was boiled in ether, chilled and filtered to give 20 g. (87% based on amine) of 2,2'-oxybis-(N-cyclohexyl-2-phenylacetamide), m.p. 139–140°.

Anal. Calcd. for $C_{28}H_{36}N_2O_3$: C, 75.00; H, 8.03; N, 6.25. Found: C, 75.62; H, 8.17; N, 6.16.

N-(3-Chlorophenyl)-2-nitroacetamide.—This was prepared by a procedure of Boyd and Leshin[6] for similar compounds. A solution of 76.8 g. (0.5 mole) of 3-chlorophenyl isocyanate and 30.5 g. (0.5 mole) of nitromethane in 500 ml. of benzene was refluxed with 69 g. (0.5 mole) of potassium carbonate for 10 hr. After cooling and filtering, the solid was stirred in 2 liters of cold water and the filtrate from this was acidified to Congo Red paper with dilute hydrochloric acid. The precipitate was collected and crystallized from benzene to give 7 g. (7%) of yellow crystals, m.p. 119.5–120.5°.

Anal. Calcd. for $C_8H_7ClN_2O_3$: C, 44.76; H, 3.26. Found: C, 44.80; H, 3.45.

N-Furfurylacetamide.—A solution of 48.5 g. (0.5 mole) of furfurylamine in 100 ml. of benzene was added slowly to 91 g. (0.9 mole) of acetic anhydride over a 15-min. period. The benzene and excess anhydride were removed by distillation and there was obtained a 64-g. (92%) yield of N-furfurylacetamide, b.p. 114–116° at 3 mm. After standing two days the liquid set to a solid, m.p. 31–33°.

Anal. Calcd. for $C_7H_9NO_2$: C, 60.43; H, 6.47. Found: C, 59.97; H, 6.60.

N-Allyl-2-chlorobenzamide.—This was prepared by the reaction of 50 g. (0.29 mole) of 2-chlorobenzoyl chloride, 16.5 g. (0.29 mole) of allylamine, 150 ml. of benzene and 60 ml. of 20% sodium hydroxide (0.30 mole). After stirring for 30 minutes, the organic layer was separated, washed with dilute hydrochloric acid and distilled to give a 48 g. (86%) yield of yellow crystals, b.p. 145–150° at 2.0 mm., m.p. 67–68°.

Anal. Calcd. for $C_{10}H_{10}ClNO$: C, 61.38; H, 5.11. Found: C, 61.30; H, 5.06.

Acid Chlorides.—The following new chlorophenylacetyl chlorides were prepared from the appropriate phenylacetic acid by the method of Schwenk and Papa[7] utilizing thionyl chloride and sulfuryl chloride: 2-chloro-2-(2-chlorophenyl)-acetyl chloride, b.p. 146–149° at 35 mm.; 2-chloro-2-(2,4-dichlorophenyl)-acetyl chloride, b.p 158–161° at 22 mm.; 2-chloro-2-(3,4-dichlorophenyl)-acetyl chloride, b.p. 163–167° at 22 mm.

Other acid chlorides needed were prepared from the corresponding acids directly with thionyl chloride.

2,3-Dichloropropionic Acid.—This material has been previously described[8,9] and obtained by other routes. In our hands the following was a more convenient synthesis.

A solution of 100 g. (1.39 moles) of acrylic acid (stabilized with methylene blue) in 400 ml. of carbon tetrachloride was stirred and treated with chlorine gas for 6 hr. The increase in weight was approximately 73 g. The solution was concentrated *in vacuo* and then distilled to give a 130-g. (66%) yield of 2,3-dichloropropionic acid, b.p. 83–86° at 3 mm., m.p. 57–58° (lit.[8,9] values, b.p. 83–86° at 2 mm.; m.p. 49°).

