

THE SYNTHESIS AND REACTIONS OF SOME 1'-SUBSTITUTED

9, 10-DIHYDRO-9, 10-METHANOANTHRACENES¹

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THE chemistry of 7-substituted bicyclo[2.2.1]heptanes (I) has been of considerable interest in recent years, particularly in connection with the behavior of the corresponding carbonium ions.⁴ Aside from the saturated parent compounds, many unsaturated and aromatic variants have been prepared and studied.⁴ An interesting group of compounds in this series which

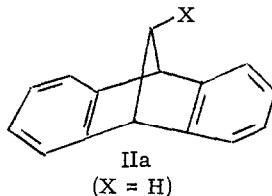
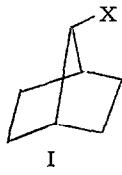
¹ The nomenclature used in the body of this Communication has been chosen to emphasize the close chemical relationship between compounds based on skeletons I and II. Thus, compounds II (b-j) will be referred to as 7-substituted dibenzobicyclo[2.2.1]heptadienes rather than the IUPAC indicated 1'-substituted 9, 10-dihydro-9, 10-methanoanthracenes.

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⁴ S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, J. Am. Chem. Soc. 77, 4183 (1955); S. Winstein and M. Shatavsky, ibid. 78,

has hitherto evaded synthesis⁵ is represented by formula II (b-j), although the unsubstituted hydrocarbon, dibenzobicyclo[2.2.1]heptadiene, IIa, was prepared recently in an ingenious two-step synthesis devised by Vaughan and Yoshimine.⁶ We wish to report the successful application of the



photochemical Wolff rearrangement to this synthetic problem, resulting in the conversion of an appropriately substituted dibenzobicyclo[2.2.1]heptadiene into the desired 7-substituted dibenzobicyclo[2.2.1]heptadienes.

Treatment of the α -diketone III⁵ with *p*-toluenesulfonylhydrazide in the usual manner⁷ gave dibenzobicyclo[2.2.1]heptadiene-2,3-dione

592 (1956); S. Winstein and E. T. Stafford, *ibid.* 79, 505 (1957);

E. E. van Tamelen and C. I. Judd, *ibid.* 80, 6305 (1958); P. D.

Bartlett and W. P. Giddings, *ibid.* 82, 1240 (1960); S. Winstein

and C. Ordronneau, *ibid.* 82, 2084 (1960); P. R. Story, *ibid.* 82,

2085 (1960); P. R. Story and M. Saunders, *ibid.* 82, 6199 (1960);

S. Winstein and R. L. Hansen, *ibid.* 82, 6206 (1960).

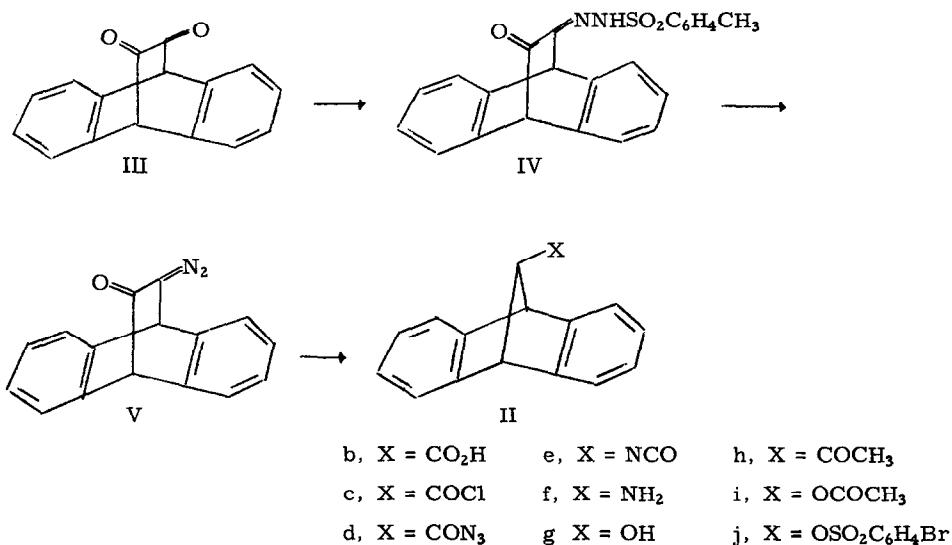
⁵ W. R. Vaughan and M. Yoshimine, *J. Org. Chem.* 22, 528 (1957).

⁶ W. R. Vaughan and M. Yoshimine, *J. Org. Chem.* 22, 7 (1957).

