# 1,2-Dibenzhydrylidenecyclohexane

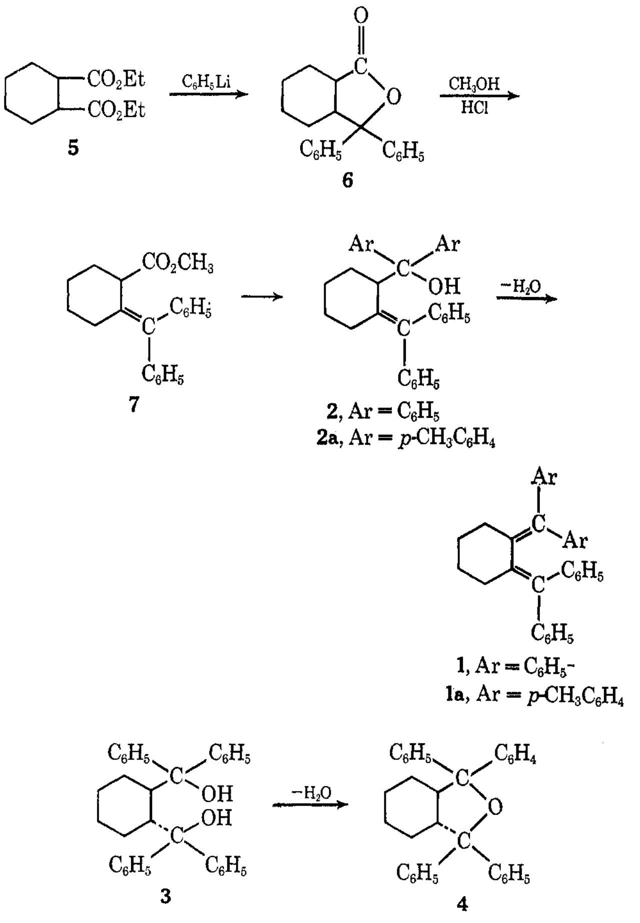
JOSEPH WOLINSKY,* STUART L. COHEN,[1]
AND KENNETH D. LOTTS[2]

*Department of Chemistry, Purdue University, Lafayette, Indiana 47907*

*Received August 13, 1970*

Nazarov and Kuznetzov[3] claimed to have prepared 1,2-dibenzhydrylidenecyclohexane (**1**) and unsaturated alcohol **2** by dehydration of *trans*-$\alpha,\alpha,\alpha',\alpha'$-tetraphenyl-1,2-cyclohexanedimethanol (**3**). All attempts to reproduce this work in our laboratory failed,[4] and instead it was found that the action of a wide assortment of dehydrating agents converted diol **3** into the phthalan **4**. In this note we report the synthesis of dienes of type **1** by an alternate route shown in Scheme I. Authentic 1,2-dibenzhydrylidencyclohexane has properties markedly different from those reported by Nazarov and Kuznetzov.[3]

SCHEME I



The addition of 2.5 equiv of phenyllithium to diethyl *cis*-1,2-cyclohexanedicarboxylate (**5**) gave crystalline lactone **6** in 25% yield. Methanolysis of lactone **6** employing anhydrous hydrogen chloride afforded the unsaturated methyl ester **7**, which was converted to unsaturated alcohol **2** by reaction with phenyllithium. Heating a benzene solution of **2** containing a trace of iodine gave diene **1**, mp 174–175°. The condensation of ester **7** with *p*-tolyllithium afforded alcohol **2a** which gave diene **1a** on dehydration with iodine.

The structure of diene **1** was confirmed by spectral analysis and by ozonolysis which afforded benzophenone. The nmr spectra of **1** displayed two distinct sets of aromatic signals at $\delta$ 6.5–6.9 (4 H) and 7.0–7.3 ppm (16 H), and very broad resonances at 2.0–2.3 and 1.4–2.0 ppm., each integrating for four protons. Examination of molecular models indicates that rotation of the $C_1$–$C_2$ bond should be prevented by overlapping of the two "inside" phenyl groups and precludes the possibility of chair–chair interconversions of the cyclohexane ring. The very broad methylene signals are consistent with this notion, since much sharper signals would be anticipated if the ring were able to invert.

