lanosta-8,25-diene, 3β-aminolanost-8-ene, or squalane at concentrations approximating those of substrate **1a**.

The inhibitory effect of 2,3-iminosqualene on the enzymic conversion of **1a** to lanosterol has been utilized to permit the accumulation of 2,3-oxidosqualene using squalene as substrate with rat liver homogenate.[2] Equilibration of 0.12 μmole of (±)-2,3-iminosqualene with 2 ml of rat liver homogenate for 5 min at 37° followed by addition of ^{14}C-labeled squalene (0.075 μmole) and *ca.* 5 mg of reduced triphosphopyridine nucleotide and aerobic incubation for 3 hr led after chromatographic isolation to 2,3-oxidosqualene in 25–30% yield.[5] The isolated labeled oxide **1a** was further identified by its transformation to labeled lanosterol by anaerobic incubation with 2,3-oxidosqualene cyclase for 1 hr (80% conversion).

The synthesis of (±)-2,3-iminosqualene was accomplished by the sequence: all-*trans*-(±)-2,3-oxidosqualene (**1a**)[2] → 2-azido-3-hydroxysqualene (HN_3) → 2-azido-3-*p*-toluenesulfonoxysqualene (*p*-toluenesulfonyl chloride–pyridine) → (±)-2,3-iminosqualene (**1b**) ($LiAlH_4$).[6] The structure of **1b** was confirmed chemically by its conversion using N-nitroso-4-nitrocarbazole to squalene and nitrous oxide.[7] Decahydro-2,3-iminosqualene was synthesized by hydrogenation of **1b** with palladium-on-charcoal catalyst in ethanol; the mass spectrum showed a peak due to the molecular ion at *m/e* 435, as expected for a decahydro derivative of **1b**, and no peak at *m/e* 425, indicating the absence of unreduced **1b**. (±)-2,3-Sulfidosqualene was obtained from the reaction of (±)-**1a** with potassium thiocyanate in ethanol;[8] independent chemical evidence for the formulation of this product as **1c** was obtained from the reaction with *n*-butyllithium which produced squalene cleanly.[9,10]

Work on various aspects of the enzymic cyclization of 2,3-oxidosqualene and its analogs is continuing.

Acknowledgments. We are indebted to Professor Konrad Bloch for numerous helpful discussions during the course of this investigation. Financial support from the National Science Foundation (Grant GP-221) and the National Institutes of Health (Grant HE-02477; Predoctoral Fellowships to P. O. de M. 1965–1967) is also gratefully acknowledged.

(5) 2,3,22,23-Dioxidosqualene was also isolated in 3–10% yield. The absence of sterol formation in this experiment was indicated by the lack of radioactivity in the sterol fraction obtained after precipitation with digitonin.

(6) New substances were characterized by infrared, nuclear magnetic resonance, and mass spectroscopy. Homogeneity was indicated by thin-layer chromatographic techniques.

(7) C. L. Bumgardner, K. S. McCallum, and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 4417 (1961).

(8) C. C. J. Culvenor, W. Davis, and N. S. Heath, *J. Chem. Soc.*, 282 (1949).

(9) F. G. Bordwell, H. M. Anderson, and B. M. Pitt, *J. Am. Chem. Soc.*, **76**, 1082 (1954).

(10) The racemic compounds **1a–c** are all liquid at room temperature. The nmr spectra of the oxide **1a** and the imine **1b** each show two sharp peaks due to the geminal methyl substituents on the three-membered ring (for **1a** at 1.25 and 1.30 ppm and for **1b** at 1.09 and 1.17 ppm, downfield from tetramethylsilane), whereas on the spectrum of the sulfide **1c** all the peaks due to methyl groups fall together at *ca.* 1.61 ppm.

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Synthesis of a Medium Ring Containing Bridge Biphenyl by Photochemically Induced Intramolecular Arylation

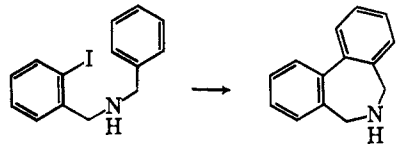
Sir:

Recent interest in intramolecular radical cyclization reactions,[1] particularly those involving aryl radicals,[2] prompts us to present details of a photochemical route to a bridged biphenyl containing a medium ring.

