# Communications TO THE EDITOR

## The Structure of a 1-Substituted Cyclohexyl Free Radical

*Sir:*

The recent communication by Greene and coworkers[1] on the nature of the cyclohexyl radical has prompted us to relate our findings in this same area. In our study, 1-hydroxycyclohexyl radicals were produced from the *cis*- and *trans*-3- and 4-*tert*-butylcyclohexanols, α- and β-cholestanol, epicoprostanol, and coprostanol with *tert*-butoxy radicals as the hydrogen-atom abstractor. These cyclohexyl radicals were caused to react with 1-octene, and the isomer ratios of the resultant tertiary alcohols were determined.

Accordingly, when 0.69 mmole of *trans*-4-*tert*-butylcyclohexanol (108.3 mg.), 0.069 mmole of 1-octene (10.8 µl.), and 0.028 mmole of *tert*-butyl peroxide (5.2 µl.) were heated at 135° for 20 hr., 5.8 mg. (31% yield based on 1-octene) of the products was both separated from the starting materials and residue and resolved to the two isomeric alcohols by thin-layer chromatography.[2] The ratio of *cis*- (*cis*-hydroxyl and *tert*-butyl) to *trans*-1-octyl-4-*tert*-butylcyclohexanol was 1.55:1.00. *Anal.* Calcd. for $C_{18}H_{36}O$: C, 80.52; H, 13.52. Found: C, 80.70; H, 13.48. Likewise, when 1.28 mmoles of β-cholestanol (0.500 g.), 0.102 mmole of 1-octene (16.0 µl.), and 0.195 mmole of *tert*-butyl peroxide (36 µl.) were treated as above, subsequent isolation of products as described above gave 7.0 mg. (28%) of α- and β-3-octyl-cholestan-3-ol in a ratio of 1.83:1.00. *Anal.* Calcd. for $C_{35}H_{64}O$: C, 83.92; H, 12.88. Found: C, 83.71; H, 12.76. The assignments of configuration of the alcohols produced were done by comparison to the pure *cis* and *trans* alcohols whose configurations had been assigned by infrared.[3] It was determined that all the products were individually stable to the conditions of the experiment and to the work-up procedure.

It was found that the Grignard reaction of octylmagnesium bromide with the appropriate ketones gave the same alcohols in good yields. A summary of the isomer ratios formed in these Grignard reactions and in the free radical reactions is given in Table I. These percentages of isomers are consistent with those determined by Eliel,[4] and essentially opposite to those of Greene and coworkers.[1] Since our work involves an alcohol radical and an olefin addition reaction as compared to a hydrocarbon radical and an abstraction reaction,[1] the results do not necessarily have to agree.

TABLE I

PER CENT AXIAL HYDROXYL PRODUCT FROM GRIGNARD AND FREE RADICAL REACTIONS[a]

| | Free radical (ultra-violet)[b] | Free radical (heat)[c] | Grignard |
|---|---|---|---|
| *cis*-3-*tert*-Butylcyclohexanol | 64 | 65 | 69 |
| *trans*-3-*tert*-Butylcyclohexanol | 66 | 67 | 69 |
| *trans*-4-*tert*-Butylcyclohexanol | 60 | 60 | 63 |
| *cis*-4 *tert*-Butylcyclohexanol | 62 | 59 | 63 |
| Epicoprostanol | .. | 36 | 35 |
| Coprostanol | .. | 36 | 35 |
| α-Cholestanol | .. | 64 | 65 |
| β-Cholestanol | .. | 57 | 65 |

[a] ±2%. [b] Peroxide decomposed by ultraviolet light. [c] Peroxide decomposed by heat.

From the results in Table I, one must conclude that the same product composition results from either isomeric starting material. On this basis and from the fact that the Grignard reaction produces the same isomer ratios as the free radical reaction, one can infer that the 1-hydroxycyclohexyl radical is planar. The preponderance of axial hydroxyl product arises from the greater ease of attack by the olefin or octylmagnesium bromide away from the 3-hydrogens (equatorial attack). The small variation in percentages can be attributed to the differences in reactions.

**Acknowledgment.**—This work was supported by the Army Research Office (Durham) under Grant No. DA-ORD-14 and in part by N.S.F. G-6580. The authors also wish to thank Dr. J. M. Bobbitt for introducing them to thin-layer chromatography.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CONNECTICUT
STORRS, CONNECTICUT
ROY J. GRITTER
ROBERT J. ALBERS

RECEIVED AUGUST 9, 1962

---

[1] F. D. Greene, C. C. Chu, and J. Walia, *J. Am. Chem. Soc.*, **84**, 2463 (1962).

[2] R. J. Gritter and R. J. Albers, *J. Chromatog.*, in press.

[3] A. R. H. Cole, P. R. Jeffries, and G. T. Mueller, *J. Chem. Soc.*, 1212 (1959).

[4] E. L. Eliel and R. V.hary Aca, *J. Org. Chem.*, **24**, 151 (1959).

---

## *n*-Butylboronic Acid as a Convenient Reagent for the Separation of Isomeric *cis,trans*-Cycloalkanediols

*Sir:*

We wish to report that esterification of *cis*-cycloalkanediols with *n*-butylboronic acid or *n*-butylboroxine yields volatile cyclic boronates, whereas *trans*-cycloalkanediols in most cases yield nonvolatile polymeric products. Consequently, the distillation of a reaction mixture of the boronic acid or boroxine with an isomeric pair of *cis,trans*-cycloalkanediols provides a convenient means for the separation of the two isomers.[1] The individual pure diols are readily recovered by transesterification with ethylene glycol. This procedure is facilitating greatly our examination of the cyclic diols obtained *via* the hydroboration–oxidation of cyclic dienes.[2–4]

In order to test the applicability of the proposed procedure, pure *cis*- and *trans*-1,4-cyclohexanediols were individually esterified with *n*-butylboroxine[5,6] and the products subjected to distillation at low pressures. In this case only the *cis* isomer can form a simple cyclic boronate, but this involves the formation of the energetically unfavorable boat form, bridged by a seven-membered ring. Nevertheless, the *cis* isomer volatilized readily at 200° and 0.05 mm., yielding a clear liquid ($n^{20}_D$ 1.4591), which was transformed into a thick sirup on standing at room temperature. *Anal.* Calcd. for $C_{10}H_{19}BO_2$: C, 65.96; H, 10.52; B, 5.94. Found: C, 65.60; H, 10.60; B, 5.78. Under the same conditions, the *trans* isomer failed to distill.

The following separation of *cis,trans*-1,3-cyclohexanediols illustrates the simplicity of the method. To 10.0 g. of the mixture (86 mmoles) was added 28.7 mmoles of *n*-butylboroxine. Benzene was added and the water of esterification removed by azeotropic distillation. The viscous product was subjected to vacuum distillation, affording 6.24 g. of distillate, b.p. 100–103° at 13 mm., $n^{20}_D$ 1.4572. *Anal.* Calcd. for $C_{10}H_{19}BO_2$: C, 65.96; H, 10.52; B, 5.94. Found: C, 66.18; H, 10.62; B, 6.12.