The ultraviolet spectrum of alcohol **2** showed a maximum at 249 nm ($\epsilon$ 10,900) which is in line with the maximum at *ca.* 256 nm ($\epsilon$ 11,200) displayed by diphenylethylene.[5] Diene **1** exhibits ultraviolet absorption at 286 nm ($\epsilon$ 7500) which is to be compared with absorption at 344 nm ($\epsilon$ 36,300) for 1,1,4,4-tetraphenyl-1,3-butadiene,[6] 351 nm ($\epsilon$ 21,400) for 1,2-dibenzhydrylidenecyclobutane,[7] and 332 and 350 nm ($\epsilon$ 9870 and 10,400) for 1,2-dibenzhydrylidenehydrindan.[8] A similar relationship exists between the ultraviolet absorption maximum found at 287 nm for 1,2-dibenzylidenecyclohexane[9] and 332 nm for 1,4-diphenyl-1,3-butadiene[9] and presumedly reflects the existence of diene **1** and 1,2-dibenzylidenecyclohexane in chair conformations where the 1,3-diene system deviates markedly from coplanarity.[10]

## Experimental Section[11]

*cis*-**2-(Hydroxydiphenylmethyl)cyclohexanecarboxylic Acid Lactone** (**6**).—A filtered solution of phenyllithium, prepared from 392 g (2.5 mol) of bromobenzene and 35 g (5.0 g-atoms) of lithium, was added to a stirred solution of 228 g (1 mol) of diethyl *cis*-1,2-cyclohexanedicarboxylate[12] in ether. The mixture was stirred at ambient temperature for 40 hr and then 650 ml of water was added. The ether phase was separated, washed with water, dried ($MgSO_4$), and evaporated to leave an oil which partly solidified. The residue was triturated repeatedly with cold hexane leaving 34 g of crude lactone **6**. Pure lactone **6**, free of *cis*-diol **3**, was obtained by several recrystallizations from hexane and showed mp 149–150° (lit.[3] mp 175–176°); ir ($CHCl_3$) 5.65 $\mu$ ($\delta$ lactone); nmr ($CDCl_3$) 1.3–1.9 (broad m, 9), 2.4 (m, 1),

---

[1] David Ross Fellow, 1966–1967.

[2] Participant in the National Science Foundation Undergraduate Research Program, 1969.

[3] I. N. Nazarov and V. N. Kuznetzov, *Bull. Acad. Soc. USSR*, 236 (1960).

[4] J. Wolinsky and M. Senyek, *J. Org. Chem.*, **33**, 3950 (1968). See this reference for the reason for our interest in these compounds.

[5] R. N. Jones, *J. Amer. Chem. Soc.*, **65**, 1818 (1943).

[6] Y. Hirschberg, E. Bergmann, and F. Bergmann, *ibid.*, **72**, 5120 (1950).

[7] K. B. Alberman, R. B. Hazeldine, and F. B. Kipping, *J. Chem. Soc.*, 3284 (1952).

[8] H. G. Heller, D. Auld, and K. Salisbury, *J. Chem. Soc., C*, 682 (1967).

[9] G. Witschard and C. E. Griffin, *J. Org. Chem.*, **29**, 2335 (1964).

[10] See E. E. Van Tamelen, S. Levin, E. Brenner, J. Wolinsky, and P. Aldrich, *J. Amer. Chem. Soc.*, **81**, 1666 (1959), and references cited therein.

[11] Melting points are uncorrected. Nmr spectra were determined with a Varian Associates A-60 spectrometer. The mass spectra were measured with a Hitachi RMU-6D spectrometer. Ultraviolet spectra were determined with a Bausch and Lomb spectronic 505. Microanalyses were performed by Dr. C. S. Yeh and associates.

[12] A. C. Cope and E. C. Herrick, *J. Amer. Chem. Soc.*, **72**, 983 (1950).

7.0–7.5 (m, 10); mass spectrum (70 eV) *m/e* (rel intensity) 292 (14), 183 (72), 165 (18), 105 (100), and 77 (66).

*Anal.* Calcd for $C_{20}H_{20}O_2$: C, 82.36; H, 7.21. Found: C, 82.48; H, 6.68.

**Methyl 2-Benzhydrylidenecyclohexanecarboxylate (7).**—A solution of 5.84 g of lactone **6** in anhydrous methanol saturated with hydrogen chloride gas was stirred at ambient temperature for 48 hr. The solvent was removed and the residue taken up in ether and washed with water, 5% sodium bicarbonate solution, and saturated salt solution. The ether solution was dried ($MgSO_4$) and evaporated leaving 6.0 g (98%) of crude ester **7**. A distilled sample of **7**, bp 162–164° (0.4 mm), crystallized slowly from hexane and showed mp 51–52°; ir 5.75 $\mu$; nmr ($CDCl_3$) 1.3–2.0 (m, 6), 2.0–2.65 (m, 3), 3.60 (s, 3, $OCH_3$), and 7.1 ppm (broad s, 10); mass spectrum (70 eV) *m/e* (rel intensity) 306 (90), 275 (12), 247 (70), 246 (90), 167 (95), and 91 (100).

