130 ma. and 12–20 v. at a temperature of 14–17°. Work-up of the solution in the usual manner gave 330 mg. of neutral material (*ca.* 81%). The mixture was subjected to preparative thin layer chromatography developed continuously for 2.5 hr., using dichloromethane–ether (98:2) as solvent. Two distinct bands were shown under short wave ultraviolet light. Elution of these bands with acetone gave 96 mg. of II (30%) and 103 mg. of V (27%). These per cents were in good agreement with those obtained from a gas chromatogram of the neutral mixture. Compound II was recrystallized from methanol, m.p. 130–132°, identical with II previously described (mixture melting point, infrared, and gas chromatography). The second product (V), was recrystallized from acetone to give a white crystalline compound, m.p. 127–130°. A second recrystallization gave raised m.p. 137.5–139°; *trans* crystallization, m.p. 160–164°. The infrared spectrum showed a broad band at 1075 cm.$^{-1}$ (ethoxyl). Analytical data indicated 20ξ-ethoxy-5α-pregnan-3β-ol, $[\alpha]^{20}D$ 11.0 ± 3.0° (*c* 0.6, chloroform).

Anal. Calcd. for $C_{23}H_{40}O_2$: C, 79.25; H, 11.57. Found: C, 79.17; H, 11.81.

Attempted Anodic Reaction of I in 2-propanol.—To a solution of 457 mg. of I in 50 ml. of 2-propanol was added 28 mg. of sodium (pH of cloudy solution 8.4). The solution was electrolyzed for 10 hr. at 30–35 ma. and 135–150 v. at 18.5–23°. Work-up in the usual manner gave 60 mg. of neutral material (*ca.* 16%). A thin layer chromatogram (dichloromethane–ether, 4:1) showed a mixture of at least ten compounds. The reaction was not further investigated.

20ξ-Methoxy-5α-pregnan-3β-ol Acetate (IIIb).—A solution of 70 mg. of crude 20ξ-methoxy-5α-pregnan-3β-ol (IIIa) in 4 ml. of pyridine containing 0.5 ml. of acetic anhydride was refluxed for 2 hr. The cooled solution was poured into ice–water (10 ml.) and the mixture extracted with 3–5 ml. portions of chloroform. Evaporation of the solvent gave a brown crystalline solid. Recrystallization from methanol gave 21 mg. of white flakes, m.p. 111–118°. Two additional recrystallizations raised the melting point to 123–126°. A mixture melting point with IIIb obtained from the anodic reaction (methanol, pH 8.6) was 122–125°. The gas chromatographic retention times and infrared spectra of both samples were identical.

5α-Pregnan-3β-ol (IV).—To a solution of 27 mg. of Δ^{20}-5α-pregnen-3β-ol (II) in 6 ml. of ethanol–dioxane (1:1) was added 96 mg. of palladium on charcoal (10%). The mixture was hydrogenated for 6 hr. at room temperature and under a pressure of 24 p.s.i., using the Parr apparatus. Removal of the catalyst by filtration and evaporation of the solvent gave a gum. The product was subjected to preparative thin layer chromatography developed continuously for 2 hr. (silica gel G; dichloromethane–ether, 95:5). Elution of the major band with acetone gave 11 mg. of white solid, m.p. 118–128°. Recrystallization from methanol gave 2.7 mg. of 5α-pregnan-3β-ol (VI) as shiny white flakes, m.p. 138–139.5°, lit.[11] m.p. 138–138.4°. The infrared spectrum showed the absence of bands at 1640 and 912 cm.$^{-1}$.

Acknowledgment.—The author wishes to thank Mr. R. B. Bradley of this Institute for the n.m.r. spectral determinations.

(11) E. P. Oliveto, L. Weber, and E. B. Hershberg, *J. Am. Chem. Soc.*, **76**, 4482 (1954).

Kolbe Electrolyses of 3-Phenyl- and 3,3-Diphenylpropanoic Acids

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The question of phenyl 1,2-migration of free radicals during Kolbe electrolyses has been examined by electrolyzing 3,3-diphenylpropanoic acid (1) in acetic acid containing acetate ion and (2) in methanol, and (3) by electrolyzing 3-phenylpropanoic acid in acetic acid containing acetate ion. The electrolysis products from 1 consisted of 1,1-diphenylpropane (IV), 3-phenyl-3,4-dihydrocoumarin (V), and 1,2-diphenylethyl acetate (VIII), along with smaller quantities of phenyl cinnamate (VI), 2-*O*-acetyl-1,1-diphenylethylene glycol (IX), and phenyl 3-acetoxy-3-phenylpropanoate (VII). The identified electrolysis products from 2 were 1,1,4,4-tetraphenylbutane (XIII) and methyl 1,2-diphenylethyl ether (XVIII). VIII and XVIII represent products of phenyl 1,2-migration. The electrolysis products from 3 consisted of *n*-propylbenzene and 2-phenylethyl acetate. Arguments are presented supporting the hypothesis that the unrearranged hydrocarbon products (IV and XIII) arose by coupling of free radicals prior to rearrangement and that the rearranged acetate and ether products (VIII and XVIII) resulted from anodic oxidation of unrearranged 2,2-diphenylethyl radicals to 2,2-diphenylethyl carbonium ions, followed by rearrangement of the latter to more stable benzylic 1,2-diphenylethyl carbonium ions which ultimately solvolyzed to the observed oxygenated products.

