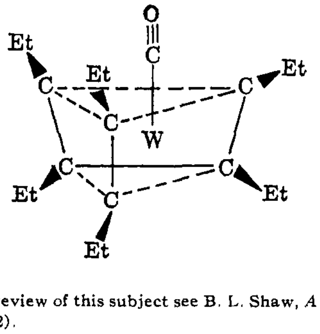
frared inspection of the oxidation residues showed no bands in the region of metal or organic carbonyl absorptions. Pyrolysis of I gave 3-hexyne with no evidence for hexaethylbenzene or other cyclic compounds that might be anticipated.[2]

The infrared spectrum is consistent with structure I. A single strong band at 2036 cm.$^{-1}$ is characteristic of a terminal metal carbonyl[3] and a band at 1702 cm.$^{-1}$ suggests an acetylene doubly π-bonded to a metal atom.[4]

The n.m.r. spectrum strongly supports the proposed structure. Whereas 3-hexyne has the typical A_2B_3 spectrum for ethyl groups consisting of a quartet and a triplet (2.30 and 1.24 p.p.m. from TMS, respectively), I has *two* equal quartets and *two* equal triplets [3.54 and 3.07 (quartets) and 1.34 and 1.09 (triplets) p.p.m. from TMS]. Since the quartets and triplets are of equal intensity, it suggests that all three acetylenic molecules are equivalent but that in each of the ligands one of the two ethyl groups is in a different environment from the other. The chemical shift of the CH_3 and CH_2 groups in the vicinity of the CO would not be expected to be the same as the ones extending in the opposite direction. Since in each case the CH_3 groups are further from the CO it is reasonable to expect less of a difference in the two types of CH_3 groups than in the two types of CH_2 groups, in excellent agreement with observation. In addition, some long-range spin coupling through the triple bond is seen in the spectrum of the hexyne, but not in the spectrum of the complex. This is further evidence that the triple bond is perturbed. The location of the multiplets is not consistent with the formation of a benzene type ring.

The effective atomic number for tungsten requires that a total of 10 electrons be donated by the acetylenic ligands. This could be accomplished if two of the three ligands served in the unusual capacity of four-electron donors, similar to that observed in the complexes $(R_3P)_2Pt$(acetylene),[4] or $ReCl(acetylene)_2$,[5] (which are also complexes of the heaviest metals in their respective sub-groups). Since the sharp proton magnetic resonance spectrum precludes paramagnetism and indicates all acetylenes are equivalent, the function of two-electron bonding and four-electron bonding must somehow be resonated throughout the entire hydrocarbon system. In this respect, this system might resemble that in cycloöctatetraeneiron tricarbonyl,[6] which shows equivalence of all hydrogens in solution, even though association of iron with the entire olefinic system would lead to a superfluity of electrons donated to the metal. In a single crystal, however, it was shown that the iron is associated with only one of the two diene systems in the ligand.[7] In view of the electron delocalization, (or at the very least a rapid tautomerism, in solution) a better representation of the bonding in I might be



Acknowledgment.—We are indebted to Miss Bonnie Ross for infrared interpretation, Dr. William Ritchey for n.m.r. interpretation and to Mrs. Jeanette G. Grasselli and Dr. Herbert Kaesz (Dept. of Chemistry, U.C.L.A.) for helpful discussions.

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RECEIVED MAY 3, 1963

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[2] For a recent review of this subject see B. L. Shaw, *Advan. Inorg. Chem. Radiochem.*, **4**, (1962).

[3] R. K. Sheline, *J. Am. Chem. Soc.*, **73**, 1615 (1951).

[4] J. Chatt, G. A. Rowe and A. A. Williams, *Proc. Chem. Soc.*, 208 (1957).

[5] R. Colton, R. Levitus and G. Wilkinson, *Nature*, **186**, 233 (1960).

[6] T. A. Manuel and F. G. A. Stone, *Proc. Chem. Soc.*, 90 (1959).

[7] B. Dickens and W. N. Lipscomb, *J. Am. Chem. Soc.*, **83**, 4862 (1961).

The Cyclohept(a)acenaphthylene Cation: Synthesis of a Pentaphenyl Derivative[1]

Sir:

The recent preparation of heptaphenylcycloheptatriene[2] by a Diels–Alder reaction of triphenylcyclopropene and tetraphenylcyclopentadienone suggests a general method for the synthesis of other difficultly accessible polyarylcycloheptatrienes,[3] which in turn may be readily converted to the corresponding polyaryltropylium ions.[4] A particularly attractive aryltropylium ion for synthesis and study, the cyclohept(a)acenaphthylene cation (I) is of interest because of similarity to the non-alternant hydrocarbon, fluoranthene, and unique ring fusion that allows extensive charge delocalization. The synthetic challenge of the cyclohept(a)acenaphthylene ring system is immense, apparently, as no derivatives have been reported prior to this work. We now wish to report the first entry into this ring system with the preparation of 7,8,9,10,11-pentaphenylcyclohept(a)acenaphthylene bromide (VI) and several interesting covalent derivatives.

