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

An Oxygen-18 Tracer Study of the Stobbe Condensation[1]

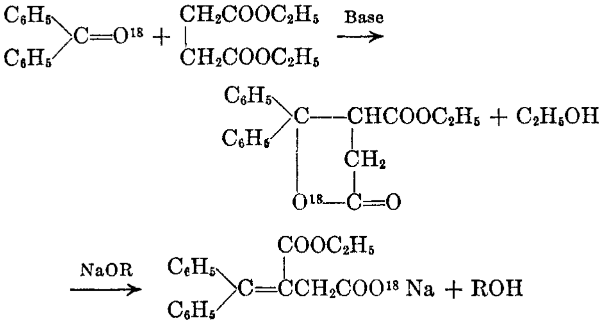
DAVID JEFFERY[2] AND ARTHUR FRY

Received February 11, 1957

A tracer study of the Stobbe condensation of diethyl succinate and benzophenone-O^{18} has been carried out. The product, β-carbethoxy-γ,γ-diphenylvinylacetic acid, has been shown to contain all of the oxygen-18 enrichment of the starting ketone. Upon degradation, all of the enrichment was found to be located in the free carboxyl group of the half-ester. These facts offer confirmatory evidence for the currently favored mechanism for the reaction. Considerable incidental information is presented concerning oxygen exchange between carboxylic acids and aqueous media.

The Stobbe condensation,[3] which consists of the base-catalyzed reaction of an aldehyde or ketone with an ester of succinic acid to give a half-ester of a substituted alkylidenesuccinic acid, has been reviewed by Johnson and Daub[4] in *Organic Reactions.* The salient features of the stoichiometry and scope of the reaction have been well established, and the reaction sequence presented by Johnson, McCloskey, and Dunnigan[5] seems to be consistent with all the known facts.

An essential feature of this mechanism is the formation of a paraconic acid ester intermediate in which the oxygen atom of the carbonyl compound becomes attached to the carbonyl carbon of one of the original ester groups. Subsequent cleavage of the lactone ring results in complete transfer of this same oxygen atom to the carboxylate anion of the resulting half-ester. This sequence is illustrated below for the reaction between benzophenone-O^{18} and diethyl succinate, the compounds used in this work.



Although no obvious reaction sequence by which it might be accomplished is apparent, it is conceivable that the oxygen-containing group which is eliminated could contain the oxygen of the carbonyl compound. The intramolecular transfer of oxygen from one carbon atom to another appeared sufficiently unusual to make it worthwhile to check this point by a tracer experiment.

DISCUSSION

The condensation of oxygen-18 labeled benzophenone and diethyl succinate was chosen as a suitable reaction for this study. The reported yields of product are high by both the potassium *t*-butoxide method[4] and the sodium hydride method.[6] The starting ketone, the product of the condensation and all degradation products are easily purified solids with characteristic melting points. Two of the four degradation procedures attempted had already been applied to the product of this reaction, β-carbethoxy-γ,γ-diphenylvinylacetic acid. The oxygen-18 labeled benzophenone was readily accessible by the method of Doering and Dorfmann.[7]

When the product of the reaction, β-carbethoxy-γ,γ-diphenylvinylacetic acid, was analyzed for oxygen-18, it was found to contain the total enrichment (1.10 atom per cent excess) of the starting ketone (1.09 atom per cent excess). This fact, in itself, shows that the ketone oxygen atom has been transferred to the product half-ester.

However, in order to establish unequivocally that the labeled atom had been transferred to the carboxylate anion, it was necessary to degrade the β-carbethoxy-γ,γ-diphenylvinylacetic acid. The several degradative procedures on which some experimental work was done were (a) an acid-catalyzed decarbethoxylation of the β-carbethoxy-γ,γ-diphenylvinylacetic acid or an acid-catalyzed decarboxylation of the γ,γ-diphenylitaconic acid arising from its hydrolysis;[8] (b) a thermal decarboxylation of the β-carbethoxy-γ,γ-diphenylvinylacetic acid; (c) a degradation of β-carbethoxy-γ,γ-diphenylvinylacetic acid according to the reaction scheme of Stobbe;[9] (d) an application of the

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[1] This work is abstracted from the M.S. thesis of David A. Jeffery, University of Arkansas, 1957, and was supported by the Atomic Energy Commission.

[2] Coulter W. Jones Scholar, 1956.

[3] H. Stobbe, *Ber.*, **26**, 2312 (1893).

