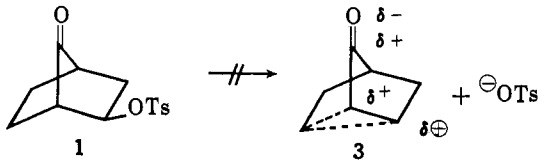
one postulate the norbornyl cation exists as a rapidly equilibrating pair of classical ions,[9,10] with both *exo*- and *endo*-norbornyl tosylates undergoing initial ionization to a classical cation. The fact that the *exo* isomer solvolyses 10^2–10^3 times faster than the *endo* isomer has been rationalized by the hypothesis that the *endo* isomer is abnormally slow due to steric hindrance to ionization of the *endo*-tosylate in the 2 position by the *endo*-hydrogen in the 6 position.[9,10] The alternate hypothesis is that the large *exo*/*endo* rate ratio observed for the solvolyses of norbornyl tosylates is due to anchimeric assistance by the 1–6 σ electrons in the solvolysis of the *exo* isomer.[1,2,11]

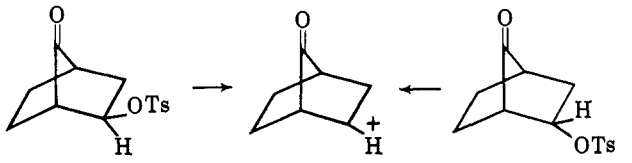
If both *exo*- and *endo*-norbornyl tosylates initially solvolyze to the same classical carbonium ion, the presence of a carbonyl function in the 7 position should have relatively little effect on the inhibition of solvolysis by the C-6 *endo*-hydrogen. Thus the *exo*/*endo* rate ratio for **1** and **2** should be 10^2–10^3 barring other effects.[8]

Alternatively, if the norbornyl *exo*/*endo* rate ratio is due to anchimeric assistance, the presence of a carbonyl function at C-7 would be expected to have drastic effects. The solvolysis of **1** should lack the rate enhancement characteristic of tosylate displacements which occur with neighboring participation because



1 **3**

the accumulation of positive charges in the transition state leading to **3** would be expected to inhibit the formation of a delocalized structure. Thus **1** would be expected to solvolyze to the classical ion, **4**. It is assumed that the *endo*-tosylate, **2**, would also solvolyze to a



1 **4** **2**

classical ion,[7,8] since it is commonly agreed upon that *endo*-norbornyl arenesulfonates solvolyze in the rate-determining step to classical ions.[1,2,9–13] If the large *exo*/*endo* rate ratio observed in the norbornyl tosylate solvolyses is due to anchimeric assistance, **1** and **2** should solvolyze with an *exo*/*endo* rate ratio of approximately 1 since anchimeric assistance would be inhibited by the presence of the carbonyl function.

The fact that **1** solvolyses 6.0 times slower (at 25°) than **2** appears to be most consistent with nonclassical carbonium ion theory. The factor of 6.0 is in amazingly good agreement with the calculations of Schleyer, who predicted[14] that the C-6 *endo*-hydrogen, rather than slowing the rate of solvolysis of the *endo*-tosylate, would actually accelerate the rate by a factor of five due to nonbonded interactions with the tosylate functions.

(12) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, 74, 1147 (1952).
(13) P. von R. Schleyer, *ibid.*, 86, 1854 (1964).
(14) P. von R. Schleyer, Symposium on Linear Free Energy Correlation, Durham, N. C., Oct. 19–21, 1964, Preprints of Papers, p. 225.

Acknowledgment. The authors are indebted to the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this work. We also wish to thank Professor Kurt Mislow for informing us of his results and for helpful discussions of this problem.

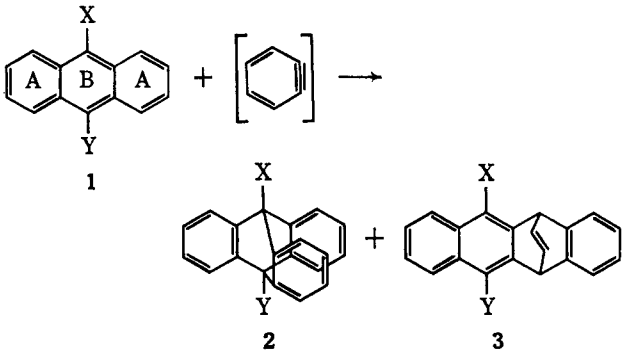
(15) National Science Foundation Cooperative Predoctoral Fellow, 1962–1963, 1964–1965.

