

of freshly distilled *N*-chloro-2-methylbutyrophenonimines (**18** and **19**) with 6 g (0.03 mole) of silver tetrafluoroborate in 75 ml of 75% dioxane-water at 80° was carried out in the manner described in the general procedure to give 3.4 g of a product mixture. The mixture was analyzed by glpc which showed the presence of three components, one of which was 2-methylbutyrophenone (**20**). The two amides, *N*-phenyl-2-methylbutanamide and *N*-(2-butyl)benzamide, expected from this reaction could not be completely resolved on several columns under a variety of conditions. The glpc trace of the product mixture indicated the presence of both amides but their relative amounts could not be ascertained. The ketone to amide ratio was 58:42. The relative amounts of 2-methylbutyrophenone and *N*-(2-butyl)benzamide (**22**) could be determined by integration of the methinyl proton resonance signals in the nmr (Table I); this permitted the calculation of the constitution of the amide mixture to be 73% *N*-phenyl-2-methylbutanamide (**21**) and 27% *N*-(2-butyl)benzamide (**22**). Extraction of the reaction mixture with aqueous acid followed by basification and back-extraction into ether gave nothing. Similarly, extraction of the basified aqueous extract in the initial

work-up with ether gave nothing. Chromatography of the reaction mixture on alumina resulted in the separation of the ketone from the amides but did not separate the amides. The ketone was characterized by comparison of its infrared and nmr spectra with that of the authentic compound. Recrystallization of the amide mixture from ethanol resulted in a pure sample of *N*-phenyl-2-methylbutanamide (**21**), mp 109–111° (lit.²⁵ mp 110–111°), whose infrared and nmr spectra were identical with the authentic compound. The nmr spectrum of the amide mixture was similar (identical except for relative intensities) to the nmr spectrum of a synthetic mixture of the two amides. Furthermore, the presence of *N*-(2-butyl)benzamide in the reaction mixture was demonstrated by tlc in two different solvent systems.

Acknowledgment.—It is a pleasure to acknowledge the partial support of the Petroleum Research Fund administered by the American Chemical Society.

(35) P. E. Verkade, *Rec. Trav. Chim.*, **36**, 204 (1917).

Lead Tetraacetate. V. Effects of a Phenyl Group on the Formation of Ethers from Phenyl-Substituted Alkyl Alcohols^{1,2}

SUNG MOON AND PAUL R. CLIFFORD

Department of Chemistry, Adelphi University, Garden City, New York 11530

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The reactions of lead tetraacetate with phenyl-substituted alcohols were studied in order to determine the effects of a phenyl group on the course of the reaction. 3-Phenylpropanol yielded chroman, and 4-phenylbutanol and 5-phenylpentanol gave tetrahydrofuran derivatives but no tetrahydropyran derivatives. 1-Phenyl-1-butanol and 1-phenyl-2-pentanol yielded cleavage products and no cyclization products. Reaction mechanisms and possible intermediates are discussed in light of these results.

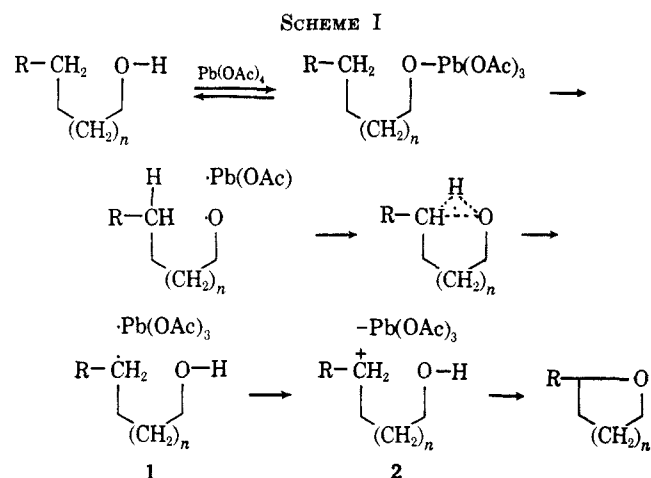
The reaction of lead tetraacetate with saturated, acyclic alcohols has been extensively studied by a number of workers.³ One of the principal products is a tetrahydrofuran derivative, although a small amount of the corresponding tetrahydropyran derivatives have also been isolated.