The distillate, 6.24 g., was treated with 0.10 mole of ethylene glycol. Distillation yielded the ethylene glycol boronate, b.p. 48–52° at 13 mm. Recrystallization of the residue from ethyl acetate yielded 2.8 g. of crystalline *cis*-1,3-cyclohexanediol, m.p. 85–86°.[7]

The residue, 7.3 g., was treated with ethylene glycol and transformed by the above procedure into 4.6 g. of *trans*-1,3-cyclohexanediol, m.p. 114–116°. The recovery was 74%. Gas chromatographic analysis indicated that the two products were essentially pure.

In the same way 5.0 g. of *cis,trans*-1,4-cyclohexanediol was converted into 1.42 g. of *cis*-, m.p. 105–107°, and 2.25 g. of *trans*-, m.p. 140–142°,[8] a recovery of 72%.

Treatment of a mixture of 68% *cis*- and 32% *trans*-1,2-cyclohexanediol with *n*-butylboroxine yielded a distillate containing both diols. Consequently, the simple separation of the 1,4- and 1,3-isomers cannot be extended to the 1,2-isomer. However, gas chromatographic examination of the distillate revealed that the first fraction contained 76% *cis*- and 24% *trans*-, whereas the second fraction contained 31% *cis*- and 69% *trans*-1,2-cyclohexanediol. Consequently, the use of an efficient fractionating column would make possible the separation of these isomeric diols.

There has been some controversy as to the precise nature of the diol produced in the hydroboration–oxidation of cyclopentadiene.[2,9,10] We observed that the 1,3-cyclopentanediol produced in this reaction was composed of two products in a ratio of 85:15 (gas chromatographic analysis). The major product possessed properties in agreement with Saegebarth's "*cis*-" and Henbest's *trans*-1,3-cyclopentanediol. Treatment of the crude product with *n*-butylboroxine, as described above for 1,3-cyclohexanediol, removed the minor peak as a volatile distillate, b.p. 80° at 10 mm., and yielded the major peak as a nonvolatile boronic ester. On this basis, the major product, b.p. 95° at 0.5 mm., m.p. 28–30°, bis-*p*-nitrobenzoate, m.p. 186–187°, and bisphenylurethane, m.p. 173–174°, is *trans*-1,3-cyclopentanediol, and the minor product, m.p. 40°, bis-*p*-nitrobenzoate, m.p. 153°, bisphenylurethane, m.p. 162–163°, is the *cis* isomer. The assignment of the *trans* configuration to the diol, m.p. 28–30°, was confirmed by the absence of a chelated hydroxyl group in the infrared spectrum at high dilution in carbon tetrachloride solution. Consequently, hydroboration–oxidation of cyclopentadiene yields the *trans*-1,3-cyclopentanediol.

From these results it appears that the use of alkylboronic acids provides a highly convenient procedure for the separation of isomeric cycloalkanediols. We are currently applying it to the study of the diols produced in the hydroboration–oxidation of cyclic dienes.[3]

RICHARD B. WETHERILL LABORATORY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA

HERBERT C. BROWN
GEORGE ZWEIFEL

RECEIVED AUGUST 22, 1962

---

(1) The preparation of the benzeneboronates of *cis*- and *trans*-1,2-cyclopentanediol and -1,2-cyclohexanediol has been previously reported: H. G. Kuivila, A. H. Keough, and E. J. Soboczenski, *J. Org. Chem.*, **19**, 780 (1954); J. G. Sugihara and C. M. Bowman, *J. Am. Chem. Soc.*, **80**, 2443 (1958).

(2) K. A. Saegebarth, *J. Org. Chem.*, **25**, 2212 (1960).

(3) G. Zweifel, K. Nagase, and H. C. Brown, *J. Am. Chem. Soc.*, **84**, 183, 190 (1962).

(4) R. Köster and G. Rotermund, *Angew. Chem.*, **74**, 252 (1962); G. Rotermund and R. Köster, *ibid.*, **74**, 329 (1962).

(5) G. F. Hennion, P. A. McCusker, E. C. Ashby, and A. J. Rutkowski, *J. Am. Chem. Soc.*, **79**, 5194 (1957).

(6) It should be pointed out that we utilized *n*-butylboronic acid and *n*-butylboroxine primarily because of their relative availability. There would be obvious advantages in utilizing more volatile derivatives, such as methylboronic acid or boroxine.

(7) M. F. Clark and L. N. Owen, *J. Chem. Soc.*, 2103 (1950), report: *cis*-, m.p. 85.5°; *trans*-, m.p. 115.5°.

(8) L. N. Owen and P. A. Robins, *ibid.*, 320 (1949), report: *cis*-, m.p. 108–110°, *trans*-, m.p. 141°.

(9) A. C. Darby, H. B. Henbest, and I. McCleanaghan, *Chem. Ind.* (London), 462 (1962).

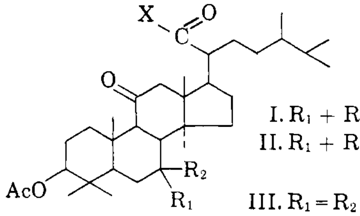
(10) H. Z. Sable and T. Posternak, *Helv. Chim. Acta*, **45**, 370 (1962).

## Transformations of Eburicoic Acid. II. Side Chain Degradation to 14-Methylandrostane Derivatives

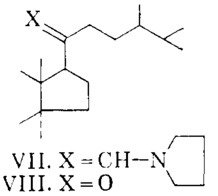
*Sir:*

In a previous paper[1] we have reported the degradation of the tetracyclic triterpene eburicoic acid to pregnane derivatives without impairment of the reactive 8,9-double bond. In this paper we wish to describe the complete removal of the eburicoic acid side chain leading to 11-oxygenated trimethylandrostane derivatives.