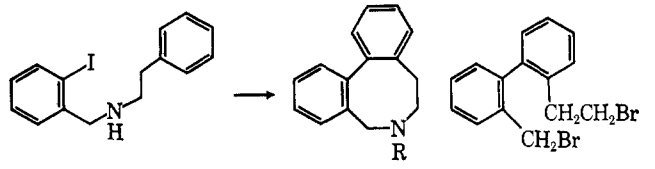
Photolysis of aryl iodides in benzene provides a useful method for the synthesis of substituted biphenyls.[3] An extension of this reaction has been employed for effecting intramolecular arylations leading to phenanthrenes,[4] and more recently to the synthesis of aporphines.[5]

The results presented in this communication demonstrate that photochemically induced intramolecular arylation may be employed not only in the formation of six-membered rings but also for constructing seven- and eight-membered cycles.

Irradiation[6] of a dilute aqueous solution of the iodoaromatic compound **I**, as the hydrochloride, gave after 200 hr the photocyclized product, 6,7-dihydro-5H-dibenz[*c*,*e*]azepine (**2**),[7] mp 74–76°, in 57% yield, together with 13% of starting material. Similarly, irradiation of N-(β-phenethyl)-2-iodobenzylamine (**3**) as the hydrochloride in water for 113 hr, under the same conditions as described above, afforded the photocyclized product **4** (R = H) in 25% yield, mp 119–120°[8] [hydrochloride mp 321–322° dec], λ_{max} 276



1 2



3 4 5

mμ (log ε 2.89), λ_{sh} 231 mμ (log ε 4.15), pmr: eight-proton multiplet, δ 7.38–6.95 (aromatic hydrogens), one-proton broad doublets, 3.83 (J = 15 Hz), 3.10 (J = 15 Hz) ($C_6H_5CH_2N$),[9] five-proton multiplet, 3.20–2.10 ($-HNCH_2CH_2$), mol wt (mass spectrum), 209, together with N-(β-phenethyl)benzylamine (10%). The

(1) C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *J. Am. Chem. Soc.*, **88**, 5361 (1966); N. C. Yang, A. Shani, and G. R. Lenz, *ibid.*, **88**, 5369 (1966).

(2) M. Tiecco, *Chem. Commun.*, 555 (1965); M. P. Cava, S. C. Havlicek, A. Lindert, and R. J. Spangler, *Tetrahedron Letters*, 2937 (1966); N. C. Yang, G. R. Lenz, and A. Shani, *ibid.*, 2941 (1966).

(3) W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965).

(4) S. M. Kupchan and H. C. Wormser, *Tetrahedron Letters*, 359 (1965); *J. Org. Chem.*, **30**, 3792 (1965).

(5) S. M. Kupchan and R. M. Kanojia, *Tetrahedron Letters*, 5353 (1966).

(6) Photolyses were carried out using a 450-w Hanovia high-pressure lamp fitted with a Pyrex sleeve.

(7) W. Wenner, *J. Org. Chem.*, **16**, 1475 (1951). We are indebted to Dr. W. E. Scott, Hoffmann-LaRoche, Nutley, N. J., for providing an authentic sample for comparison.

(8) All new compounds gave satisfactory analyses.

(9) The nonequivalence of the benzylic hydrogens indicates the eight-membered ring exists predominantly in one conformation at room temperature. Studies on the temperature dependence of the spectrum of this compound are under investigation.

structure of the bridged biphenyl **4** (R = H) was established by an independent synthesis *via* its N-benzyl derivative **4** (R = $CH_2C_6H_5$) (hydriodide, mp 235–238°) from benzylamine and the dibromide **5**.[10]

The extension of the reaction to other bridged biphenyls containing medium-size rings is under investigation.

(10) S. R. Ahmed and D. M. Hall, *J. Chem. Soc.*, 3383 (1959).

(11) N.A.S.A. Trainee, 1964–1967.

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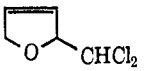
Additions and Corrections

Halomethyl–Metal Compounds. II. The Preparation of *gem*-Dihalocyclopropanes by the Reaction of Phenyl(trihalomethyl)mercury Compounds with Olefins [*J. Am. Chem. Soc.*, **87**, 4259 (1965)]. By DIETMAR SEYFERTH, JAMES M. BURLITCH, RICHARD J. MINASZ, JEFFREY YICK-PUI MUI, HARRY D. SIMMONS, JR., ARNO J. H. TREIBER, and SUSAN R. DOWD. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.

On page 4265, formula IV should be



Nuclear Magnetic Resonance Spectroscopy. The Configurational Stability of Primary Grignard Reagents. Structure and Medium Effects [*J. Am. Chem. Soc.*, **87**, 4878 (1965)]. By GEORGE M. WHITESIDES and JOHN D. ROBERTS. The Gates and Crellin Laboratories of Chemistry, California Institute of Technology, Pasadena, California.