Paul G. Gassman, James L. Marshall[15]
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210
Received June 14, 1965

Novel Products from the Reaction of Benzyne with Anthracenes

Sir:

Benzyne reacts with anthracene (**1a**) to produce triptycene (**2a**)[1] and is thereby reacting in a Diels–Alder manner with the more reactive **B** ring of the anthracene molecule. We have found that benzyne also reacts in Diels–Alder fashion with the A ring of anthracene and that the relative amounts of A-ring and B-ring addition products can be modified by substituents appended to the anthracene system.



1 **2** **3**

1a, X = Y = H
b, X = CN, Y = H
c, X = Y = CN
d, X = Y = C_6H_5

Benzyne was generated from anthranilic acid diazotized *in situ* by the procedure of Friedman and Logullo[1f] and condensed with anthracene (**1a**), 9-anthronitrile (**1b**), and 9,10-anthracenedicarbonitrile (**1c**) to give A-ring adducts (**3**) and B-ring adducts (**2**) as well as recovered starting material. Table I shows the results which were obtained by vapor-phase chromatographic analyses of the reaction mixtures.

The A-ring and B-ring adducts were isolated from larger-scale reactions (20–50 g. of the appropriate anthracene) by column chromatography (Florisil and/or neutralized alumina) and crystallization techniques. The B-ring adducts (9-X, 10-Y-triptycenes) were identified by their spectral properties, especially their ultraviolet and n.m.r. spectra, as recorded in Table II. The ultraviolet spectra showed only nonconjugated phenyl absorption, and the n.m.r. spectra were sym-

(1) (a) G. Wittig and R. Ludwig, *Angew. Chem.*, 68, 40 (1956); (b) G. Wittig, *Org. Syn.*, 39, 75 (1959); (c) M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, 82, 3802 (1960); (d) E. LeGoff, *ibid.*, 84, 3786 (1962); (e) G. Wittig and R. W. Hoffmann, *Chem. Ber.*, 95, 2718 (1962); (f) L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, 85, 1549 (1963); (g) M. Stiles, R. G. Miller, and U. Burckhardt, *ibid.*, 85, 1792 (1963); (h) H. Günther, *Chem. Ber.*, 96, 1801 (1963).

Table I.[a] Reaction of Benzyne with Anthracene Systems[b]

Substrate	% recovered starting material	% B-ring adduct	% A-ring adduct	B-ring/A-ring
1a	43	45	1.5	30
1b	74	21	5	4
1c	88	4	4	1

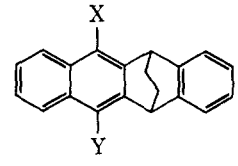
[a] Vapor-phase chromatographic analyses were made by comparing standard solutions of the authentic reaction mixture components with the reaction mixtures on an F & M Model 720 gas chromatograph equipped with SE-30 silicone rubber on Diatoport W columns. The precision of the results was approximately 5%. [b] Two reactions of each substrate with benzyne were carried out on different scales. All reactions were carried out in refluxing methylene chloride (40°) with the anthranilic acid added as an acetone solution.

Table II. Physical Data for Compounds **2**, **3**, and **4**

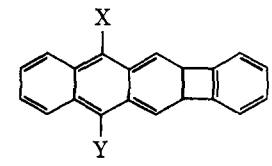
Product[a]	M.p., °C.	Ultraviolet max., mμ[b]	N.m.r. max., τ[c,d]
2a	253–254	272, 279	2.50–3.10 (12), 4.57 (2)
2b	292–294	270, 278	2.19–3.02 (12), 4.54 (1)
2c	300–302	269, 277	2.14–2.89 (12)
3a	145–146	268, 276, 288, 297, 310, 324	2.23–3.14 (12), 4.82 (2)
3b	221–222	272, 279, 294, 306, 319, 334	1.86–3.07 (11), 4.33 (1), 4.77 (1)
3c	275–276	282, 291, 317, 333, 350	1.80–3.00 (10), 4.26 (2)
4a	169–171	259, 267, 271, 278, 289, 306, 320	2.15–3.01 (10), 5.61 (2), 8.22 (4)
4b	170–171	268, 274, 284, 296, 309, 313, 328	1.80–2.96 (9), 5.08 (1), 5.59 (1), 8.22 (4)