[4] W. S. Johnson and G. H. Daub, *Org. Reactions*, **6**, 1 (1951).

[5] W. S. Johnson, A. L. McCloskey, and D. A. Dunnigan, *J. Am. Chem. Soc.*, **72**, 514 (1950).

[6] G. H. Daub and W. S. Johnson, *J. Am. Chem. Soc.*, **70**, 418 (1948); **72**, 501 (1950).

[7] W. von E. Doering and E. Dorfman, *J. Am. Chem. Soc.*, **75**, 5595 (1953).

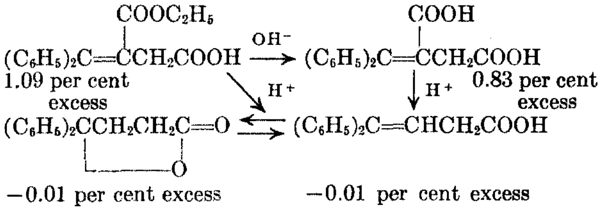
[8] W. S. Johnson, J. W. Petersen, and W. P. Schneider, *J. Am. Chem. Soc.*, **69**, 74 (1947).

[9] H. Stobbe, *Ann.*, **308**, 104 (1899).

Hunsdiecker degradation[10] of the silver salt of β-carbethoxy-γ,γ-diphenylvinylacetic acid.

During the application of these methods considerable incidental information concerning the oxygen exchange reaction of the carboxylic acids involved was also obtained. The very fact that the product half-ester contained all of the enrichment of the starting ketone demonstrates the lack of exchange between β-carbethoxy-γ,γ-diphenylvinylacetic acid and the aqueous acetic and hydrochloric acids and 1*N* aqueous ammonium hydroxide used in its work-up procedure.

When the method of Johnson, Peterson, and Schneider[8] for the acid-catalyzed decarbethoxylation of β-carbethoxy-γ,γ-diphenylvinylacetic acid or the acid-catalyzed decarboxylation of its hydrolysis product, γ,γ-diphenylitaconic acid, was tried on oxygen-18 labeled compounds, it was found that the equilibrium mixture of γ,γ-diphenylvinylacetic acid and γ,γ-diphenylbutyrolactone produced contained no excess oxygen-18. This result, which was not unexpected, indicates that exchange of the carboxyl group oxygen with the aqueous reaction medium was essentially complete under these conditions.

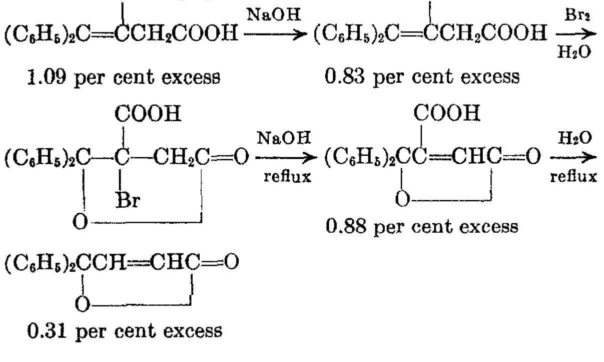


This exchange probably takes place by the mechanism proposed by Bender, Stone, and Dewey[11] for the acid-catalyzed oxygen exchange of substituted benzoic acids with water. The mechanism involves addition of a molecule of water to the carboxylic acid to give an ortho acid, which can break down to give the exchange products.

It is noteworthy that the basic hydrolysis of β-carbethoxy-γ,γ-diphenylvinylacetic acid to γ,γ-diphenylitaconic acid shown above resulted in partial loss of oxygen-18 enrichment (1.10 atom per cent excess in the half-ester and only 0.83 atom per cent excess in the dibasic acid). This fact is not in line with the conclusions reported in Dole's review article[12] to the effect that carboxyl groups undergo exchange only in the presence of strong acids, while the oxygen of peptide bonds, amides, and ureas does not undergo exchange in either acidic or alkaline medium. It is not inconceivable that the exchange may occur during the working-up of the γ,γ-diphenylitaconic acid, but this would imply an extremely fast rate of exchange at low temperature, which appears unlikely, especially in view of the fact that there was no exchange in the acidic work-up of the original half-ester. The approximate agreement of the oxygen-18 analysis values for γ,γ-diphenylitaconic acid (0.83 atom per cent excess) and γ,γ-diphenylaconic acid (0.88 atom per cent excess) also suggests that exchange must have occurred during hydrolysis since no apparent exchange was observed in this conversion.

