and decompose any alkyl chlorosulfite present. The organic layer was separated, dried, and concentrated by evaporation of the ether. The extent of the reaction was determined by glpc analyses on an 11-ft Carbowax 20M column, 10% on 70–80 Anakrom AS, using a column temperature of 125° and a helium flow rate of 60 ml/min. The composition of the alkyl chlorides was determined by a combination of glpc and infrared analyses. Glpc analyses using a 20 ft × $\frac{1}{8}$ in. 10% tris(cyanoethoxy)propane on 110–120 Anakrom AS column (column temperature, 35°; injector, 45°; detector, 55°; nitrogen flow rate, 40 ml/min) gave the percentage composition of three components: Δ^2-cyclopentenylcarbinyl chloride, *trans*-2-chlorobicyclo[3.1.0]hexane and 4-chlorocychlohexene, and *cis*-2-chlorobicyclo[3.1.0]hexane. The structural identities of the alkyl chloride components in peaks two and three were established by nmr and ir comparison with authentic standards. The ratio of the components in the second peak (*trans*-2-chloride and 4-chlorocyclohexene) was determined by infrared analyses using base-line calculations employing the 780-cm^{-1} band of 4-chlorocyclohexene. An analytical sample of the only previously unreported chloride, Δ^2-cyclopentenylcarbinyl chloride, was prepared by glpc.

Anal. Calcd for C_6H_9Cl: C, 61.95; H, 7.80. Found: C, 61.91; H, 7.67.

The nmr spectrum (60 Mc) of Δ^2-cyclopentenylcarbinyl chloride shows a complex band for the two olefinic hydrogens centered at τ 4.27, an asymmetrical doublet at 6.58 (CH_2Cl), a complex splitting pattern for an allylic tertiary proton in the region 6.72–7.35, and a complex four-proton band in the region 7.40–8.70. A 100-Mc spectrum reveals that the absorption centered at τ 4.27 is an AB pattern (J_{AB} = 5.7 Hz, $\Delta\nu_{AB}$ = 17.1 Hz) with additional splitting by the three adjacent allylic (Al) protons ($J_{A\text{-}Al} \cong J_{B\text{-}Al} \cong$ 2Hz). The infrared spectrum shows a high-energy C–H stretching frequency at 3050 and a C=C band at 1600 cm^{-1}.

Registry No.—Δ^2-Cyclopentenylcarbinol, 13668-59-2; thionyl chloride, 7719-09-7; **6**, 13668-60-5.

Acknowledgment.—The authors gratefully acknowledge the generous support of this research by the Air Force Office of Scientific Research (AF-34-65) and the National Science Foundation (Grant GP-6228).

A Convenient Synthesis of the True 6,7-Acechrysene

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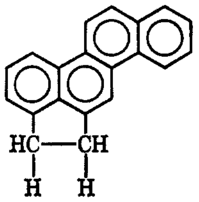
Received April 26, 1968

A general interest in the spectral properties of dialkyl chrysenes led us to synthesize 6,7-acechrysene (I). Previous attempts to synthesize this compound had led to compounds with physical data that did not fit the structural assignment.[1,2]

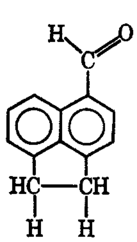
Our method of preparation of I began with the formylation of acenaphthene to form 5-acenaphthenecarboxyaldehyde (II). Treatment of 5-acenaphthenecarboxyaldehyde with benzylmagnesium chloride gave a carbinol which was dehydrated with potassium hydrogen sulfate to the known 5-styrylacenaphthene (III).[3] Photocyclization of III with ultraviolet light was by methods described by Mallory and coworkers.[4,5]

The structure for I is based upon identification of the chrysene nucleus by ultraviolet spectrophotometry and nmr spectrometry. 1-Methylchrysene has ultraviolet maxima at 260, 269, 297, 310, and 323 mμ; I has ultraviolet maxima at 262.5, 272, 302, 314.5, and 329 mμ. Chrysene has well separated complex band chemical shifts centered at (tetramethylsilane = 0) 458, 477, and 521 cps with an applied frequency of 60 Mc.[6] I has chemical shift bands at 448, 465 and 503 cps. Identification of the ace grouping in I is based upon a chemical shift of 182 cps and a parent mass of 254. Assignment of the ace-group substitution on the chrysene nucleus is based upon the method of synthesis (migration of methyl groups during photocyclization has never been noted) and comparison of the infrared spectra of I (11.8, 12.4, 13.2, and 13.4 μ) with 6-methylchrysene (11.5, 12.2, and 13.2 μ). Aromatic adjacent free hydrogen out-of-plane vibration analysis indicates that substitution is in position 6 and 7 of the chrysene ring.

