

Journal of Labelled Compounds

ABSTRACTS

In the following part of this journal, information on methods of synthesizing labelled compounds and related problems (analysis, assaying, purifying, radiodecomposition, storage) will regularly be given. The references cover articles drawn from 40 primary periodicals and also from N.S.A. and C.A.

A point will be made of singling out each of the above mentioned aspects in the abstracts, particularly where the greater part of the article deals with applications of labelled compounds¹. This journal will likewise contain author and subject indexes at the end of each volume.

The articles are abstracted by H. Dworschak, CID (Euratom).

¹ The work on this information project was started in May 1964. The results obtained until December 1964 have been published in Euratom reports EUR 2212.e and EUR 2212.e suppl., the latter of which contains author and subject indexes.

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1 — SYNTHESIS

1.1 — Deuterium and Tritium Compounds

1.1.1 — General

65-1

GORDON B. E., MADISON J. J.

Labeling of hydrocarbons by exchange. Conditions for high yield.U. S. At. E. C. CONF-398-1, 23 pp. (1963)
CA 61, 15615 d (1964)

Studies were made on the exchange between D_2O or D_2 and some hydrocarbons. Al_2O_3 and Co/Mo/S were evaluated as catalysts. D_2 is a more effective reagent than D_2O . Yields as high as 86 % were observed in a few hrs. Normal alkanes and cyclanes exchange at similar rates, but isoalkanes (isopentane) exchange more rapidly.

1.1.2 — Aliphatic Compounds

65-2

BÜCHI G., KOLLER E., PERRY C. W.
Bicycloionones and Tricycloionones.

J. Am. Chem. Soc. 86, 5646 (1964)

Tetradeuteriotricycloionone was prepared by refluxing a solution of tricycloionone in C_2H_5OD/C_2H_5ONa . In the same run tetradeuterioepitricycloionone was obtained.

65-3

COREY E. J., ATKINSON R. F.

A Test for Hydrogen Rearrangement in the Deamination of Cyclopropylamine to Allyl Alcohol.

J. Org. Chem. 29, 3703 (1964)

1.1 — Cyclopropane-dicarboxylic acid was dissolved in deuterium oxide; the solution was then frozen and dried in vacuo, and the process was repeated. Then the acid was decarboxylated. It was degraded with sodium azide to yield the urethane, which was hydrolyzed to cyclopropylamine-1-d (94,4 atom % D).

65-4

CRAM D. J., GOSSER L.

Electrophilic Substitution at Saturated Carbon. XXI. Isoracemization Reactions Involving Ion-Pair Intermediates.

J. Am. Chem. Soc. 86, 5457 (1964)

(+)-2-Phenylbutyronitrile-2-d was prepared from the corresp. acid through the acid chloride and amide. No exchange was observed during this conversion. (97 atom % D).

65-5

CRAM D. J., UYEDA R. T.

Electrophilic Substitution at Saturated Carbon. XXII. Intramolecular Hydrogen Transfer Reactions in Base-Catalyzed Allylic Rearrangements.

J. Am. Chem. Soc. 86, 5466

Optically active 3-Phenyl-1-butene-3-d (I) was prepared as follows :

In hydrotroponitrile α -H was exchanged for D and the nitrilgroup saponified. By the method of Arndt-Eistert the homohydrotropic acid- β -d (3-deuterio-3-phenyl butanoic acid) (II) was built. On the stage of the diazoketone the D-content dropped to 88 atom % II was reduced, transformed to the bromide from which by the Hofmann elimination I was formed.

65-6

CRAM D. J., WINGROVE A. S.

Electrophilic Substitution at Saturated Carbon. XXIV. Trifluoromethyl as a Carbanion-Stabilizing Group.

J. Am. Chem. Soc. 86, 5490 (1964)

O-Deuterated benzylmethylmalonic acid was decarboxylated, the acids resolved into the enantiomers and treated with sulfur tetrafluoride. No D was lost in this transformation to 2-deuterio-2-methyl-3-phenyl-1,1,1-trifluoropropane (97 atom % D). When 2-phenylbutyronitrile was treated with $D_2O(NaOD)$ and after saponification the corresp. acids were resolved and than treated as above 2-deuterio-2-phenyl-1, 1, 1-trifluorobutane (98 atom % D) was obtained.

65-7

KWART H., SCALZI F. V.

Observations Regarding the Mechanism and Steric Course of the α -Bromination of Carboxylic Acid Derivatives. An Electrophilic Substitution Reaction in Non-polar Media.

J. Am. Chem. Soc. **86**, 5496 (1964)

α -Deuteriocyclohexanecarboxylic acid (I) was prepared from unlabeled I by bromination (Br_2/P) and heating the brominated acid with zinc powder-acetic anhydride and D_2O , giving a total yield of 73 % with 7,36 atom % D (88,35 % α -deuteration).

65-8

LESZCZYNSKI Z., WELLS P. B.

Selectivity of metallic catalysts and stereoselectivity of platinum and palladium catalysts in the reaction of butadiene with deuterium.