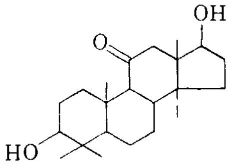
Methyl 3-acetyl 24ξ-methyllanostane-3β-ol-7,11-dione-21-oate (I)[2] obtained from methyl acetyl dihydroeburicoate[3] in two steps was converted into the 7-thioethylene ketal (II), m.p. 227–228°; $[\alpha]^{21}_{\mathrm{D}}$ +24°[4]; *Anal.* Found: C, 67.81; H, 9.13; S, 10.39; with ethanedithiol and boron trifluoride-etherate in 88% yield and II reduced with sponge nickel in alcohol in 85% yield to the 11-keto ester III, m.p. 166–167°; $[\alpha]^{21}_{\mathrm{D}}$ +52°; *Anal.* Found: C, 74.71; H, 10.28. The strongly hindered, alkali-resistant carbomethoxy group of III was converted by anhydrous lithium iodide in refluxing collidine[5] in 95% yield to the acid IV,[6] m.p. 286–287°; *Anal.* Found: C, 74.37; H, 9.56; which was converted in 85% yield to the acid chloride V with thionyl chloride at 5°; m.p. 220–221°; $[\alpha]^{23}_{\mathrm{D}}$ +26°; *Anal.* Found: C, 72.46; H, 9.74; Cl, 6.50. The extremely stable acid chloride was reduced in 85% yield with a stream of hydrogen in boiling toluene in the presence of 10% palladium on charcoal to the aldehyde VI, m.p. 171–172°; $[\alpha]^{20}_{\mathrm{D}}$ +53°; $\lambda^{\mathrm{Nujol}}_{\mathrm{max}}$ 3.72 μ (CHO); n.m.r. $\tau_{21\mathrm{H}}$ = 0.62; *Anal.* Found: C, 76.86; H, 10.37, which formed an oxime but no dinitrophenylhydrazone. The aldehyde VI was converted into the pyrrolidyleneamine VII with *p*-toluenesulfonic acid in refluxing benzene[7]; $\lambda^{\mathrm{MeOH}}_{\mathrm{max}}$ 228 mμ (ε 4820); 237 mμ (ε 4980) and the latter ozonized directly in ether solution at −35° followed by reduction of the ozonide with zinc and acetic acid. Alumina chromatography gave the pure 20-ketone VIII, m.p. 194–195°; $[\alpha]^{20}_{\mathrm{D}}$ +90°; *Anal.* Found: C, 76.87; H, 10.42; which was stable to perphthalic acid for 2 weeks but rearranged with trifluoroperacetic acid[8] in methylene chloride in the presence of sodium monohydrogen phosphate in 48 hr. to yield after saponification with hot methanolic potassium hydroxide the known 4,4,14-trimethylandrostane-3β,17β-diol-11-one (IX)[9]; m.p. 275–276° (block); $[\alpha]^{20}_{\mathrm{D}}$ +54° (dioxane); *Anal.* Found: C, 75.97; H, 10.66. Identity was confirmed by conversion into the 3,17-diacetate, m.p. 246–248°[9] and the 3,17-diketone, m.p. 175–178° (block)[9], as well as by direct comparison with samples of IX and its diacetate kindly supplied by Prof. O. Jeger. As a minor product there was obtained the 17β-carboxylic acid X,[10] m.p. 315°, identified as the methyl ester,[10] m.p. 240–241°; $[\alpha]^{23}_{\mathrm{D}}$ +60°.



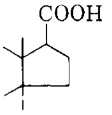
I. $R_1 + R_2 = O$, $X = OCH_3$
II. $R_1 + R_2 = S–CH_2$, $X = OCH_3$
S–CH₂
III. $R_1 = R_2 = H$, $X = OCH_3$
IV. $R_1 = R_2 = H$, $X = OH$
V. $R_1 = R_2 = H$, $X = Cl$
VI. $R_1 = R_2 = X = H$



VII. X = CH–N
VIII. X = O



IX



X

THE SQUIBB INSTITUTE FOR MEDICAL RESEARCH
NEW BRUNSWICK, NEW JERSEY

G. W. KRAKOWER
JAMES W. BROWN
JOSEF FRIED

Received August 28, 1962

---

(1) D. Rosenthal, J. Fried, P. Grabowich, and E. F. Sabo, *J. Am. Chem. Soc.*, **84**, 877 (1962).

(2) R. M. Gascoigne, A. Robertson, and J. J. H. Simes, *J. Chem. Soc.*, 1830 (1953).

(3) F. N. Lahey and P. H. A. Strasser, *ibid.*, 873 (1951).

(4) All rotations in chloroform. Melting points in capillary tubes unless otherwise indicated.

(5) F. Elsinger, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, **43**, 113 (1960). *Cf.* also E. Taschner and B. Liberek, *Roczniki chem.*, **30**, 323 (1956).

(6) It was necessary to reacetylate the crude product because of some deacetylation during the reaction.

(7) Removal of water was achieved by allowing the refluxing solvent to pass through a thimble filled with calcium carbide.

(8) W. D. Emmons and G. B. Lucas, *J. Am. Chem. Soc.*, **77**, 2287 (1955).

(9) W. Voser, M. V. Mijovic, H. Heusser, O. Jeger, and L. Ruzicka, *Helv. Chim. Acta*, **35**, 2414 (1952).

(10) J. Fried and E. F. Sabo, *J. Am. Chem. Soc.*, **84**, 4356 (1962).

---

## On the Mechanism of the Acid-catalyzed Hydrolysis of Heteroaromatic Ethers[1]

*Sir:*

We wish to report the first definitive experiment designed to elucidate the mechanism of the acid-catalyzed cleavage of alkoxy ethers of heteroaromatic compounds.

It is well known that α- and γ-alkoxypyrimidines and similarly constituted aromatic heterocycles undergo hydrolysis much more readily than the corresponding aromatic carbocycle. It has been

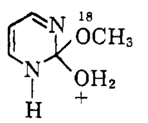
---

(1) This research was supported by a National Science Foundation Coöperative Graduate Fellowship, October 1, 1959–September 30, 1961, and by the Research Board of the Graduate College of the University of Illinois, Grant No. 56-92-62.

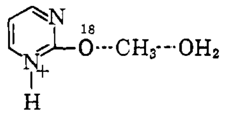
tacitly assumed that this ease of reaction is closely related to the facile nucleophilic displacement of diverse α- and γ-substituted heteroaromatic compounds.[2] On this basis it has been concluded that their mechanisms are congruent and involve a nucleophilic attack at the α- or γ-position of the heterocyclic ring followed by an elimination of the extant functional group (pathway A).[2c]

However, an alternate mechanism can be written for the hydrolysis of α- and γ-alkoxyheterocycles, *viz.*, a nucleophilic displacement of the alkyl group involving a heterolytic cleavage of the alkyl-oxygen bond (pathway B).[3]

In the specific example of the acid-catalyzed hydrolysis of 2-methoxypyrimidine, pathway A would proceed *via* intermediate *A* while pathway B would afford transition state *B*. By selecting an appropriately labeled precursor, it should be possible to distinguish between these pathways for for former liberates methanol-$O^{18}$, whereas *B*, the latter, gives methanol with the normal distribution of oxygen isotopes.



*A*



*B*

2-Methoxypyrimidine-$O^{18}$ was prepared from 2-chloropyrimidine and sodium methoxide-$O^{18}$ in phenyl ether. We have allowed this labeled ether to react with 2 *N* sulfuric acid at 100° for 4 hr. and have isolated a 75% yield of methanol.[4] Mass spectrographic analysis[5] reveals that this methanol retains a *minimum of 90%* oxygen-18. These data are consistent with pathway A as the major reaction course involving intermediate *A* as part of the over-all scheme.

This work not only provides evidence for the mechanism of cleavage of these ethers but also lends further support to the two-step intermediate complex mechanism put forward for aromatic nucleophilic displacement reactions.[2,6]

Additionally, we have evidence suggesting that under other conditions, part of the reaction may indeed proceed *via* the nucleophilic displacement described in pathway B. The mechanistic implications of our data as well as the base-catalyzed cleavage of these esters are being studied in greater detail.

DEPARTMENT OF CHEMISTRY
COLLEGE OF PHARMACY
UNIVERSITY OF ILLINOIS
CHICAGO 12, ILLINOIS

RALPH DANIELS
LEE T. GRADY
LUDWIG BAUER

RECEIVED SEPTEMBER 6, 1962

---

[2] (a) J. Hine, "Physical Organic Chemistry," 1 ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 369 ff.; (b) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951); (c) R. O. Clinton and C. M. Suter, *J. Am. Chem. Soc.*, **70**, 491 (1948); (d) J. D. Reinheimer, J. T. Gerig, R. Garst, and B. Schrier, *ibid.*, **84**, 2770 (1962).