⁷ M: P. Cava, R. L. Little and D. R. Napier, *J. Am. Chem. Soc.*

80, 2257 (1958).

monotoluenesulfonylhydrazone (IV) (m. p. 195.5-196.5° (dec.); Found: C, 68.83; H, 4.54; N, 7.24; S, 8.01. $C_{23}H_{18}N_2O_3S$ requires: C, 68.63; H, 4.51; N, 6.96; S, 7.97%). Extraction with ether of a stirred suspension of IV in dilute, aqueous sodium hydroxide gave, in high yield, crystalline 3-diazodibenzobicyclo[2.2.2]octadien-2-one (V) (m. p. 149-151° (dec.); $\lambda\lambda_{\text{max}}^{\text{KBr}}$: 4.80, 5.99 μ ; $\lambda\lambda_{\text{max}}^{\text{EtOH}}$ (log ϵ): 252 (4.06), 273 (3.75), 280 (3.80), 305 (3.60) m μ ; Found: C, 77.58; H, 4.28; N, 11.44. $C_{16}H_{10}N_2O$ requires: C, 78.03; H, 4.09; N, 11.38%). Irradiation⁸ of a solution of V in aqueous dioxane gave dibenzobicyclo[2.2.1]heptadiene-7-carboxylic acid (IIb) (m. p. 255-256°; $\lambda\lambda_{\text{max}}^{\text{EtOH}}$ (log ϵ): 253 (2.96)



⁸ For a description of the apparatus see J. Meinwald and P. G.

Gassman, J. Am. Chem. Soc. 82, 2857 (1960).

inflection, 272 (3.18), 279 (3.30) m μ ; Found: C, 81.51; H, 5.25; molecular weight (Rast), 251. $C_{17}H_{12}O_2$ requires: C, 81.33; H, 5.12%; M. W., 236) in 16% yield.

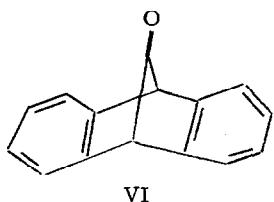
Curtius degradation⁹ of the acid IIb, via the acid chloride (IIc), the acid azide (IId), and the isocyanate (IIe), gave 7-dibenzobicyclo[2.2.1]-heptadienylamine (IIf) (m. p. 196-198° (dec.); $\lambda\lambda_{\text{max}}^{\text{EtOH}}$ (log ϵ): 254 (2.96) inflection, 272 (3.19), 278 (3.29) m μ ; Found: C, 86.82; H, 6.11; N, 6.75. $C_{15}H_{13}N$ requires: C, 86.92; H, 6.32; N, 6.76%). Treatment of a cold solution of the amine IIf in dilute hydrochloric acid with sodium nitrite gave exclusively dibenzobicyclo[2.2.1]heptadien-7-ol (IIg) (m. p. 184-185°; $\lambda\lambda_{\text{max}}^{\text{EtOH}}$ (log ϵ): 254 (2.89) inflection, 272 (3.18), 278 (3.29) m μ ; Found: C, 86.71; H, 5.96. $C_{15}H_{12}O$ requires: C, 86.51; H, 5.81%). The absence of any skeletal rearrangement in the course of the deamination is evident from the close similarity of the ultraviolet spectra of the alcohol and the amine. The structure of the alcohol, IIg, is supported by an independent synthesis as well as by oxidation to the 7-keto compound, VI, described below.

Methyl lithium reacted smoothly with acid IIb to give 7-acetyl-dibenzobicyclo[2.2.1]heptadiene (IIh) (m. p. 163-164°; Found: C, 86.78; H, 6.20. $C_{17}H_{14}O$ requires: C, 87.15; H, 6.02%). Baeyer-Villiger oxidation of IIh, followed by lithium aluminum hydride reduction of the

⁹ P. A. S. Smith in Organic Reactions, Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chap. 9.

resultant acetate IIi (m. p. 164-164.5°; Found: C, 81.41; H, 5.82. $C_{17}H_{14}O_2$ requires: C, 81.58; H, 5.64%) gave IIg identical with that obtained via nitrous acid deamination of IIf. Acetolysis of the p-bromo-benzenesulfonate IIj (m. p. 159-159.5°; Found: C, 58.59; H, 3.72; Br, 19.03; S, 7.50. $C_{21}H_{15}O_3BrS$ requires: C, 59.02; H, 3.54; Br, 18.70; S, 7.50%) also proceeded without rearrangement, giving the corresponding acetate, IIi, quantitatively. This solvolysis showed good first order kinetics, and gave a rate constant ($20.3 \pm 0.2 \times 10^{-6}$ sec. $^{-1}$ at $75.30 \pm .02^\circ$) in accord with expectations, based on the data of Bartlett and Giddings.⁴ Thus, it is unlikely that the carbonium ion derived from IIj derives any special benefit from the possibility of symmetrical charge distribution over both aromatic rings.

Oppenauer oxidation of IIg with aluminum isopropoxide and p-benzoquinone in benzene at room temperature for 3.5 days yielded anthracene, the product to be expected from decarbonylation of dibenzobicyclo[2.2.1]heptadien-7-one (VI).¹⁰ When the reaction period was



¹⁰ Cf. the analogous result obtained by Bartlett and Giddings in the oxidation of anti-benzobicyclo[2.2.1]heptadien-7-ol.⁴

shortened to 1 day, or when the oxidation was carried out using chromium trioxide in pyridine at 4° for 32 hours, the infrared spectrum of the crude reaction product contained a peak of medium intensity at 5.58 μ , characteristic of a 7-keto bridged system.¹¹ Chromatography of this crude oxidation product at 4° has given small amounts of a crystalline fraction (VI) with intense absorption at 5.58 μ .

¹¹ The carbonyl absorption of the closely related benzobicyclo[2.2.1]-hepten-7-one is reported by Bartlett and Giddings⁴ to occur at 5.58 μ .