Przemysl Chem. **43** (9), 508-15 (1964)

CA **61**, 14502g (1964)

The results of comparative study on the reaction of 1, 3-butadiene (I) with D in the presence of Pt and Pd catalysts are given. Methods of kinetic study and of the analysis of reaction products, based on chromatographic analysis and sepn. as well as on mass spectrometric analysis and nuclear magnetic resonance, are described.

65-9

PREMUZIC E., REEVES L. W.

Conformational Studies by Nuclear Magnetic Resonance. Part VI. Adjacent Deuterated 2-, 3-, and 4-Methyl-cyclohexanol Esters, Cyclohexyl Nitrite, and Cyclooctyl Acetate.

J. Chem. Soc. **1964**, 4817

2-, 3-, and 4-methylcyclohexanols and their acetate esters were prepared labeled with deuterium in the α -positions to the hydroxy group by basic exchange of the protons in the corresp. ketones. To

obtain ketones with less than 2 % of α -protons six exchange steps with 99,8 % D_2O were necessary.

65-10

SAMUELSSON B.

Prostaglandins and Related Factors.

27. Synthesis of tritium-labeled prostaglandin E_1 and studies on its distribution and excretion in the rat.

J. Biol. Chem. **239**, 4091 (1964)

Prostaglandin E_2 from sheep vesicular gland was hydrogenated with tritium gas by Pd on activated carbon and the product separated by reversed phase partition chromatography. The fraction, containing tritiated prostaglandin E_1 was purified. Yield 6 % (based on tritium gas), sp. act. 50 mc/ μmole .

65-11

STREITWIESER A. Jr., VERBIT L., STANG P.

A Convenient Preparation of Methanol-d.

J. Org. Chem. **29**, 3706 (1964)

Dimethyl carbonate, (400 g), deuterium oxide (100 g) and 16 g dimethyl sulfate were refluxed. After 72 hr. the hydrolysis was complete. Methanol was distilled directly from the reaction flask. It was found to contain 98,6 % D.

65-12

TIETZ A., LINDBERG M., KENNEDY E. P.

A New Pteridine-requiring Enzyme System for the Oxidation of Glyceryl Ethers.

J. Biol. Chem. **239**, 4081 (1964)

Selachyl alcohol was hydrogenated (PtO_2 , cyclohexane) with tritium gas (1.5 c). After chromatography on a column of silicic acid with carrier compound *D-batyl alcohol* was obtained with a final sp. activity of 7×10^5 c.p.m./ μmole . The purity was established by thin layer chrom. and gas-liquid chrom. of the isopropylidene derivative.

See also: **65-51**, mevalonic acid.

1.1.3 — *Aromatic Compounds*

65-13

BANCROFT K. C. C., BOTT R. W., EABORN C.

Aromatic Reactivity. Part XXIX. Diphenylmethane and Fluorene in Detritiation. *J. Chem. Soc.* **1964**, 4806

(2-³H) *Diphenylmethane* (I) from O-bromochlorobenzene (Grignard, T₂O) → (2-³H) chlorobenzene (Grignard, benzaldehyde) → diphenylmethanol (LiAlH₄-AlCl₃) → I. (3-³H) *Diphenylmethane* (II) was received from m-bromochlorobenzene, n-butyl-lithium and T₂O, than as above.

(1-³H) *Fluorene* (III) from 1-bromofluoren-9-one, 1-bromofluoren-9-one, 1-bromofluorene (by Wolff-Kishner), than Grignard reagent.

(3-³H) *Fluorene* (IV) from 2-aminofluoren-9-one, the corresp. 3-bromoderivative, deamination, than as described for III.

(4-³H) *Fluorene* (V) from diphenic acid, 4-carboxy-fluoren-9-one, its amid, 4-aminofluoren-9-one, 4-bromo... Clemmensen-red; Grignard reagent.

65-14

COOK D.

Deuterated aromatic materials.

U. S. Patent 3.132.188, May 5, 1964

CA **61**, 16009g (1964)

C₆H₆-d can be prepd. by contacting equimolar quantities of an appropriate pyridine hydrohalide with a H₂O-sol. alkali metal tetraphenylboron in the presence of D₂O.

65-15

CRAM D. J., GOSSER L.

Electrophilic Substitution at Saturated Carbon. XX. Stereochemical Fates of Ammonium Carbanide and Related Ion Pairs.

J. Am. Chem. Soc. **86**, 5445 (1964)

2-Carboxy-9-methylfluorene-9-d (I) was obtained by proton-exchange. 97-99 atom % D from which 95-100 % were in the 9-position (NMR). I was resolved through the quinine salt in the optically pure enantiomers.

65-16

HORNER L., MAYER D., MICHAEL B., HOENDERS H.

Der H-D-Austausch zwischen toluol und deuteriumgas in gegenwart von raney-nickel.

Ann. Chemie **679**, 1 (1964)

Study on the catalysed H-D exchange between toluene and deuterium gas.

1. Each proton is accessible to the exchange.
2. More than 50 % of the deuterium is located in the side chain.
3. An equal distribution was found between the m- and p-position.
4. D-content in the o-position was much lower.

65-17

MERCER W. A.

ed.