[3] See J. F. Bunnett and E. Buncell, *ibid.*, **83**, 1117 (1961), for similar considerations in the hydrolysis of alkyl ethers of carbocyclic compounds.

[4] In a control experiment under identical conditions we have established that neither the oxygen atom of water nor that of 2-hydroxypyrimidine exchanges with the oxygen atom of methanol. The methanol used for this study was labeled with 10% $O^{18}$ and was purchased from Yeda, Rehovoth, Israel.

[5] These analyses were determined at 7.0 volts and 40 μamp. on a Consolidated Electrodynamics Corp. 21-130 mass spectrograph. We are indebted to Mr. R. M. Sherrill of Northwestern University for the mass spectrographic analyses.

[6] J. F. Bunnett, *Quart. Rev.*, **12**, 1 (1958).

---

## The Photoinitiated Arylation of Trivalent Phosphorus Compounds

*Sir:*

The limitations of the various available methods for the establishment of aryl-phosphorus bonds are well known.[1] As part of an effort to develop new procedures for the formation of this bond,[2] we have examined the photolysis of aromatic iodo compounds in the presence of triphenylphosphine and several trialkyl phosphites and find that the processes constitute convenient and apparently general one-step syntheses of the corresponding triphenyl-(aryl)phosphonium iodides and dialkyl arylphosphonates. Kharasch has recently shown that the photolysis of aryl iodides in the presence of aromatics leads to the homolytic arylation of the substrate in useful yields.[3] Since the attack of free radicals on trivalent phosphorus derivatives has been demonstrated previously[4] and shown to lead to the formation of carbon-phosphorus bonds by chain processes in two instances,[5] it was anticipated that the photolysis reaction would proceed by a similar mechanism. However, in the triphenylphosphine reaction all indications point to a non-chain reaction.

A solution of triphenylphosphine (19 mmoles) and iodobenzene (19 mmoles) in chlorobenzene (65 ml.) in a Vycor reaction vessel under an atmosphere of dry nitrogen was irradiated for 46 hr. at 65° with an unfiltered 100-watt Hanovia mercury resonance lamp. The precipitated product was recrystallized from chloroform-benzene to give tetraphenylphosphonium iodide (I) (22.5%), m.p. 323-326° (lit.,[6a] m.p. 337°). The addition of azobisisobutyronitrile to the reaction mixture did not alter the yield, but

---

[1] L. D. Freedman and G. O. Doak, *Chem. Rev.*, **57**, 481-485 (1957); P. C. Crofts, *Quart. Rev.*, **12**, 347-363 (1958).

[2] C. E. Griffin and N. T. Castellucci, *J. Org. Chem.*, **26**, 629 (1961).

[3] W. Wolf and N. Kharasch, *ibid.*, **26**, 283 (1961); W. Wolf, N. Kharasch, and T. Erpelding, 142nd National Meeting, American Chemical Society, Atlantic City, N. J., September 13, 1962, Abstracts, p. 87Q.

[4] For principal citations, see A. C. Poshkus and J. E. Herweh, *J. Am. Chem. Soc.*, **84**, 555 (1962); C. Walling, O. H. Basedow, and E. S. Savas, *ibid.*, **82**, 2181 (1960).

[5] F. Ramirez and N. McKelvie, *ibid.*, **79**, 5829 (1957); C. E. Griffin, *Chem. Ind.* (London), 415 (1958); J. I. G. Cadogan and W. R. Foster, *J. Chem. Soc.*, 3071 (1961).

[6] (a) L. Horner and H. Hoffmann, *Chem. Ber.*, **91**, 45 (1958); (b) L. Horner and H. Hoffmann, *ibid.*, **91**, 50 (1958); (c) L. Horner, H. Hoffmann, H. G. Wippel, and G. Hassel, *ibid.*, **91**, 52 (1958).

an increase in reaction time to 159 hr. gave 36% of I. In analogous fashion the following triphenyl(aryl)phosphonium iodides resulted from irradiation of chlorobenzene solutions of triphenylphosphine and the aryl iodide at 40–70°: *p*-tolyl (36% 346-hr. reaction time), m.p. 209–225° (lit.,[6a] m.p. 207–209°); *p*-anisyl (18%, 249 hr.), m.p. 217–218° (lit.,[6b] m.p. 209°); *p*-biphenylyl (II) (9%, 137 hr.), m.p. 209–214°; *p*-hydroxyphenyl[7] (III) (42%, 57 hr.), m.p. 255–289°. Compounds II and III were converted by ion exchange to the corresponding bromides: II bromide, m.p. 195–216°; III bromide, m.p. 279–280° (lit.,[6c] m.p. 254–262°).[8] The reaction is not restricted to triphenylphosphine, but can be extended to trialkylphosphines. Thus irradiation of a solution of iodobenzene and tri-*n*-butylphosphine in chlorobenzene for 118 hr. gave tri-*n*-butyl(phenyl)phosphonium iodide (6.4%), m.p. 151–152.5°.

A series of added inhibitors (hydroquinone, 2,6-di-*t*-butylphenol, air, iodine) produced no significant change in the yield of phosphonium salt in the reaction between triphenylphosphine and iodobenzene.

As a synthetic method for tetraarylphosphonium halides, this method supplements currently available methods[9] such as the diazo and cobalt salt methods reported by Horner[6] and may be more useful in certain instances. Thus III could not be prepared directly by Horner, but required a three-stage synthesis.[6c]

Under carefully controlled conditions, the photochemical phenylation of trialkyl phosphites with iodobenzene leads to acceptable yields of the corresponding dialkyl phenylphosphonates. A mixture of trimethyl phosphite (50 mmoles) and iodobenzene (50 mmoles) in a double-walled water cooled Vycor vessel was irradiated for 16 hr. at 7–10° with an unfiltered 450-watt Hanovia mercury resonance lamp. Fractionation of the reaction mixture gave iodomethane (39.6%), dimethyl phenylphosphonate (38.0%), and an inseparable mixture of dimethyl methylphosphonate and iodobenzene. The identity of the products was confirmed by infrared spectroscopy and v.p.c. analysis.

Without careful choice of conditions the alkyl iodide undergoes an Arbuzov reaction with the trialkyl phosphite to form dialkyl alkylphosphonate at the expense of the phenylphosphonate. When the above reaction was conducted at 50° only 3.9% of the phenylation product was obtained; the remainder of the phosphite was converted quantitatively to dimethyl methylphosphonate. In accord with its mechanism, the Arbuzov process was expected to be less important with the higher trialkyl phosphites. Thus triisopropyl phosphite underwent phenylation forming diisopropyl phenylphosphonate (26%), isopropyl iodide, and diisopropyl isopropylphosphonate, when irradiated for 24 hr. at 28–30°. A comparable yield was obtained using tri-*n*-butyl phosphite, but v.p.c. analysis indicated the presence of several side products, one of which was possibly di-*n*-butyl phosphite; biphenyl and 4-iodobiphenyl, the expected side products of a free radical arylation, were absent.