Recently, with the intention of developing a system in which the possibility of bridged radical intermediates could be critically evaluated, we have succeeded[2] in generating the 1,2,2-triphenylethyl-1-C^{14} radical (I)

$Ph_2CH—\dot{C}^{14}HPh$ (I) $\quad Ph_2\dot{C}HCH_2\cdot$ (II) $\quad Ph\dot{C}HCH_2Ph$ (III)

by the decarbonylation of 2,3,3-triphenylpropionaldehyde-2-C^{14}. The label redistribution in the monomeric decarbonylation product, 1,1,2-triphenylethane, indicated that radical I had undergone phenyl 1,2-rearrangement to the extent of 5–14% during its transitory existence. In considering methods by which radical intermediates might be produced to broaden the above studies, the Kolbe electrolysis reaction appeared potentially applicable. While phenyl 1,2-shifts are observed frequently and are well-documented for radical intermediates produced by a variety of other techniques,[2] the situation regarding such rearrangements during Kolbe electrolyses is less straightforward. Urry[3] has reported the formation of rearranged products (isobutylbenzene, 2-methyl-3-phenyl-1-propene, and 1-phenyl-2-methyl-1-propene) along with unrearranged products (*t*-butylbenzene, ethyl β-phenylisovalerate, 2,2-dimethyl-2,2-diphenylhexane, and neophyl β-phenylisovalerate) during the Kolbe electrolysis (*ca.* 2 ma./cm.^{2}) of β-phenylisovaleric acid in ethanol. More recently, on the other hand, Breederveld and Kooyman[4] noted specifically the absence of rearranged products on Kolbe electrolysis of β-phenylisovaleric acid under slightly different conditions (methanol and methanol–acetic acid solvents, *ca.* 150 ma./cm.^{2}). Accordingly, it appeared initially pertinent to ascertain if Kolbe electrolysis would lead

(1) The authors are grateful to the National Science Foundation for a grant (G9479) which supported part of this study.

(2) W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 29 (1964).

(3) W. H. Urry, Abstracts of Papers, 12th National Organic Chemistry Symposium of the American Chemical Society, Denver, Colo., 1951, p. 36.

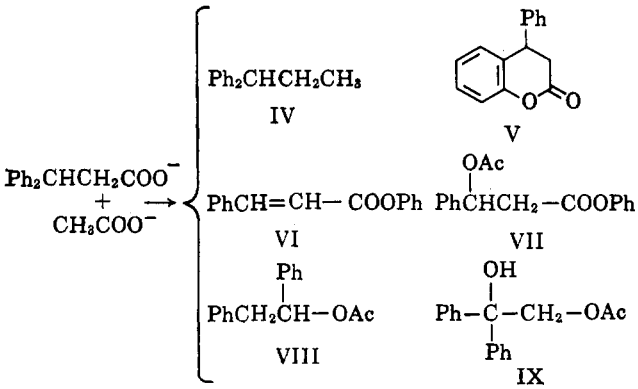
(4) H. Breederveld and E. C. Kooyman, *Rec. trav. chim.*, **76**, 297 (1957).

to phenyl 1,2-rearrangement in radical systems somewhat analogous to I. We, therefore, undertook to study the electrolysis of 3,3-diphenylpropanoic acid, rearrangement of whose initial 2,2-diphenylethyl primary radical (II) into the more stable secondary benzyl radical (III) might be readily detected by ordinary (*i.e.*, nonlabeling) techniques.

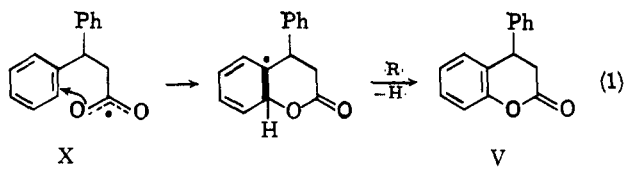
Sodium 3,3-diphenylpropanoate was electrolyzed in glacial acetic acid solution containing sodium acetate (whose concomitant electrolysis might provide methyl radicals[4] to couple with II or III), and the crude product was chromatographed on acid-washed alumina. Seven fractions resulted, which afforded the six discrete products summarized in Chart I.

CHART I

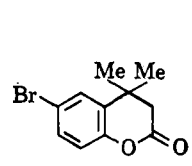
PRODUCTS FROM ELECTROLYSIS OF $Ph_2CHCH_2COO^-$ AND CH_3COO^- IN ACETIC ACID



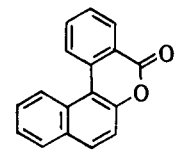
The only hydrocarbon product recovered, 1,1-diphenylpropane (IV), could be accounted for by the coupling at or near the electrode surface of unrearranged 2,2-diphenylethyl radicals (II) with methyl radicals. No rearranged hydrocarbon [*e.g.*, (a) the dimer of III or (b) 1,2-diphenylpropane, the coupling product of III with $CH_3\cdot$] was observed. The absence of such products indicates either that radical II does not here rearrange to III or, if it does, that III follows a path other than coupling. The formation of 4-phenyl-3,4-dihydrocoumarin (V) presumably results from the homolytic cyclization of the initially produced propionoxy radical (X, eq. 1) prior to its de-



carboxylation. Analogous radical cyclizations have been reported in the Hunsdiecker decarboxylations of silver β-phenylisovalerate to produce the lactone (XI)[5a] and of silver 3,3-diphenylpropanoate to produce the lactone (V),[5b] as well as in the thermal decomposition of *t*-butyl *o*-(1-naphthyl)perbenzoate to produce the lactone (XII).[6] The presence of unrearranged 2-*O*-acetyl-1,1-diphenylethylene glycol (IX) in the crude electrolysis product seemed possibly due to the intermediate formation of 1,1-diphenylethylene,