The radical name 2,3-dimethylbutyl mentioned in the last paragraph on page 4884 and in the first column of page 4885 should actually be 3-methyl-2-butyl.

Substituent Effects. VII. The ^{19}F Nuclear Magnetic Resonance Spectra of Substituted 1- and 2-Fluoronaphthalenes [*J. Am. Chem. Soc.*, **89**, 379 (1967)]. By W. ADCOCK and M. J. S. DEWAR. Department of Chemistry, The University of Texas, Austin, Texas 78712.

On page 381, in the Experimental Section, line 3, 29% should read 20%. In Table XIII, third column, third entry, +1.14 should read −1.14.

The Crystal and Molecular Structure of 2,4-Dithiouracil [*J. Am. Chem. Soc.*, **89**, 1249 (1967)]. By ELI SHEFTER and HENRY G. MAUTNER. Department of Pharmaceutics, School of Pharmacy, State University of New York at Buffalo, Buffalo, New York, and the Department of Pharmacology, Yale University School of Medicine, New Haven, Connecticut.

On page 1250 in line 6 of the Experimental Section the linear absorption coefficient μ should be 67 cm^{-1} and not 6.7 cm^{-1}. The statement "the low absorption coefficient and" should be deleted from the last sentence of the third paragraph of the Experimental Section.

Cyclosemigramicidin S [*J. Am. Chem. Soc.*, **89**, 1278 (1967)]. By MICHINORI WAKI and NOBUO IZUMIYA. Laboratory of Biochemistry, Faculty of Science, Kyushu University, Fukuoka, Japan.

In Table I, the values in the second and third columns for the fourth row of entries (-Gly^4-Pro-OH) should be 0 and 100, respectively; those for the fifth row of entries (-D-Ala^4-) should be 25 and 75, respectively.

Total Synthesis of *dl*-Atisine [*J. Am. Chem. Soc.*, **89**, 1483 (1967)]. By WATARU NAGATA, TSUTOMU SUGASAWA, MASAYUKI NARISADA, TOSHIO WAKABAYASHI, and YOSHIO HAYASE. Shionogi Research Laboratory, Fukushima-ku, Osaka, Japan.

On page 1485, in the first column, line 5, **4a** should read 4a. On page 1486, in the first column, line 4, mp 110–130° should read mp 110–112°. On page 1491, in the second column, line 6, **2**, bp 140–160° should read **3**, bp 140–160°. On page 1492, in the first sentence in the second column under the heading (±)-**4aα-Cyano-1α-formyl-7-methoxy-1,2,3,4,4a,9,10,10a,β-octahydrophenanthrene (9)**, 30.4 g should read 30.4 mg. On page 1494, in the second column, line 12, in a by a mix- should read in **a** by a mix-. On page 1497, in the first column, nine lines up from the bottom, $C_{22}H_{32}O_2N$ should read $C_{22}H_{32}O_3N_2$. On page 1498, In the first column, lines 42 and 52, **acetoxy ketone 39a** and **hydroxy ketone 34a** should read **acetoxy ketone 39b** and **hydroxy ketone 39a**, respectively. On page 1499, in the second column, line 21, $C_{22}H_{31}N_2O$ should read $C_{22}H_{31}NO_2$.

The Stereochemistry of the Pentacyclic Oxindole Alkaloids [*J. Am. Chem. Soc.*, **89**, 1739 (1967)]. By MAURICE SHAMMA and ROBERT J. SHINE, Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania; IVAN KOMPIŠ and T. STICZAY, Slovak Academy of Sciences, Institute of Chemistry, Bratislava, Czechoslovakia, F. MORSINGH, Department of Chemistry, University of Malaya, Kuala Lumpur, Malaya; and J. POISSON and J-L. POUSSET, Faculté de Pharmacie de Paris, Laboratoire de Pharmacie Galénique, Paris 6, France.

In Table I, the correct heading for the last column is $[\alpha]_D$, deg ($CHCl_3$).

Anodic Oxidations of Medium Ring Cycloalkanecarboxylic Acids [*J. Am. Chem. Soc.*, **89**, 2139 (1967)]. By JAMES G. TRAYNHAM and JOHN S. DEHN. Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana.

The formula for bicyclo[7.1.0]nonane in the illustration should be replaced by one for bicyclo[6.1.0]octane.