Thermal decarboxylation of β-carbethoxy-γ,γ-diphenylvinylacetic acid containing 1.10 atom per cent excess oxygen-18 in refluxing quinoline using copper chromite as a catalyst gave carbon dioxide with 0.69 atom per cent excess oxygen-18. Presumably the chief source of carbon dioxide would be the free carboxyl group of the half-ester, indicating that at least part of the enrichment was located there. However, since exchange of some kind or dilution with unenriched carbon dioxide had obviously taken place, and since all efforts to isolate crystalline products from the residue failed, this experiment must be regarded as inconclusive.

The experimental work done by Stobbe[9] on the compound β-carbethoxy-γ,γ-diphenylvinylacetic acid suggested a means of degrading this compound and establishing the position of the labeling. This series of reactions is outlined below and involved hydrolysis of the half-ester to the diacid, γ,γ-diphenylitaconic acid, followed by bromination of the diacid to give γ,γ-diphenyl-β-bromoparaconic acid which was subsequently dehydrohalogenated to yield γ,γ-diphenylaconic acid. Subsequent dissolution of the γ,γ-diphenylaconic acid in a large excess of water, and refluxing, led to decarboxylation to give γ,γ-diphenylcrotonlactone. The γ,γ-diphenylcrotonlactone should contain the total enrichment of the β-carbethoxy-γ,γ-diphenylvinylacetic acid if there were no exchange of the oxygen of the carboxyl group with the reaction medium during the course of such a series of reactions.



When this reaction sequence was carried out on the labeled compounds, the oxygen-18 results indicated above were obtained. It should be noted that exchange with the aqueous medium did not occur during the conversion of γ,γ-diphenylitaconic acid to γ,γ-diphenylaconic acid, but that partial exchange did occur during the decarboxylation of the latter compound to γ,γ-diphenylcroton-

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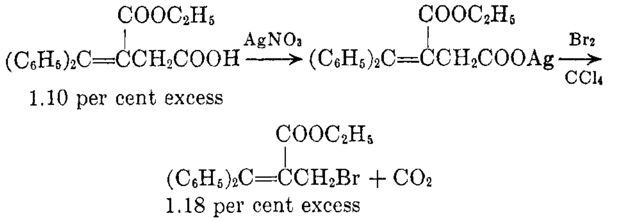
[10] J. Kleinberg, *Chem. Revs.*, **40**, 381 (1947).

[11] M. L. Bender, R. R. Stone, and R. S. Dewey, *J. Am. Chem. Soc.*, **78**, 319 (1956).

[12] M. Dole, *Chem. Revs.*, **51**, 263 (1952).

lactone. This last observation is in accord with the evidence put forth by Long and Friedman[13] through an oxygen-18 study of the hydrolysis of γ-butyrolactone. This lactone upon acidic hydrolysis is known to form an equilibrium mixture of lactone and γ-hydroxybutyric acid. When this reaction was carried out in oxygen-18 enriched water it was found that exchange of the oxygen of the carboxylic acid group of the γ-hydroxybutyric acid with water took place in both acidic and alkaline media. The fact that *any* enrichment remained in the γ,γ-diphenylcrotonlactone indicates clearly that *at least part* of the original enrichment was in the free carboxyl group of the β-carbethoxy-γ,γ-diphenylvinylacetic acid.

A final conclusive proof that all of the original enrichment of the benzophenone was in the free carboxyl group of the half-ester is found in the results of the Hunsdiecker degradation. When the silver salt of β-carbethoxy-γ,γ-diphenylvinylacetic acid (1.10 atom per cent excess oxygen-18) was treated with bromine, the carbon dioxide evolved contained all of the enrichment (1.18 atom per cent excess).



$$(C_6H_5)_2C{=}\overset{\overset{\displaystyle COOC_2H_5}{|}}{C}CH_2COOH \xrightarrow{AgNO_3} (C_6H_5)_2C{=}\overset{\overset{\displaystyle COOC_2H_5}{|}}{C}CH_2COOAg \xrightarrow[CCl_4]{Br_2}$$

1.10 per cent excess

$$(C_6H_5)_2C{=}\overset{\overset{\displaystyle COOC_2H_5}{|}}{C}CH_2Br + CO_2$$

1.18 per cent excess

The results of this study are in full agreement with the mechanism involving a paraconic acid ester intermediate as proposed by Johnson, McCloskey, and Dunnigan.[5] These results, however, do not rule out the possibility of a mechanism such as condensation of the ketone with diethyl succinate to yield the diester which in turn may be partially hydrolyzed. This last possibility appears to be highly unlikely in view of the evidence presented by Johnson and Daub,[4] and we feel that the essential features of the Johnson, McCloskey, and Dunnigan[5] mechanism have been unequivocally established.