*Anal.* Calcd for $C_{21}H_{22}O_2$: C, 82.36; H, 7.21. Found: C, 82.44; H, 7.28.

**1-(Hydroxydiphenylmethyl)-2-benzhydrylidenecyclohexane (2).**—To a solution of phenyllithium, prepared from 7.8 g of bromobenzene and 0.7 g of lithium, in ether was added an ether solution of 5 g of unsaturated ester **7**. After stirring for 2.5 hr the reaction was worked up in the usual manner to give, after crystallization from hexane, 6.8 g of pale yellow solid. A pure sample of unsaturated alcohol **2** was obtained by recrystallization from hexane (Norit) and showed: mp 154.5–156.5° (lit.[3] mp 112–113°); ir ($CHCl_3$) 2.8 $\mu$ (OH); nmr 1.4–2.0 (m, 8), 2.3 (s, 1), 2.3–2.9 (m, 2), 3.85 (broad s, 1), 6.5–6.9 (m, 5) and 7.0–7.3 ppm (m, 15); uv $\lambda_{max}^{EtOH}$ 249 nm ($\epsilon$ 10,900); mass spectrum (70 eV) *m/e* (rel intensity) no molecular ion, 412 (4), 249 (12), 248 (56), 247 (17), 205 (5), 184 (16), 183 (100), 169 (7), 117 (14), 105 (56), 91 (24), and 77 (32).

*Anal.* Calcd for $C_{32}H_{30}O$: C, 89.26; H, 7.03. Found: C, 88.96, H, 7.11.

**1,2-Dibenzhydrylidenecyclohexane (1).**—A solution of alcohol **2** in benzene containing several crystals of iodine was refluxed for 24 hr. The solution was washed with sodium bisulfite solution and evaporated to leave 1.26 g of solid. Recrystallization from hexane afforded 333 mg of white solid, mp 174–175° (lit.[3] mp 247–248°). An analytical sample was prepared by sublimation *in vacuo:* nmr ($CDCl_3$) 1.4–2.0 (m, 4), 2.0–2.3 (m, 4), 6.5–6.9 (m, 4), and 7.0–7.3 ppm (m, 16); uv $\lambda_{max}^{EtOH}$ inflection at 240 nm ($\epsilon$ 15,400), 286 (7500); mass spectrum (70 eV) *m/e* (rel intensity) 413 (37), 412 (100), 335 (40), 297 (14), 291 (14), 215 (19), 167 (19), and 165 (24).

*Anal.* Calcd for $C_{32}H_{28}$: C, 93.21; H, 6.79. Found: C, 93.09; H, 6.82.

A solution of 300 mg of **1** diene in methylene chloride was ozonized at −78° for 8 min at which time the solution turned blue. The solution was flushed with nitrogen to remove excess ozone and was then added to a stirred solution of 8 ml of 30% hydrogen peroxide in 8 ml of 10% sodium hydroxide solution. The mixture was extracted with ether affording 206 mg of solid which was converted into a 2,4-dinitrophenylhydrazone derivative, mp 239–241°, which did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone derivative of benzophenone.

**2-Benzhydrylidene-1(hydroxydi-*p*-tolylmethyl)cyclohexane (2a).**—The reaction of *p*-methylphenyllithium, prepared from 10.26 g (0.06 mol) of *p*-bromotoluene and 0.833 g (0.12 g-atom) of lithium, with 6.40 g (0.02 mol) of methyl-2-benzhydrylidenecyclohexanecarboxylate gave after the usual work-up and recrystallization from hexane 6.3 g (69%) of **2a**: mp 167–169°; $\lambda_{max}^{EtOH}$ 251 nm ($\epsilon$ 13,700); nmr ($CDCl_3$) 1.2–2.0 (m, 7), 2.21 (s, 6, $CH_3Ar$), 2.3–2.8 (m, 2), 3.80 (broad s, 1), 6.35–6.80 (m, 4), 6.82 (s, 4), and 6.90–7.12 ppm (m, 10); mass spectrum (70 eV) *m/e* (rel intensity) no molecular ion, 440 (16) 248 (21), 212 (19), 211 (100), 119 (48), and 91 (30).