This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research under Grant No. AF-AFOSR-62-48. We are indebted to Professor L. Horner and Mr. G. Witschard for providing authentic samples of phosphonium salts.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH 13, PENNSYLVANIA

JOHN B. PLUMB
CLAIBOURNE E. GRIFFIN

RECEIVED SEPTEMBER 7, 1962

---

[7] Reaction carried out in the absence of solvent by irradiating a melt of *p*-iodophenol in excess (6:1) triphenylphosphine at 90°.

[8] Satisfactory analytical data were obtained for all compounds and mixture melting point determinations were carried out where authentic samples were available. The yields reported are not optimal; the phosphonium salt precipitates as it is formed and coats the surface of the reaction vessel rendering it opaque to irradiation. By refinement of the apparatus, higher yields should be readily obtainable.

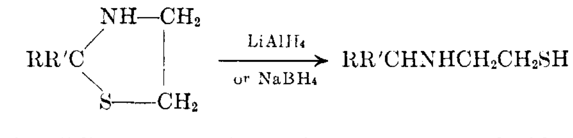
[9] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, N. Y., 1950, chap. 5.

---

## A New Synthesis of β-Aminomercaptans

*Sir:*

β-Aminomercaptans, *e.g.*, $RR'CHNHCH_2CH_2SH$ have recently received considerable attention as radiation-protective agents.[1] Most current syntheses of these compounds are based on amines, $RR'CHNH_2$ as starting materials.[2] We now wish to report a convenient synthesis of β-aminomercaptans from carbonyl compounds $RR'C{=}O$, including such natural products as 3-cholestanone. The synthesis involves metal hydride reduction of intermediate thiazolidines



Thiazolidines are available from ketones and aldehydes by well described methods[3] and are smoothly reduced to the desired products by either sodium borohydride or a stoichiometric amount (0.5 mole) of lithium aluminum hydride. An excess of lithium aluminum hydride must be avoided because it leads to hydrogenolysis of the product $RR'CHNHCH_2CH_2SH$ with loss of sulfur to RR'-

---

[1] *Cf.* Symposium on Radiation-protective Agents, 141st National Meeting, American Chemical Society, Washington, D. C., March 28, 1962.

[2] D. D. Reynolds, M. K. Massad, D. L. Fields, and D. L. Johnson, *J. Org. Chem.*, **26**, 5109 (1961); D. D. Reynolds, D. L. Fields, and D. L. Johnson, *ibid.*, **26**, 5116, 5119, 5125 (1961). See also C. W. Schimelpfenig, *ibid.*, **27**, 3323 (1962).

[3] (a) I. R. Schmolka and P. E. Spoerri, *J. Am. Chem. Soc.*, **79**, 4716 (1957); (b) E. D. Bergmann and A. Kaluszyner, *Rec. trav. chim.*, **78**, 289 (1959); (c) "The Chemistry of Penicillin," ed. by H. T. Clarke, J. R. Johnson, and R. Robinson, Princeton University Press, Princeton, N. J., 1949, pp. 921 ff.

$CHNHCH_2CH_3$. The mechanism of this unexpected reaction is under investigation; overreduction does not occur with sodium borohydride. Examples of the reaction are shown in the table. The yields refer to distilled materials.

| R | R′ | Yield, % |
|---|---|---|
| *n*-$C_4H_9$ | H | 60[a] |
| $C_6H_5$ | H | 70[a] |
| $C_2H_5$ | $CH_3$ | 35[a] |
| $C_6H_5$ | $CH_3$ | 56[b] |
| Cyclohexylidene | | 57[a] |
| 4-*t*-Butylcyclohexylidene[c] | | 65[d] |
| 3-Cholestanylidene[e] | | 75[f] |

[a] Identical in physical properties and infrared spectrum with sample prepared by Reynolds and co-workers; *cf*. ref. 2. We are grateful to Dr. Reynolds for the infrared spectra of his samples. [b] B.p. 127–128° (7 mm.). *Anal*. Calcd. for $C_{10}H_{15}NS$; C, 66.24; H, 8.34; N, 7.73. Found: C, 66.21; H, 8.46; N, 7.72. [c] M.p. 57–58°. *Anal*. Calcd. for $C_{12}H_{23}NS$; C, 67.56; H, 10.87; N, 6.57. Found: C, 67.93; H, 10.93; N, 6.44. Stereochemistry undetermined. [d] B.p. 116.5° (1 mm.). *Anal*. Calcd. for $C_{12}H_{25}NS$: C, 66.91; H, 11.70; N, 6.51. Found: C, 66.95; H, 11.60; N, 6.57. [e] C. Djerassi, N. Crossley, and M. A. Kielczewski, *J. Org. Chem.*, **27**, 1112 (1962). [f] M.p. 142–143°. *Anal*. Calcd. for $C_{29}H_{53}NS$; C, 77.78; H, 11.93; N, 3.13. Found: C, 77.49; H, 11.92; N, 3.11.

The following preparation will exemplify the method: To a stirred solution of 15 g. of 2-phenylthiazolidine in 350 ml. of anhydrous ether, 37 ml. of a 0.93 *M* solution of lithium aluminum hydride was added dropwise over a period of 15 min., followed by boiling at reflux for 30 min. The solution was cooled, 4 ml. of water was added, and the precipitated metal hydroxides were filtered with the aid of Celite. The filtrate was dried over magnesium sulfate and concentrated to give 13.3 g. of crude product; another 1.3 g. was recovered from the precipitate by dissolution in aqueous sodium potassium tartrate (200 ml., 20%) and ether extraction. The product (10.7 g., 70%) distilled at 105–108° (1–1.5 mm.), $n^{25}D$ 1.5594; its infrared spectrum was essentially identical with that of N-benzyl-2-mercaptoethylamine,[2] b.p.[2] 101° (0.7 mm.), $n^{25}D$ 1.5598.[2] Reduction of 2.8 g. (0.018 mole) of the thiazolidine derived from cyclohexanone with 2 g. (0.053 mole) of sodium borohydride in propanol-2 (2.5 hr., *ca.* 55°) gave 1.7 g. (60%) of N-cyclohexyl-2-mercaptoethylamine.

The stereochemistry of the product was checked in the reduction of the thiazolidine derived from 4-*t*-butylcyclohexanone (itself of unknown stereochemistry). Excess lithium aluminum hydride yielded 4-*t*-butylcyclohexyl-N-ethylamine in 90% yield; comparison of the infrared spectrum of the product with spectra of *cis*- and *trans*-4-*t*-butylcyclohexyl-N-ethylamine (from the corresponding N-acetyl-4-*t*-butylcyclohexylamines by lithium aluminum hydride reduction) and mixtures thereof indicated the product to be over 85% *trans* (equatorial) isomer.