Mihailovic^{3b} has proposed the following mechanism for the formation of cyclic ethers (see Scheme I).

On the other hand, it was found that an ether oxygen, substituted at the proper carbon, caused the formation of six-membered ethers.^{3b} Presumably, the oxygen atom stabilizes such an intermediate as **1** or **2**, causing the formation of the six-membered ethers. With these results in mind, the reactions of lead tetraacetate with 3-phenylpropanol, 4-phenylbutanol, and 5-phenylpentanol were investigated in order to study the effect of a phenyl group on the course of the reaction.

Results

The results of these reactions are shown in Scheme II. The percentages listed are obtained from gas



chromatographic analysis of the reaction mixtures. The products were isolated by gas chromatography and identified by comparison of their infrared and nmr spectra with those of authentic samples.

In an attempt to obtain authentic samples of **9** and **12**, 1-phenyl-1-butanol (**14**) and 1-phenyl-2-pentanol (**15**), respectively, were treated with lead tetraacetate. Neither of the cyclization products were obtained, but considerable amounts of carbon-carbon bond cleavage products were obtained (Scheme III).

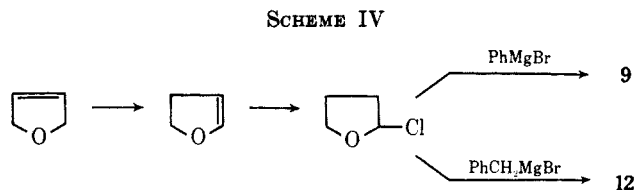
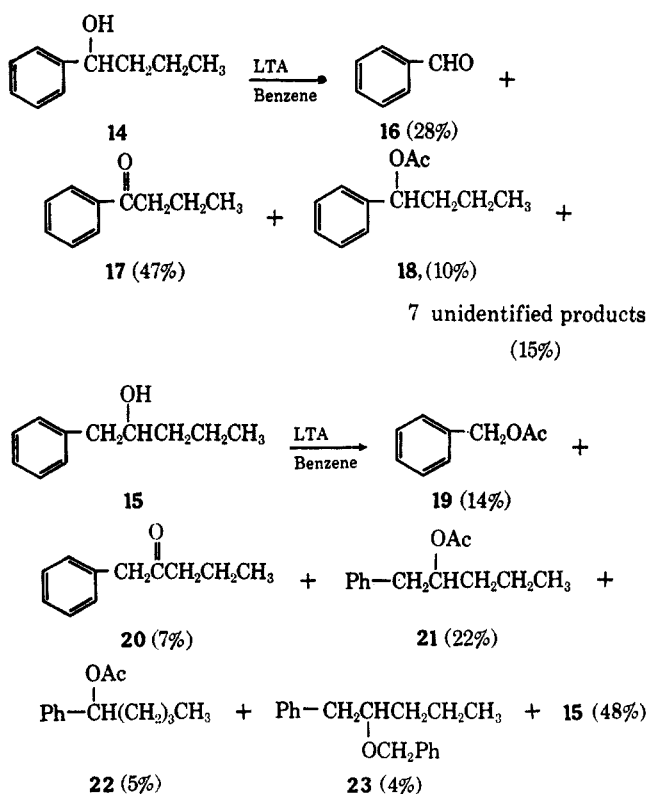
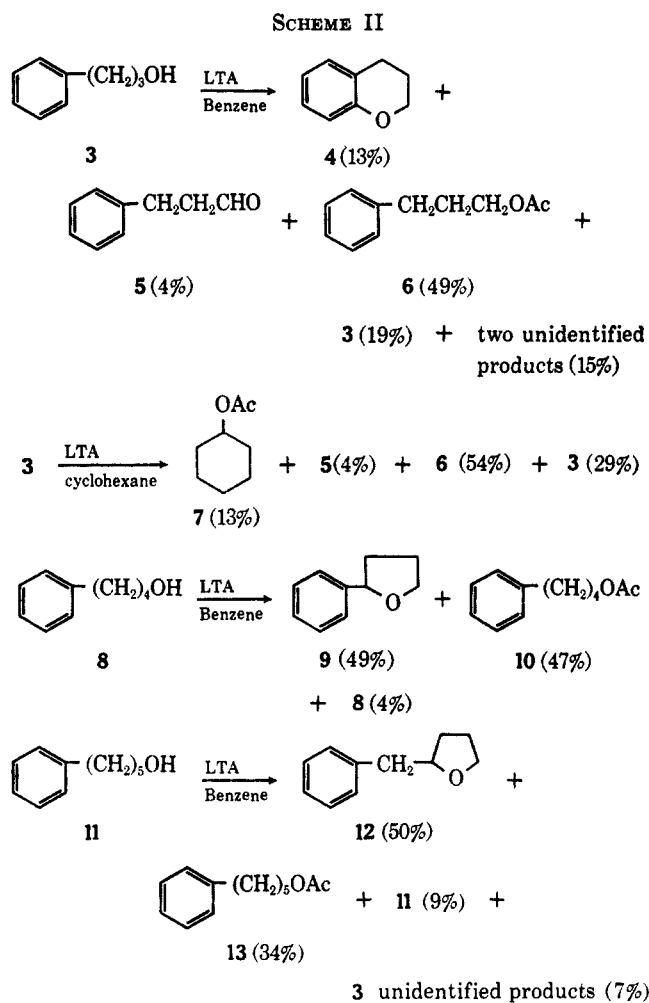
Authentic samples of **9** and **12** were obtained as shown in Scheme IV. The over-all yields were low. Therefore, lead tetraacetate oxidation of **8** and **11** is a