2,3-Dichloro-2-methylpropionic Acid.—In a manner similar to the preceding experiment, 86 g. (1.0 mole) of methacrylic acid in 500 ml. of carbon tetrachloride was treated with chlorine for 2 hr. Distillation, after solvent removal, gave 31 g. of methacrylic acid, b.p. 40–60° at 2 mm. followed by 2,3-dichloro-2-methylpropionic acid, yellow oil, b.p. 106–112° at 2 mm., $n^{25}D$ 1.4670. The yield was 47 g. (47%) and the conversion was 30%. The material is quite unstable, rapidly losing HCl.

Anal. Calcd. for $C_4H_6Cl_2O_2$: neut. equiv., 157. Found: neut. equiv., 151.

2,4-Dichlorophenylacetic Acid.—To a solution of 380 ml. of concd. sulfuric acid in 520 ml. of water there was added 500 g. (2.7 moles) of 2,4-dichlorophenylacetonitrile.[10] After heating to boiling and stirring for 3 hr. the mixture was filtered and the solid was crystallized from alcohol to give 104 g. (71.5%) of 2,4-dichlorophenylacetic acid, m.p. 52–53°.

Anal. Calcd. for $C_8H_6Cl_2O_2$: Cl, 34.63. Found: Cl, 33.85.

Herbicidal Assay.—The method employed has been described by Hamm and Speziale.[2] All of the amides described in this paper were shown to be relatively non-phytotoxic in pre-emergence tests.

Acknowledgment.—The authors wish to express their gratitude to Drs. P. C. Hamm and E. G. Jaworski for evaluation data and to Mrs. Winifred Harden, Mrs. Geneva Kratzer, Mr. Donald Stoltz and Mr. J. Danby for analytical data. Several helpful discussions with Dr. A. J. Speziale are gratefully acknowledged.

ST. LOUIS, MO.
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[6] R. N. Boyd and R. Leshin, THIS JOURNAL, **75**, 2762 (1953).

[7] E. Schwenk and D. Papa, *ibid.*, **70**, 3626 (1948).

[8] G. S. Simpson, *ibid.*, **40**, 674 (1918).

[9] P. Karrer and W. Klarer, *Helv. Chim. Acta*, **7**, 930 (1924).

[10] E. A. Falco, S. DuBreuil and G. H. Hitchings, THIS JOURNAL, **73**, 3758 (1951).

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

The Diazotization of 3,3-Dimethyl-1-butylamine-1-^{14}C

BY WILLIAM H. SAUNDERS, JR.

RECEIVED JULY 17, 1956

The reaction of 3,3-dimethyl-1-butylamine-1-^{14}C with nitrous acid yields an alcohol mixture which was shown to contain 57% 3,3-dimethyl-1-butanol and 43% 2,3-dimethyl-2-butanol. The former is produced with less than 1% isotope-position rearrangement. The significance of these results is discussed.

Isotopic tracer studies on the diazotization of amines of the type $RCH_2CH_2NH_2$ have revealed that the tendency of R to migrate follows the order $Ar > CH_3 > H > ArCH_2$.[1] Since very little is known about the migration aptitudes of branched alkyl groups, a study of the case where R = *t*-butyl was undertaken. This system is also of interest in that it bears structural resemblances to systems reported to undergo 1,3-shifts of methyl.[2]

The synthetic scheme employed is outlined in Fig. 1. Use of carbon-^{14}C dioxide in the first step led to the desired 3,3-dimethyl-1-butylamine-1-^{14}C

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[1] (a) A. W. Fort and J. D. Roberts, THIS JOURNAL, **78**, 584 (1956); (b) J. D. Roberts and M. Halmann, *ibid.*, **75**, 5759 (1953); (c) J. D. Roberts and J. A. Yancey, *ibid.*, **74**, 5493 (1952); (d) J. D. Roberts and C. M. Regan, *ibid.*, **75**, 2069 (1953).