The facile reduction of thiazolidines to β-mercaptoethylamines is of particular interest in the light of a recently reported synthesis of the latter[4] in which some pains were taken to circumvent such a reduction by first opening the thiazolidines with iodine or by carrying out the condensation of their carbonyl precursors not with mercaptoethylamine but with its disulfide prior to sodium borohydride reduction. It should also be pointed out that thiazolidines may be intermediates in the hydride reduction of N-substituted 2-phenyl-4-thiazolidinones to N-substituted β-mercaptoethylamines.[3a]

This work was supported by Petroleum Research Fund grant 266-A and by National Institutes of Health grant RG-8848.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

ERNEST L. ELIEL
ERNEST W. DELLA
MILORAD M. ROGIĆ

RECEIVED SEPTEMBER 24, 1962

---

[4] T. P. Johnston and A. Gallagher, *J. Org. Chem.*, **27**, 2452 (1962).

---

## A Novel Synthesis of Quinolines and Dihydroquinolines

*Sir:*

In the preparation of 1,1-dimethyl-*N*(*p*-tolyl)-propargylamine (I) by Hennions's method[1] (alkylation of *p*-toluidine with 3-chloro-3-methyl-1-butyne using copper as a catalyst), the formation of an unexpected isomeric by-product was observed. This material (b.p. 73° at 0.08 mm., $n^{25}D$ 1.5760; hydrochloride m.p. 129–130°; C, H, N analysis of free base and of hydrochloride satisfactory) was not acetylenic; an IR band in the free base at 2.96 μ was not seen in the hydrochloride and hence is attributed to NH. Hydrogenation resulted in the absorption of only one mole of hydrogen.

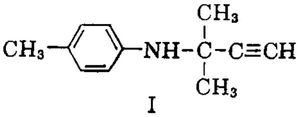
The assignment of the dihydroquinoline structure (II) was confirmed by the n.m.r. spectra of this material and its hydrogenated derivative.

The n.m.r. spectrum of the hydrochloride salt of II showed single bands at 8.30 τ (6H), assigned to the two methyl groups at $C_2$; at 7.65 τ (3H), assigned to the methyl group at $C_6$; and at 2.98 τ (1H) (overlapping a doublet), assigned to the proton at $C_5$. A typical AB pattern with doublets centered at 4.19 τ (1H), 3.49 τ (1H), and a coupling constant of 12 c.p.s. was seen for the hydrogens at $C_3$ and $C_4$. The remaining aromatic protons were doublets centered at 2.89 τ (1H) and 2.22 τ (1H).

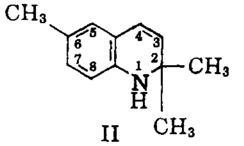
The n.m.r. spectrum of the hydrochloride salt of the hydrogenated material showed single bands at 8.48 τ (6H), 7.66 τ (3H), and at 2.85 τ (1H) (overlapping a doublet); triplets centered at 7.91 τ (2H) and 7.08 τ (2H); and doublets centered at 2.84 τ (1H) and 2.25 τ (1H).

---

[1] G. F. Hennion and R. S. Hanzel, *J. Am. Chem. Soc.*, **82**, 4908–4912 (1960).



I



II

Further evidence for this unusual cyclization reaction was obtained from the facts that (a) I could be cyclized to II under the original alkylation conditions; (b) in the same way quinoline was obtained from *N*-propargylaniline (presumably through the intermediacy of 1,2-dihydroquinoline); (c) either quinaldine or lepidine could be prepared when the appropriately substituted propargylaniline was used. Treatment of aniline hydrochloride with 3-methyl-1-butyne-3-ol in methanol for 18 hours at 200° failed to produce either I or II.

The use of silver chloride as the catalyst in the treatment of the 3-chloro-3-methyl-1-butyne with *p*-toluidine allowed the isolation of the acetylenic amine (I), in a 60% yield, contaminated by only a small amount of the dihydroquinoline (II). I was converted to II in an 87% yield by refluxing for three days a mixture of I in aqueous ether, using copper powder and/or cuprous chloride as catalysts.

Further studies of the generality of this reaction are now under way and will be reported in detail at a later date.

THE LILLY RESEARCH LABORATORIES
ELI LILLY AND COMPANY
INDIANAPOLIS, INDIANA

NELSON R. EASTON
DONALD R. CASSADY

RECEIVED AUGUST 24, 1962

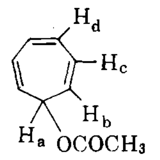
---

## Carbon–Carbon Bond Formation in Catalytic Hydrogenolysis: Differences in Behavior of Adsorbed Isomeric $C_7H_7$ Radicals[1]

*Sir:*

Catalytic cleavage with hydrogen of a C-X bond results, in general, solely in the replacement of X by hydrogen. Coupling products have been observed in the hydrogenolysis of benzotrichloride,[2] and in the desulfurization of sulfur compounds with degassed Raney nickel or nickel.[3] The conversion of aromatic halides to biaryls with palladium catalysts in alcoholic base requires no hydrogen and differs from catalytic hydrogenolysis in the usual sense.[4] There is no previous record of coupling of purely hydrocarbon groups under classical, neutral hydrogenolysis conditions. We have found that such coupling occurs extensively with certain 7-substituted cycloheptatrienes, but is totally absent with their benzylic isomers.

A mixture of cuprous bromide (0.13 g.), cycloheptatriene (92.0 g.), and *t*-butyl peracetate (52.8 g.) in benzene was refluxed for 24 hr.[5] Distillation afforded 0.9 g. of 7-*t*-butoxycycloheptatriene and 18.8 g. (31%) of cycloheptatrienyl acetate (I)[6], b.p. 70° (3.6 mm.), $n^{22.5}\text{D}$ 1.5104, $\lambda_{\text{max}}^{C_6H_{12}}$ 256 m$\mu$ (log $\epsilon$, 3.73) $\nu_{\text{max}}^{\text{neat}}$ 696, 727, 741, and 1735 cm.$^{-1}$. *Anal.* Calcd. for $C_9H_{10}$: C, 72.0; H, 6.7; mol. wt., 150; Found: C, 72.0; H, 7.15; mol. wt., 160. The structure of I is confirmed by its n.m.r. spectrum[7] ($\tau$ values in p.p.m.: 8.49, singlet ($CH_3$); 5.47, triplet ($H_a$); 4.97, quadruplet ($H_b$); 4.25, quadruplet ($H_c$); 3.84, doublet ($H_d$); $J_{ab}$ = 5.0 c.p.s., $J_{bc}$ = 9.4 c.p.s., $J_{cd}$ = 3.0 c.p.s.), and its quantitative conversion to tropylium bromide and acetic acid with hydrogen bromide. Hydrogenation of I (1.0 g.) in ethyl acetate at room temperature and atmospheric pressure with 5% palladium–charcoal (0.50 g.) resulted in the uptake of 3.25 molar equivalents of hydrogen. Distillation gave only dicycloheptyl. Interrupting the hydrogenation after absorption of 0.64 molar equivalents of hydrogen furnished ditropyl.