(1) Part IV: S. Moon and W. J. Campbell, *Chem. Commun.*, 470 (1966).

(2) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

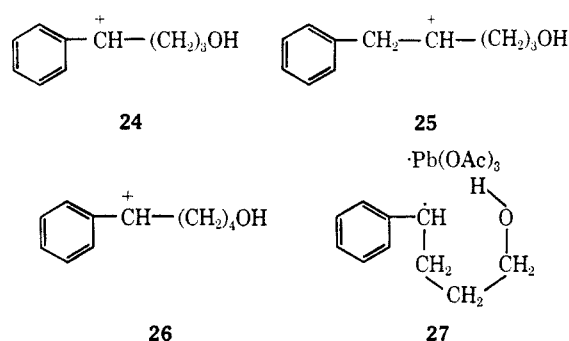
(3) For leading references, see (a) R. Criegee, "Oxidation in Organic Chemistry," Part A, K. B. Wiberg, Ed., Academic Press Inc., New York, N. Y., 1965, pp 278–366; (b) M. Lj. Mihailovic and M. Miloradovic, *Tetrahedron*, **22**, 723 (1966); (c) K. Heusler and J. Kalvoda, *Angew. Chem. Intern. Ed. Engl.*, **3**, 525 (1964).

synthetically useful procedure for **9** and **12** (Scheme II).



Discussion

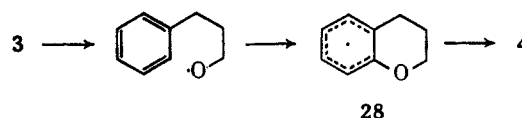
The most significant result of this work is that a phenyl group has little effect on the course of the reaction of alcohols with LTA. Thus, **8** and **11** gave only tetrahydrofuran derivatives and no tetrahydropyran derivatives. Furthermore, the yields of ethers **9** and **12** were about the same, although one would expect a higher yield of **9** because the phenyl group should stabilize intermediate **24**, but not **25**. Apparently, **26** is



not sufficiently stabilized by the phenyl group to yield a six-membered ether. As mentioned earlier, the oxygen atom in place of the phenyl group activates the carbon atom to which it is attached sufficiently to cause the formation of the tetrahydropyran derivative. Abstraction of a benzyl proton to form the benzyl free radical **27** would have to pass through a seven-membered, cyclic transition state. Apparently the low probability of such an abstraction occurring, combined with the inherent strain in such a seven-membered ring, are destabilizing factors overriding the expected stabilization by the phenyl group.