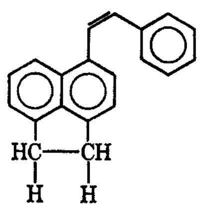
The above physical data is sufficient evidence that compound I is 6,7-acechrysene. The compound (mp 181–182°; C, 93.99; H, 6.18) reported by Fieser, *et al.*,[1] in the attempted synthesis of 6,7-acechrysene by a dehydrogenation of dihydroacechrysene was not 6,7-acechrysene.[7] The compound reported by Vardanyan, *et al.*[2] (mp 238–239°; uv maxima 283, 294, 306 and 318 mμ), in the attempted synthesis of 6,7-acechrysene by the dehydration and dehydrogenation of 3-keto-1,2,3,11,12,12a-hexahydro-6,7-acechrysene was also not 6,7-acechrysene. It must be reemphasized that substituted aromatics prepared by dehydrogenation at high temperatures and/or with strong catalysts before the advent of infrared spectroscopy, mass spectrometry and proton resonance spectrometry should be critically examined for correct structural assignment.[8]



I



II



III

Experimental Section[9]

5-Acenaphthaldehyde (II) was prepared by methods described by Hinkel, *et al.*[10] (yield 70%), and Fieser and Jones[11] (yield

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[1] L. F. Fieser, M. Fieser, and E. B. Hershberg, *J. Amer. Chem. Soc.*, **58**, 1463 (1936).

[2] S. A. Vardanyan, P. A. Zagorets, and G. T. Tatevosyan, *Zh. Obshch. Khim.*, **23**, 867 (1953).

(3) G. Drefahl and K. Ponsold, *Chem. Ber.*, **93**, 472 (1960).

(4) F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. Savitz, *J. Amer. Chem. Soc.*, **84**, 4361 (1962).

(5) C. S. Wood and F. B. Mallory, *J. Org. Chem.*, **29**, 3373 (1964).

(6) R. H. Martin, N. Defay, F. Geerts-Evrard, and S. Delavarenne, *Tetrahedron*, **20**, (4), 897 (1964).

(7) L. F. Fieser, Harvard University, personal communication, 1968.

(8) A. Lacassagne, N. P. Buu-Hoi, F. Zajdela, and F. A. Vingiello, *Naturwissenschaften*, **55**, (1), 43 (1968).

85%). The time-consuming steam distillation purification method by Fieser was eliminated and replaced with Hinkel sodium bisulfite product purification procedure without loss of yield. Recrystallizations from ethanol–water gave pale yellow crystals: mp 87–88° (lit.[10] mp 87–88°); infrared λ_{max}^{KBr} 6.0 (CO), 6.3 (aromatic C═C), 6.7, 8.3, 8.7, 10.9, 12.0, and 12.9 μ; mass spectrum (70 eV) *m/e* (relative intensity) 153 (1000), 182 (943), 152 (585), 181 (413), 76 (366).

5-Styrylacenaphthene (III).—A Grignard reagent was prepared from 1.75 ml (0.015 mol) of benzyl chloride in 25 ml of anhydrous ether. A mixture of 1.85 g (0.01 mol) of II and 500 ml of anhydrous benzene was added and the resulting mixture was refluxed 2 hr. This mixture was decomposed with 1 *N* H_2SO_4. The organic layer was separated, concentrated (2.5 g) and combined with 0.17 g of potassium hydrogen sulfate. The mixture was heated 10 min at 200°. The residue was dissolved in an excess of benzene and passed through a 15 × 2 cm alumina column using hexane as the eluting solvent. Fractions (100 ml) yielded 0.40 g (30%) of III from fractions 3, 4 and 5: mp 96° (MeOH) [lit.[3] mp 94° (MeOH)]; infrared λ_{max}^{KBr} 6.3 (aromatic C═C), 6.7, 10.4 (*trans* HC═CH), 12.0, 12.3, 13.0 (shoulder), 13.5 and 14.6 μ; mass spectrum (70 eV) *m/e* (relative intensity) 256 (1000), 255 (321), 257 (279), 128 (217), 119.5 (192).

6,7-Acechrysene (I).—Eastman Spectro Grade cyclohexane (400 ml), 0.0292 g (1.2×10^{-4} mol) of iodine and 0.2054 g (8×10^{-4} mol) of III were placed in a 2 l. round-bottomed flask fitted with a 3 in. Vycor filter disk and reflux condenser. This mixture was irradiated with a 140-W Hanovia Quartz lamp for 4 hr. The solvent was evaporated and the residue eluted through a 15 × 2 cm basic alumina column with benzene. Recrystallization of the residue from ethanol–benzene (1:1) gave 0.15 g (74%) of I: mp 185° (*Anal.* Calcd for $C_{20}H_{14}$: C, 94.45; H, 5.55. Found: C, 94.63; H, 5.52); ultraviolet $\lambda_{max}^{cyclohexane}$ 272 mμ (ε 2.09×10^5), 262.5 (1.06×10^5), 329 (2.01×10^4), 314.5 (1.98×10^4), 302 (1.60×10^4); infrared λ_{max}^{KBr} 6.2, 6.3 (aromatic C═C), 11.6, 12.4, 13.2, 13.4 μ; mass spectrum (70 eV) *m/e* (relative intensity) 126 (1000), 254 (906), 113 (612), 127 (580), 125 (540); nmr (C_6D_6) δ 3.04 (CH_2), 8.39 (H-β, m), 7.75 (H-α, m), and 7.46 (H-α3, m).