*Anal.* Calcd for $C_{34}H_{34}O$: C, 89.04; H, 7.47. Found: C, 88.98; H, 7.69.

**1-Benzhydrylidene-2-*p*-tolylidenecyclohexane (1a).**—A solution of 0.458 g of **2a** in benzene containing a trace of iodine was heated at reflux for 1 day. The solvent was removed and the residue recrystallized from hexane to yield 392 mg (89%) of a white solid: mp 185–186°; $\lambda_{max}^{EtOH}$ 286 nm ($\epsilon$ 11,000); nmr ($CDCl_3$) 1.2–2.0 (m, 4), 2.0–2.98 (m, 2), 2.22 (s, 3, $CH_3Ar$), and 6.30–7.35 ppm (m, 18); mass spectrum (70 eV) *m/e* (rel intensity) 440 (100), 363 (31), and 349 (14).

*Anal.* Calcd for $C_{34}H_{32}$: C, 92.68; H, 7.32. Found: C, 92.68; H, 7.42.

**Registry No.**—**1**, 27621-80-3; **1a**, 27621-81-4; **2**, 27621-82-5; **2a**, 27621-83-6; **6**, 27621-84-7; **7**, 27621-85-8.

---

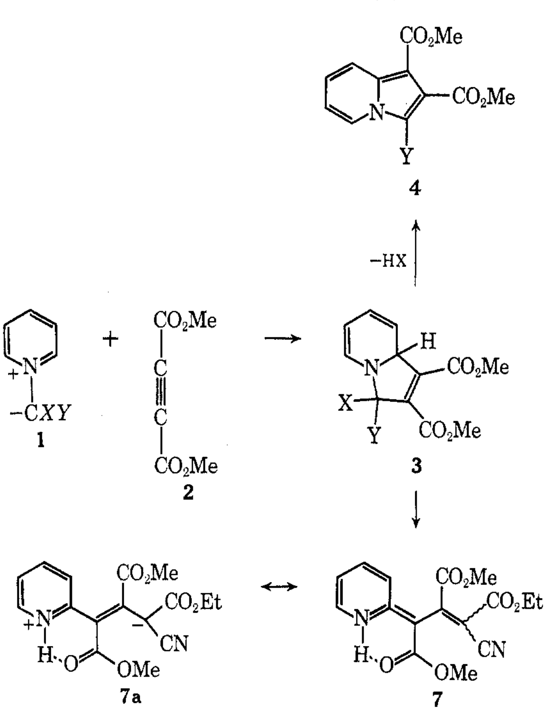
# A Novel 1,3-Dipolar Addition Reaction of Pyridinium Carbethoxycyanomethylide

James E. Douglass* and Joseph M. Wesolosky

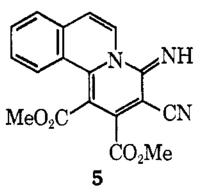
*Department of Chemistry, Marshall University,*
*Huntington, West Virginia 25701*

*Received September 18, 1970*

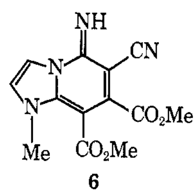
Numerous pyridinium, and related heteroaromatic, ylides (**1**) have been reported to react with dimethyl acetylenedicarboxylate (**2**) to yield indolizines (**4**) *via* the intermediate dihydroindolizines (**3**).[1-3]



In a few cases, however, these 1,3-dipolar additions give other products as well. For example, Linn and coworkers[2] found that isoquinolinium dicyanomethylide reacts with **2** to yield the iminoquinolizine **5** in addition to the expected benzindolizine. At about the same time Boekelheide and Fedoruk[4] reported the isolation of compound **6** from the reaction of 3-methyl-1-imidazolium dicyanomethylide with **2**, rather than the anticipated diazapentalene.



**5**



**6**

---

[1] C. A. Henrick, E. Ritchie, and W. C. Taylor, *Aust. J. Chem.*, **20**, 2467 (1967).

[2] W. J. Linn, O. W. Webster, and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3652 (1965).

[3] V. Boekelheide and K. Fahrenholtz, *ibid.*, **83**, 458 (1961).

[4] V. Boekelheide and N. A. Fedoruk, *ibid.*, **90**, 3830 (1968).