The reaction of acecyclone (IIa)[5] and triphenylcyclopropene (IIIa) in refluxing xylene solution for 4–7 hr. yielded 70–75% of a crystalline orange solid, m.p. 304–306° (*Anal.* Calcd. for $C_{47}H_{32}$: C, 94.59; H, 5.41; mol. wt., 597. Found: C, 94.40; H, 5.56; mol. wt., 605) and 15–20% of a mixture of two unidentified crystalline ketones. Acetonitrile solutions of the hydrocarbon showed absorption maxima at 402 ($\log \epsilon$ 4.11), 339 (4.18), 303 (4.38) and 248 (4.64) mμ. The analytical and spectral data, including infrared, are consistent with the 9H-cyclohept(a)acenaphthylene structure IVa; however, the lack of model compounds in this series does not permit ruling out isomeric structures on these data alone. Accordingly the carboxylic acid IVb, m.p. 326–329° (*Anal.* Calcd. for $C_{42}H_{28}O_2$: C, 89.33; H, 5.00. Found: C, 89.52; H, 5.14), $\lambda_{\max}^{\mathrm{MeCN}}$ 397 (3.94), 339 (3.98), 297 (4.26) and 244 (4.60) mμ, was synthesized from acecyclone and diphenylcyclopropenecarboxylic acid (IIIb) in the above manner. The close similarity of the ultraviolet spectra of IVa and IVb suggests nearly identical chromophoric systems in support of the proposed structures.

Considering further the problem of possible isomerization under refluxing xylene conditions, the reaction of acecyclone with triphenylcyclopropene was run in refluxing benzene and in benzene–chloroform solution at room temperature.[6] The hydrocarbon product from

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[1] (a) This research was supported in part by the National Science Foundation, Grant No. GP-254, for which grateful acknowledgment is made; (b) Polyarylcycloheptatrienes. Part IV; (c) a preliminary report of portions of this work was presented at the 14th Annual Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tennessee, November, 1962.

[2] M. A. Battiste, *Chem. Ind.* (London), 550 (1961).

[3] Although alkylcyclopentadienones are generally unstable, with certain modifications it seems reasonable that this method may be extended to the preparation of alkylcycloheptatrienes.

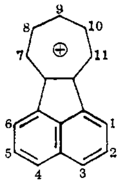
[4] *Cf.* M. A. Battiste, *J. Am. Chem. Soc.*, **83**, 4101 (1961).

[5] W. Dilthey, I. ter Horst and W. Schommer, *J. prakt. Chem.*, **143**, 189 (1935).

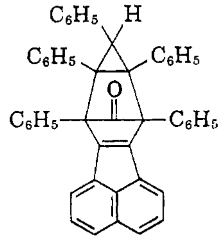
[6] Due to the limited solubility of acecyclone in cold organic solvents this reaction is extremely sluggish, taking 5–6 weeks to yield appreciable adduction products. In this interval considerable decarbonylation of the adduct V occurs despite the mild conditions of reaction and work-up.

each reaction was identical in all respects with the hydrocarbon obtained from the xylene reaction. In addition, the room temperature reaction yielded small amounts of a bright yellow crystalline ketone, m.p. 195–197° dec. (*Anal.* Calcd. for $C_{48}H_{32}O$: C, 92.28; H, 5.16. Found: C, 92.12; H, 5.14), formulated as V on the basis of its thermal behavior (vigorous evolution of gas on melting) and strong carbonyl absorption at 5.65 μ.[2,7]

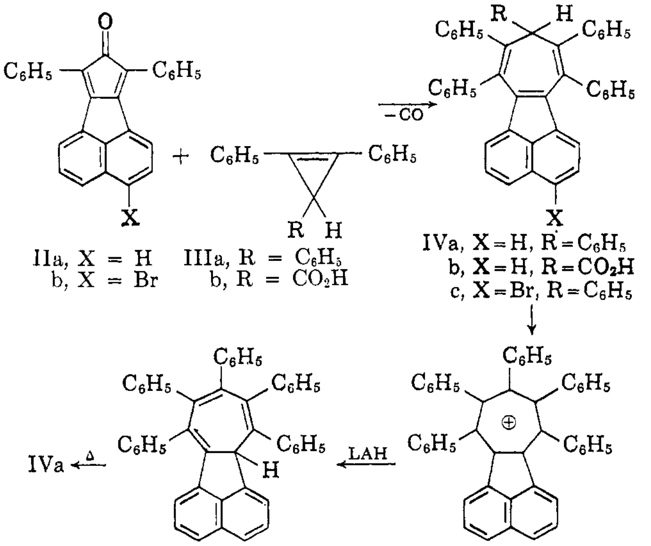
Solutions of IVa in bromine–carbon tetrachloride slowly evolved hydrogen bromide over a period of several days while depositing in very poor yields the crude amorphous bromide salt VI. The major product in almost 70% yield was a bromine-containing orange solid, m.p. 195–198° (*Anal.* Calcd. for $C_{47}H_{31}Br$: C, 83.55; H, 4.62; Br, 11.83. Found: C, 83.42; H, 4.38; Br, 11.96.), soluble in carbon tetrachloride, benzene and acetonitrile, λ_{max}^{MeCN} 410 (4.17), 342 (4.22), 309 (4.42) and 252 (4.67) mμ. It seemed clear that nuclear substitution of the naphthalene ring had occurred and that the 3-position was the most likely for attack. This was confirmed by direct comparison and identification of the brominated product with independently prepared IVc, available from triphenylcyclopropene (IIIa) and 3-bromoacecyclone (IIb), the latter prepared from 3-bromoacenaphthoquinone and dibenzyl ketone.



