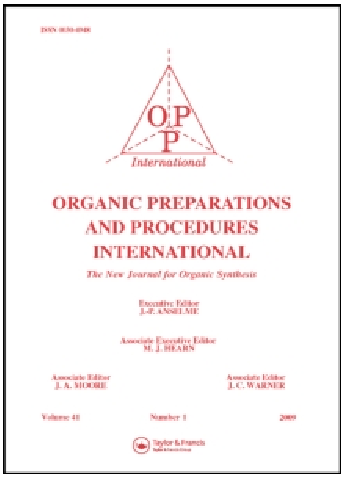


Organic Preparations and Procedures International

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

APPROACHES TO THE SYNTHESIS OF 1-DIPHEIWLCYCLOPROPENYLIDENE-4-(CYCLOPEIMTADIENYLIDENE)-2,5-CYCLOHEXADIENE

T. Niem[a]; M. D. Rausch[a]
[a] Department of Chemistry, University of Massachusetts, Amherst, Massachusetts

To cite this Article Niem, T. and Rausch, M. D.(1976) 'APPROACHES TO THE SYNTHESIS OF 1-DIPHEIWLCYCLOPROPENYLIDENE-4-(CYCLOPEIMTADIENYLIDENE)-2,5-CYCLOHEXADIENE', Organic Preparations and Procedures International, 8: 6, 271 — 278

To link to this Article: DOI: 10.1080/00304947609355641

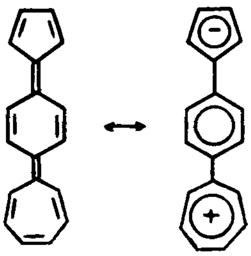
URL: http://dx.doi.org/10.1080/00304947609355641

ORGANIC PREPARATIONS AND PROCEDURES INT. 8(6), 271-278 (1976)

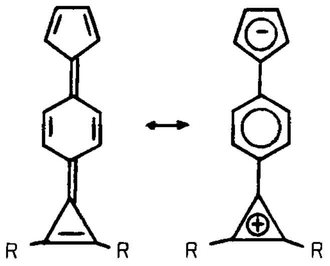
APPROACHES TO THE SYNTHESIS OF 1-DIPHENYLCYCLOPROPENYLIDENE-4-(CYCLOPENTADIENYLIDENE)-2,5-CYCLOHEXADIENE[†]

T. Niem and M. D. Rausch[*]
Department of Chemistry, University of Massachusetts
Amherst, Massachusetts 01003

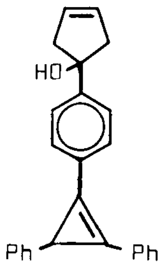
In the area of polycyclic cross-conjugated π-systems, the hydrocarbons I and II having an inserted p-phenylene ring between the two aromatic rings of sesquifulvalene and calicene, respectively, would be of interest in regard to their possible aromaticity. Several derivatives of I have recently been prepared.[1-3] However, the parent hydrocarbon IIa and its derivatives are still unknown. We now report the synthesis of carbinol III which could serve as a possible intermediate for the synthesis of the diphenyl derivative IIb.



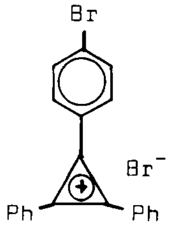
I



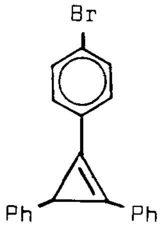
II a. R = H
b. R = Ph



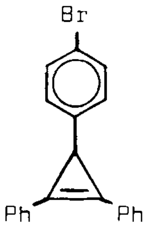
III



IV



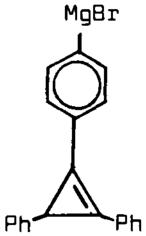
V



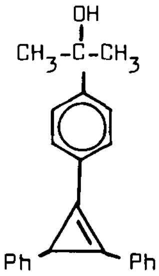
VI

1-p-Bromophenyl-2,3-diphenylcyclopropenium bromide IV was prepared in 84% yield from a reaction of p-bromodiphenylacetylene and benzal chloride followed by treatment with hydrogen bromide, according to the general procedure of Breslow and Cheng.[4,5] Salt IV was subsequently reduced with lithium aluminum hydride to give a mixture of two cyclopropene isomers, V and VI. One of these isomers was produced in a major amount, as judged by thin layer and gas chromatography of the products. Isomer V is assigned as the major product, since it would be anticipated as the major product on a statistical basis. After several crystallizations from ethanol, a single isomer (assigned as V) was obtained. The nmr spectrum of this product exhibited a singlet at τ 6.86, assigned to the methine proton of the cyclopropenyl group, while the IR spectrum contained a band at 1830 cm^{-1} which is characteristic of a cyclopropene ring bearing two phenyl substituents.[6]

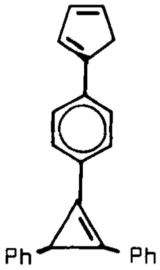
The Grignard reagent VII was prepared by treatment of 1-p-bromophenyl-2,3-diphenylcyclopropene V and an equivalent amount of 1,2-dibromoethane with magnesium in tetrahydrofuran. It was characterized by a reaction with acetone to produce the carbinol derivative VIII in 34% yield. When the Grignard reagent



VII



VIII



IX

VII, prepared by reacting V with magnesium using ethyl bromide as an entrainer,[7] was allowed to react with 3-cyclopentenone,[8] the carbinol III was obtained in 40% yield.