[a] All compounds had proper elemental analyses and mass spectra showing peaks corresponding to the molecular ions. [b] Ultraviolet spectra were obtained in cyclohexane with a Perkin-Elmer Model 202 spectrophotometer. [c] Nuclear magnetic resonance spectra were obtained in deuteriochloroform with a Varian Model A-60 spectrometer. [d] The number following the τ value represents the number of protons. All absorptions were multiplets except for the 4.57 and 4.54 values of **2a** and **2b**, respectively, which were singlets.

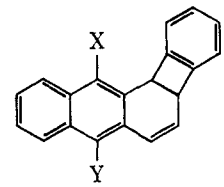
metrical and definitive for the triptycene systems, as shown by the aromatic proton absorption and bridgehead proton absorption. The A-ring adducts (6-X-11-Y-5,12-dihydro-5,12-ethenonaphthacenes) were similarly identified by their spectral properties, recorded in Table II. The ultraviolet spectra supported the presence of the naphthalene moieties, and the n.m.r. spectra were consistent but not definitive for the proposed 1,4 A-ring adducts because the vinyl proton absorption was not separated from the aromatic proton absorption, although low vinyl proton absorption was not unexpected.[2] Consequently, adducts **3a** and **3b** were hydrogenated to the corresponding 6-X-11-Y-5,12-dihydro-5,12-ethanonaphthacenes (**4**), and the n.m.r. spectra of these compounds (Table II) showed clearly the ethano proton absorption at τ 8.22. The field positions of the bridgehead proton absorption for **3b** (τ 4.33 and 4.77) and **4b** (τ 5.08 and 5.59) ruled out an adduct such as **5** which would be expected to show the bridgehead proton peaks at more nearly the same value; furthermore, if **5** were hydrogenated to a naphthalene system, all of the benzylic protons would be found at a lower field position than τ 8.22. The symmetry of the bridgehead proton absorption of both the nonhydrogenated and hydrogenated materials ruled out the possibility of 1,2 A-ring adducts such as **6** or **7**.



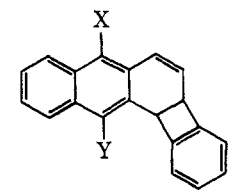
4



5



6



7

Significantly, the relative proportion of A-ring adduct increased with the addition of cyano groups to carbon atoms 9 and 10 of anthracene. In the case of **1c**, equal amounts of A-ring and B-ring adducts were formed, albeit in low yield. Thus the cyano groups deactivated the B ring toward Diels–Alder addition but had little effect on the A-ring addition. The formation of 1,4 A-ring adducts is reasonable in light of the reaction of benzyne with benzene and naphthalene to give 1,4 adducts in low yields.[2]

Maleic anhydride and dimethyl acetylenedicarboxylate have been reported to react only with the A ring of 9,10-diphenylanthracene (**1d**).[3-5] However, the reactivities of the above dienophiles are considerably different from that of benzyne and therefore do not predict the product(s) for the reaction of benzyne with **1d**. In a preliminary experiment similar to those described above, benzyne reacted with **1d** to give both A-ring and B-ring products in a 1:10 B:A ratio. Thus a significant amount of B-ring adduct was formed. Moreover, in a study of the reactions of maleic anhydride and dimethyl acetylenedicarboxylate with 9-bromo-, 9-chloro- and 9-nitro-10-phenylanthracene, B-ring and A-ring adducts were isolated from the maleic anhydride reactions, but only A-ring adducts were found for the reactions employing dimethyl acetylenedicarboxylate.[6]

The data observed in this report correlate well with relative yield data for the reaction of benzyne with 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone), 2,5-bis(*p*-dimethylaminophenyl)-3,4-diphenylcyclopentadienone, and 2,5-di-*p*-anisyl-3,4-diphenylcyclopentadienone.[7] In these reactions the electron-releasing groups promoted the reactivity of the respective tetracyclone toward benzyne, whereas the electron-withdrawing groups in the present report lowered the reactivity of the anthracene B ring toward benzyne. These results support electrophilic character for benzyne.