EXPERIMENTAL

Preparation of oxygen-18 labeled β-carbethoxy-γ,γ-diphenylvinylacetic acid. Benzophenone-O^{18}, m.p. 47–48°, containing 1.10 atom per cent excess oxygen-18 was prepared according to the procedure of Doering and Dorfman[7] and treated with diethyl succinate and sodium hydride[14] according to the method of Daub and Johnson.[6] The crude β-carbethoxy-γ,γ-diphenylvinylacetic acid, m.p. 124.5–125°, was obtained in 97.5 per cent yield. Recrystallization from benzene-petroleum ether gave a product of m.p. 123.5–124°, reported[4] m.p. 123–124.5°, which contained 1.09 atom per cent excess oxygen-18.

Preparation of oxygen-18 labeled γ,γ-diphenylitaconic acid. Oxygen-18 labeled β-carbethoxy-γ,γ-diphenylvinylacetic acid containing 1.09 atom per cent excess oxygen-18 was refluxed in 2*N* sodium hydroxide for 3 hr. After cooling, acidification with 6*N* hydrochloric acid, and recrystallization from dilute ethanol, γ,γ-diphenylitaconic acid was obtained in 89.9 per cent yield. The acid melted at 169–170°, reported[9] m.p. 170–171°, and contained 0.83 atom per cent excess oxygen-18.

Acid-catalyzed decarbethoxylation of β-carbethoxy-γ,γ-diphenylvinylacetic acid. β-Carbethoxy-γ,γ-diphenylvinylacetic acid containing 1.09 atom per cent excess oxygen-18 was treated with a mixture of acetic and hydrobromic acids according to the procedure of Johnson, Petersen, and Schneider.[8] γ,γ-Diphenylvinylacetic acid was isolated in 64 per cent yield, and upon recrystallization from dilute ethanol melted at 116–117°, reported[8], m.p. 117–118.5°. γ,γ-Diphenylbutyrolactone, m.p. 91.5–92°, reported[8] m.p. 90–91° was also isolated in 30 per cent yield. The γ,γ-diphenylvinylacetic acid contained −0.01 atom per cent excess oxygen-18. The lactone was not analyzed for oxygen-18.

Acid-catalyzed decarboxylation of γ,γ-diphenylitaconic acid. γ,γ-Diphenylitaconic acid containing 0.83 atom per cent excess oxygen-18 was decarboxylated following the procedure of Johnson, Petersen, and Schneider[8] used above. γ,γ-Diphenylvinylacetic acid, m.p. 117–118°, and γ,γ-diphenylbutyrolactone, m.p. 91–92°, were isolated in 63 and 35 per cent yields, respectively. The γ,γ-diphenylbutyrolactone contained −0.01 atom per cent excess oxygen-18. The acid was not analyzed for oxygen-18.

Attempted thermal decarboxylation of β-carbethoxy-γ,γ-diphenylvinylacetic acid. One-half gram of oxygen-18 labeled β-carbethoxy-γ,γ-diphenylvinylacetic acid was dissolved in 3 ml. of quinoline in a 25 ml. two-necked flask fitted with a dropping funnel and reflux condenser. A trace of copper chromite catalyst was added and the temperature was maintained at the reflux temperature of quinoline for a period of 2.5 hr. Nitrogen, previously dried by passage through Fieser's solution, sulfuric acid, a magnesium perchlorate tube, and an Ascarite tube, was used as a sweep gas. The carbon dioxide evolved was collected in a sample tube maintained at liquid nitrogen temperature. Excess nitrogen was pumped off prior to oxygen-18 analysis of the carbon dioxide. The reaction mixture was taken up in ether and washed 5 times with dilute hydrochloric acid to remove quinoline. The ether extract was dried over magnesium sulfate and upon filtration and subsequent evaporation of the ether yielded an intractable dark red oil. The evolved carbon dioxide contained 0.69 atom per cent excess oxygen-18.