An intermediate such as **2** was also postulated by Jeger and co-workers⁴ in the formation of an ether from an optically active alcohol, (+)-4*R*-4,8-dimethylnonanol, on treatment with LTA. However, our work suggests that an intermediate **2**, if it exists, does not play an important role in determining the products.

It is interesting to note that 3-phenylpropanol yielded a cyclization product on treatment with LTA,⁵ whereas none was obtained from 2-phenylethanol.⁶ Presumably, cyclization of 3-phenylpropanol proceeds by the following path suggested by Mihailovic.^{3b}



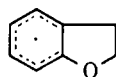
The transition state proposed involves the six-membered ring **28**. In the case of 2-phenylethanol, how-

(4) D. Hauser, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **47**, 1883 (1964).

(5) Recently, the formation of chroman (**4**) from 3-phenylpropanol on treatment with LTA was reported.^{3b}

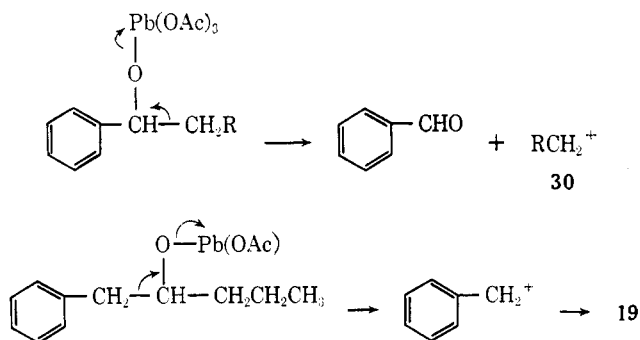
(6) S. Moon and J. M. Lodge, *J. Org. Chem.*, **29**, 3453 (1964).

ever, the transition state would involve the five-membered cyclic structure **29**. The latter transition state

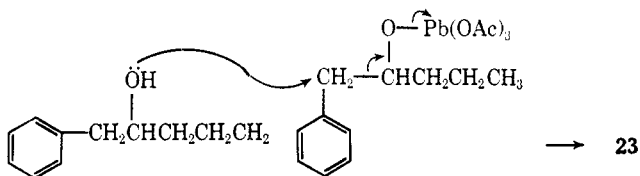
**29**

is probably of high energy and the competing reaction, leading to the cleavage product, benzyl acetate, may assume importance due to the stability of the intermediate benzyl free radical.⁷

Failure of the formation of **9** and **12** from **14** and **15** was unexpected. Secondary, aliphatic alcohols⁸ do form ethers on treatment with LTA. The formation of benzyl acetate from **15**, and benzaldehyde from **14**, can best be explained by the following mechanisms. However, in spite of a thorough search for their presence (by means of distillation and gas chromatography), no products arising from the intermediate **30** were detected.



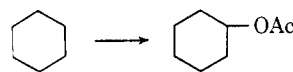
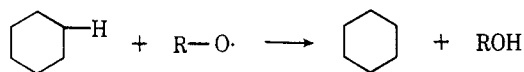
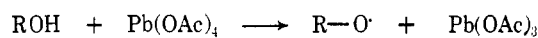
The formation of 2-(1-phenylpentyl) benzyl ether (**23**) can be rationalized by the following mechanism, similar to one proposed⁶ for the formation of 3-buten-1-yl allyl ether from 3-buten-1-ol.



The route by which the rearrangement product **22** is formed is not immediately apparent.

Noteworthy also is the difference in products obtained from 3-phenylpropanol in different solvents. In particular, while 13% of chroman (**4**) is formed in benzene, none is found in cyclohexane. On the other hand, 13% cyclohexyl acetate is formed in cyclohexane while no phenyl acetate is found in benzene. It was previously found⁹ that whenever an alcohol is treated with LTA in cyclohexane, a small amount of cyclohexyl acetate is obtained.