Unfortunately, several attempts to dehydrate III to form the cyclopentadienyl derivative IX have not been successful. The dehydration methods included: (a) an etheral solution of III with 35% sulfuric acid; (b) an alcoholic solution of III with hydrochloric acid; (c) refluxing acetic anhydride; (d) thionyl chloride and pyridine; (e) *p*-toluenesulfonyl chloride and pyridine. If a suitable conversion of III to IX can be developed, it should be possible to dehydrogenate the latter intermediate to form the diphenyl derivative IIb, based on similar methods used for the synthesis of various phenylated analogs of I.[3]

EXPERIMENTAL

IR spectra were recorded on a Beckman IR-10 spectrophotometer. Nmr spectra were determined on a Varian A-60 spectrometer with tetramethylsilane as internal standard. The elemental analyses were performed by the Microanalytical Laboratory, University of Massachusetts.

<u>1-p-Bromophenyl-2,3-diphenylcyclopropenium Bromide</u> (IV).--To a nitrogen-flushed 250-ml flask equipped with a nitrogen inlet and bubbler, reflux condenser, pressure-equalizing addition funnel and mechanical stirrer, was added 10.0 g (39 mmol) of p-bromodiphenylacetylene,[9,10] 18.3 g (0.16 mmol) of potassium tert-butoxide (MSA Research Corp.), and 150 ml of dry benzene. To the mixture was slowly added with stirring under nitrogen 12.3 g (76 mmol) of freshly distilled benzal chloride. The viscous brown reaction mixture was stirred vigorously and refluxed for 3 h. Cold water was then added to dissolve the inorganic salt, the layers were separated, and the aqueous layer was extracted twice with 75 ml portions of ether. The combined extracts were dried (Na_2SO_4). After filtration, the organic solution was saturated with anhydrous hydrogen bromide to precipitate the product. The precipitate was collected on a Buchner funnel and washed with dry ether to yield 14.0 g (84%) of product. An analytically pure sample was obtained by recrystallization from acetonitrile, mp 236-240°; nmr (CF_3COOH) τ 1.35-1.80 (6H, m, H_{ortho}), 1.90-2.30 (8H, m, $H_{m,p}$); ir (KBr) 1400 cm^{-1} (s, cyclopropenium ring).

<u>Anal</u>. Calcd. for $C_{21}H_{14}Br_2$: C, 59.19; H, 3.31; Br, 37.50. Found: C, 59.10; H, 3.35; Br, 37.55.

<u>1-p-Bromophenyl-2,3-diphenylcyclopropene (V)</u>.--To a 500-ml flask equipped with a condenser and a magnetic stirring bar, was added 5.3 g (141 mmol) of lithium aluminum hydride and 250 ml of dry ethyl ether. Solid 1-p-bromophenyl-2,3-diphenylcyclopropenium bromide (IV) (20.0 g, 47 mmol) was added in small portions under nitrogen to the mixture at 0°. After stirring at room temperature

for 24 h, the reaction mixture was quenched by the dropwise addition of water. The layers were separated; the ether layer was washed with water, dried (Na_2SO_4) and evaporated to dryness. The residue was purified by two recrystallizations from Skellysolve-B to yield 7.2 g (46%) of a white solid. An analytical sample was obtained by recrystallization from ethanol, mp 113-114°; nmr ($CDCl_3$) τ 6.86 (1H, s, $H_{methine}$), 2.33-3.00 (14H, m, H_{Ar}); ir ($CHCl_3$) 1830 cm^{-1} (m, C=C).

Anal. Calcd. for $C_{21}H_{15}Br$: C, 72.63; H, 4.35. Found: C, 72.35; H, 4.47.