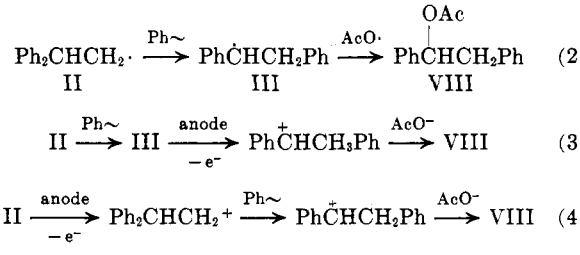
XI



XII

since it has been reported[7] that ethylene results in good yield during the electrolysis of sodium propionate. The possibility that such a mechanism was responsible for formation of IX was strengthened by our observation that the electrolysis of sodium acetate in acetic acid in the presence of 1,1-diphenylethylene afforded the monoacetate (IX) in good yield.[8] The remaining oxygenated substances (VI, VII, and VIII) in Chart I represent rearrangement products. The phenyl cinnamate (VI) and phenyl 3-acetoxy-3-phenylpropanoate (VII) products clearly have arisen from a phenyl 1,4-migration, though it is not clear at present if this migration involved radical or carbonium ion intermediates (see below). Similar phenyl 1,4-migrations have been observed during the Hunsdiecker decarboxylation of silver 3,3,3-triphenylpropanoate,[9,10] as well as during the Kolbe electrolysis of the same acid.[4] The 1,2-diphenylethyl acetate (VIII) derivative in Chart I represents the only observed product of phenyl 1,2-migration. It was unaccompanied by detectible amounts of unrearranged 2,2-diphenylethyl acetate.

Three paths, as summarized in eq. 2, 3, and 4, appeared possible *a priori* for the formation of the rearranged acetate (VIII). The Hofer–Moest oxidations



postulated in eq. 3 and 4 are analogous to those described by Corey,[11] who found that electrolytically generated aliphatic radicals readily undergo further oxidation to carbonium ions, especially when the latter can be resonance-stabilized. Benzylic radicals apparently oxidize with even greater ease, since the electrolyses of mono-, di-, and triphenylacetic acids afford progressively decreasing amounts of coupling products and increasing amounts of solvolysis products.[12,13] Similarly, our present attempts to electrolyze the sodium salt of 2,3,3-triphenylpropanoic acid in methanol yielded no coupling product, but only methyl 1,2,2-triphenylethyl ether in 53% yield.

It would appear that the coupling mechanism (eq. 2) is incapable of explaining the formation of the rear-

(5) (a) C. E. Berr, Dissertation, University of California at Los Angeles, 1952; (b) U. K. Pandit and I. P. Dirk, *Tetrahedron Letters*, **14**, 891 (1963).

(6) D. F. DeTar and C. C. Chu, *J. Am. Chem. Soc.*, **82**, 4969 (1960).

(7) C. L. Wilson and W. J. Lippincott, *ibid.*, **78**, 4290 (1956).

(8) This novel electrolytic hydroxylation of alkenes has been explored in greater detail and will be described fully in a forthcoming communication.

(9) J. W. Wilt and D. Oathoudt, *J. Org. Chem.*, **21**, 1550 (1956); **23**, 218 (1958).

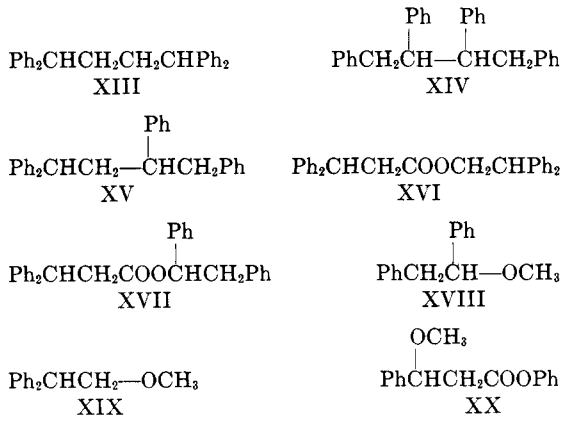
(10) J. W. Wilt and J. L. Finnerty, *ibid.*, **26**, 2173 (1961).

(11) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *J. Am. Chem. Soc.*, **82**, 2645 (1960).

(12) R. P. Linstead, B. R. Shephard, and B. C. L. Weedon, *J. Chem. Soc.*, 3624 (1952).

(13) B. Wladislaw and A. M. J. Ayres, *J. Org. Chem.*, **27**, 281 (1962).

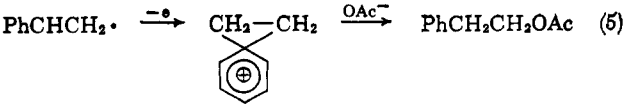
ranged acetate (VIII). Should mechanism 2 have intervened, one would certainly anticipate recovering as well unrearranged 2,2-diphenylethyl acetate—perhaps even as the predominant isomer—since the less stable radical II should be more reactive than the more stable III in such a process. Unrearranged acetate, however, was not detected. Furthermore, Swarc[14] has estimated the lifetime of the acetoxy radical to be only 10^{-9}–10^{-10} sec., and has suggested that such radicals can react only in their original "cage" and not in the surrounding solution. To confirm these conclusions regarding mechanism 2, 3,3-diphenylpropanoic acid was electrolyzed in methanol solvent rather than acetic acid. Should mechanism 2 prevail, one would expect in methanol the coupling products 1,1,4,4-tetraphenylbutane (XIII, from II), 1,2,3,4-tetraphenylbutane (XIV, from III), and 1,1,3,4-tetraphenylbutane (XV, from II + III), as well as the esters XVI and XVII (from $Ph_2CHCH_2COO\cdot$ with II and III). If the oxidation–solvolysis paths 3 or 4 prevailed, however, the anticipated solvolysis products should be methyl 1,2-diphenylethyl ether (XVIII), with possibly a small amount of methyl 2,2-diphenylethyl ether (XIX, if path 4). The principal products from the above electrolysis in methanol, on chromatographic separation, proved to be the unrearranged coupling product (XIII) and the rearranged ether (XVIII). Small amounts of the lactone (V) and the 1,4-migration product, phenyl 3-methoxy-3-phenylpropanoate (XX), were also obtained. None of the unrearranged ether (XIX) nor the other coupling products (XIV–XVII) could be recovered from the crude electrolysis product. These results appear to confirm the above conclusion that the rearranged acetate (VIII) resulting from phenyl 1,2-migration is formed by solvolysis of a cationic intermediate (eq. 3 or 4) and not by the radical coupling path (eq. 2).



