

SOME REACTIONS OF THE ACENAPHTHYLENYL DIANION

Thomas S. Cantrell

Chemistry Department, American University

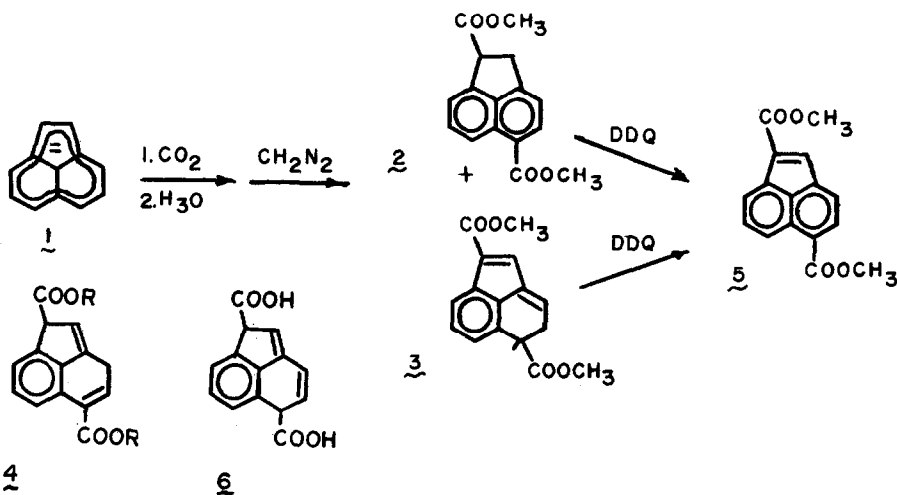
Washington, D. C. 20016

(Received in USA 22 November 1972; received in UK for publication 3 April 1973)

Reports have recently appeared of the preparation and characterization of the 14π -electron species acenaphthylenyl dianion, ⁽¹⁾ as well as mention of its protonation and deuteration.^{1,2,3} We describe here our observations on the products of reaction of 1 with carbon dioxide and with benzophenone.

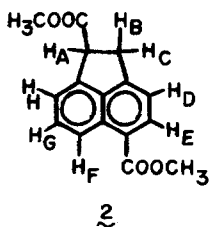
Generation of 1 from acenaphthene and n-butyllithium in THF at 0°. followed by carboxylation with powdered dry ice gave a mixture of dicarboxylic acids, mp 266-280° (dec). For characterization, these were converted to the corresponding methyl esters, which were easily separated by chromatography on silica gel with 4:1 hexane - chloroform as eluant. The faster moving ester 2 (white needles, mp 110-111°, 16% overall) showed the following spectral parameters: ir(KBr): 1712 and 1738 cm^{-1} ; uv (CH₃OH) 309 ($\epsilon = 49,000$) nm; nmr : see Table I; m/e 270 (P,100), 211 (40), and 210 (23). Its structure was initially deduced from analysis of its nmr spectrum and from the similarity of its nmr and uv spectra to those of methyl acenaphthene-5-carboxylate (4), mp 71° ⁴[uv(CH₃OH) 316 ($\epsilon = 7900$) and 239 ($\epsilon = 29,500$) nm]. The less rapidly eluted ester, 3 [mp 77-78°, 25%; ir(KBr) 1740 and 1708 cm^{-1} ; uv(CH₃OH) 309 ($\epsilon = 12,000$) and 227 (49,000) nm;

nmr; see Table I; m/e 270 (P, 53), 211 (38), and 210 (100)] exhibits an ultraviolet spectrum qualitatively similar to that of 8,8-dimethyl-benzofulvene (λ_{\max} 342 ($\epsilon = 1500$), 320 (5000), 308 (6000), and 261 (30,000) nm.⁵ Both 2 and 3 on refluxing in benzene with



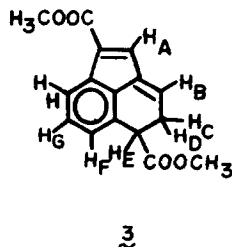
2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) gave dimethyl acenaphthylene-1,5-dicarboxylate, 5, in > 80% yield as fluffy orange needles, mp 114-115° [ir(KBr) 1710 cm⁻¹; uv(CH₃OH) 334 ($\epsilon = 17,500$), 319 (11,500), 248 (27,000), and 226 (29,000) nm; nmr: τ 1.7 - 2.5 (6H, m), 5.95 (3H, s), and 6.02 (3H, s); m/e 268 (P, 76) and 238 (100)].