Preparation of oxygen-18 labeled γ,γ-diphenyl-β-bromoparaconic acid. Twenty-five grams of the oxygen-18 labeled γ,γ-diphenylitaconic acid prepared above was suspended in 50 ml. of water. To this mixture, 14 g. of bromine was added dropwise. The mixture was stirred for a period of 3 hr. during which time the resinous mass initially formed on addition of bromine was broken up into fine crystalline particles. The mixture was filtered and the residue on the filter was washed thoroughly with water and dried. Thirty-one grams of a crude mixture was obtained which was fractionally crystallized from benzene to yield 10.5 g. of a bromine containing compound melting at 150–170° with decomposition; reported for γ,γ-diphenyl-β-bromoparaconic acid[9], m.p. 170–171°. The filtrate was concentrated to give a brownish colored crystalline mass which was not further purified. Repeated attempts to further purify the bromine containing compound by crystallization failed to give a sharp melting point and as a result this material was not analyzed for oxygen-18.

Preparation of γ,γ-diphenylaconic acid. Three grams of the crude γ,γ-diphenyl-β-bromoparaconic acid prepared above was dissolved in 100 ml. of 3% sodium hydroxide solution

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[13] F. A. Long and L. Friedman, *J. Am. Chem. Soc.*, **72**, 3692 (1950).

[14] In preliminary experiments both the potassium *t*-butoxide and the sodium hydride methods were investigated. The labeled experiments utilized only the sodium hydride method.

and refluxed for 2 hr. The cooled solution was diluted to 10 times its original volume and acidified with 6*N* hydrochloric acid. The resulting precipitate was filtered and dried, yielding 2.17 g. (94.8 per cent) of γ,γ-diphenylaconic acid. A portion of this was recrystallized from benzene for oxygen-18 analysis. The purified acid melted at 136–137°, reported[9] 138–139°, and contained 0.88 atom per cent excess oxygen-18.

Preparation of γ,γ-diphenylcrotonlactone. Two grams of γ,γ-diphenylaconic acid was dissolved in 500 ml. of water and refluxed for 1 week. The solution was concentrated and extracted with ether. The ethereal solution was extracted with a 5 per cent solution of sodium carbonate to remove acidic material. The ethereal solution was concentrated and 0.15 g. of γ,γ-diphenylcrotonlactone was obtained which was further purified by recrystallization from ether to give a product of m.p. 130–131°, reported[9] m.p. 130–131°. The compound contained 0.31 atom per cent excess oxygen-18.

Silver salt degradation of β-carbethoxy-γ,γ-diphenylvinylacetic acid. The silver salt of β-carbethoxy-γ,γ-diphenylvinylacetic acid was treated with bromine in refluxing carbon tetrachloride in the usual Hunsdiecker degradation procedure.[10] The carbon dioxide evolved during the reaction was swept out of the system by helium and trapped in a sample tube at liquid nitrogen temperature after first passing through a dry ice trap to condense bromine vapor. The crude product obtained from the carbon tetrachloride solution was further purified by recrystallization from an ether-petroleum ether mixture, to give ethyl α-benzhydrilidene-β-bromopropionate. The purified product melted at 96–97°.

Anal. Calcd. for $C_{18}H_{17}BrO_2$: C, 62.62; H, 4.96; Br, 23.15. Found: C, 62.56; H, 4.92; Br, 22.98. The carbon dioxide contained 1.18 atom per cent excess oxygen-18. The bromide was not analyzed for oxygen-18.

Analysis of organic compounds for oxygen-18. The procedure employed in this laboratory was one recently reported by Doering and Dorfman.[7] This method involved the pyrolysis of oxygen-containing organic compounds over carbon at 1120° to carbon monoxide followed by oxidation of the carbon monoxide by iodine pentoxide to carbon dioxide. The apparatus was essentially that described by Dinerstein and Klipp.[15] Helium was used as a sweep gas and was passed through Fieser's solution and concentrated sulfuric acid prior to passage through the reduction tube. The effluent gases were passed through a U-tube cooled in dry ice-isopropyl alcohol to condense iodine vapor; the carbon dioxide was finally collected in a sample trap immersed in liquid nitrogen.

The apparatus had an apparent memory effect for the sample which had immediately preceeded. At most, two consecutive analyses were required to remove this effect and give reproducible results with a given compound. The precision of this method for determining oxygen-18 concentration in organic compounds is excellent as can be seen from the reproducibility of the results shown in Table I. No suitable explanation is at hand for the fairly large difference between the oxygen-18 value for β-carbethoxy-γ,γ-diphenylvinylacetic acid and the carbon dioxide obtained from its degradation.