[2] (a) F. C. Whitmore, K. C. Laughlin, J. F. Matuszeski and J. D. Surmatis, *ibid.*, **63**, 756 (1941); (b) W. A. Mosher and J. C. Cox, *ibid.*, **72**, 3701 (1950); see, however, M. F. Ansell, M. A. Davis, J. W. Hancock and W. J. Hickinbottom, *Chemistry & Industry*, 1483 (1955), who cast doubt on the identity of the starting material used by Mosher and Cox.

(III), and direct reduction of I afforded unequivocally labeled IV for the blank degradation.

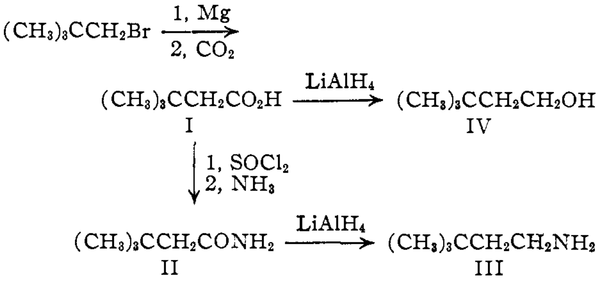


Fig. 1.—Preparation of starting materials.

Preliminary experiments with inactive III and nitrous acid resulted in 30–32% yields of a mixture of hexyl alcohols. No olefinic products were obtained although the method of product isolation (ether extraction) was such that 3,3-dimethyl-1-butene (b.p. 41°) would be lost, and small quantities of rearranged olefins might escape detection. The infrared spectrum of the alcohol mixture was compared with the spectra of four alcohols which might reasonably result from the reaction: 3,3-dimethyl-1-butanol (IV), 3,3-dimethyl-2-butanol (V, 1,2-shift of H), 2,3-dimethyl-2-butanol (VI, 1,2-shift of H followed by 1,2-shift of CH_3), and 2-methyl-2-pentanol (VII, 1,3-shift of CH_3). In this manner V and VII were shown to be absent and the mixture was found to contain 57.7 ± 1.7% of IV and 42.3 ± 1.7% of VI (see Experimental for details).

The diazotization of III was repeated using labeled amine and the reaction mixture diluted with inactive samples of IV and VI. Subsequent separation of IV and VI and radioassay as appropriate derivatives (see Table I) gave 36% as the total alcohol yield and the composition of the mixture as 56.3% IV and 43.7% VI, in excellent agreement with the infrared analysis. The degradation of IV is outlined in Fig. 2 and radioassays on the products recorded in Table I. From these data the extent of isotope-position rearrangement in the formation of IV was only 0.83%, and in the blank degradation only 0.02% rearrangement occurred.

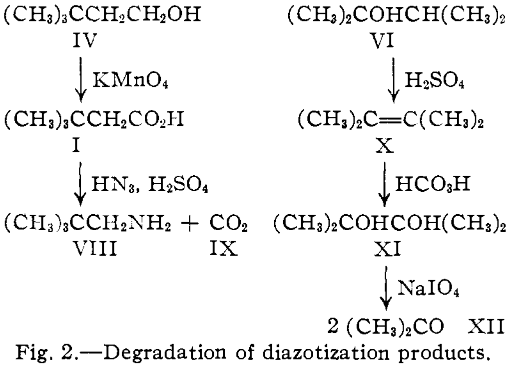


Fig. 2.—Degradation of diazotization products.

