

synthesis,¹⁵ this point remains to be defined for β -sitosterol.

(15) L. W. Parks, *J. Am. Chem. Soc.*, **80**, 2023 (1958).

(16) Postdoctoral trainee in the training program for Steroid Biochemistry.

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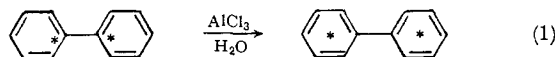
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THE WORCESTER FOUNDATION FOR
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The Rearrangement of Diphenyl¹

Sir:

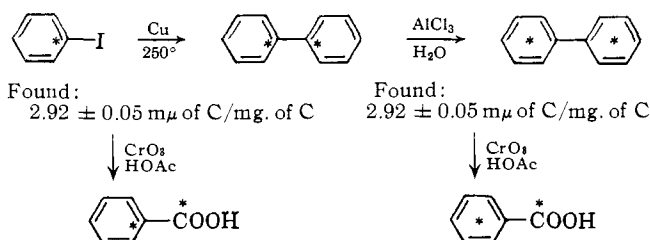
We wish to report unequivocal evidence for the water promoted, aluminum chloride induced intramolecular rearrangement of the benzene rings in diphenyl



When diphenyl-1,1'-C¹⁴, prepared in 80% yield *via* an Ullmann reaction² on iodobenzene-1-C¹⁴, was heated to 100° for 30 min. with 10 mole % of aluminum chloride and 1 mole % of water, the radioactivity, originally localized at the two connecting carbons, had been randomly distributed. Recovered active diphenyl was also shown to be randomized when the reaction was carried out for 12 hr. in a refluxing benzene solution. The degradation method used is outlined in Scheme I.

SCHEME I

SYNTHESIS AND DEGRADATION OF ACTIVE DIPHENYL



Found:
2.92 \pm 0.05 μ of C/mg. of C

Found:
2.92 \pm 0.05 μ of C/mg. of C

Calcd.
for no rearrangement:
4.99 μ of C/mg. of C

Calcd.
for complete rearrangement:
2.92 μ of C/mg. of C

Found:
4.95 \pm 0.06 μ of C/mg. of C

Found:
2.92 \pm 0.05 μ of C/mg. of C

The view that the reaction is intramolecular³ is supported by the following facts: (1) The inactive benzene used in the solvent experiments was devoid of activity at the end of a run within the precision of our assay methods.⁴ (2) A rearrangement carried out with inactive diphenyl in benzene-1-C¹⁴ yielded diphenyl having an activity indicating less than 0.001% intermolecularity.

The isomerizations in benzene were carried out by refluxing 0.5 g. of diphenyl-1,1'-C¹⁴ in 10 ml. of benzene containing 50–100 mg. of aluminum chloride and 5–10 mg. of water for various periods of time. The diphenyl,

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.

(2) The benzoic acid obtained by oxidation of the unrearranged diphenyl-1,1'-C¹⁴ showed no loss in specific activity. This indicated *inter alia* that the Ullmann reaction proceeds without rearrangement. The iodobenzene-1-C¹⁴ was prepared in 76% yield from aniline-1-C¹⁴ (*cf.* H. J. Lucas and E. R. Kennedy, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 351) supplied by Nuclear Research Chemicals, Inc., Orlando, Florida.

(3) G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **28**, 1912 (1963).

(4) D. R. Christman, M. E. Day, P. R. Hansell, and R. C. Anderson, *Anal. Chem.*, **27**, 1935 (1955). The authors are indebted to Dr. D. R. Christman and Mrs. C. T. Paul for the activity assays.

isolated after quenching the reaction mixture and evaporating the benzene, was oxidized⁵ by stirring for 5 hr. at 40–50° with 3.0 g. of chromium trioxide in 35 ml. of glacial acetic acid, furnishing benzoic acid in 35–47% yields.

As a secondary check on the exchange, radioactive benzene alone was treated with the aluminum chloride-water catalyst. Carrier diphenyl was added after the reaction had been quenched. The isolated and purified diphenyl had an activity indicating a benzene to diphenyl conversion of less than 0.01%.⁶

Our experimental data do not allow us to distinguish between a hydrogen abstraction⁷ mechanism and a proton addition⁸ mechanism to develop the positive charge on the *ortho* carbon. The latter pathway followed by a 1,2-shift and proton loss seems to us the simplest explanation, although other mechanisms cannot be excluded at this stage. If a proton addition mechanism is operative during this facile rearrangement of diphenyl in the presence of a water promoted Lewis acid, some doubt is thrown on the stability of polyaryls⁹ under conditions of electrophilic substitution reactions. Furthermore it seems to us that the significance of isomer distribution in diphenyl¹⁰ would require some re-examination.

(5) J. C. Colbert and C. L. Hensley, *J. Am. Chem. Soc.*, **62**, 3257 (1940).

(6) The yield of diphenyl from benzene in the absence of diphenyl may well be greater than in the presence of diphenyl, the latter presumably complexing better with the catalyst than benzene.

(7) A. Streitwieser, Jr., and L. Reif, *J. Am. Chem. Soc.*, **82**, 5003 (1960).

(8) R. H. Allen, *ibid.*, **82**, 4856 (1960); *cf.* H. C. Brown and C. R. Smoot, *ibid.*, **78**, 2176 (1956); H. Steinberg and F. L. J. Sixma, *Rec. trav. chim.*, **81**, 185 (1962); E. Ünseren and A. P. Wolf, *J. Org. Chem.*, **27**, 1509 (1962).

(9) P. Kovacic and F. W. Koch, *ibid.*, **28**, 1864 (1963).

(10) M. J. S. Dewar, T. Mole, D. S. Urch, and E. W. T. Warford, *J. Chem. Soc.*, 3572 (1956); L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 1242 (1962); R. Baker, R. W. Bott, and C. Eaborn, *J. Chem. Soc.*, 2136 (1963).

(11) Visiting professor at Brookhaven National Laboratory, June 14, 1963–September 4, 1963, from University of Groningen, Holland.

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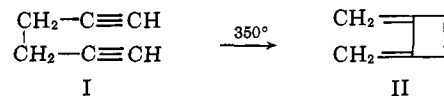
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RECEIVED AUGUST 28, 1963

3,4-Dimethylenecyclobutene by Thermal Rearrangement of 1,5-Hexadiene

Sir:

We have found that 1,5-hexadiene (I) rearranges at 350° giving 3,4-dimethylenecyclobutene (II) in 85% yield. The reaction is conducted in a flow system, using



a Pyrex tube (12 mm. \times 65 cm.) packed with glass helices as the reaction vessel. The diene is vaporized and swept through the reaction tube in a stream of nitrogen. It is important that the hydrocarbon be vaporized before it reaches the reaction zone. If the liquid is allowed to drop directly onto the helices, it ignites each time a drop hits, and after a short time a vigorous reaction occurs filling the apparatus with soot. This trouble is not experienced when the hydrocarbon is vaporized first. Complete conversion of I occurs at 350° using a hydrocarbon feed rate of 6 ml./hr. and a nitrogen flow of 2400 ml./hr. The v.p.c. tracing of the product shows a single peak.

The infrared and ultraviolet spectra are in agreement with those reported for II by Blomquist and Maitlis.¹ The boiling point which we observe (72°) is substan-

(1) A. T. Blomquist and P. M. Maitlis, *Proc. Chem. Soc.*, 332 (1961).