Application of radiochemistry techniques in food processing research. Radioisotopic tracer techniques in evaluation and improvement of industry practices for removal of pesticide residues from foods. (SAN-1023)

N. S. A. **18**, 43160 (1964)

DDT-³H was prepared by the Wilzbach technique. Extensive purification of the crude sample was required to get a homogeneous preparation. Chemical degradation of the DDT-³H established that 92 % of the tritium was in the benzylic-H position.

65-18

STREITWIESER A. Jr., KLEIN H. S.

Secondary Isotope Effects in Solvolysis of Various Deuterated Benzhydryl Chlorides.

J. Am. Chem. Soc. **86**, 5170 (1964)

Bromobenzene-d₅ (I) was prepared from benzene-d₆, bromobenzene-4-d (II) > 95 % D from p-dibromobenzene via the mono-Grignard reagent, bromobenzene-4, 6-d₃ (III > 99 %) from aniline by proton exchange and Sandmeyer reaction. From III bromobenzene-2, 6-d₂ (IV) was obtained by nitration reduction

and deamination. Bromobenzene-3, 5-d₂ (V) was prepared from acetanilide-2, 4, 6-d₃ by bromination, hydrolysis and deamination. From each bromobenzene the corresponding benzhydrol was prepared via the Grignard reagent and ethyl formate.

1.1.4 — *Heterocyclic Compounds*

65-19

DUFFIELD A. M., BUDZIKIEWICZ H., DJERASSI C.

Mass Spectrometry in Structural and Stereochemical Problems. LVIII. A Study of the Fragmentation Processes of Some Lactams.

J. Am. Chem. Soc. **86**, 5536 (1964)

5- and 6-membered 3, 3-d₂-lactams (also N-methylated) were prepared by exchange. 5, 5-d₂-2-Pyrrolidone was obtained by LiAlD₄-reduction of succinimide.

N-d₈-Methyl-2-pyrrolidone (and -piperidone resp.) were built by treating the lactam with NaH and subsequently with CD₃I.

65-20

WILLIAMS D. L.

Synthesis of labeled deoxynucleotide Dimers.

(LA-3132- S (p. 270-2).

N. S. A. **18**, 43545 (1964)

The thymidine dimer, tpt, labeled with tritium, was prepared. Methods and results are described.

1.1.5 — *Alkaloids*

1.1.6 — *Carbohydrates*

1.1.7 — *Peptides, Amino Acids, Proteins*

1.1.8 — *Steroids*

65-21

GURST J. E., DJERASSI C.

Mass Spectrometry in Structural and Stereochemical Problems. LIX. Mechanism of the Formal Loss of Acetone from 2-Oxo-5 α -steroids.

J. Am. Chem. Soc. **86**, 5542 (1964)

1, 1, 3, 3-d₄-5 α -Androstan-2-one was obtained by exchange in methanol-d.

5 α -d₁-Androstan-2-one was prepared from the 3-keto-isomer by bromination, reduc-

tion, forming the epoxide, second reduction and oxidation. By the same procedure androstan-2-ones, labeled in the following positions were built : 6, 6-d₂, 4, 4-d₂, 1 α -d₁, 9 α -d₁.

65-22

OERTEL G. W., KAISER E., BRUEHL P.

Biogenesis of steroid conjugates.

Med. Forsch. **1** (5), 169-70 (1963)

CA **61**, 14977c (1964)

Lipophilic, solvolyzable steroid conjugates were biosynthesized by incubation of 7 α -dehydroepiandrosterone-³H (I), I sulfate (II), and cortisol-1, 2-³H (III) with homogenates of guinea pig livers and adrenals. I gave with the liver 5.5 % and with adrenals 5.6 %, II 8.2 % and 10.6 %, and III 3.6 % and 2.9 % sulfatidylsteroids resp.

65-23

SHAPIRO R. M., DJERASSI

Mass spectrometry in structural and stereochemical problems. LVI. Fragmentation and hydrogen transfer reactions of 4, 4-dimethyl-5 α -androstan-3-one and related ketones.

Tetrahedron **20** (9), 1987-98 (1964)

CA **61**, 14741e (1964)

A series of deuterium labeled steroids was prepared by catalytic reduction and keto-enole equilibration, in detail : 4, 4-dimethyl-5 α -androstan-3-one-labeled in pos. 1, 2; 1; 5 α ; 6,6; 7,7; 7; 2,2;

1.2 — **Carbon-13 and -14 Compounds**

1.2.1 — *General*

65-24

Distribution of radioactivity in some organic compounds, labeled by the reaction ¹⁴N (n, p) ¹⁴C.

Thesis, Amsterdam, Universiteit, 1963. 107 p.

N. S. A. **16**, 41556 (1964)

Theoretical aspects of the recoil-labeling process: activity distribution in a series

of toluenes- ^{14}C obtained by recoil-labeling; activity distribution in toluenes obtained by irradiation of toluene-1- ^{14}C and activity distribution in quinoline- ^{14}C obtained by recoil-labeling.

1.2.2 — Aliphatic Compounds

65-25

BENES J., DOBIASOVA M., VERES K.
Synthesis of methylmalonic acid- $^{14}\text{CH}_3$; Side reactions in the alkylation of ethyl malonate.