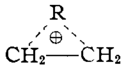
TABLE I

^{14}C-ACTIVITY MEASUREMENTS

Compound	Microcuries/mmole[a]
Degradation of 3,3-dimethyl-1-butanol-x-^{14}C	
$(CH_3)_3CCH_2CH_2OH$ as $(CH_3)_3CCH_2CONH_2$	0.2413 ± 0.0010^b
$BaCO_3$	$0.2460 \pm .0011$
$(CH_3)_3CCH_2NH_2$ as benzoyl derivative	$(2.00 \pm 0.06) \times 10^{-3}$
Degradation of 3,3-dimethyl-1-butanol-1-^{14}C	
$(CH_3)_3CCH_2CH_2OH$ as $(CH_3)_3$—CCH_2CONH_2	$1.188 \pm .002^{b,c}$
$BaCO_3$	$1.204 \pm .005^c$
$(CH_3)_3CCH_2NH_2$ as benzoyl derivative	$(2.21 \pm .02)^c \times 10^{-4}$
Isotope dilution analysis	
$(CH_3)_3CCH_2CH_2NH_2$ as $(CH_3)_3$-CCH_2CONH_2	$2.102 \pm .003^b$
$(CH_3)_3CCH_2CH_2OH$ as $(CH_3)_3$-CCH_2CONH_2	$0.2413 \pm .0010^b$
$(CH_3)_2COHCH(CH_3)_2$ as acetone 2,4-dinitrophenylhydrazone	$0.1921 \pm .0009^d$

[a] Samples were converted to carbon dioxide by wet combustion. The carbon dioxide was counted in an ionization chamber on a Cary model 31 vibrating reed electrometer. See O. K. Neville, THIS JOURNAL, **70**, 3499 (1948). Figures are corrected for background and represent mean values of two or more combustions with average deviations. [b] Combustion proceeded more reluctantly with this amide (II) than with the other compounds so that the values, even though consistent, may be slightly low. [c] Mean of two or more counts on carbon dioxide from a single combustion. [d] Corrected for a statistical factor of two.

The products obtained show that no 1,3-shift of methyl[2] has occurred and thus provide only negative evidence on the structural requirements for this process. The presence of VI but not V suggests that the formation of VI may involve essentially concerted migration of hydrogen and methyl, the pinacolyl cation having no independent existence. It is interesting that the present results parallel those obtained in a reversible carbonium-ion reaction involving the same system, namely, the production of 2,3-dimethylbutane from 3,3-dimethyl-1-chlorobutane and isobutane in the presence of aluminum chloride.[3] Since VIII contains only 0.83% of the activity, of IV, it is clear that the bridged ion XIII (R = *t*-butyl) is not involved in the reaction to any significant extent.



XIII

Interpretation of the lack of *t*-butyl migration is rather difficult. The present result does fit qualitatively into the correlation[1a] with Kharasch's electronegativity series.[4] When two alkyl groups are in direct competition, however, a different order usually prevails. It has been reported that benzyl > methyl in pinacol-type rearrangements.[5] Less is known concerning branched alkyl groups, but in migrations to oxygen secondary[6] and tertiary[7] alkyl migrate better than primary alkyl. Recently an intramolecular carbon-to-carbon migration[8] was found to involve migration of a tertiary group in preference to a primary one. It is not, of

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[3] L. Schmerling, *ibid.*, **67**, 1778 (1945).

[4] M. S. Kharasch and A. L. Flenner, *ibid.*, **54**, 674 (1932).

[5] M. Tiffeneau and J. Levy, *Bull. soc. chim. France*, [4] **49**, 1661 (1931); results are summarized on pp. 1698–1699.

[6] W. D. Emmons and G. B. Lucas, THIS JOURNAL, **77**, 2287 (1955).

[7] R. P. Jacobsen, *J. Biol. Chem.*, **171**, 61 (1947).

[8] S. Winstein, R. Heck, S. Lapporte and R. Baird, *Experientia*, **12**, 138 (1956).

course, unusual that the order of migration aptitudes should vary with the nature of the reaction.[9] For instance, the system RCH_2CH_2X should be freer of steric complications than the other examples cited. It does not seem possible at present, however, to provide a satisfactory over-all interpretation of these variations.[10]

Acknowledgment.—Part of this work was carried out during the summer of 1954, when the author held a Summer Research Grant from E. I. du Pont de Nemours and Co.

Experimental[11]

Neopentyl Bromide.—Neopentyl alcohol was prepared by the action of lithium aluminum hydride on pivalic acid. The alcohol was converted to neopentyl bromide by the action of phosphorus tribromide and quinoline.[12] The fraction taken as pure bromide had b.p. 105–107°, $n^{25}D$ 1.4367 (lit.[12] b.p. 105°, $n^{20}D$ 1.4370).