Cyclohexyl acetate may be formed by the following mechanism. The formation of cyclohexyl acetate strongly suggests that a free-radical mechanism¹⁰ operates in the reaction of LTA with alcohols.



Experimental Section¹¹

Reaction of 3-Phenylpropanol with LTA. A. In Benzene.—A mixture of 32.6 g of LTA, 10.0 g of 3-phenylpropanol, and 250 ml of benzene was refluxed for 18 hr. It was cooled to room temperature and was filtered. The precipitate was washed with 40 ml of benzene. The combined organic layers were washed with water, 10% Na₂CO₃, and water and dried over anhydrous magnesium sulfate. The organic layer was concentrated by distillation and the residue was distilled, yielding 7.1 g of product, bp 40–127° (0.2 mm). Gas chromatography (silicone rubber, programmed from 100 to 250°) showed seven components, four of which were identified¹² as 3-phenylpropanol (**5**, 4%), 2,3-benzo-5,6-dihydro-γ-pyrone (chroman) (**4**, 13%), 3-phenylpropanol (**3**, 19%), and 3-phenylpropyl acetate (**6**, 49%). The nmr spectrum of **4** had absorptions at τ 2.87 (4 H, multiplet), 5.90 (2 H, triplet, $J = 5$ cps), 7.27 (2 H, triplet, $J = 6$ cps), and 7.98 (2 H, triplet, $J = 5$ cps).

B. In Cyclohexane.—A mixture of 3.26 g of LTA, 1.0 g of 3-phenylpropanol, and 25 ml of cyclohexane was refluxed for 18 hr. It was cooled to room temperature and the products were isolated as described for the reaction in benzene. Gas chromatography (silicone rubber, programmed from 100 to 250°) showed four components which were identified¹² as cyclohexyl acetate (**7**, 13%), **5** (4%), **6** (54%), and **3** (29%).

3-Phenylpropanol.—3-Phenylpropanol was prepared from 3-phenylpropanol and LTA in pyridine according to the method of Partch.¹³ The product was isolated by gas chromatography (silicone rubber, 160°).

Reaction of 4-Phenylbutanol¹⁴ with LTA.—A mixture of 2.94 g of LTA, 1.0 g of 4-phenylbutanol, and 25 ml of benzene was refluxed for 18 hr. The products were isolated as described above. Distillation through a short-path distillation column gave 0.47 g of product, bp 42–99° (0.2 mm). Gas chromatography (silicone rubber, programmed from 100 to 250°) showed three components which were identified as 2-phenyltetrahydrofuran (**9**, 49%), 4-phenylbutanol (**8**, 4%), and 4-phenylbutyl acetate (**10**, 47%).

Reaction of 5-Phenylpentanol¹⁵ with LTA.—A mixture of 2.67 g of LTA, 1.0 g of 5-phenylpentanol, and 25 ml of benzene was refluxed for 18 hr. The products were isolated as previously described. Distillation through a short-path distillation column gave 0.48 g of product, bp 43–109° (0.2 mm). Gas chromatography (silicone rubber, programmed from 100 to 250°) showed six components, three of which were identified as 2-benzyltetrahydrofuran (**12**, 50%), 5-phenylpentanol (**11**, 9%), and 5-phenylpentyl acetate (**13**, 34%).

2-Chlorotetrahydrofuran.—2-Chlorotetrahydrofuran was prepared according to the method of Normant.¹⁶ 2,3-Dihydrofuran (15 g), obtained from 2,5-dihydrofuran,¹⁷ was treated with dry, gaseous hydrochloric acid at 0° for 25 min; large amounts of a black polymer were formed. The crude mixture was stirred under reduced pressure for 2 min and then was distilled, giving 2.5 g of product, bp 32–37° (20 mm). The product is a

(11) For gas chromatographic analysis, an F & M Model 720 gas chromatograph was used. Infrared spectra were recorded with a Perkin-Elmer Infracord Model 337 and a Varian A-60 nmr spectrometer was used to record the nmr spectra. Lead tetraacetate was purchased from Arapahoe Chemical, Inc., and used without purification.