Coll. Czechoslov. Chem. Commun. **29**, 3178 (1964)

65-26

GOTTSCHALK G., SCHLEGEL H. G.
Preparation of ^{14}C -D(-)- β -hydroxybutyric Acid from $^{14}\text{CO}_2$ using « Knallgas » Bacteria (Hydrogenomonas).

Nature **205**, 308 (1965)

« Knallgas » bacteria of the Hydrogenomonas type incorporate $^{14}\text{CO}_2$ into poly- β -hydroxybutyric acid (PHBA) in a hydrogen-oxygen atmosphere in the absence of a source of nitrogen PHBA can be depolymerized to D(-)- β -hydroxybutyric acid (HBA) by using either hydrazine or enzymatic hydrolysis. From 5 mc. of barium carbonate ^{14}C (sp. act. 20-26 mc./m.mole), a yield of 3-3.5 mc. of HBA (60-70 per cent theoretical) with a sp. act. of 12-20 mc./m.mole was obtained.

65-27

MARAGOUDAKIS M. E., KING T. E., CHELDELIN V. H.

Acidic amino acids from α -hydroxy- γ -keto (^{14}C) glutarate in rat liver and larvae of the blowfly *Sarcophaga bullata*.

Biochim. Biophys. Acta **95**, 646 (1964)

α -Hydroxy- γ -ketoglutarate- ^{14}C (I) was prepd. by acidifying a soln. of oxalmalate- ^{14}C to pH 3 by addn. of 3N HCO_2H and evapg. in vacuo. Identity and purity of I was established by paper chromatography of its 2, 4-dinitrophenylhydrazone (II) and catalytic redn. of II to γ -hydroxyglutamate.

65-28

MAYORAL J. B.

Biosynthesis of glycine and serine; precursor behavior of dihydroxyacetone- ^{14}C .

Rev. Fac. Cienc. Univ. Oviedo **5** (1), 89-105 (1964)

CA **61**, 15139d (1964)

Dihydroxyacetone-(carbonyl- ^{14}C) (I) was prepared from glycolic acid-1- ^{14}C via the diazoketone, which was decomposed with sulfuric acid. Overall yield 35 % I with the label in position 1 and 3 was prep. starting from H^{14}CHO .

65-29

SCHMIDT L. H., BUBNER M.

Synthesis of glyceryl tri (palmitate-1- ^{14}C).

Kernenergie **6** (2), 82-3 (1963)

CA **61**, 14522a (1964)

To palmitoyl chloride-1- ^{14}C from palmitic acid and SOCl_2 glycerol in abs. pyridine is added and the whole is kept 3 days at room temp. and then refluxed 2 hrs. 695.3 mg. title compd., activity 5.77 mc.

65-30

SCHMIDT L. H., BUBNER M., DOERR D.

Synthesis of dicyclohexylammonium nitrite-1, 1'- $^{14}\text{C}_2$ (II).

Kernenergie **6** (8), 411-13 (1963)

CA **61**, 14546a (1964)

From $(\text{CH}_2)_6\text{Br}_2$ and K^{14}CN cyclohexanone-1- ^{14}C was prepared, which was transformed to dicyclohexylamino-1, 1- ^{14}C (I) by catalytic reduction in the presence of NH_3 . I was treated with NaNO_2 to yield II.

65-31

STOCKER J. H.

Quantitative Studies in Stereoselective Addition Reactions by Isotope Dilution. Additions of Organometallic Reagents Leading to 2, 3-Dicyclohexyl-2, 3-butane-diol. A Strong Halide Effect.

J. Org. Chem. **29**, 3593 (1964)

Benzoic acid-7- ^{14}C (sp. act. 4 mc/mole) was hydrogenated (Rh on Al_2O_3) to

cyclohexanecarboxylic acid-7-¹⁴C and methylated (I) (yield : 90 %). I was condensed with Na to the Ketol, which was oxidized with copper acetate to 1,2-dicyclohexylethanedione-1,2-¹⁴C₂ (II) (78 %, 2,75 mc/mole).

Benzil-¹⁴C was treated with CH₃Li and by addition of the corresp. unlabeled *meso*- or *d*, 1-glycol the pure enantiomere was isolated, which was hydrogenated to *meso*- or *d*, 1-2, 3-dicyclohexyl-2, 3-butanediol-2, 3-¹⁴C₂ (III).

65-32

WESTOO G.

The metabolism of sorbic acid in the mouse.

Acta Chem. Scand. **18** (6), 1373-8 (1964)
CA **62**, 901e (1965)

Sorbic acid-1-¹⁴C was prepd. by refluxing malonic acid-1-¹⁴C with crotonaldehyde and pyridine for 2.5 hrs. The product was purified by chromatography first on 1 : 1 mixt. of kieselguhr and silica gel with C₆H₆ and later on kieselguhr treated with dichlorodimethylsilane.

See also: 65-50

65-51

1.2.3 — *Aromatic Compounds*

65-33

EFREMOV A. A., ZEL'VENSKII Ya. D.

Preparation of some organochlorosilanes tagged with ¹⁴C.