3,3-Dimethylbutyric-1-^{14}C Acid.—Neopentylmagnesium bromide was prepared from 9.1 g. (0.060 mole) of neopentyl bromide and 1.5 g. (0.060 mole) of magnesium in 100 ml. of dry ether. This was carbonated in an apparatus similar to one described by Calvin, *et al.*[13] Carbon dioxide was obtained by the action of concd. sulfuric acid on 5.9 g. (0.030 mole) of barium carbonate containing 1 millicurie of ^{14}C. The Grignard was decomposed with ice and sulfuric acid, the product extracted with ether, and the extract dried. The ether was removed and the residue distilled under reduced pressure. The pot residue was scavenged twice with 1.0-g. portions of inactive acid. The yield was 4.2 g. of b.p. 98–100° (28 mm.), or 63% (deducting material used in scavenging).

Inactive acid for cold runs and for dilution was prepared by the action of sodium hypobromite on methyl neopentyl ketone.[14]

3,3-Dimethylbutyramide-1-^{14}C.—To 20.2 g. (0.17 mole) of thionyl chloride was added dropwise 17.0 g. (0.15 mole) of 3,3-dimethylbutyric-1-^{14}C acid. The mixture was heated on the steam-bath for an hour and then added dropwise with stirring to 200 ml. of liquid ammonia. The ammonia was allowed to evaporate and the residue extracted three times with hot chloroform. The chloroform extract was concentrated to 100 ml., filtered, and treated with 200 ml. of hexane. The solution was cooled and the amide collected; yield 8.6 g. (51%), m.p. 127–131°. Another recrystallization gave material of m.p. 130.5–131.5° (lit.[14] 132°).

3,3-Dimethyl-1-butylammonium-1-^{14}C Perchlorate.—In the thimble of a Soxhlet extractor was placed 7.6 g. (0.066 mole) of 3,3-dimethylbutyramide-1-^{14}C, and in the boiler was placed 3.8 g. (0.10 mole) of lithium aluminum hydride in 300 ml. of dry ether. The ether was refluxed for ten hours and the reaction mixture hydrolyzed.[15] The ethereal solution of the amine was neutralized with 2 *N* perchloric acid, the ether evaporated, and the residue dried under aspirator vacuum at 70–80°. The solid was recrystallized from a mixture of *n*-butyl alcohol and hexane. There was obtained 7.6 g. (57%) of white solid, m.p. 299–302° dec. Further concentration of the filtrate yielded 2.3 g. of less pure material (m.p. 285–288° dec.). An analytical sample had m.p. 298–301° dec.

Anal. Calcd. for $C_6H_{16}NClO_4$: C, 35.74; H, 8.00. Found: C, 35.59; H, 8.06.

Diazotization of 3,3-Dimethyl-1-butylamine-1-^{14}C.—A solution of 6.11 g. (0.0302 mole) of 3,3-dimethyl-1-butylammonium-1-^{14}C perchlorate in 50 ml. of water was heated to 40–50° and treated with 2 ml. of 2 *N* perchloric acid and 2.4 g. (0.035 mole) of sodium nitrite in 10 ml. of water. After two hours there was added another 0.40 g. of sodium nitrite and 5 ml. of 2 *N* perchloric acid. The mixture was left standing overnight and then treated with a final 5 ml. of 2*N* perchloric acid. There was added 4.82 g. of inactive 3,3-dimethyl-1-butanol and 4.82 g. of inactive 2,3-dimethyl-2-butanol. The mixture was extracted four times with ether (alcohol-free), the extracts concentrated under a Vigreux column, and the residual alcohol mixture distilled from 10% sodium hydroxide (to hydrolyze any alkyl nitrite present). The distillate was extracted four times with alcohol-free ether and the extract dried over sodium sulfate and then over Drierite. The ether was removed through a Vigreux column and the residue fractionated through a small spinning-band column. Four fractions were taken: (1) 1.40 g., b.p. 33–115°; (2) 3.17 g., b.p. 115–119°; (3) 0.86 g., b.p. 119–141°; (4) 3.89 g., b.p. 141–144°. Previous experiments with synthetic mixtures had demonstrated that fraction 2 was pure 2,3-dimethyl-2-butanol and that fraction 4 was pure 3,3-dimethyl-1-butanol.