Solvolysis path 3 for the formation of rearranged acetate (VIII) involves phenyl 1,2-rearrangement of the initial 2,2-diphenylethyl radical (II), prior to anodic oxidation of the rearranged radical (III) to the rearranged 1,2-triphenylethyl carbonium ion. Solvolysis path 4 entails anodic oxidation of the initial radical II to the unrearranged 2,2-triphenylethyl carbonium ion, followed by a phenyl 1,2-shift to the rearranged carbonium ion. One might anticipate a preference for path 3, since this involves not only the rearrangement of an unstable primary aliphatic radical (II) to a more stable secondary benzyl radical (III), but also the relief of perhaps appreciable B-strain at C-2 in II. Furthermore, the benzylic radical III should presumably undergo anodic oxidation more readily than the primary radical II.[12,13] Against path 3, however, was our failure to detect either the dimer of III from electrolysis in methanol, or the $CH_3\cdot$ + III coupling product, 1,2-diphenylpropane, from electrolysis in acetic acid. In favor of path 4 was our exclusive isolation of XIII, the dimeric coupling product of II, from electrolysis in methanol, and of the unrearranged $CH_3\cdot$ + II coupling product (IV) from electrolysis in acetic acid.

While the preponderence of evidence thus appeared to favor the solvolysis mechanism 4, it seemed desirable to establish experimentally the fact that anodic oxidation and subsequent solvolysis could in fact occur on a primary alkyl radical in the present system. To this end sodium 3-phenylpropanoate was electrolyzed with sodium acetate in acetic acid. Here, after initial decarboxylation, the primary 2-phenylethyl radical cannot rearrange to a more stable secondary benzylic radical (*i.e.*, no hydrogen 1,2-shift should occur[15]), no coupling with the acetoxy radical should take place (see above), and any acetate product must arise by anodic oxidation of the 2-phenylethyl radical to the 2-phenylethyl carbonium ion, followed by solvolysis. Chromatographic separation of the crude electrolysis product from sodium 3-phenylpropanoate afforded the unrearranged $CH_3\cdot$ coupling product, *n*-propylbenzene, and the solvolysis product, 2-phenylethyl acetate. The isolation of the latter acetate appears to confirm the supposition that the anodic oxidation of the primary radical in path 4 can occur, and to render this path as the more probable mechanism in the present case. We plan to test this conclusion experimentally by electrolysis studies with C^{14}-labeled analogs. The finding of Muhs[16] that, in the Kolbe electrolysis of aliphatic acids, the rearranged products appear exclusively monomeric while the dimeric products prove to be unrearranged, supports our suggestion that rearranged products arise *via* cationic intermediates which cannot undergo self-coupling.

To test for possible anchimeric assistance by the β-phenyl group in the above production of the 2-phenylethyl acetate solvolysis product, sodium propionate itself was electrolyzed under similar conditions. β-Phenyl participation has been proposed as occurring during several solvolysis reactions of 2-phenylethyl derivatives.[17] The electrolysis product was examined by vapor–liquid partition chromatography and found to be primarily ethyl acetate. The isolation of ethyl acetate indicates that phenyl participation need not intervene in the above anodic oxidations of 2-phenylethyl or 2,2-diphenylethyl radicals and, specifically, that bridged phenonium ions (eq. 5) are not prerequisites in these instances.



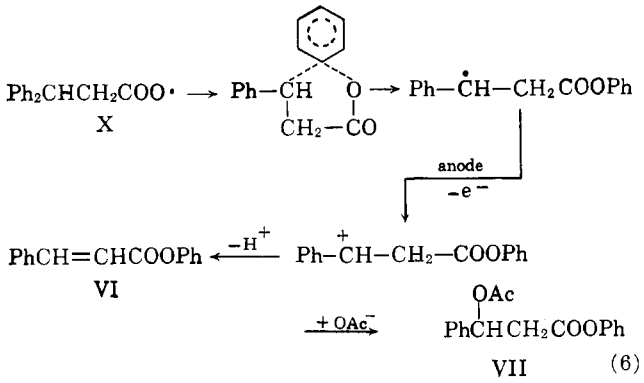
(14) L. Herk, M. Feld, and M. Swarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

(15) D. Y. Curtin and V. C. Kauer, *J. Org. Chem.*, **25**, 880 (1960); L. H. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959).

(16) M. A. Muhs, *Dissertation Abstr.*, **14**, 765 (1954).

(17) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p. 575 ff.

One possible rationalization for the formation of the phenyl 1,4-migration products (VI and VII) in the 3,3-diphenylpropanoate system (Chart I) is shown in eq. 6. We have no direct experimental evidence, however, bearing on the validity of this suggestion.



(6)

Experimental

3,3-Diphenylpropanoic acid was prepared by the aluminum chloride-catalyzed alkylation of benzene with cinnamic acid according to the procedure of Homes and Hill.[18] The purified product had m.p. 154–155°, in agreement with the reported value.[18]

Electrolysis of 3,3-Diphenylpropanoic Acid in Acetic Acid.—The electrode unit consisted of two platinum foil electrodes (1.25 × 1.25 cm.) spaced approximately 2 mm. apart and joined to wires sealed into a tapered glass head (⅋ 29/42, female) equipped with a gas exit tube. The cell compartment (30 ml.), fitted to receive the electrode unit, was equipped with a water jacket for thermostating. The electrolysis apparatus was energized by a 12-v. Heathkit battery eliminator.