An appropriately substituted anthracene might well be used as a diagnostic tool to test for the equivalency of benzyne generated under various conditions. One

(2) R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1963).
(3) I. Gillet, *Bull. soc. chim. France*, 17, 1141 (1950).
(4) J. W. Cook and L. Hunter, *J. Chem. Soc.*, 4109 (1953).
(5) J. Rigaudy and N. K. Cuong, *Compt. rend.*, 253, 1705 (1961).
(6) J. Rigaudy and K. V. Thang, *ibid.*, 260, 2527 (1965).
(7) F. M. Beringer and S. J. Huang, *J. Org. Chem.*, **29**, 445 (1964).

molecule incorporates two different sites with which benzyne can react, and relative reactivity ratios can easily be obtained. This method would be somewhat simpler and more versatile than that reported previously.[8] To this end, benzyne was generated from diphenyliodonium-2-carboxylate[1d] and allowed to react with **1b** and **1c**. B:A values of 3 and 1, respectively, were obtained in comparison with values of 4 and 1 for benzyne generated from benzenediazonium-2-carboxylate in methylene chloride–acetone at 40°. Considering the change in solvent (diglyme) and temperature (160°), these values indicate that this method is valid. The cyano group limits the usefulness of **1b** and **1c** because this group interferes with Grignard intermediates and strong bases. Further work in this area with A-ring and/or B-ring substituents is in progress.

Acknowledgment. The author wishes to thank Dr. T. H. Regan for n.m.r. spectra and Mr. G. P. Happ and Mr. D. P. Maier for mass spectra.

(8) R. Huisgen and R. Knorr, *Tetrahedron Letters*, 1017 (1963).

B. H. Klanderman
Research Laboratories, Eastman Kodak Company
Rochester, New York 14650
Received June 5, 1965

Oxidation of Carbohydrates with Dimethyl Sulfoxide Containing Phosphorus Pentoxide

Sir:

Recently oxidation of alcohols to ketones and aldehydes with dimethyl sulfoxide has been reported. Pfitzner and Moffatt[1] found that primary and secondary hydroxyl groups of carbohydrates and steroidal alcohols were oxidized to the corresponding aldehydes and ketones with dimethyl sulfoxide containing both dicyclohexylcarbodiimide and phosphorus compounds such as phosphoric acid or pyridinium phosphate. This procedure was applied to the synthesis of streptose by Dyer, *et al.*[2] Traynelis, *et al.*,[3] also reported the oxidation of arylcarbinols to the corresponding aldehydes with dimethyl sulfoxide.

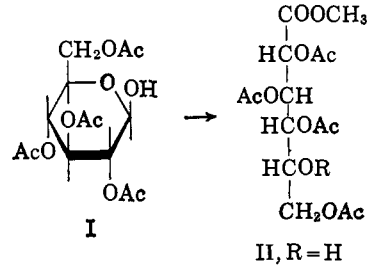
In the course of our work[4] on the syntheses of nucleosides and polysaccharides with phosphorus pentoxide as dehydrating agent, we have observed that phosphorus pentoxide accelerated the oxidation of the various hydroxyl groups of carbohydrates and other compounds with dimethyl sulfoxide to the corresponding aldehydes, ketones, and carboxylic acids. We wish to report some results of the oxidation of carbohydrates with this reagent.

(1) K. E. Pfitzner and J. G. Moffatt, *J. Am. Chem. Soc.*, 85, 3027 (1963).
(2) J. R. Dyer, W. E. McGonigal, and K. C. Rice, *ibid.*, 87, 654 (1965).
(3) V. J. Traynelis and W. L. Hergenrother, *ibid.*, 86, 298 (1964).
(4) Paper presented at the annual meeting of the Agricultural Chemical Society of Japan, Tokyo, April 1–4, 1965. For example, the reaction of 2,3,4,6-tetra-O-acetyl-β-D-glucopyranose with theophylline in N,N-dimethylformamide in the presence of phosphorus pentoxide produced 7-(2′,3′,4′,6′-tetra-O-acetyl-β-D-glucopyranosyl)theophylline. When dimethyl sulfoxide was used as solvent, however, no nucleoside was isolated. The polymerization of hexoses, pentoses, hexosamines, or uronic acids was observed as the result of the reaction in a mixture of dimethyl sulfoxide and phosphorus pentoxide. These results will be published elsewhere.