Oxidation of 3,3-Dimethyl-1-butanol.—A mixture of 3.7 g. (0.036 mole) of 3,3-dimethyl-1-butanol and 30 ml. of 6 *N* sulfuric acid was cooled in an ice-bath, stirred, and treated portionwise with 5.1 g. (0.032 mole) of potassium permanganate over one-half hour. After two hours the mixture was decolorized with sulfur dioxide and extracted with ether. The extract was dried over sodium sulfate, concentrated, and the residue fractionated *in vacuo*. There was obtained 1.95 g. (47%) of 3,3-dimethylbutyric acid, b.p. 97–99° (28 mm.). A portion was converted to the amide, m.p. 131–132°, for radioactivity assay.

Decarboxylation of 3,3-Dimethylbutyric Acid.—The procedure followed closely the one described for *cis*-cyclopentane-1,3-dicarboxylic acid,[16] except that the reaction proceeded with sufficient vigor to make heating unnecessary. From 0.73 g. of 3,3-dimethylbutyric acid was obtained 0.89 g. of barium carbonate and 0.56 g. neopentylamine hydrochloride. The latter was converted to N-neopentylbenzamide by the Schotten–Baumann method. After several recrystallizations from ethanol–water, white needles of m.p. 112.5–113.5° were obtained.

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96. Found: C, 75.35; H, 8.92.

Dehydration of 2,3-Dimethyl-2-butanol.—The procedure was essentially as previously described for 2-methyl-2-butanol.[17] The reaction of 3.1 g. (0.022 mole) of 2,3-dimethyl-2-butanol with 25 ml. of 18 *N* sulfuric acid gave a product which was diluted with xylene, dried over Drierite, and fractionated to yield 1.13 g. (60%) of 2,3-dimethyl-2-butene, b.p. 70–72°, $n^{20}D$ 1.4112 (lit.[18] b.p. 72.9–73.2°, $n^{20}D$ 1.4115).

Hydroxylation of 2,3-Dimethyl-2-butene.—The procedure was essentially that employed by Roberts, McMahon and Hine[17] on 2-methyl-2-butene. From 1.1 g. (0.013 mole) of 2,3-dimethyl-2-butene, 20 ml. of 90% formic acid, and 5 ml. of 30% of hydrogen peroxide was obtained a pale yellow sirup. This was taken up in 5 ml. of water, the solution cooled in ice, and the solid pinacol hydrate collected; yield 1.0 g. (34%), m.p. 42–46°.

Periodate Cleavage of Pinacol.—A mixture of 0.76 g. (3.4 mmoles) of pinacol hydrate, 0.73 g. (3.8 mmoles) of sodium metaperiodate in 50 ml. of water, and 10 drops of 2 *N* perchloric acid was allowed to stand at room temperature for 12 days. The mixture was diluted with water and 40 ml. distilled at 80 mm. into a trap cooled by Dry Ice. One-third of the solution was treated with 0.5 g. of 2,4-dinitrophenylhydrazine in 100 ml. of 2 *N* hydrochloric acid.

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[9] C. J. Collins, THIS JOURNAL, **77**, 5517 (1955), has studied a system in which the relative migration aptitudes of phenyl and hydrogen can be reversed merely by changing the reaction conditions.

[10] The possibility that alkyl groups are more or less uniformly poor migrators in the present series cannot be discounted. The results of Roberts and Halmann[1b] on methyl may be high, since they obtained poor yields of 1-propanol and, unfortunately, worked at rather low activity levels where trace contamination by active impurities could seriously affect the observed counts.