I

The quantitative experiments presented in the table were carried out under comparable conditions (1–2 mmoles of compound with 150–250 mg. of 5% palladium–charcoal in 3 ml. of ethyl acetate at room temperature and atmospheric pressure), and the products were determined by gas–liquid chromatography. The extent of dicycloheptyl formation is evidently not independent of the substituent. Simple reduction is significant with the ethers, but hydrogenolysis to cycloheptane competes favorably with coupling only with the amine.[8] 7-Benzyloxycycloheptatriene, which affords a direct comparison of the reductive cleavage of the isomeric $C_7H_7$ groups, gave only about 10% of products (cyclo-

---

[1] Chemistry of Cycloheptatriene. III. K. Weiss and Sister M. Lalande, C.S.J., *J. Am. Chem. Soc.*, **83**, 3117 (1960), and J. M. Cinnamon and K. Weiss, *J. Org. Chem.* **26**, 2644 (1961) are considered parts I and II respectively.

[2] W. Borsche and G. Heimburger, *Ber.*, **48**, 452 (1915); M. Busch and H. Stöve, *ibid.*, **49**, 1063 (1916).

[3] G. M. Badger and W. H. F. Sasse, *J. Chem. Soc.*, 3862 (1957); G. Badger, N. Kowanko, and W. H. F. Sasse, *ibid.*, 1658 (1960); H. Hauptmann, W. F. Walter, and C. Marino, *J. Am. Chem. Soc.*, **80**, 5832 (1958) and earlier papers.

[4] M. Busch and W. Weber, *J. prakt. Chem.*, **146**, 1 (1936); R. Baltzly and A. P. Phillips, *J. Am. Chem. Soc.*, **68**, 261 (1946); F. R. Mayo and M. D. Hurwitz, *ibid.*, **71**, 776 (1949).

[5] *Cf.*, M. S. Kharasch, G. Sosnovsky, and N. C. Yang, *ibid.*, **81**, 5819 (1959).

[6] The reaction of dicycloheptatrienyl ether and acetic anhydride reported by M. E. Volpin, I. S. Akhrem, and D. N. Kursanov, *J, Gen. Chem. USSR*, **28**, 326 (1958), yields an inseparable mixture of I, tropone, and unchanged ether.

[7] Kindly taken by M. Melchior, Esso Research Engineering Company, Linden, N. J.

[8] Tropylium salts over platinum oxide reportedly give only cycloheptane [W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **76**, 3203 (1954); R. B. Turner, H. Prinzbach, and W. von E. Doering, *ibid.*, **82**, 3451 (1960)].

TABLE I
HYDROGENATION OF $C_7H_7X$ AND $C_6H_5CH_2X$

$C_7H_7$—

| X | Molar equiv. $H_2$ absorbed | Products (mole/mole $C_7H_7X$) $(C_7H_{13})_2$ | $C_7H_{14}$ | HX | $C_7H_{13}X$ | Other |
|---|---|---|---|---|---|---|
| $-OCOCH_3$ | 3.32 | 0.23 | 0 | 0.51 | 0.07 | [a] |
| $-OCH_3$ | 3.36 | 0.34 | 0.04 | 0.75 | 0.29 | |
| $-OCH_2C_6H_5$ | 3.16 | 0.25 | [b] | 0.53 | 0.30 | 0.20[c] |
| $-OC_4H_9$-*tert* | 3.33 | [d] | | | [d] | |
| $-N(CH_2)_5$ | 3.88 | 0.28 | 0.23 | [e] | 0 | [f] |

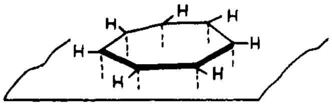
$C_6H_5CH_2$—

| X | Molar equiv. $H_2$ absorbed | Products (mole/mole $C_6H_5CH_2X$) $C_6H_5CH_3$ | HX | $(C_6H_5CH_2)_2$ |
|---|---|---|---|---|
| $-OCOCH_3$ | 0.76 | 0.63 | 0.75 | 0 |
| $-OCH_3$ | 0.87 | 0.92 | 0.72 | 0 |
| $-N(CH_2)_5$ | 0.78 | 0.85 | [e] | 0 |

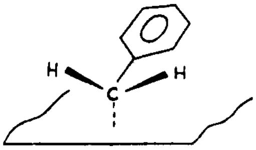
[a] Unidentified material *ca.* 0.04 mole. [b] Trace of cycloheptane possibly present. [c] Containing 0.06 mole of toluene, 0.03 mole of benzaldehyde, 0.02 mole of cycloheptanone, and 0.09 mole of cycloheptanol. [d] Approximately equimolar amounts of dicycloheptyl and cycloheptyl *t*-butyl ether; the pure saturated ether was not available for quantitative estimation. [e] Piperidine could not be detected on the columns used, but was isolated from the reaction mixture as its hydrochloride. [f] *Ca.* 0.08 mole of unidentified material.

heptanol and cycloheptanone) corresponding to scission of the benzyl–oxygen bond.

The formation of dicycloheptyl, and particularly the formation of ditropyl from I, can only be explained by the dimerization of cycloheptatrienyl (tropyl) radicals.[9] The planar tropyl radical, which has identical electron densities at each position, can be envisioned as $\pi$-bonded to the surface[10] (II). The benzyl radical, for which simple molecular orbital theory predicts that 4/7 of the odd electron is at the $CH_2$-group, is probably attached by an $sp^3$-bond (III). This arrangement retains *ca.* 40 kcal./mole of benzenoid stabilization, whereas a similar attachment of the tropyl radical would cause loss of most of its stabilization energy. Dimerization of tropyl radicals is favored by their symmetry, and by their strong attachment and consequent stabilization[11] and domination of the surface. Benzyl radicals, which are not stabilized to the same extent by the surface, and which can dimerize only in specific orientations, are more likely to react with hydrogen.



II



III

Neither dibenzyl, nor benzylcycloheptane were detected with any of the cycloheptatriene derivatives. These products might have arisen from the isomerization of tropyl to benzyl radicals, which has been estimated to be exothermic by about 20 kcal./mole in the gas phase.[12]

**Acknowledgment.**—Support of this work by a Frederick Gardner Cottrell grant from Research Corporation is gratefully acknowledged.

WM. H. NICHOLS CHEMICAL LABORATORY
NEW YORK UNIVERSITY
NEW YORK 53, NEW YORK
CHARLES M. ORLANDO, JR.

DEPARTMENT OF CHEMISTRY
NORTHEASTERN UNIVERSITY
BOSTON 15, MASSACHUSETTS
KARL WEISS[13]

RECEIVED AUGUST 6, 1962

---

[9] For previous speculations regarding the mechanism of hydrogenolysis see E. R. Alexander, A. G. Pinkus, and F. W. Stone, Brookhaven Conf. Rept., Chem. Conf. No. 4, 1950, p. 100; R. Baltzly and P. B. Russell, *J. Am. Chem. Soc.*, **75**, 5598 (1953); W. A. Bonner and J. A. Zderic, *ibid.*, **78**, 3218 (1956). Evidence for the participation of adsorbed radicals in hydrogenation is discussed by G. C. Bond, *Quart. Rev.* (London), **8**, 279 (1954); T. I. Taylor in "Catalysis," Vol. 5, P. H. Emmett, ed., Reinhold Publishing Corp., New York, N. Y., 1957, p. 257; C. Kemball, *Proc. Chem. Soc.*, 264 (1960); R. P. Eischens and W. A. Pliskin in "Advances in Catalysis," Vol. 10, D. D. Eley, *et al.*, ed., Academic Press, Inc., New York, N. Y., 1958, p. 1.