(12) The products were isolated by gas chromatography and identified by comparison of their infrared spectra with those of authentic samples and by their retention times on gas chromatography.

(13) R. E. Partch, *Tetrahedron Letters*, 3071 (1964).

(14) Prepared from β -benzoylpropionic acid [L. F. Somerville and C. F. H. Allen, *Org. Syn.*, **2**, 81 (1943)] by Clemmenson reduction, followed by treatment with lithium aluminum hydride.

(15) Prepared from β -benzoylbutyric acid by the method described in ref 13.

(16) H. Normant, *Compt. Rend.*, **228**, 102 (1949).

(17) R. Paul, M. Fluchaire, and G. Collardeau, *Bull. Soc. Chim. France*, 668 (1950).

(7) The cleavage reactions may occur by an analogous carbonium ion.

(8) V. M. Micovic, R. I. Mamuzic, D. Jeremic, and M. Lj. Mihailovic, *Tetrahedron Letters*, 2091 (1963).

(9) S. Moon and E. Baum, unpublished results.

(10) J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 3609 (1965).

colorless liquid which decomposed on standing. It could be stored by keeping it in the cold and in the dark.

2-Phenyltetrahydrofuran.—Phenylmagnesium bromide was prepared from 0.75 g of bromobenzene and 0.3 g of magnesium. To the Grignard reagent was added 0.5 g of 2-chlorotetrahydrofuran in ether and the mixture was refluxed for 1 hr. It was then cooled, poured onto ice, and acidified with 5% sulfuric acid. The layers were separated and the ether layer was washed with water and was dried. The ether was removed by distillation, giving 0.9 g of crude product. 2-Phenyltetrahydrofuran was isolated by gas chromatography (silicone rubber, 140°). The nmr spectrum showed absorptions at τ 7.75 (5 H, singlet), 5.19 (1 H, triplet, $J = 7$ cps), 6.05 (2 H, multiplet), and 8.00 (4 H, multiplet).

2-Benzyltetrahydrofuran.—2-Benzyltetrahydrofuran (**12**) was prepared from 0.86 g of 2-chlorotetrahydrofuran and benzylmagnesium chloride. Isolation of the product as described before gave 1.1 g of crude product. The pure sample was isolated by gas chromatography (silicone, rubber, 120°). The nmr spectrum showed absorptions at τ 2.87 (5 H, singlet), 6.26 (3 H, a broad multiplet), 7.25 (2 H, triplet, $J = 5$ cps), and 8.28 (4 H, multiplet). Gas chromatography also indicated that small amounts of two other products were present, one of which had the same retention time as biphenyl.

Reaction of 1-Phenyl-1-butanol with LTA.—A mixture of 1.0 g of 1-phenyl-1-butanol, prepared from benzaldehyde and propylmagnesium bromide, 2.94 g of LTA, and 25 ml of benzene was refluxed for 18 hr. The crude product was isolated as described before and distillation through a short-path distilla-

tion column gave 0.52 g of product, bp 33–105° (0.2 mm). Gas chromatography (silicone rubber, programmed from 100 to 261°) showed ten components, three of which were identified¹² as benzaldehyde (**16**, 28%), phenyl propyl ketone (**17**, 47%), and 1-phenyl-1-butyl acetate (**18**, 10%).

Reaction of 1-Phenyl-2-pentanol with LTA.—A mixture of 2.67 g of LTA, 1.0 g of 1-phenyl-2-pentanol, and 25 ml of benzene was refluxed for 18 hr. The crude product was distilled through a short-path distillation column, giving 0.41 g of product, bp 32–152° (0.2 mm). Gas chromatography (silicone rubber, programmed from 100 to 261°) showed six components which were identified¹² as benzyl acetate (**19**, 14%), benzyl propyl ketone (**20**, 7%), 1-phenyl-2-pentanol (**15**, 48%), 1-phenyl-2-pentyl acetate (**21**, 22%), 1-phenyl-1-pentyl acetate (**22**, 5%), and 2-(1-phenylpentyl) benzyl ether (**23**, 4%).