[11] Melting points and boiling points are uncorrected. Analyses by Miss A. Smith and by Micro-Tech Laboratories, Skokie, Ill. Infrared spectra were run by Mr. C. A. Whiteman on a Perkin–Elmer model 12B infrared spectrophotometer.

[12] L. H. Sommer, H. D. Blankman and P. C. Miller, THIS JOURNAL, **76**, 803 (1954).

[13] M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. E. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 177.

[14] A. H. Homeyer, F. C. Whitmore and V. H. Wallingford, THIS JOURNAL, **55**, 4209 (1933).

[15] L. H. Amundsen and L. S. Nelson, *ibid.*, **73**, 242 (1951).

[16] J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

[17] J. D. Roberts, R. E. McMahon and J. Hine, *ibid.*, **72**, 4327 (1950).

[18] I. Schurman and C. E. Boord, *ibid.*, **55**, 4932 (1933).

The product was recrystallized several times from ethanol to yield material of m.p. 125–126°.

3,3-Dimethyl-1-butanol-1-^{14}C.—The reduction of 6.0 g. (0.052 mole) of 3,3-dimethylbutyric-1-^{14}C acid with 2.0. g. (0.053 mole) of lithium aluminum hydride gave 3.8 g. (72%) of 3,3-dimethyl-1-butanol-1-^{14}C, b.p. 142–143°. The same procedure was used to prepare inactive material of b.p. 144°, n^{20}D 1.4146 (lit.[19] b.p. 141–143°, n^{23}D 1.4160).

2,3-Dimethyl-2-butanol.—The reaction of methylmagnesium iodide with methyl isopropyl ketone gave a 71% yield of 2,3-dimethyl-2-butanol, b.p. 115–120°. The sample for infrared spectra had b.p. 118°, n^{25}D 1.4157 (lit.[20] b.p. 118.7°, n^{25}D 1.4151).

3,3-Dimethyl-2-butanol.—The reduction of 3,3-dimethyl-2-butanone (pinacolone) with lithium aluminum hydride yielded 78% of 3,3-dimethyl-2-butanol, b.p. 116–118°. Fractionation gave a center cut of b.p. 119.5°, n^{20}D 1.4160 (lit.[21] b.p. 120.4°, n^{20}D 1.4148).

2-Methyl-2-pentanol.—The reaction of *n*-propylmagnesium bromide with acetone gave 51% of 2-methyl-2-pentanol, b.p. 121–125°. Fractionation gave a center cut of b.p. 122°, n^{20}D 1.4130 (lit.[22] b.p. 119.3°, n^{25}D 1.4089).

Analysis of Alcohol Mixture from Diazotization.—Infrared spectra of 3,3-dimethyl-1-butanol (IV), 3,3-dimethyl-2-butanol (V), 2,3-dimethyl-2-butanol (VI) and 2-methyl-2-pentanol (VII) were compared with the infrared spectrum of the alcohol product from a cold run on the diazotization. The spectrum of V had strong peaks at 7.77 and 9.93 μ, which were absent in the spectrum of the mixture. Similarly, VII showed strong absorption at 11.18 and 11.34 μ, where the mixture showed no peaks. Calculations based on the above peaks showed that no more than a small percentage of V or VII could be present. Comparison of the spectra of IV and VI with that of the mixture gave an approximate composition of 60% IV and 40% VI. Three synthetic mixtures of IV and VI bracketing this composition were prepared and plots of optical density *vs.* composition at 10.05, 10.60, 10.96 and 11.71 μ made. The composition of the unknown was thus found to be 57.7 ± 1.7% IV.

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[19] R. C. Huston and A. H. Agett, *J. Org. Chem.*, **6**, 123 (1941).

[20] F. Hovorka, H. P. Lankelma and J. W. Bishop, THIS JOURNAL, **63**, 1097 (1941).

