtained from the corresponding ionylideneacetic acids via the acid chlorides and dimethylcadmium. These ketones have maximum absorption at the same wave length (285 mμ) but have differently shaped curves (see Table I and Fig. 1). The α- and β-ionylideneacetones were proven[7] to be genuine α-β isomers by their preparation from the α- and

Fig. 1.—Ultraviolet absorption spectrum (in 95% ethanol) of α- and β-ionylideneacetone (II α, β, R—CO—CH$_3$) and two of its homologs (III, α, β, R—CO—CH$_2$-CH$_2$CH$_3$ and IV α, β, R—CO—CH(CH$_3$)$_2$).

(17) No α,α-dimethylglutaric acid could be isolated from experiments in which geronic acid was treated with hydrogen peroxide and dilute sulfuric acid.

β-ionylideneacetonitriles and by ozonization. In an effort to investigate the generality of this spectral phenomenon, the corresponding n-propyl (IIIα,β) and isopropyl (IVα,β) ketones were prepared. These pairs of ketones displayed absorption spectra curves almost identical to those obtained for the α- and β-ionylideneacetones (see Table I and Fig. 1). Each pair of α- and β-ketones had maxima at almost the same wave length, the α-isomer displaying a high sharp curve while the corresponding β-isomer had a broad flat curve. The α- and β-n-propyl ketones (IIIα,β) and the α- and β-isopropyl ketones (IVα,β) were shown to be true α-β isomers by ozonization. The β-isomers yielded geronic acid and the α-isomers isogeronic acid.

TABLE I

THE ABSORPTION SPECTRA[a] OF SOME HOMOLOGS OF α- AND β-IONYLIDENEACETONE

Compound	$\lambda_{max.}$ (mμ)	ϵ
α-Ionylideneacetone (IIα)	285	14500
β-Ionylideneacetone (IIβ)	285	11600
1-(α-Ionylidene)-2-pentanone (IIIα)	283.5	18400
1-(β-Ionylidene)-2-pentanone (IIIβ)	283	10100
1-(α-Ionylidene)-3-methyl-2-butanone (IVα)	280	17900
1-(β-Ionylidene)-3-methyl-2-butanone (IVβ)	283	10600

[a] In 95% ethanol.

Besides the spectral anomaly of the ketones discussed above and the spectral behavior of the α- and β-esters, other anomalies are: (1) the absorption spectra of β-ionone semicarbazone[18] and (2) the fact that the extinction coefficients of most of the α- compounds are higher than those of the corresponding β-isomers[7] even though the latter has one more conjugated double bond than the former. In most series of compounds containing increasing numbers of conjugated double bonds the extinction coefficients increase in the same direction.[8] The remarkable ease with which the extinction coefficients of the α- and β-esters (Iα,β) can be varied is very striking and indicates the possible presence of a mixture of stereoisomers in each (α or β) isomer. The extinction coefficients reported in the literature for these α- and β- esters show no consistency.[2,3,7] Even in this Laboratory samples of the β-ester have been prepared, all made presumably under the same conditions, exhibiting a constant maximum (283 mμ) but with extinction coefficients varying from 17,000 to 22,000. Similarly with the α-ester, samples with constant maximum (272 mμ) exhibited extinctions between 14,000 and 19,000. All of these preparations were analytically pure. An interesting example of this variation in extinction coefficient was reported by Sobotka and co-workers.[3c] Starting with a β-ester sample with $\epsilon = 12550$, by saponifying to the acid and re-

(18) Burawoy, J. Chem. Soc., 20 (1941).

esterifying with ethanol, these workers obtained a so-called "purified" ester with $\epsilon = 34,000$.

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Experimental

Ethyl α- and β-Ionylideneacetates.—These esters were prepared from the commercial ionones by the method described previously.[7] A slightly higher yield was obtained when the dehydration of the intermediate crude hydroxy-ester was carried out in boiling benzene containing one or two grams of p-toluenesulfonic acid. The properties of the esters obtained were the same as has already been reported (see text) with the exception that the hump at 236 mμ, previously[7] reported for the ester derived from α-ionone, gradually disappeared after several redistillations yielding an ester with λ_{max}. 272 mμ (ϵ 16,000–17,000).