2-(1-Phenylpentyl) Benzyl Ether.—A mixture of 0.13 g of sodium, 1.0 g of 1-phenyl-1-pentanol, and 40 ml of benzene was refluxed for 20 hr. It was cooled to room temperature and 0.75 g of benzyl chloride was added. The mixture was then stirred for 5 min and refluxed for 23 hr. After cooling to room temperature, 1.0 ml of methanol was added. This solution was washed with water until the washings were neutral. After drying over anhydrous magnesium sulfate, the benzene was removed by distillation. Gas chromatography (silicone rubber, 175°) indicated the presence of 2-(1-phenylpentyl) benzyl ether as well as some residual starting material. The nmr spectrum had absorptions at τ 2.80 (10 H, singlet), 5.60 (2 H, singlet), 6.42 (1 H, multiplet), 7.22 (2 H, doublet, $J = 5$ cps), 8.59 (4 H, multiplet), and 9.11 (3 H, multiplet).

10,12-Dihydrocyclohept[b]fluorene and Other Derivatives of Cyclohept[f]indene¹

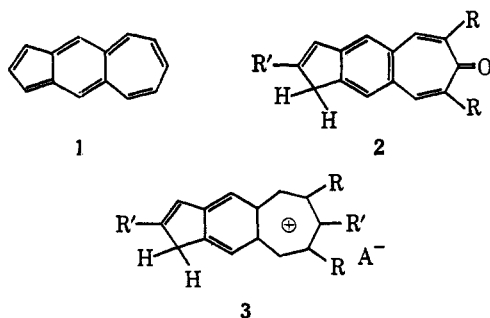
MARTIN G. GRIFFITH AND JOSEPH A. DIXON

Whitmore Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

Received June 2, 1967

A synthesis of 10,12-dihydrocyclohept[b]fluorene (**9**) and cationic (**10**) and anionic (**12**) derivatives is reported. Delocalization energies, charge densities, and bond orders were calculated for cyclohept[f]indene (**1**) and for cyclohept[b]fluorene (**4**). The theoretical results suggest that **1** and **4** should have as much aromatic character as azulene, although **4** may have more polyolefinic character. Attempts at formation of **4** by elimination of HBF₄ from **10** or by reaction of **10** with **12** were unsuccessful. The electronic spectra of **10** and **12** are related to those of fluorene and **9** and show significant bathochromic and hypsochromic effects.

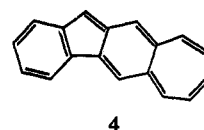
In recent years several attempts at synthesis of the cyclohept[f]indene (**1**) system have been reported. Derivatives such as **2** and **3** have been prepared by Bertelli^{2,3} (R = C₆H₅, R' = H) and by Bordwell and Winn⁴ (R = CH₃, R' = C₆H₅). Neither ketone dis-



played any tendency to exist in the enol form, according to nmr and infrared spectra. Furthermore the

tropylium salts, **3**, reacted with trimethylamine to produce polymeric material, rather than the fully unsaturated hydrocarbon formed by the elimination of HA.

This paper is a report on compounds related to a benzo derivative of **1**, cyclohept[b]fluorene (**4**).



Hückel and SCF Calculations.—In Table I are listed theoretical delocalization energies (DE's) for **1** and **4**; naphthalene and azulene are included for comparison. The values for DE per electron indicate that **1** and **4** should have at least as much resonance stabilization as azulene, although still less than ordinary benzenoid systems.

The Hückel and self-consistent field (SCF) charge densities and bond orders for azulene, cyclohept[f]indene, and cyclohept[b]fluorene are recorded in Tables II–IV. The densities and bond orders of **1** are very similar to those of azulene, a stable nonbenzenoid

(1) From the Ph.D. Thesis of M. G. G., June 1967.

(2) D. J. Bertelli, *J. Org. Chem.*, **29**, 3032 (1964).

(3) D. J. Bertelli, *ibid.*, **30**, 891 (1965).

(4) F. G. Bordwell and M. Winn, *ibid.*, **32**, 42 (1967).