[21] F. C. Whitmore and P. L. Meunier, *ibid.*, **55**, 3721 (1933).

[22] F. H. Norton and H. B. Hass, *ibid.*, **58**, 2147 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Preparation and Geometry of *o,o'*-Bridged Biphenyls Containing Sulfur or Selenium in the Bridge

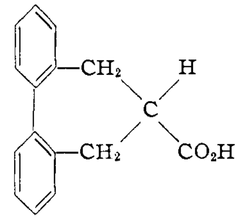
BY WILLIAM E. TRUCE AND D. D. EMRICK

RECEIVED JUNE 21, 1956

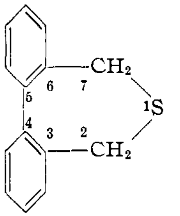
2,7-Dihydro-3,4-5,6-dibenzoheteropins (1-heterodibenzo[a,c] [3,5]-cycloheptadienes) have been prepared where the hetero function is represented by sulfide, selenide, sulfone, methylsulfonium and methylselenonium groups. As predicted from molecular models, these materials, with the exception of the sulfonium compound, show ultraviolet absorption maxima at shorter wave lengths than the corresponding carbocyclic and other seven-membered ring *o,o'*-bridged biphenyls, indicative of enhanced non-coplanarity and accompanying asymmetry in the biphenyl system. 2,7-Dihydro-3,4-5,6-dibenzothiepin-1-dioxide-2',3''-dicarboxylic acid has been obtained in optically active form. This is the first example of demonstrable activity in a seven-membered ring *o,o'*-bridged biphenyl not having auxiliary 6,6'-biphenylic hindering groups.

The fact that Bell could not resolve the seven-membered ring bridged biphenyl[1] I has left open the question of whether or not in a seven-membered ring bridged biphenyl auxiliary hindering groups in the biphenyl 6,6'-positions are necessary to obtain optical activity. Presumably, a seven-membered ring all carbon atom 2,2'-bridged biphenyl is sufficiently close to coplanarity so that relatively moderate bond stretching and bond angle distortion cause racemization.[2]

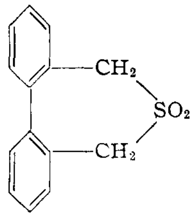
Fischer–Hirschfelder–Taylor molecular models indicate that the presence of large hetero atoms (sulfur or the even larger selenium) in 2,2'-bridged biphenyls would be more likely to develop enantiomorphism.[3] The increasing covalent radii[4] of carbon, sulfur and selenium, respectively, give a theoretical basis for this prediction. Accordingly, 2,7-dihydro-3,4-5,6-dibenzothiepin (1-thia[a,c][3,5]dibenzocycloheptadiene) (IIA), 2,7-dihydro-3,4-5,6-dibenzothiepin-1-dioxide (III), the methylsulfonium iodide (IVA) of the former, 2,7-dihydro-3,4-



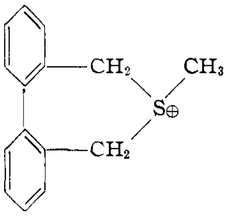
I



II A, S = sulfur
B, S = selenium



III



IV A, S = sulfur
B, S = selenium

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[1] F. Bell, *J. Chem. Soc.*, 5047 (1952). The inability of Bell to obtain activity in compounds of the dibenzo[a,c][3,5]cycloheptadiene type is being checked by current studies of Iffland and Siegel (University of West Virginia, private communication) involving optically active compounds of this type in which activity is maintained by auxiliary biphenylic 6,6'-diamino groups which are then subjected to deamination under very mild conditions. The latter studies should prove very illuminating.

[2] K. E. Howlett, D. M. Hall and E. E. Turner, *ibid.*, 1249 (1955).

[3] *Cf.* M. H. Beeby, F. G. Mann and E. E. Turner, *ibid.*, 1923 (1950).

[4] L. Pauling, *Proc. Natl. Acad. Sci.*, **18**, 292 (1932).