2-[p-(2,3-Diphenyl-1-cyclopropenyl)-phenyl]-2-propanol (VIII).-- To a nitrogen-flushed 50 ml flask equipped with a magnetic stirring bar, condenser, addition funnel, and nitrogen inlet, were added 0.14 g (5.5 mmol) of magnesium and 1.0 g (2.8 mmol) of 1-p-bromophenyl-2,3-diphenylcyclopropene (V) in 15 ml of dry tetrahydrofuran. A solution of 0.5 g (2.8 mmol) of 1,2-dibromoethane in 10 ml of tetrahydrofuran was added dropwise under nitrogen to the mixture. After about 20% of the solution was added, the reaction was initiated by crushing a piece of magnesium with a stirring rod. The reaction flask was then immersed in an oil bath at 40° and the remainder of the dibromoethane solution was added dropwise over a period of 1 h. Stirring was continued for 30 min at this temperature and the reaction mixture was then cooled to 0°. A solution of 0.21 g (35 mmol) of acetone[11] in 10 ml of tetrahydrofuran was added dropwise over 1 h and the reaction mixture was stirred for an additional 2 h. The resulting white suspension was hydrolyzed with cold saturated ammonium chloride solution. The mixture was extracted with ether. The ether extracts were washed with water, dried (Na_2SO_4) and evaporated in vacuo. The residual oil was dissolved in a minimum amount of benzene and chromatographed on a column of alumina. Triphenylcyclopropene was obtained by eluting with Skellysolve-B. Elution with benzene gave 0.32 g (34%) of a light yellow product. Several recrystallizations from Skellysolve-B afforded analytically pure white crystals of mp 124-125°; nmr ($CDCl_3$) τ 8.50 (6H, s, H_{methyl}), 8.21 (1H, s, H_{OH}), 6.77 (1H, s, $H_{methine}$), 2.22-2.82 (14H, H_{Ar}).

Anal. Calcd. for $C_{24}H_{22}O$: C, 88.30; H, 6.79; O, 4.90. Found: C, 88.20; H, 6.85; O, 5.00.

1-[p-(2,3-diphenyl-1-cyclopropenyl)-phenyl]-3-cyclopentene-1-ol (III).--To a nitrogen-flushed 50-ml flask were added 0.14 g (5.6 mmol) of magnesium and 1.0 g (2.8 mmol) of 1-p-bromophenyl-2,3-diphenylcyclopropene (V) in 15 ml of dry ethyl ether. A solution of 0.3 g (2.8 mmol) of ethyl bromide in 10 ml of dry ether was added dropwise under nitrogen to the mixture. After about 20% of the solution was added, the reaction was initiated by crushing a piece of magnesium with a stirring rod. The reaction mixture was then heated to reflux and the remainder of the ethyl bromide solution was added dropwise over 45 min with stirring. Stirring was continued for 3 h. The reaction mixture was cooled to 0° and a solution of 0.48 g (5.6 mmol) of 3-cyclopentenone[8] in 100 ml of dry ethyl ether was added dropwise over 30 min. Stirring was continued for 3 h at this temperature. The reaction mixture was quenched with cold 2N hydrochloric acid. The ether layer was separated, washed with 10% sodium carbonate solution, water, and dried (Na_2SO_4). The dried ether layer was evaporated and the residual oil was subjected to preparative thin layer chromatography on 20 x 20 cm silica plates. Elution with benzene afforded 0.44 g (40%) of crude product. Trituration of the solid with Skellysolve-B followed by recrystallization from the same solvent yielded analytically pure white crystals, mp 99-100°; nmr ($CDCl_3$) τ 7.88 (1H, s, H_{OH}), 7.16-7.37 (4H, broad s, $H_{methylene}$), 6.80 (1H, s, $H_{methine}$), 4.30 (2H, broad s, H_{vinyl}), 2.28-3.02 (14H, m, H_{Ar}); ir ($CDCl_3$) 3610 cm^{-1} (m, O-H), 1836 cm^{-1} (m, C=C).

Anal. Calcd. for $C_{26}H_{22}O$: C, 89.11; H, 6.33; O, 4.56; MW, 350. Found: C, 88.98; H, 6.30; O, 4.60; MW (osmometric in benzene), 335.

REFERENCES

† Abstracted from the Ph.D. Thesis of T. Niem, University of Massachusetts, Amherst, Massachusetts, 1972. Presented at the 166th National ACS Meeting, Chicago, Illinois, August 27-31, 1973; Abstract ORGN 91.

1. K. Takahashi, I. Oikawa, and K. Takase, Chem. Lett., 1215 (1974).
2. K. Takahashi and K. Takase, Tetrahedron Lett., 245 (1975).
3. T. Niem and M. D. Rausch, J. Org. Chem., In press.
4. R. Breslow and H. W. Cheng, J. Am. Chem. Soc., 83, 2367 (1961).
5. W. Broser and M. Brockt, Tetrahedron Lett., 5331 (1968).
6. R. Breslow and P. Dowd, J. Am. Chem. Soc., 85, 2732 (1963).
7. When 1,2-dibromoethane was used as entrainer, VII did not react with 3-cyclopentenone to yield III, and only the starting materials were recovered.
8. H. W. Hess and H. C. Brown, J. Org. Chem., 32, 4139 (1967).
9. C. E. Castro, E. J. Gaughan, and D. C. Owsley, ibid., 31, 4071 (1966).

10. R. D. Stephens and C. E. Castro, ibid., 28, 3313 (1963).

11. Acetone was purified by distillation from potassium permanganate.

(Received Oct. 19, 1976; in revised form Dec. 1, 1976)