Dry Distillation of Barium α- and β-Ionylideneacetate.—The dry barium salts (ca. 20 g.) were ground in a mortar with an equal volume of powdered soft glass and heated on a sand-bath under a vacuum of 2 mm. No appreciable decomposition occurred when the mixture was heated slowly to 150–200°. At higher temperatures, 350–450°, a small yield of a dark red liquid condensed at tap water temperatures while water and dark decomposition products collected in a trap cooled in a Dry Ice-acetone mixture. The residue was a black infusible tar. In two experiments the Pyrex flasks, softened by the high temperature necessary for the decomposition, imploded. The dark red distillate on redistillation yielded 0.5–2.5 g. of a fraction boiling 80–110° at 2 mm. All of the samples of this fraction from several runs on both the α- and β-salts had the same absorption spectra: λ_{max}. 220–225 mμ ($E_{1 cm.}^{1\%}$ 500–650), λ_{max}. ca. 260 mμ ($E_{1 cm.}^{1\%}$ 190–200), λ_{min}. 240 mμ ($E_{1 cm.}^{1\%}$ 160–180). The high maximum at ca. 220 mμ indicated that the liquid was almost pure α-ionone (λ_{max}. 227 mμ, $E_{1 cm.}^{1\%}$ 600).

Ozonization of Ethyl α- and β-Ionylideneacetate.—Although the ozonization of the α- and β-esters was attempted under a wide variety of combinations of solvents and concentration and with varying amounts of ozone, the best results were obtained by a modification of the procedures of Karrer and co-workers.[11] The following is an example of the ozonization of the β-ester. A solution of 3.0 g. (0.0115 mole) of the ester in 30 ml. of carbon tetrachloride, cooled in an ice-bath, was subjected to a stream of ozonized oxygen containing 2.5% ozone at the rate of eighteen liters per hour for six hours. The ice-bath was removed to allow the reaction mixture to come to come to room temperature while ozone continued to pass through for two more hours (total moles ozone = 0.173, a five-fold excess). During this latter period glacial acetic acid was added periodically to replace the carbon tetrachloride as it evaporated. The ozonide solution was then added to a mixture of 20 ml. of 0.2 N sulfuric acid and 13 ml. of 30% hydrogen peroxide and the mixture allowed to stand overnight. Several ml. more of hydrogen peroxide was added and the mixture was refluxed for one hour. The water and acetic acid were removed by evaporation at 2 mm. in a bath at 35°. The oily residue[19] was taken up in ether (75–100 ml.) and extracted with four 25-ml. portions of 5% sodium carbonate. After acidification with 6 N sulfuric acid and saturation with salt the solution was successively extracted with one 75-ml. and four 50-ml. portions of ether. The combined ether extract was evaporated on the steam-bath and under vacuum. The residue was dissolved in 30 ml. of hot water and treated with 3.0 g. of sodium acetate and 3.0 g. of semicarbazide hydrochloride. The semicarbazone was collected in a tared centrifuge cone, washed with cold

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(19) In one case the residue exploded violently at this point.

water and dried. The crude semicarbazone (0.509 g., 20% yield) melted 135–145° and after recrystallization from ethyl acetate and ethanol a pure product (m. p. 159–160.5°) was obtained which showed no depression in melting point when mixed with some geronic acid semicarbazone obtained from ozonization of β-ionone. The absence of any isogeronic acid semicarbazone in the crude semicarbazone was indicated by the lack of anything but a trace of substance insoluble in hot ethyl acetate.[11]

The crude semicarbazone obtained from ozonization of the α-ester usually melted 175–190°. Recrystallization from ethanol gave a material of m. p. 194–196° which showed no depression in melting point when mixed with a sample of pure isogeronic acid prepared by ozonization of α-ionone.