The solution of 3,3-diphenylpropanoic acid (5.37 g.) and sodium acetate (1.59 g.) in acetic acid (30 ml.) was electrolyzed (0.2-amp. current) in the above cell for 38 hr. (12 f./mole), with continual magnetic stirring and external cooling (cell contents, 32–38°). The majority of solvent was then removed by evaporation at reduced pressure, and the residue was dissolved in ether. The ether solution was extracted twice with 5% aqueous ammonium hydroxide (discard), then was washed with water, dried (magnesium sulfate), filtered, and evaporated, affording 3.85 g. of thick, amber oil. A portion (1.98 g.) of the crude product was chromatographed on silicic acid using hexane–benzene mixtures gradually enriched in benzene, then benzene and finally ether as eluent, collecting 50-ml. portions of eluate. Residues from the evaporation of each portion were examined by infrared spectroscopy and thin layer chromatography (t.l.c.), and similar residues were combined yielding a total of seven fractions (fractions 1–7, in order of appearance) which totaled 1.73 g. (87.4%).

Fraction 1 (66 mg.) was rechromatographed [silica–(hexane–ether), 100:1] to give 63 mg. of clear oil, homogeneous by t.l.c. and having an R_f value and infrared spectrum identical with those of authentic 1,1-diphenylpropane (IV), prepared independently. A spot during t.l.c. corresponding to 1,2-diphenylpropane was absent, as were infrared bands at 1005 and 2849 cm.$^{-1}$ which proved characteristic of the latter hydrocarbon. Fraction 2 (50 mg.) solidified and was recrystallized from ethanol, m.p. 73–75°. It showed t.l.c. behavior identical with that of phenyl cinnamate (VI, m.p. 74–76°), showed no mixture melting point depression (74–76°) with this ester, and displayed an infrared spectrum superimposable on that of an authentic sample. Fraction 3 (oil, 107 mg.) had an R_f value by t.l.c. identical with that of authentic 1,2-diphenylethyl acetate (VIII) and different from that of 2,2-diphenylethyl acetate. Its infrared spectrum was identical with the spectrum of 1,2-diphenylethyl acetate, with the exception of three very weak bands (1198, 1169, 738 cm.$^{-1}$) not present in the spectrum of the authentic sample. Its retention time in gas chromatography (180°) on a silicone rubber column was identical with the retention time of authentic 1,2-diphenylethyl acetate. The identity of fraction 3 was confirmed by treatment of a portion (56 mg.) with an ether solution containing an excess of lithium aluminum hydride. The mixture was heated under reflux for 1 hr., then processed as usual to produce 40 mg. of oil which solidified. Recrystallization from hexane–benzene gave a sample of 1,2-diphenylethanol, m.p. 63–66°, which showed no mixture melting point depression (64–66°) with an authentic sample and gave an infrared spectrum identical with that of the authentic sample. Fraction 4 (oil, 168 mg.) showed two spots by t.l.c. The lower R_f spot was identical in position and hue to one of authentic 4-phenyl-3,4-dihydrocoumarin (V), while the faster travelling spot corresponded to 1,2-diphenylethyl acetate (VIII). A portion of fraction 4 was gas chromatographed (200°) on a silicone rubber column, and the presence of 4-phenyl-3,4-dihydrocoumarin (55%) was confirmed by peak enhancement with an authentic sample. Fraction 5 (solid, 253 mg.) was recrystallized from ethanol, m.p. 81.5–83.5°. It showed similar t.l.c. behavior, an identical infrared spectrum, and no mixture melting point depression (81.5–83.5°) with authentic 4-phenyl-3,4-dihydrocoumarin (m.p. 83–84°). Fraction 6 (oil, 471 mg.) displayed a strong carbonyl stretching frequency at 1750 cm.$^{-1}$ as well as ester C—O stretching bands[19] at 1140, 1163, 1196, and 1231 cm.$^{-1}$. The n.m.r. spectrum (tetramethylsilane internal standard taken as zero, deuteriochloroform, Varian A60 n.m.r. spectrometer) of a distilled portion of fraction 6 was consistent with the structure, phenyl 3-acetoxy-3-phenylpropanoate (VII). The benzylic methynyl proton, coupled to the two nonequivalent methylene protons (6.0 and 8.5 c.p.s.), appeared as a quartet centered at 6.3 p.p.m. The spectrum displayed another quartet centered at 3.08 and a sharp acetate methyl band at 2.01 p.p.m. Several bands appeared in the aromatic region of the spectrum between 6.8 and 7.5 p.p.m. The integrated band intensities from low to high field were in the ratio 10:1:2:3. Fraction 6 (169 mg.) was purified by rechromatographing on silicic acid (20 g.) using ether–hexane (1:10) as eluent. The first 100 ml. of eluate was discarded and the next 25 ml. was evaporated to yield 90 mg. of clear oil, homogeneous by t.l.c.

Anal. Calcd. for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.98; H, 5.81.

Confirmation of the identity of fraction 6 as phenyl 3-acetoxy-3-phenylpropanoate (VII) was obtained by pyrolysis of a 90 mg. sample for 5 min. at 400° (Woods metal bath). The crude product, a dark oil, was chromatographed on silicic acid (benzene eluent) to yield an amber oil which solidified. Recrystallization from ethanol gave a sample of solid, m.p. 70.5–76°, which was shown by its mixture melting point (73.5–76°) and the identity of its t.l.c. behavior and infrared spectrum with those of an authentic sample, to consist of phenyl cinnamate (VI) (m.p. 76–78°). Fraction 7 showed the presence of four components by t.l.c., and its infrared spectrum showed the presence of both ester and hydroxylic compounds. A portion (115 mg.) of the crude fraction was dissolved in ethanol (6 ml.) and treated with water (4 ml.) containing potassium hydroxide (1.7 g.). The mixture was heated under reflux for 5 hr. and allowed to stand at 25° for 4 days, then was evaporated to about half its volume at reduced pressure. The aqueous residue (A) was extracted with ether, and the extracts were washed with water, dried, and stripped of solvent to give 18 mg. of viscous, amber oil which solidified. This was chromatographed on silicic acid (5 g.) using benzene, gradually enriched with ether, as eluent. Evaporation of the first 250 ml. of eluent afforded 12 mg. of pale oil which crystallized. The solid was treated with a few drops of benzene and the supernatant solution was separated and treated with a little hexane, affording white needles, m.p. 119–120.5°. The infrared spectrum of these was identical with that of authentic 1,1-diphenylethylene glycol (m.p. 120–122°), and a mixture melting point gave no depression. The aqueous alkaline residue (A) above was acidified and extracted with ether, yielding ultimately 73 mg. of dark, acidic oil from which no crystalline material could be recovered chromatographically. Another portion (227 mg.) of fraction 7 was chromatographed on silicic acid (25 g.) using benzene as eluent. Evaporation of the first 150 ml. yielded 196 mg. of thick oil which proved to contain four components by t.l.c. Its infrared spectrum showed O—H, C=O, and C—O stretching frequencies. One of the spots by t.l.c. corresponded both in position and color under ultraviolet illumination to the spot corresponding to authentic 2-*O*-acetyl-1,1-diphenylethylene glycol (IX).