2,3,4,6-Tetra-O-acetyl-β-D-glucopyranose (1 mmole) (I; m.p. 134°, $[\alpha]^{28}D$ +2.2° (*c* 1.2, $CHCl_3$)) was heated in anhydrous dimethyl sulfoxide containing phosphorus pentoxide (1.2 mmoles as P_4O_{10}) at 60–65° for 10–15 hr. The syrup obtained by extracting the reaction mixture with chloroform followed by concentration was dissolved in methanol, and to the solution were added ether and petroleum ether to incipient turbidity. After allowing the solution to stand in a refrigerator, methyl 2,3,4,6-tetra-O-acetyl-D-gluconate (II) crystallized; yield 20–30%, m.p. 111–112°, $[\alpha]^{28}D$ +13.9° (*c* 1.4, $CHCl_3$). *Anal.* Calcd. for $C_{15}H_{22}O_{11}$: C, 47.62; H, 5.86; OCH_3, 8.21. Found: C, 47.29; H, 5.74; OCH_3, 7.9. The infrared spectrum[5] of II showed OH absorption at 3500 cm.$^{-1}$. The n.m.r. spectrum[6] showed the presence of four O-acetyl groups (δ 2.0–2.2), one O-methyl group (δ 3.75, $COOCH_3$), and six hydrogens (δ 3.8–4.2, 3 H; δ 5.1–5.8, 3 H). Acetylation of II gave methyl 2,3,4,5,6-penta-O-acetyl-D-gluconate (III); m.p. 123–124°, $[\alpha]^{28}D$ +8.2° (*c* 1.1, $CHCl_3$). All the physical constants of III were in good agreement with those reported.[7] No OH absorption was observed in the infrared spectrum, and five acetyl CH_3 signals were observed at δ 2.0–2.2 in the n.m.r. spectrum.

Methylsulfonylation of II gave methyl 2,3,4,6-tetra-O-acetyl-5-O-(methylsulfonyl)-D-gluconate (IV); m.p. 143°, $[\alpha]^{28}D$ −4.9° (*c* 1.33, $CHCl_3$), ν_{max}^{KBr} no OH absorption, 1350 and 1185 cm.$^{-1}$ (sulfonyloxy), n.m.r. δ 2.0–2.2 (O-acetyl, 4 CH_3), 3.1 (S-CH_3, 1 CH_3), 3.75 ($COOCH_3$, 1 CH_3), 4.2–4.4 (2 H), and 4.9–5.6 (4 H). *Anal.* Calcd. for $C_{16}H_{24}O_{13}S$: C, 43.3; H, 5.25; S, 7.00; OCH_3, 6.79. Found: C, 42.7; H, 5.28; S, 6.94; OCH_3, 6.1. On the basis of the analysis of coupling constants of six hydrogens of II, III, and IV, in addition to the evidence mentioned above, it is concluded that the hydroxyl group of II is attached to C-5 of the original carbon chain of the D-glucopyranose molecule.

Scheme I



The mechanism of formation of methyl ester in this oxidation is not yet known, although some novel reactions of dimethyl sulfoxide in connection with methylation have recently been reported.[8,9]

Oxidation of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (1.0 mmole) (V; m.p. 108–109°, $[\alpha]^{28}D$ −13.5° (*c* 1.0, $CHCl_3$)) at room temperature for 24

(5) Spectra were measured with KBr pellets.
(6) Chemical shifts were expressed as p.p.m. downfield from tetramethylsilane as internal standard and measured at 60 Mc. in $CDCl_3$.
(7) G. B. Robbins and F. W. Upson, *J. Am. Chem. Soc.*, 62, 1074 (1940).
(8) H. Metzger, H. König, and K. Seelert, *Tetrahedron Letters*, 15, 867 (1964).
(9) D. H. Ball, E. D. M. Eades, and L. Long, Jr., *J. Am. Chem. Soc.*, 86, 3579 (1964).