I



V



IIa, X = H
b, X = Br

IIIa, R = C_6H_5
b, R = CO_2H

IVa, X = H, R = C_6H_5
b, X = H, R = CO_2H
c, X = Br, R = C_6H_5

VII

VI

N-bromosuccinimide in refluxing carbon tetrachloride (catalytic amounts of azobisisobutyronitrile added) improved the yields of pure VI to about 30% after digestion of the crude solid in acetonitrile–acetone. The amorphous crimson salt, m.p. 321–324° dec. (*Anal.* Found: C, 83.36; H, 4.64; Br, 11.63) showed absorption maxima in acetonitrile solution at 475 (4.17), 355 (4.35) and 278 (4.35) mμ. Addition of one drop of ammonium hydroxide completely destroyed this spectrum with the appearance of new bands at 355 (4.13) and 337 (sh) (4.02) mμ, λ_{min} 311 (3.87) mμ. Fluoroboric acid restored the original spectrum with virtually no change, establishing the reversibility of hydrolysis without rearrangement.

Lithium aluminum hydride reduction of an ether suspension of VI afforded 78% of a crystalline yellow hydrocarbon isomeric with IVa (*Anal.* Found: C, 94.58; H, 5.42). The infrared and nuclear magnetic resonance spectra of this isomer bear close resemblance to the respective spectra of IVa; however, in the ultraviolet there are striking differences, the yellow isomer showing absorption at 340 (4.23) and 325 (sh) (4.11) mμ, λ_{min} 299 (3.94) mμ. This spectrum is similar to that for hydrolyzed solutions of VI although the bands are somewhat shifted to the blue. On heating to around 200° this same yellow hydrocarbon is converted to the apparently more stable 9H-isomer IVa. While this work was in progress, a report[8] of similar thermal isomerizations of substituted cycloheptatrienes appeared in which evidence was presented that isomerization occurred *via* a 1,5-transannular shift of hydrogen. Consideration of this evidence with the above chemical and physical data leads us to propose VII for the structure of the isomeric hydrocarbon. Further support for this structure was obtained on closer examination of the nuclear magnetic resonance spectra of both IVa and VII.[9] An explanation for the apparent mode of reduction, and perhaps for hydrolysis also, probably lies in steric approach control of the attacking nucleophile.[10]

Further studies of the cyclohept(a)acenaphthylene ring system are currently in progress with immediate attention focused on the preparation of the parent cation I. Simple molecular orbital calculations of the Hückel type suggest I should have unique stability among aryl-fused tropylium ions with a calculated gain in delocalization energy on ionization of 1.99–2.38 β.[11]

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[7] C. F. H. Allen, T. Davis, D. W. Stewart and J. A. VanAllan, *J. Org. Chem.*, **20**, 306 (1955).

[8] A. P. ter Borg, H. Kloosterziel and N. Van Meurs, *Proc. Chem. Soc.*, 359 (1962).

[9] The n.m.r. spectra will be reproduced and fully discussed later in a more detailed publication.

[10] *Cf.* K. Conrow, *J. Am. Chem. Soc.*, **83**, 2343 (1961), for pertinent data on isomer distribution obtained on complex hydride reductions of the methyltropylium ion.

[11] The author is grateful to Dr. J. Nordling and Mr. M. Alvarez of the Quantum Theory Project, University of Florida, for their invaluable aid in the computational programming for these calculations, the details of which will be published separately.

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RECEIVED MAY 4, 1963

The Stereospecific Acid- and Base-Catalyzed Ring Opening of a Substituted Cyclopropanol[1]

Sir:

We recently have reported several convenient methods for the synthesis of substituted cyclopropanols.[2] Our interest in these compounds was stimulated originally by reports of their tautomerization. Cottle,[3] for instance, noted that cyclopropanol was readily converted to propionaldehyde in basic solution. Cyclopropanols also undergo acid catalyzed tautomerizations. *We wish to report that cis-1-methyl-2-phenylcyclopropanol (I) is isomerized to 4-phenyl-2-butanone (II) by different, stereospecific pathways in acidic and basic solution.*

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[1] Supported by a grant from the National Science Foundation.

[2] C. H. DePuy, L. R. Mahoney and K. L. Eilers, *J. Org. Chem.*, **26**, 3616 (1961); C. H. DePuy, G. M. Dappen and R. A. Klein, *ibid.*, **27**, 3742 (1962).

[3] J. K. Magrane, Jr., and D. L. Cottle, *J. Am. Chem. Soc.*, **64**, 484 (1942).