Zh. Obshch. Khim. **34** (8), 2622-5 (1964)
CA **61**, 14703c (1964)

Different methyl- or phenyl substituted chlorosilanes were prepared from SiCl₄ and the corresp. Grignard reagent. The app. used for handling the latter is shown.

65-34

PATSCHKE L., BARZ W. GRISEBACH H.

Über den Einbau von 5.7.4'-Trihydroflavanon- (2.6.8.10-¹⁴C₄) (III) in Cyanidin

und die Isoflavone Biochanin-A und Formonnetin.

Z. Naturforsch. **19b**, 1110 (1964)

Phloroglucinol-(2.4.6-¹⁴C₃) (I) was synthesized from ethyl malonate-(2-¹⁴C) (33 %) and condensed with *p*-carbethoxycoumaryl chloride; the resulting product (20 %) was saponified to form 5.7.4'-trihydroxyflavanone-(6.8.10-¹⁴C₃) (85 %) (II). The latter compound was mixed with 5.7.4'-trihydroxyflavanone-(2-¹⁴C) to yield III. The sp. act. of II was 0,3 mc/mmole.

1.2.4 — *Heterocyclic Compounds*

65-35

BLAKE J., WILLSON C. D.,
RAPOPORT H.

3-Pyrrolidinones by Intramolecular Condensation.

J. Am. Chem. Soc. **86**, 5293 (1964)

From *N*-(2-carboxy ethyl) glycine-1-¹⁴C and *i*-butylene the corresp. *t*-butyl ester (I) was prepared (34,3 %). I was transformed to *t*-butyl *N*-ethoxycarbonyl-*N*-(2-*t*-butoxycarbonyl ethyl) glycinate-1-¹⁴C (II) (86 %), which was transformed to *t*-butyl 1-ethoxycarbonyl-4-oxopyrrolidine-3-carboxylate (III) (70 %).

65-36

BOULANGER P., SACQUET E., OSTEUUX R., CHARLIER H.

Formation of ¹⁴CO₂ from labeled lysine Δ¹-piperidine-2-carboxylic acid, and pipercolic acid in the germ-free rat.

Compt. Rend. **259** (4), 932-3 (1964)
CA **61**, 16547e (1964)

Uniformly labeled L-lysine was oxidatively deaminated to Δ¹-piperidine-2-carboxylic acid (I) enzymically, and DL-pipercolic acid (II) was prepd. by catalytic redn. of I.

65-37

HARKNESS D. R., TSAI L., STADTMAN E. R.

V. Stoichiometry of Riboflavin Degradation to Oxamide and Other Products,

Oxidation of ^{14}C -Labeled Intermediates and Isolation of the Pseudomonad Effecting These Transformations.

Arch. Biochem. Biophys. **108**, 323 (1964)
3, 4-Dimethyl-6-carboxy- α -pyrone-methyl- ^{14}C (I) was obtained by incubating 6,7-dimethyl-quinoxaline-2, 3-diol-methyl- ^{14}C (sp. act. 2.5×10^4 cpm/ μmole) (II) with cells. (Synthesis of II will be described elsewhere).

1.2.5 — *Alkaloids*

1.2.6 — *Amino Acids, Peptides*

65-38

HARTMANN H., HEIDBERG J.

Untersuchungen über die Kinetik der Spaltung von Di- und Tripeptiden. III. Mitt. : über die rasche Spaltung von Serinpeptiden in rein wässriger Lösung.

Z. Naturforsch. **19b**, 1095 (1964)

^{14}C -Carbobenzoxy-alanine (-glycine) labeled in the carboxy group, and serine benzyl ester are combined by ethyl chloroformate in THF. After hydrogenation the free dipeptides were obtained with yields in the range of 70 %.

65-39

PAN F., NATORI Y., TARVER H.

Studies on selenium compounds. II. Metabolism of selenomethionine and selenoethionine in rats.

Biochim. Biophys. Acta **93**, 521 (1964)

To DL-Se-benzylselenohomocysteine Na was added and than ($1\text{-}^{14}\text{C}$) ethyl iodide to yield DL-(Et- $1\text{-}^{14}\text{C}$) selenoethionine. The recovery of total radioactivity was 82 %. In a similar way DL-(Me- ^{14}C) selenomethionine was prepared (yield : 69 %).

65-40

TAYLOR K. W., PARRY D. G., SMITH G. H.

Biosynthetic labeling of mammalian insulins in vitro.

Nature **203**, 1144-5 (1964)

CA **61**, 14975h (1964)

Insulin may be labeled by incubating either fresh ox or rat pancreas with ^{14}C -labeled amino acids.

Special purification methods must be used to ensure radiochem. purity. A high concn. of glucose in the incubating medium appears to be important in achieving a rapid rate of incorporation into insulin.

1.2.7 — *Carbohydrates*

65-41

HATCH M. D.

Sugar Accumulation by Sugar-Cane Storage Tissue : the Role of Sucrose Phosphate.