The isotopic $CO^{16}O^{18}/CO^{16}O^{16}$ ratios were determined in a Consolidated Model 21-401 mass spectrometer. The heights of the 46 and 44 mass/charge peaks were assumed to be proportional to the $CO^{16}O^{18}$ and $CO^{16}O^{16}$ concentrations, respectively. The $CO^{16}O^{18}$ value used here neglects any contribution from the $C^{13}O^{16}O^{17}$ peak, which is considered to be negligible. For each sample the mass spectrum was scanned at least five times, and the values reported are averages of the ratios obtained.

Calculations and results.[16] In calculating the results of these experiments, the main problem involved is proper treatment of the dilution of the oxygen-18 enrichment which takes place during pyrolysis of the organic compound and the subsequent oxidation of the carbon monoxide to carbon dioxide. In the benzophenone, all of the oxygen-18 is concentrated in the one oxygen position. For comparison purposes, these calculations attribute all of the *excess* oxygen-18 (over that normally present) in all of the other compounds to a single position also. This procedure makes no assumption concerning the actual position in the molecule which contains excess oxygen-18, or even concerning the number of positions which contain excess oxygen-18. It does assume that the oxygen introduced into the organic compounds from other sources than benzophenone (including that introduced from the iodine pentoxide in the oxidation of carbon monoxide to carbon dioxide) is of normal isotopic composition.

TABLE I

RESULTS OF MASS SPECTROMETER ANALYSES

Compound	$(n + 1)$	$c_1 \times 10^3$	$c_2 \times 10^3$	Excess atom Per Cent $y \times 100$
Benzophenone	2	14.39	3.66	1.07
		15.52	3.91	1.12
		14.96	3.82	1.11
		14.60	3.83	1.08
			Average	1.10
β-Carbethoxy-γ,γ-diphenylvinylacetic acid	8	6.38	3.66	1.08
		6.66	3.86	1.11
		6.58	3.83	1.09
			Average	1.09
γ,γ-Diphenylitaconic acid	8	5.95	3.91	0.81
		6.06	3.91	0.85
			Average	0.83
γ,γ-Diphenylvinylacetic acid	4	3.82	3.85	−0.01
γ,γ-Diphenylbutyrolactone	4	3.84	3.88	−0.01
CO_2 from thermal decarboxylation of β-carbethoxy-γ,γ-diphenylvinylacetic acid	2	10.83	3.89	0.69
γ,γ-Diphenylaconic acid	4	6.18	3.95	0.89
		6.15	3.95	0.88
		6.16	3.95	0.88
			Average	0.88
γ,γ-Diphenylcrotonlactone	4	5.55	3.94	0.32
		5.47	3.94	0.30
		5.53	3.94	0.32
			Average	0.31
CO_2 from silver salt degradation of β-carbethoxy-γ,γ-diphenylvinylacetic acid	2	15.81	3.93	1.18
		15.78	3.93	1.17
			Average	1.18

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(15) R. A. Dinerstein and R. W. Klipp, *Anal. Chem.*, 21, 545 (1949).

(16) The authors are indebted to Dr. T. C. Hoering of this laboratory for several helpful discussions of the mass spectrometer analytical techniques and methods of calculation.

It can readily be shown that the excess atom fraction of oxygen-18 of a single position to which all enrichment is attributed, y, can be related to the observed mass spectrometer ratios by the following equation:

$$y = (n + 1)\left[\frac{c_2}{2 + c_2} - \frac{c_1}{2 + c_1}\right]$$

where c_1 = $CO^{16}O^{18}/CO^{16}O^{16}$ ratio in tank carbon dioxide as measured on the mass spectrometer

c_2 = $CO^{16}O^{18}/CO^{16}O^{16}$ ratio in enriched carbon dioxide as measured on the mass spectrometer

and n = the number of atoms of oxygen of normal isotopic composition which are added to the single enriched atom during analysis.

Using this equation and the values of n, c_1, and c_2 determined experimentally, the results given in Table I were calculated.