(18) R. B. Homes and A. J. Hill (to American Cynamid Co.), U. S. Patent 2,423,025 (June 24, 1947).

(19) A. D. Cross, "Introduction to Practical Infrared Spectroscopy," Butterworths Scientific Publications, London, 1960, p. 64.

The authentic samples used for t.l.c., melting point, and infrared comparisons with the products from the previous electrolysis were prepared in the following ways.

1,2-Diphenylethyl Acetate (VIII).—This compound (VIII) was prepared by acetylation of authentic 1,2-diphenylethanol (4 g.) with acetic anhydride (3 ml.) in refluxing acetic acid (40 ml.) during 4 hr. Solvent evaporation, followed by chromatographic purification (silicic acid) of the residue afforded the pure oily ester, which was t.l.c. homogeneous and had infrared stretching bands for C=O and C—O at 1740 and 1230 cm.$^{-1}$, respectively.[19] Its reduction with lithium aluminum hydride regenerated 1,2-diphenylethanol. **2,2-Diphenylethyl acetate** was prepared by lithium aluminum hydride reduction of 2,2-diphenylacetic acid, followed by acetylation, as described above, of the resulting 2,2-diphenylethanol. The crude, solid acetate was recrystallized from ethanol to give white crystals, m.p. 55.5–57°, C=O infrared band at 1725 cm.$^{-1}$ and C—O band at 1250 cm.$^{-1}$.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 79.78; H, 6.64.

1,1-Diphenylpropane (IV) was prepared by the reduction of 3,3-diphenylpropanoic acid with excess lithium aluminum hydride in ether. The crude, oily 3,3-diphenyl-1-propanol product, showing no carbonyl absorption in the infrared, was converted to its tosylate by the procedure of Cram.[20] The latter in turn was reduced with lithium aluminum hydride in ether solution, affording a clear, oily product. This was purified by chromatographing on neutral alumina (grade II), using hexane as eluent. The purified oil was homogeneous by t.l.c. and showed an n.m.r. spectrum consistent with that of 1,1-diphenylpropane. The aromatic protons appeared at 7.1 p.p.m. The benzylic methynyl proton, split by the two adjacent methylene protons (8.5 c.p.s.), appeared as a triplet centered at 3.7 p.p.m. The three methyl protons, also coupled to the two methylene protons (7.5 c.p.s.), showed as a triplet centered at 0.9 p.p.m. The two methylene protons, coupled to both the adjacent methynyl and three methyl protons, appeared as a quintuplet centered at 2.1 p.p.m. The material had b.p. 281°, in agreement with the recorded boiling point (278.5–280.5°)[21] for 1,1-diphenylpropane. **1,2-Diphenylpropane** was prepared by the dehydroxylation of 1,2-diphenyl-1-propanol[22] with Raney nickel[23] in refluxing ethanol. The crude product, whose t.l.c. behavior revealed the presence of some unchanged starting material, was purified by chromatographing twice on neutral alumina. The n.m.r. spectrum of the t.l.c. homogeneous oily product was consistent with 1,2-diphenylpropane. The three methyl protons, coupled to the adjacent methynyl proton (5.5 c.p.s.), appeared as a doublet centered at 1.1 p.p.m. A multiplet, centered at 2.7 p.p.m., represented the benzylic methylene and methynyl protons. The aromatic protons appeared around 7.5 p.p.m. The oil had b.p. 275°, in agreement with the reported value[21] of 280–282°.

4-Phenyl-3,4-dihydrocoumarin (V), m.p. 83–84°, was prepared from phenol and cinnamic acid after the procedure of Simpson and Stephen.[24] **1,1-Diphenylethylene glycol** was prepared by the permanganate hydroxylation of 1,1-diphenylethylene after the method of Clark and Owen,[25] the purified sample having m.p. 120–122°.[26] A portion of this glycol was converted into **2-*O*-acetyl-1,1-diphenylethylene glycol (IX)** by treatment with excess acetic anhydride in pyridine (1:1). The crude solid product crystallized from hexane–benzene as white needles, m.p. 93–93.5°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.97; H, 6.32.