Biochem. J. **93**, 521 (1964)

Sucrose phosphate (I), phosphorylated at the 6-position of fructose and containing radioactivity only in the fructose moiety was prepared from (U- ^{14}C) fructose-6-P (8.8 μmoles , 70×10^6 ipm), UDP-glucose and buffer with germ UDP-glucose-fructose-6-P glucosyltransferase. 60 % of the radioactivity was recovered in I.

1.2.8 — *Steroids*

65-42

SCHULSTER D., WHITEHEAD J. K., KELLIE A. E.

Synthesis of 3-Hydroxy-19-nor (21- ^{14}C) pregna-1, 3, 5 (10)-trien-20-one (I) from (^{14}C) Methyl Iodide.

Biochem. J. **93**, 512 (1964)

Starting from 3-benzoyloxy-oestra-1,3,5(10)-trien-17-one the cyanohydrin was built. After dehydration ^{14}C -labeled methyl Grignard reagent was added to form the unsaturated methyl ketone, which was hydrogenated catalytically. 22 mg of I were obtained with a sp. act. of 1,03 mc(mmmole).

1.3 — Halogen Labeled Compounds

65-43

BUBNER M., SCHMIDT L. H.

Synthesis of pentachlorophenol- $^{36}\text{Cl}_5$.

Kernenergie **6** (2), 82 (1963)

CA **61**, 14567d (1964)

PhOH is treated with dried Cl gas at 100° for 25 hrs. The resulting hexachlo-

rophenol- $^{36}\text{Cl}_6$ is treated with a soln. that is supersatd. with SO_2 . After precipitation of the product with $\text{H}_2\text{O}/\text{HCl}$ it is filtered and recrystd. from C_6H_6 .

1.4 — Phosphorus-32 Compounds

65-44

BOVE J.-M., YOT P., MELAMED R., MOREL G.

Préparation de ribonucléosides et de déoxyribonucléosides 5' monophosphates marqués au phosphore 32.

Bull. Soc. Chim. Biol. **46**, 1027 (1964)

The 5'-monophosphates of ribonucleosides (AMP, CMP, UMP, GMP, sp. act. : $2,5 \times 10^6$ cpm/ μmole) and deoxyribonucleosides are obtained by spec. hydrolysis of ribo- and deoxyribonucleic acids isolated from *Escherichia coli* grown in the presence of ^{32}P .

65-45

HOARD D. E., OTT D. G.

The conversion of mono- and oligodeoxyribonucleotides to their 5'-triphosphates.

(LA-3132-MS, p. 242-4)

N. S. A. **18**, 43541 (1964)

A method is described for the chemical synthesis of mono- and oligonucleotides bearing a 5'-triphosphate group. It appears to be universally applicable and particularly useful for small-scale reactions with isotopically labeled compounds.

65-46

PFITZNER K. E., MOFFATT J. G.

An improved synthesis of 2-cyanoethyl phosphate- ^{32}p .

Biochem. Biophys. Res. Commun. **17**, (2), 146-9 (1964)

CA **61**, 14523a (1964)

$\text{H}_3^{32}\text{PO}_4$ (5 mc.) was treated with Et_3N and pyridine and each time evapd. to dryness. The final residue was dissolved in 1.0 ml. 2-cyanoethanol and 0.07 ml. Et_3N and 1.0 ml. trichloroacetonitrile added. After an hr. the mixture was evapd. and treated with ether and H_2O . The Ba salt of 2-cyanoethyl phosphate was isolated.

1.5 — Sulfur-35 Compounds

65-47

OBOLENTSEV R. D., NIKITIN Yu. E.

Isotopic exchange of sulfur in organosulfur compounds.

Khim. Seraorgan. Soedin., Soderzhashch. v Neft. i Nefteprod., Akad. Nauk SSSR, Bashkirak. Filial 6, 252-4 (1964)

CA **61**, 14483e (1964)

In the exchange reaction between thiophene and its homologs and Na_2S , the rate of exchange was slow at 30° (4 %) and increased with temp., e.g. 49 % at 98° .

1.6 — Oxygen-18 Compounds

65-48

McNUTT W. S., DAMLE S. P.

Tetraoxypteridine Isomerase.

J. Biol. Chem. **239**, 4272 (1964)

^{18}O -Tetraoxypteridine was prepared from uniformly labeled ^{18}O -oxalic acid, obtained from diethyl oxalate and H_2^{18}O , and diaminouacil. H_2SO_4 . H_2O . The reaction product was chromatographed on a column of DEAE-cellulose. 13 Ultraviolet-absorbing components were present of which tetraoxypteridine was the major one (33 % of theory).

1.7 — Nitrogen- 15 Compounds

65-49

CARLIN R. B., MAGISTRO A. J., MAINS G. J.

An ^{15}N tracer Study of the Transformations of Acetophenone 2,6-Xylylhydrazone under the Conditions of the Fischer Indole Synthesis.

J. Am. Chem. Soc. **86**, 5300 (1964)

2,6-Xylylhydrazine- ω - ^{15}N was prepared in 71 % yield by diazotation with ^{15}N enriched sodium nitrite (5,2 %) and reduction. In the course of the reaction 2,6-xyldine was isolated and was shown to contain only traces of ^{15}N .