Registry No.—I, 4766-40-9.

Acknowledgment.—We would like to thank Dr. Morton Jacobs of International Flavor and Fragrances, Inc., for obtaining the nmr spectrum.

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[9] Melting points were determined in a capillary and were uncorrected. Infrared, ultraviolet, nmr and mass spectra were taken on a Perkin-Elmer 521 spectrophotometer, Beckman DK-2 spectrophotometer, Varian HA-100 spectrometer and CEC 104 mass spectrometer. The alumina used for chromatography was basic alumina from Arthur H. Thomas. Elemental analyses were performed by Galbraith Laboratories.

[10] L. E. Hinkel, E. E. Ayling, and J. H. Beynon, *J. Chem. Soc.*, 339 (1936).

[11] L. F. Fieser and J. E. Jones, *J. Amer. Chem. Soc.*, **64**, 1666 (1942).

Organolithium Compounds and Acetylenes. VI. p-Chlorodiphenylacetylene[1]

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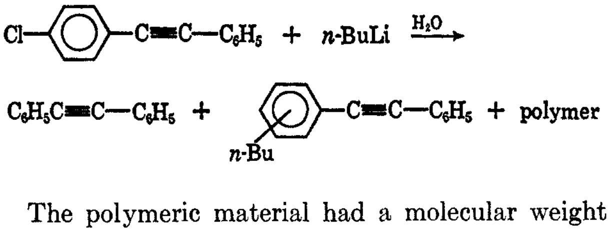
To determine the effect of substituents on addition, metalation, and electron-transfer reaction of organolithium compounds and acetylenes, *p*-chlorodiphenylacetylene was prepared and its reaction with *n*-butyllithium was studied.[2]

The reaction of *o*-chlorodiphenylacetylene and *n*-butyllithium has recently been reported to give an 80% yield of 1-(*o*-chlorophenyl)-2-phenyl-1-hexene after hydrolysis.[3]

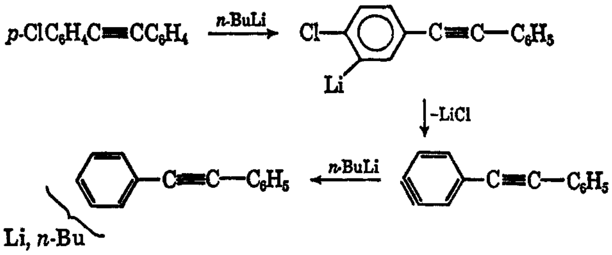
Our results with *p*-chlorodiphenylacetylene are markedly different. When 2.2 mol of *n*-butyllithium in ethyl ether were treated with 1.0 mol of *p*-chlorodiphenylacetylene, there was obtained after hydrolysis 14% diphenylacetylene, 27% an equimolar mixture of *n*-butyldiphenylacetylenes, 3% starting material, and a moderate amount of polymeric material (eq 1).



(1)

The polymeric material had a molecular weight of 2400, contained only a trace of chlorine, and had aromatic and aliphatic protons in approximately a 3:1 ratio. This mixture was not further identified.

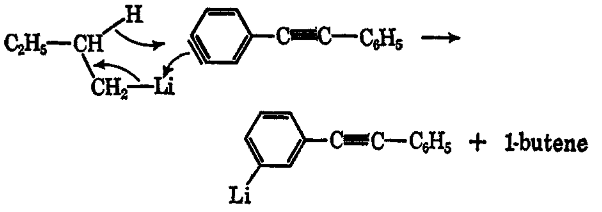
There is no precedent for direct nucleophilic substitution of chlorine by *n*-butyllithium under these conditions. It is most likely that the *n*-butyldiphenylacetylenes arise *via* a benzyne intermediate (eq 2).



(2)

This would yield two *n*-butyl derivatives in equal amounts as is observed. Although chloroaromatics do not generally yield benzyne intermediates under these conditions the electron-withdrawing effect of the acetylenic bond would be expected to facilitate metalation of the hydrogen *ortho* to the chlorine.

Diphenylacetylene could arise by direct halogen–metal interconversion but it could also arise from the benzyne as indicated in eq 3. This kind of phenomenon



(3)

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[1] (a) Research supported by AFOSR(SRC)-OAR, U. S. Air Force Grant No. 720-65. (b) For paper V, see J. E. Mulvaney, S. Groen, L. T. Carr, Z. G. Gardlund and S. L. Gardlund, *J. Amer. Chem., Soc.* **91**, 388 (1969).

[2] Unlike bromides and iodides an aromatic chloride does not generally undergo halogen–metal interconversion or induce *ortho* metalation when treated with organolithium compounds. H. Gilman and R. G. Jones, *Org. Reactions*, **6**, 342 (1951). H. Gilman and J. W. Morton, *ibid.*, **7**, 267 (1954).

[3] R. E. Dessy and S. A. Kandil, *J. Amer. Chem. Soc.*, **88**, 3027 (1966).