The rate of absorption of ozone by the esters was quite slow as indicated by the fact that excess ozone could be detected in the stream of oxygen issuing from the ozonide solution even at the very beginning of the ozonolysis. Using appreciably smaller or larger amounts of ozone decreased the yield of geronic acid obtainable. Using acetic acid as the only solvent also gave a markedly lower yield. The ozonide is partially insoluble in the carbon tetrachloride and thus is protected somewhat from "over-ozonization."

Ozonization of a Mixture of the Ethyl α- and β-Ionylideneacetates.—A mixture of 2.0 g. each of the α- and β-esters was ozonized by a procedure similar to the one described above. A sample (264 mg.) of the crude mixture of semicarbazones (m. p. 135–160°) was extracted with 10 ml. of boiling ethyl acetate. The insoluble residue, 107 mg., was almost pure isogeronic acid semicarbazone, m. p. 186–188°, and recrystallization from 7.5 ml. of ethanol yielded 80 mg. of pure isogeronic acid semicarbazone, m. p. 192–194°. On cooling, the ethyl acetate solution deposited 83 mg. of geronic acid semicarbazone which after two recrystallizations from ethanol (1.0 ml.) had a m. p. 159.5–160°.

Isolation of α,α-Dimethylglutaric Acid from Ozonization of the Ethyl α- and β-Ionylideneacetates.—The aqueous solution from which the geronic or isogeronic acid semicarbazone had precipitated was treated with 10 ml. of concentrated hydrochloric acid, saturated with salt and extracted with many portions of ether. After evaporating the ether, the α,α-dimethylglutaric acid was extracted from the residue by a procedure (*via* copper salts) which was essentially that used by Karrer and co-workers.[11] The final product crystallized very slowly on standing (three to fourteen days) and was purified by recrystallization from benzene–petroleum ether.

From 3.0 g. of the β-ester was obtained 281 mg. (15% yield) of crude acid, m. p. 64–72°. Recrystallization yielded pure α,α-dimethylglutaric acid, m. p. 82–83.5° (Karrer[11] reports m. p. 82–83°).

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.52; H, 7.61.

Two grams of the α-ester yielded 193 mg. (16% yield) of α,α-dimethylglutaric acid as shown by m. p. and mixed m. p. with the product isolated above from ozonization of the β-ester.

Preparation of 1-(α- and β-Ionylidene)-2-pentanone (IIIα,β) and 1-(α- and β-Ionylidene)-3-methyl-2-butanone (IVα,β).—These ketones were prepared from the corresponding α- and β-ionylideneacetyl chlorides and the proper dialkyl cadmium (propyl or isopropyl) by the procedure already described for the preparation of the α- and β-ionylideneacetones.[7] The yields were low (30–40%) and the products were contaminated with small amounts of impurities of similar boiling point. However, analyses and catalytic hydrogenations indicated purities of approximately 95%. We were unable to prepare crystalline ketone derivatives. The absorption spectra of these ketones are listed in Table I.

Summary

The use of the absorption spectra of the ethyl α- and β-ionylideneacetates as a means of determin-

ing the position of the ring double bond has been shown to lead to inconclusive results. These esters were shown to be genuine α-β isomers by ozonolysis experiments.

The α- and β-ionylidene-propyl and -isopropyl

ketones were prepared and their absorption spectra measured. The spectral anomaly exhibited by the previously reported α- and β-ionylidene-acetones was found to persist in these homologs.