Electrolysis of Sodium 3,3-Diphenylpropanoate in Methanol.—A solution of 3,3-diphenylpropanoic acid (2.67 g.) in absolute methanol (25 ml.) containing sodium (27 mg.) was electrolyzed in the manner described above. It was not possible to maintain a constant current since a white precipitate, which obstructed the current flow, formed at the anode. This difficulty was largely overcome by reversing the electrode polarity every 5 min. The electrolysis was continued for a period of 20 hr., whereupon the mixture was processed as before to yield 1.56 g. of crude sirup. This was chromatographed on 200 g. of silicic acid, using benzene–hexane mixtures gradually enriched in benzene, and finally ether as eluents. Residues from eluate evaporation, combined as before, afforded 5 fractions totalling 97.3% of the charge. These are described below in order of their appearance in the column eluates. Fraction 1 (13%) solidified and was recrystallized from hexane as white needles, m.p. 119–122°. The infrared and n.m.r. spectra of the product were consistent with 1,1,4,4-tetraphenylbutane (XIII), whose reported[27] melting point is 122°. The aromatic protons appeared as a multiplet centered at 7.2, the methynyl protons as a multiplet around 4.1, and the methylene protons as a triplet (4.0 c.p.s.) centered around 2.02 p.p.m. The integrated band intensities for each proton type, respectively, were 10:1:2. Fraction 2 (4.5%) was an oil whose small quantity precluded further purification and characterization. Its t.l.c. behavior suggested the presence of one major component along with one or more minor ones. Fraction 3 (1.1%) crystallized and was recrystallized from hexane–benzene to provide a few milligrams of white solid, m.p. 137–139°. Its infrared spectrum was quite similar to that of 1,1,4,4-tetraphenylbutane, showing no absorption bands attributable to functional groups. The reported melting point for 1,1,3,3-tetraphenylpropane is 139°, but sufficient material was not available for further characterization. Fraction 4 (12.7%) proved to be a clear oil which was homogeneous on t.l.c. Its infrared spectrum and t.l.c. R_f value were identical with those of authentic methyl 1,2-diphenylethyl ether (XVIII) described below and distinctly different from those of authentic methyl 2,2-diphenylethyl ether. Fraction 5 (68.8%) was a crude oil whose t.l.c. behavior suggested the presence of at least four components. One of the t.l.c. spots was identical in position and hue with that of 4-phenyl-3,4-dihydrocoumarin (V). Further attempts at column chromatographic separation of fraction 5 led to no further identifiable products.

Methyl 1,2-Diphenylethyl Ether (XVIII).—1,2-Diphenylethanol (1 g.) was methylated by dissolving in methyl iodide (25 ml.) and stirring in the presence of silver oxide (10 g.), Drierite (10 g.) and glass beads[28] for a period of 30 hr. The crude product was a thick oil (1 g.), which was chromatographed on silicic acid (100 g.) using benzene as eluent. Evaporation of the first 100 ml. of eluate left a pale oil, which was rechromatographed in the same way. Its infrared spectrum showed no OH absorption, and its n.m.r. spectrum was consistent with the structure of the desired ether. The aromatic protons appeared from 6.9–7.3 p.p.m. The benzylic methynyl proton, coupled to two nonequivalent methylene protons (7.0 and 7.5 c.p.s.) revealed a quartet centered at 4.2 p.p.m. A sharp peak at 3.09 p.p.m. was superimposed on a sextet centered at 2.9 p.p.m. The integrated band intensities from low to high field were 10:1:5.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.94; H, 7.56.

Methyl 2,2-diphenylethyl ether, an oil, was prepared from 2,2-diphenylethanol in the manner described before, then purified twice by similar column chromatography. The n.m.r. spectrum showed a quartet around 4.19 p.p.m., corresponding to the methynyl proton coupled to two nonequivalent methylene protons (6.0 and 8.0 c.p.s.). The methylene protons appeared as a triplet centered at 3.75, and the methyl protons as a sharp singlet at 3.12 p.p.m. The integrated band intensities were 10:1:2:3.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.94; H, 7.56.

Electrolysis of 3-Phenylpropanoic Acid in Acetic Acid.—A solution of 3-phenylpropanoic acid (2.89 g.) and sodium acetate (1.43 g.) in acetic acid (25 ml.) was electrolyzed as above for 21 hr. (0.2 amp., 8 f./mole). The mixture was treated with excess ammonium hydroxide and the basic solution was extracted thoroughly with ether. The extracts were washed, dried, and evaporated to yield 534 mg. of neutral, amber oil. This was chromatographed on 50 g. of silicic acid, with ether as eluent, affording 411 mg. of clear oil, which was examined by gas chromatography on diethylene glycol succinate (150°) and silicone rubber (120°) columns. Authentic samples of *n*-propylbenzene, 2-phenylethyl acetate, and 3,4-dihydrocoumarin were used for identification purposes. The observed retention times showed that *n*-propylbenzene and 2-phenylethyl acetate were present but that 3,4-dihydrocoumarin was absent. In a duplication of

(20) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 2863 (1949).

(21) P. Sabatier and M. Murat, *Compt. rend.* **155**, 385 (1912); *Ann. chim.* (Paris), [9] **4**, 287 (1915).

(22) M. Tiffeneau, *ibid.*, [8] **10**, 192, 353 (1907); M. F. Kayser, *ibid.*, [11]**6**, 145 (1936).

(23) J. A. Zderic, W. A. Bonner, and T. W. Greenlee, *J. Am. Chem. Soc.*, **79**, 1696 (1957).

(24) D. Simpson and J. Stephen, *J. Chem. Soc.*, 1382 (1956).

(25) M. F. Clark and L. N. Owen, *ibid.*, 315 (1949).

(26) P. Weidenkoff, *Ber.*, **39**, 2063 (1906).

(27) K. Ziegler, H. Colonius, and O. Schäfer, *Ann.*, **473**, 56 (1929).

(28) W. A. Bonner, *J. Am. Chem. Soc.*, **73**, 3126 (1951).

the above electrolysis the two products were separated by column chromatography and their identities were confirmed by comparison of their infrared spectra with those of authentic samples.

Electrolysis of Propionic and Acetic Acids.—A mixture of propionic acid (6.8 g.), acetic acid (20 g.), and sodium acetate (2.1 g.) was electrolyzed as above (0.3 amp.) for a period of 6 hr. All material boiling below 120° was distilled directly from the reaction mixture, and the distillate was examined by gas chromatography using three different column packings. Peak enhancement, using authentic ethyl acetate, confirmed the presence of this ester, which was calculated to have been formed in about 13% yield from the propionic acid precursor.