[10] *Cf.* J. J. Rooney, F. G. Gault, and C. Kemball, *Proc. Chem. Soc.*, 407 (1960).

[11] *Cf.* D. Bijl, H. Kainer, and A. C. Rose-Innes, *Nature*, **174**, 830 (1954).

[12] A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

[13] To whom inquiries should be addressed.

---

## Reaction of Benzyne with Acetylenic Compounds

*Sir:*

Diazotization of anthranilic acid, or a substituted anthranilic acid, yields an arenediazonium-2-carboxylate which can be pyrolyzed[1] or photolyzed[2] to produce benzyne or a substituted benzyne.[3] Earlier reports have described the reactions of benzyne, generated in this way, with dienes,[1] carboxylic acids,[1] *t*-butyl alcohol,[3] aryl azides,[4] and simple aromatic hydrocarbons such as benzene and naph-

---

[1] M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960).

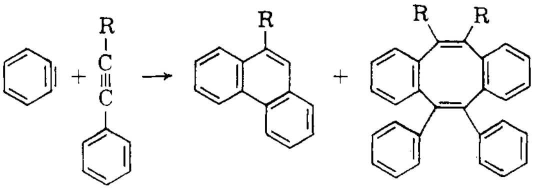
[2] R. S. Berry, G. N. Spokes, and M. Stiles, *ibid.*, **82**, 5240 (1960); **84**, 3750 (1962).

[3] M. Stiles, R. G. Miller, and U. Burckhardt, paper submitted to *J. Am. Chem. Soc.*

[4] R. Huisgen and P. Knorr, *Naturwissenschaften*, **48**, 716 (1961).

thalene,[5] as well as the dimerization and trimerization reactions.[2] This communication deals with the reaction of benzyne with compounds containing the acetylenic linkage. These latest results reveal a kind of reactivity not encountered in previous studies of the benzyne intermediate. In particular, the reaction of phenylacetylene takes a course altogether different from that of sodium phenylacetylide.[6]

Heating suspensions of benzenediazonium-2-carboxylate (I) in phenylacetylene (II, R = H) produced a hydrocarbon mixture from which two products could be readily isolated. Crystallization from ether or, more efficiently, chromatography on alumina, afforded a 29% yield of 5,6-diphenyldibenzo[*ae*]cycloöctatetraene (IV, R = H), m.p. 195.5–196.0°; the ultraviolet spectrum exhibited shoulders at 288 mμ (log ε 3.95) and 240 mμ (4.49). *Anal.* Found: C, 94.14; H, 5.77; mol. wt. 357.[7] From the more soluble fractions phenanthrene was isolated (8%).

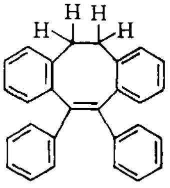


II III IV

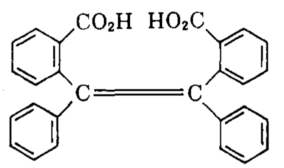
1-Phenylpropyne (II, R = $CH_3$) proved less reactive toward benzyne than phenylacetylene, but the recognizable products were analogous. 9-Methylphenanthrene (III, R = $CH_3$) was obtained in 3.6% yield, together with only 0.5% of 5,6-dimethyl-11,12-diphenyldibenzo[*ae*]cycloöctatetraene (IV, R = $CH_3$), m.p. 207–208°. *Anal.* Found: C, 93.71; H, 6.30. This hydrocarbon was identical with one prepared by Blomquist and Bottomley.[8]

Treatment of I with diphenylacetylene (II, R = $C_6H_5$) either in hexane solution or as the pure melt led to nearly complete recovery of the hydrocarbon and no recognizable products.

The hydrocarbon IV (R = H) rapidly absorbed one equivalent of hydrogen (palladium–charcoal) to form a dihydro derivative (V), m.p. 183–184°, $\lambda_{max}$ 283 mμ (log ε 4.04), shoulder 230 mμ (log ε 4.41). *Anal.* Found: C, 93.69; H, 6.11. The n.m.r. spectrum[9] of the dihydro compound exhibited, in addition to the aromatic proton resonances, a 12-line multiplet symmetrical about τ = 6.84; ratio of integrated intensities of aromatic and aliphatic protons was 4.6 to 1.0. The multiplet is apparently of the $A_2B_2$ type, which is consistent with the structure V if the ring is relatively rigid.



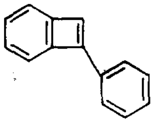
V



VI

Oxidation of hydrocarbon IV (R = H) with potassium permanganate in refluxing acetone gave a diacid (VI) m.p. 296–298° (68%). *Anal.* Found: 79.58; H, 4.89; neut. equiv., 217. (Methyl ester, m.p. 167–168°: Found: C, 80.28; H, 5.35.) The diacid was decarboxylated by heating with copper powder in refluxing quinoline for 1.5 hr. to tetraphenylethylene (34%). Oxidation of the diacid with alkaline permanganate gave *o*-benzoylbenzoic acid (8.5%).[10]

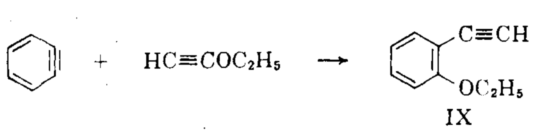
The hydrocarbon IV is apparently formed by dimerization of the benzocyclobutadiene VII.



VII

Whether phenanthrene is formed by a competing rearrangement of VII or by an independent 1,4-cycloaddition cannot be decided at present. The latter path is more consistent with the observation that the ratio of III to IV does not change appreciably when the reaction between I and II is carried out in ligroin solution rather than in pure II.

One attempt to extend the 1,2-cycloaddition reaction led to a surprising result. Ethoxyacetylene reacted with benzyne to produce a 37% yield of 2-ethoxyphenylacetylene IX, b.p. 42–44° (0.1–0.2 mm.) $n^{26}D$ 1.5529. *Anal.* Found: C, 87.98; H, 6.99. (Silver salt: Found: Ag, 42.0.) The compound IX was identical with a sample prepared by alkylation of 2-ethynylphenol[11] with diethyl sulfate.



IX

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF MICHIGAN
ANN ARBOR, MICHIGAN

MARTIN STILES[12]
URS BURCKHARDT
ARMIN HAAG

RECEIVED OCTOBER 9, 1962

---

(5) R. G. Miller and M. Stiles, paper submitted to *J. Am. Chem. Soc.*

(6) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **3**, 197 (1958).

(7) Determined from crystal density and unit cell volume, by Professor C. E. Nordman.

(8) C. G. Bottomley, thesis, Cornell University, 1961. We are grateful to Professor Blomquist for a sample of this compound.

(9) Obtained through the courtesy of Dr. J. Heeschen of the Dow Chemical Company.

(10) The diacid VI was also obtained by Blomquist and Bottomley (ref. 8) who proved the structure in the same way.

(11) V. Prey, *Chem. Ber.*, **76**, 156 (1943).

(12) Grateful acknowledgment is made of a grant from the Petroleum Research Fund of the American Chemical Society for financial support of this work.