Investigations on the Stereoisomerism of Unsaturated Compounds. VIII. The Catalytic Hydrogenation of Butadiene[1]

BY WILLIAM G. YOUNG, RICHARD L. MEIER, JEROME VINOGRAD, HOWARD BOLLINGER, LOUIS KAPLAN AND SEYMOUR L. LINDEN

The catalytic hydrogenation of butadiene derivatives by Paal[2] led to the belief that in the presence of highly dispersed platinum or palladium, only completely hydrogenated products were formed even though the reaction was interrupted when only one mole of hydrogen had been absorbed per mole of diene. Lebedev and Yakubchik[3] studied the reduction of several conjugated systems using platinum as a catalyst and obtained evidence for the formation of all possible dihydro-addition products. Since their conclusions were based entirely on the interpretation of the curves for the variation of the rate of absorption of hydrogen with time without verification by chemical analysis, the validity of the work was questioned by other workers.[4,5,6] Ingold and Sha[5] were unable to establish the presence of any dihydro-addition products after 50% hydrogenation of ethyl muconate, and sorbic and vinylacrylic acids. On the basis of this work Ingold and Sha[5] concluded that formation of dihydro products during the hydrogenation of conjugated systems was not the general case. On the other hand, many other workers,[4,7] have reported that the partial catalytic hydrogenation of several butadiene derivatives gave rise to the formation of intermediate dihydro addition products.

The present investigation was undertaken in an attempt to clarify the situation by presenting additional evidence that the formation of intermediate dihydro-addition products is indeed the general case. It is our contention that most of the common low pressure hydrogenation catalysts exhibit a considerable degree of selectivity permitting in certain cases the isolation of dihydro products in excellent yields from partial hydrogenation of conjugated carbon–carbon double bonds. Butadiene was chosen for study because the re-

action products readily lend themselves to analysis by several methods.

The hydrogenation of butadiene was studied in the presence of four catalysts, platinum (from platinum oxide), palladium (from palladium oxide), palladium on barium sulfate and Raney nickel. The hydrogenations were carried out at one to two atmospheres pressure in 95% ethanol. In preliminary experiments butadiene was hydrogenated to various degrees and the reaction products analyzed for butane, butene and butadiene by the micro methods of Blacet and Leighton.[8] The analyses were calculated from equations (1) and (2) as follows

$$H = 2N + N_1 \tag{1}$$
$$N + N_1 + N_2 = 1 \tag{2}$$

H is moles of hydrogen absorbed and N, N_1 and N_2 are the mole fractions of butane, butene and butadiene, respectively. Equation (1) represents the fact that at any given time the moles of hydrogen absorbed are equivalent to the sum of the moles of butene plus twice the moles of butane formed. N, the mole fraction of butane, is estimated by combustion of the butane after the unsaturated hydrocarbons have been removed. Since the amount of hydrogen absorbed at any given time is accurately known, the values of N_1 and N_2 can be calculated from the simultaneous solution of equations (1) and (2).

Figures 1 and 2 are typical of graphs obtained when per cent. composition is plotted against per cent. hydrogenation. The concentrations of butadiene, butane and butene were found to vary linearly with increase in degree of hydrogenation

(1) A portion of this paper was presented before the Division of Organic Chemistry at Cincinnati, April, 1940.

(2) Paal, *Ber.*, **45**, 2221 (1912).

(3) Lebedev and Yakubchik, *J. Chem. Soc.*, 823, 2190 (1928); 220 (1929).

(4) Farmer, et al., *ibid.*, 688 (1933); 304, 1929 (1934).

(5) Ingold and Sha, *ibid.*, 885 (1933).

(6) Campbell and Campbell, *Chem. Rev.*, **31**, 77 (1942).

(7) Muskat and Knapp, *Ber.*, **64**, 779 (1931); Dupont and Pacquot, *Compt. rend.*, **205**, 805 (1937); Issacs and Wilson, *J. Chem. Soc.*, 202, 574, 810 (1936).

TABLE I

COMPOSITION AT THE CRITICAL POINT OF THE HYDRO-CARBON MIXTURE FROM HYDROGENATION OF BUTADIENE IN 95% ETHANOL

Catalyst	Temp., °C.	% Hydro-genation	% C_4H_6	% C_4H_8	% C_4H_{10}
Pt	−12	70	0	61	39
Pd	−12	54	0	94	6
Pd–BaSO₄	− 8	80	0	40	60
Ni	− 8	83	0	34	66

(8) Blacet and Leighton. *Ind. Eng. Chem., Anal. Ed.*, **3**, 266 (1931).