See also : 65-50

1.8 — Miscellaneous**1.9 — Double-Labeled Compounds**

65-50

BINSCH G., LAMBERT J. B.,
ROBERTS B. W., ROBERTS J. D.**Nitrogen-15 Magnetic Resonance Spectroscopy. II. Coupling Constants.**J. Am. Chem. Soc. **86**, 5564 (1964)

N-methyl-¹³C-phthalimide-¹⁵N was prepared by heating potassium phthalimide-¹⁵N with methyl-¹³C iodide. It was converted to the methyl-¹³C-amine-¹⁵N (I), which was condensed with benzaldehyde to form benzalmethyl-¹³C-amine-¹⁵N (II). I was also converted to ¹⁵N-methyl-¹³C-N'-phenylthiourea. The following ¹⁵N- labeled

compounds were prepared : nitrobenzene, aniline diethylaniline, azobenzene, azoxybenzene, hydrazobenzene, benzamide, benzonitrile, diphenylketimine.

65-51

GOODWIN T. W., WILLIAMS R.
J. H.**A Mechanism for the Cyclization of an Acyclic Precursor to Form β -Carotene.**Biochem J. **94**, 5c (1965)

(2-¹⁴C, 4R-³H)mevalonic acid and (2-¹⁴C, 4 S-³H)mevalonic acid, two stereospecifically labeled mevalonic acid specimens were a gift from Cornforth, I. W. (Cornforth, R. H. Donninger C.) and Popjak G. A. the synthesis of which will be published in Proc. Roy. Soc. 1965.

2 — RADIODECOMPOSITION STABILITY STORAGE

65-52

KHARLAMOV V. T., SHUBNYA-
KOWA L. P.**Radioactive decomposition of γ -irradiated methionine.**Zh. Prikl. Khim., **37** : 1714-18 (1964)N. S. A. **18**, 41552 (1964)

Synthesized methionine-³⁵S with a specific activity of 1 μ C/g was analyzed by paper chromatography. Observation of γ -irradiated powder specimens and their aqueous solutions in air and in inert atmospheres showed a strong oxygen effect on radiochemical decomposition.

3 — PURIFICATION, SEPARATION

65-53

GANT P. L., YANG K.

Chromatographic Separation of Isotopic Methanes.J. Am Chem. Soc. **86**, 5063 (1964)

The four possible deuterium- or tritium labeled methanes are separated chromatographically by using a charcoal column. Retention times progressively decrease with increasing D or T substitutions. This decrease is consistent with the expected decrease in polarizabilities with increasing D or T substitutions. The recovery of pure CT₄ is described.

65-54

GLIEMANN J., DOLE V. P.

Incorporation of Formate into Lipids of Adipose Tissue.J. Biol. Chem. **239**, 4062 (1964)

By acidification and evaporation nonvolatile contaminants (0,01 %) were excluded.

Countercurrent distribution in isopropyl ether-phosphate buffer (pH 5.2) showed that contamination with acetate and longer chain fatty acids did not exceed 0.1 % of the total activity of formic acid.

65-55

HARTRODT W.

Radioactive labeled organic compounds. I. A simple paper chromatographic method for determining the purity of Rose Bengale-¹³¹I.

Nucl. Med. 3(4), 382-96 (1963)

CA 61, 16417e (1964)

Rose Bengale-¹³¹I preps. in solns., varied in sp. activity between 0.026 and 0.25 mc./mg./ml. and in free inorg. ¹³¹I between 0.0 and 4.7%. Chromatographs on paper (Schleicher-Schüll 2045a) using BuOH-2N HOAc (1 : 1). R_f values for inorg. ¹³¹I and Rose Bengale-¹³¹I were, resp., 0.23 ± 0.02 and 0.94 ± 0.01.

65-56

ROHR W., BASSHAM J. A.

Two-dimensional high-voltage, low-temperature paper electrophoresis of ¹⁴C-labeled products of photosynthesis with ¹⁴CO₂.

Anal. Biochem. 9(3), 343-50 (1964)

CA 61, 16418d (1964)

The sepn. of early products of ¹⁴CO₂ redn. during photosynthesis in algae by 2-dimensional high-voltage low-temp. paper electrophoresis is described.

See also : 65-12, D-batyl alcohol

See also : 65-27, α-hydroxy-γ-ketoglutarate

65-32, sorbic acid

4 — ANALYSIS**4.1 — Substances****4.1.1 — Determination of activity****65-57**

ANDREWS P., HOUGH L., PICKEN J. M.

The Biosynthesis of Polysaccharides. Incorporation of D-(-1-¹⁴C) glucose and D-(6-¹⁴C) glucose into plumleaf polysaccharides.

Biochem. J. 94, 75 (1965)

After the precursors had been metabolized the polysaccharides were isolated from the leaves. Both the specific activities and the distribution of ¹⁴C along the carbon chains of the monosaccharides were determined.(D-galactose, D-glucose, D-xylose and L-arabinose).

65-58

BLAEDEL W. J., EVENSON M. A.

A continuous isotope derivative procedure with direct readout for amino acids.

(CONF-692-1). From Symposium on Radiochemical Methods of Analysis, Salzburg, Austria, Oct. 1964.