Electrolysis of 2,3,3-Triphenylpropanoic Acid. A. In Methanol.—2,3,3-Triphenylpropanoic acid[2] (685 mg.) in methanol (20 ml.) containing sodium (26 mg.) was electrolyzed as above for a period of 17 min., after which the crude product was recovered by solvent evaporation. The residue was dissolved in ether, and the solution was extracted with dilute aqueous sodium hydroxide. Ether extraction of the acidified aqueous layer afforded 290 mg. of unchanged acid. Evaporation of the original ether layer yielded 351 mg. of crude product. This was chromatographed on acid-washed alumina (grade III, benzene–hexane eluent) to provide 172 mg. of white solid, m.p. 67.5–68°, after recrystallization from dilute methanol. The sample gave no mixture melting point depression, and displayed an infrared spectrum identical with that of authentic methyl 1,2,2-triphenylethyl ether. The latter sample, m.p. 66.5–68°, was prepared by the methylation of 1,2,2-triphenylethanol, as described before,[28] using methyl iodide and silver oxide.

Anal. Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 86.82; H, 6.87.

B. In Acetic Acid.—A mixture of 2,3,3-triphenylpropanoic acid (450 mg.) and sodium acetate (200 mg.) in acetic acid (20 ml.) was electrolyzed as described above (8 f./mole). The mixture was evaporated to dryness, dissolved in ether and extracted with ammonium hydroxide solution (discard). Evaporation of the ether solvent yielded 370 mg. of crude product which was chromatographed on acid-washed alumina (grade III, benzene–hexane eluent), affording 260 mg. of white solid. This was recrystallized from ethanol, m.p. 147–149°. The product showed no mixture melting point depression and had an infrared spectrum superimposible on that of authentic 1,2,2-triphenylethyl acetate, m.p. 155–156°.[29]

(29) W. A. Bonner and C. J. Collins, *J. Am. Chem. Soc.*, **75**, 5372 (1953).

Wheat Bran Phenols[1]

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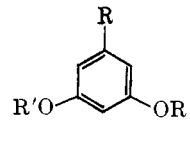
A mixture of 5-*n*-alkylresorcinols is found to be present in the nonsaponifiable fraction of wheat bran. The structures of two phenols are shown to be 5-*n*-nonadecylresorcinol and 5-*n*-heneicosylresorcinol by analysis and synthesis.

While much effort has been expended in the past on investigations of the chemical constitution of wheat, only little is known about the composition of the nonsaponifiable portion of wheat bran.[2] On undertaking an investigation of the latter and initially carrying out alumina chromatography, we encountered the presence of hydrocarbons, steroids, and a phenolic material. The unusual presence of a phenolic constituent, designated at first as substance A, in the nonsaponifiable fraction of a plant extract aroused our attention and led to a structure analysis which constitutes the major portion of this communication.

Early elemental analyses of crystalline substance A, m.p. 84–85°, pointed to a $C_{13}H_{24}O$ formula. Its infrared spectrum showed hydroxyl and aromatic absorption bands and its ultraviolet spectrum was characteristic of a phenolic compound. Its phenolic character was confirmed by the preparation of a crystalline methyl ether and acetate. The infrared spectrum of the ester revealed no hydroxyl peaks and only a 5.65-μ band in the carbonyl region. Inspection of the n.m.r. spectra of substance A and its two derivatives indicated the presence of aromatic hydrogens. The ratio (2:1) of the intensities of the O-methyl signal *vs.* the aromatic hydrogen signal in the methyl ether as well as the same ratio of the acetyl methyl signal *vs.* the aromatic hydrogen signal in the ester showed that A was a monoalkylated dihydric phenol of a $C_{26}H_{48}O$ formula. A positive mercuric nitrate test[3] suggested it was an alkylresorcinol. An n.m.r. analysis of the six dimethoxytoluenes (*vide infra*) and comparison of their spectra with the spectrum of the dimethyl ether of substance A established that A was a 5-alkylresorcinol.

The resistance of A to hydrogenation over palladium–charcoal and the absence of olefinic hydrogen signals in its n.m.r. spectrum indicated that the alkyl side chain was saturated. The n.m.r. signal of the side chain was composed of a benzylic two-proton multiplet at 2.33–2.75 p.p.m. (deuterioacetone solution with an internal tetramethylsilane standard), a broad methylene *ca.* 36-proton singlet at 1.32 p.p.m., and a methyl three-proton multiplet at 0.82–1.05 p.p.m. Thus substance A appeared to be 5-*n*-eicosylresorcinol (Ia).



Ia, R = $(CH_2)_{19}CH_3$; R′ = H
b, R = $(CH_2)_{18}CH_3$; R′ = Me
c, R = $(CH_2)_{20}CH_3$; R′ = Me
d, R = $(CH_2)_{18}CH_3$; R′ = H
e, R = $(CH_2)_{20}CH_3$; R′ = H
f, R = $(CH_2)_{16}CH_3$; R′ = Me
g, R = $(CH_2)_{22}CH_3$; R′ = Me
h, R = $(CH_2)_{24}CH_3$; R′ = Me

In view of the fact that all previously reported naturally occurring *n*-alkylphenols have been shown to possess side chains containing odd numbers of carbon atoms in agreement with biosynthetic arguments (*vide infra*), the structure Ia was anomalous. The first indication of the heterogeneity of substance A was the wide melting ranges of its diacetate and dimethyl ether. As a consequence the vapor phase chromato-

(1) This work was carried out under contracts with the U. S. Department of Agriculture and authorized by the Research and Marketing Act. The contracts were supervised by the Northern Utilization Research Branch and the Western Utilization Research and Development Division of the Agricultural Research Service.

(2) M. T. Ellis, *Biochem. J.*, **12**, 160 (1918); R. J. Anderson and F. P. Nabenhauer, *J. Am. Chem. Soc.*, **46**, 1717 (1924); M. Gažo and V. Špringer, *Pol'nohospodárstvo*, **7**, 807 (1960); *Chem. Abstr.*, **55**, 8694*b* (1961).

(3) A. Butenandt and F. H. Stodola, *Ann.*, **539**, 40 (1939).