Condensation of 1 with benzophenone gave 32% of a diol, 7, as white prisms, mp 250-251°, whose nmr [τ 2.48 and 2.86, (AB, J=8), 2.68 and 2.69 (both s, 5H each), 2.96 (10H, s), 3.01(1H,d, J = 7), 3.93 (2H, d), 5.30 (2H, s, br), and 6.67 (2H, s, br OH)], uv[λ_{\max} (CHCl₃) 324 ($\epsilon = 1000$), 303 (sh, 6300), 295 (8100), 284 (6800), and 252 (1400)], and mass [m/e 530 (P, 0.1), 500 (1), 482 (4), 406 (7), 318 (100), 240 (56), and 182 (80)] spectra were consistent with its formulation as the acenaphthene derivative 7. Attempts to dehydrate 7 using various reagents, including sulfuric acid-acetic acid, toluenesulfonic acid-xylene, and thionyl chloride-pyridine, were unsuccessful. However brief (2 min) heating of 7 above its melting point gave benzophenone⁶ and 8, 1-(α -hydroxybenzhydryl) acenaphthene, mp 206-207° (55%; nmr: τ 2.3-2.9 (14H, m), 3.75 (2H, d, J=7), 4.96 (1H, t, J=6, H-1), 6.69 (2H, d, J=6), and 8.03 (1H, s, OH); τ (CHCl₃): 308 ($\epsilon = 2600$), 302 (sh, 3100), 293 (4400), and 283 (3800) nm; m/e (336 (P, 0.4), 318 (12), 182 (100), 154 (61), and 105 (24)

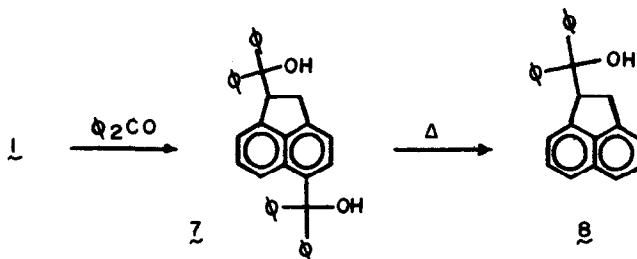


τ	1.28	H_H	$J_{AB} = 7.8$
	1.71	H_E	$J_{AC} = 4.2$
	2.41	$H_{F,G}$	$J_{BC} = 9.1$
	2.7	H_D	$J_{BD} = 1.3$
	5.91	H_A	$J_{DE} = 7.4$
	6.3	$H_{B,C}$	$J_{FG} = 6.9$
	6.02	$COOCH_3$	$J_{CH} = 6.6$
	6.22		$J_{FH} = 2.4$

Table I
NMR Parameters



τ	1.96	H_B	$J_{BC} = 8.5$
	2.3-2.6	$H_{A,F,G,H}$	$J_{DE} = 4.2$
	5.44	H_E	$J_{CE} = 7.5$
	5.93	$H_{C,D}$	
	6.05	$COOCH_3$	
	6.20		



The production of acenaphthene and dideutero- and dimethyl-acenaphthenes by 1,5-hydrogen migrations from C-5 to C-2 of the initially formed isoacenaphthenes was reported by Freedman, et al.¹ The presently reported formation of the 3, 4-dihydroacenaphthylene **2** is intriguing, since **2** must arise by a novel, previously unobserved type of 1,5-hydrogen transfer, i.e., from C-1 to C-4. Structure **4** is ruled out in favor of **2** for the major ester on the basis of the large couplings observed for the protons on the two saturated carbons (J_{CE} and J_{DE} in Table I) and on the close correspondence of the major esters UV spectrum and that expected for **2**. The isolation of **2** as the major product from carboxylation of **1** is especially surprising, since the resonance energy of **2**, a benzofulvene, should be less than that of the isomeric acenaphthene,

2, by 20 kilocalories. No isoacenaphthene intermediates were detected in the present study, even though their spectral properties should permit ready detection of such substances (e.g., 6).⁷

ACKNOWLEDGEMENTS

The author wishes to thank Dr. Herman Yeh and Mr. William Landis of the National Institutes of Health for 100 MHz nmr spectra and mass spectra, respectively, of the compounds reported herein.

Bibliography

1. (a) L.D. Kershner, J.M. Gaidis, and H.H. Freedman, J. Amer. Chem. Soc., 94, 985 (1972).
(b) H.H. Freedman, Private Communication.
2. R.G. Lawler and C.V. Ristagno, ibid., 91, 1534 (1969).
3. J.M. Gaidis, L.D. Kershner, and H.H. Freedman, Abstracts 162nd National ACS Meeting, Washington, D.C., Fall, 1971, Org. Div., No. 80.
4. (a) F.R. Lorrman, J. Amer. Chem. Soc., 47, 212 (1925).
(b) H. Gilman, W. Langham, and F.W. Moore, ibid., 62, 2327 (1940).
5. A. Pullman, B. Pullman, E.D. Bergmann, G. Berthier, Y. Hirshberg, and Y. Sprinzak, Bull. Soc. Chim. Fr., 702 (1951).
6. Identified by comparison with an authentic sample.
7. (a) G. Wittig, H. G. Reppe and T. Eicher, Ann., 643, 47 (1961).
(b) W. Tochtermann and B. Knickel, Chem. Ber., 102, 3508 (1969).