N. S. A. 18, 41314 (1964)

It is possible to incorporate alanine into non-labile Co(III) complex on a continuous

basis. The reaction is quantitative and rapid, and the labeled derivative is stable toward reduction and substitution for at least several hours, which is ample for the isotope derivative procedure.

65-59

HATTORI T., AOKI H., MATSUZAKI I., MARNO B.

Liquid Scintillation Counting of ³H-Nucleic Acids.

Anal. Chem. 37, 159 (1965)

Nucleic acids, labeled with ³H-adenine, were purified, placed in a vial, digested by hydrochloric acid and than radioassayed by addition of a hyamine-dioxane solvent system.

65-60

KRANE S. M., STONE M. J., GLIMCHER M. J.

The presence of protein phosphokinase in connective tissue and the phosphorylation of enamel proteins in vitro.

Biochem. Biophys. Acta 97, 77 (1965)

The amount of ³²P in the γ-position of (³²P) ATP was determined by converting it to 6-phosphogluconic acid with hexokinase, glucose-6-phosphate dehydroge-

nase, glucose and NADP (^{32}P) P_i was then determined on aliquots before and after hydrolysis in 1 N HCl.

4.1.2 — *Determination of Radiochemical Pattern*

6561

BIRCH A. J., DJERASSI C., DUTCHER J. D., MAJER J., PERLMAN D., PRIDE E., RICKARDS R. W., THOMSON P. J.

Studies in Relation to Biosynthesis. Part XXXV. Macrolide Antibiotics. Part XII. Methymycin.

J. Chem. Soc. 1964, 5274

The biosynthesis of the antibiotic methymycin has been investigated by growing *Streptomyces venezuelae* in media containing a series of ^{14}C precursors. Convenient degradative routes are employed modifications where necessary to improve yields for isotope work.

65-62

BIRKINSHAW J. H., DRYLAND A. M. L.

Studies in the Biochemistry of Microorganisms 116. Biosynthesis of β -Nitropropionic acid by the mould *penicillium atrovenetum* G. Smith.

Biochem. J. 93, 478 (1964)

Aspartic acid and β -nitropropionic acid, received from (2- ^{14}C) pyruvate and (1- ^{14}C) acetate as precursors in biosynthesis were degraded. The rate of labeling of each carbon atom could be obtained separately.

65-63

FLOSS H. G., RETTIG A.

Biosynthese des Gentisins.

Z. Naturforsch. 19b, 1103 (1964)

Gentisin, by biosynthesis from sodium acetate-1- ^{14}C , was degraded to gentisic acid and phloroglucinol by melting with alkali. The latter was further transformed to bromopicrin.

65-64

HUGHES C. A., LETCHER R., WARREN F. L.

The Senecio Alkaloids. Part XVI. The Biosynthesis of the «Necine» Bases from Carbon-14 Precursors.

J. Chem. Soc. 1964, 4974

After application of (2- ^{14}C) ornithine hydrochloride and sodium (2- ^{14}C) acetate to *Senecio isatideus* D. C. and to *S. sceleratus* Schweikerdt, resp. the radioactive alkaloids isolated were hydrolysed to yield radioactive retronecanol. This base was degraded, mainly by successive Hofmann reactions, and the reaction products further oxidised by the Kuhn-Roth technique.

See also : 65-57

4.2 — **Apparatus**

65-65

TAMERS M. A., DIEZ M.

Determination of ^{14}C and Tritium in Blood and Other Biological Materials.

Intern. J. Appl. Rad. Isotopes 15, 697 (1964)

A sample convertor was designed which is capable of accepting any type of substance containing ^{14}C or tritium, without preliminary treatment, and transforming it, quantitatively, to another chemical compound that can be counted with precision by liquid scintillation techniques. A further advantage of the method is illustrated by tests showing its capability of removing a variety of other isotopes present in the original sample that would interfere with the ^{14}C determinations.

65-66

YAMAGUCHI M., HUGHES D. L., HOWARD F. D.

Absorption of $^{14}\text{CO}_2$ from a gas stream and preparation of $\text{Ba}^{14}\text{CO}_3$ precipitates

for counting with Geiger-Müller tubes. Intern. J. Appl. Radiation Isotopes **15**(9), 545-8 (1964)

CA **61**, 13871h (1964)

Periodic samples are collected in a bacteriological fermentation-type tube and continuous samples in an inclined scrubber. CO_2 is trapped with NaOH and precipitated with BaCl_2 . Increasing amts. of BaCO_3 in the sample decrease the counts measured. The results in the different samples are within 4 % of the mean value.

4.3 — Radiochem. Methods for Analysis of Complex Compounds 65-67

RAKOVIC M., TALPOVA H.
A nondestructive determination of phosphorus in various kinds of animal tissues with neutron activation analysis.

Chem. Zvesti **18**(9), 669-75 (1964)

CA **61**, 15110f (1964)

A nondestructive detn. of P in animal tissues was carried out with the 20-hr. activation in the stream 1.5×10^{12} thermal neutrons/cm.²/sec. and with the direct measurement of the impulses with a Geiger-Mueller tube after a 14-day waiting period.