FAYETTEVILLE, ARK.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF OREGON]

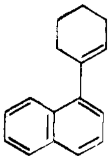
Coplanarity and Chromatographic Adsorbability of Some Isomeric Naphthylcycloalkenes and Polycyclic Aromatic Hydrocarbons[1,2]

L. H. KLEMM, DAVID REED,[3] AND C. D. LIND[4]

Received January 21, 1957

Binary mixtures (dissolved in isooctane) of (a) isomeric α- and β-substituted naphthalenes bearing phenyl, cyclohexenyl (I and IV), and cyclopentenyl (II and III) groups; (b) II and IV, and; (c) anthracene and phenanthrene, were investigated by down-flow frontal analysis for relative chromatographic adsorbability on silicic acid impregnated with picric acid or 2,4,7-trinitrofluorenone. In cases (a) and (b) the more nearly coplanar β-substituted naphthalene was adsorbed more tenaciously while in (c) little difference in adsorbability was evident. Results were consistent with data for displacement analysis of binary mixtures from alumina. The characteristics of impregnated silicic acid as an adsorbent are described. In particular it is proposed that adsorption of the substrate occurs principally *via* a steady-state process in which the impregnant molecules serve as "active sites" for molecular compound formation on the surface of the ground mass, silicic acid.

A survey of published observations reveals that coplanarity factors may play an important part in chromatographic adsorbabilities of conjugated isomeric biaryls and arylalkenes on alumina. Thus Orchin and Reggel[5] found that 2,2′-binaphthyl (effectively coplanar) was held more tenaciously than the more twisted 1,2′-binaphthyl. For mixtures of the geometric isomers of stilbene, 4,4′-dimethylstilbene, and 4,4′-dimethoxystilbene the coplanar *trans* form was adsorbed more strongly in every case.[6] A mixture of the three possible 1,4-diphenylbutadienes, moreover, showed the order of adsorbability *trans-trans* (coplanar) > *trans-cis* > *cis-cis* (noncoplanar).[7] Also indicative of such an effect are the findings of Orchin and coworkers[5,8] that adsorbabilities of certain conjugated iso-π-electronic (though not isomeric) aromatic hydrocarbons fall in the orders: fluoranthene > mixed 1- and 2-phenylnaphthalenes > 1-phenylnaphthalene; benzofluoranthene > 1,2′-binaphthyl;[9] and perylene > 1,1′-binaphthyl.[10] The authors report herewith semiquantitative studies on the relative adsorbabilities of various other such pairs of hydrocarbons (usually isomeric substituted naphthalenes) on alumina, silicic acid impregnated with picric acid (TNP) or 2,4,7-trinitrofluorenone (TNF),[11] and silicic acid alone.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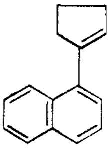
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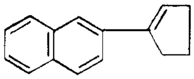
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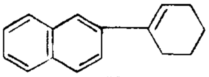
IV

In studies with alumina, limited approximately equimolar amounts of the isomeric pairs I plus IV

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[1] Supported (in part) by the Petroleum Research Fund of the AMERICAN CHEMICAL SOCIETY and (in part) through sponsorship by the Office of Ordnance Research, U. S. Army, contract number DA-04-200-ORD-176.

[2] Part of this material was presented at the Symposium on Polycyclic Hydrocarbons at the Atlantic City Meeting of the AMERICAN CHEMICAL SOCIETY, September, 1956. Part IX in the series on Chemical Reactivities of Arylcycloalkenes. For paper VIII see L. H. Klemm, J. W. Sprague, and E. Y. K. Mak, *J. Org. Chem.*, 22, 161 (1957).

[3] Research assistant, 1955–56.

[4] Research associate, 1956.

[5] M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **69**, 505 (1947).

[6] L. Zechmeister and W. H. McNeely, *J. Am. Chem. Soc.*, **64**, 1919 (1942).

[7] Alumina containing 25% of celite was used; J. H. Pinckard, B. Wille, and L. Zechmeister, *J. Am. Chem. Soc.*, **70**, 1938 (1948).

[8] M. Orchin and R. A. Friedel, *J. Am. Chem. Soc.*, **68**, 573 (1946).

[9] *Cf.* M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **73**, 436 (1951).

[10] In the last of these cases the alumina was diluted with the apparently relatively inactive Super-Cel.

[11] The use of silica gel impregnated with a polynitroaromatic complexing agent for gross separation of hydrocarbon mixtures into aromatic, hydroaromatic and alkenic, and saturated hydrocarbons was reported by M. Goldewicz, *Nature*, **164**, 1132 (1949).