## PREPARATIVE UV-VIS LASER PHOTOCHEMISTRY: MOLECULAR OXYGEN TRAPPING OF THE PATERNO-BUCHI TRIPLET DIRADICALS DERIVED FROM 1,4-DIOXENE.

Waldemar ADAM\*(\*), Ulrike KLIEM(\*) and Vittorio LUCCHINI(\*)

Institut für Organische Chemie'\*', Universität Würzburg, D-8700 WÜRZBURG, FRG. Dipartimento di Chimica Organica''', Universitá di Padova, I-35131 PADOVA, Italy.

SUMMARY: Argon ion laser irradiation of CCl4 solutions of 1.4-dioxene and benzophenone or p-benzoguinone under oxygen pressure affords the 1,2,4-trioxanes 4a, b (cis ring junction by NOE 'H-NMR differential spectroscopy), resulting from trapping of the corresponding triplet preoxetane diradicals.

Our recent demonstration<sup>(1)</sup> that short-lived triplet diradicals, generated by laser photolysis of azoalkanes, can be trapped by triplet molecular oxygen in the form of stable peroxides, encouraged us to attempt trapping of the transient triplet species observed<sup>(2)</sup> in the Paterno-Büchi reaction of 1.4-dioxene and benzophenone (Eq.1). Although the feasibility of such oxygen trapping of triplet preoxetane intermediates (especially for resonance-stabilized cases) has been previously demonstrated,<sup>(3)</sup> the rather short triplet lifetime of <u>2a</u> ( $\tau_{T}$  ~ 1.6 ns<sup>(2)</sup>) presented a challenging test of our oxygen trapping technique<sup>(4)</sup>. Besides providing chemical proof for the spectroscopically observed triplet preoxetane species 2a, the 1,2,4-trioxanes <u>4</u> resulting from oxygen trapping constitute useful model compounds for the natural antimalarial agent Qinghaosu<sup>(5)</sup>. In view of the efficient quenching of triplet ketones by molecular oxygen, the short lifetime of the triplet Paterno-Büchi diradical intermediates 2. and the photolabile nature of the 1,2,4-trioxanes 4, the high intensity and monochromicity of the argon ion laser (COHERENT Model CR-18) was essential for these trapping experiments.



Irradiation of a ca. 0.2 <u>M</u> solution each of 1,4-dioxene and benzophenone, contained in a Griffin-Worden tube under 10 atm oxygen pressure,<sup>(4)</sup> was carried out with the UV output (333.6, 351.4 and 363.8 nm ca. 2.8 W) of the argon ion laser for 6 h at -5°C. After flash chromatography of the crude photolysate on silica gel at -20°C, eluting with a 50:50:1 mixture of dichloromethane-petroleum ether (50-70°C)-ethyl acetate, the oxetane <u>3a</u> (9%), the 1,2,4-trioxane <u>4a</u> (7%)<sup>(4)</sup>, and ethylene glycol diformate (24%)<sup>(7)</sup>, besides 50% unreacted benzophenone, were obtained.

Although the 1,2,4-trioxane <u>4a</u> structure (positive peroxide test with KI-HOAc) was consistent with the spectral and analytical data <sup>(\*)</sup>, the <u>cis</u> versus <u>trans</u> ring junction of the 1,2,4-trioxane moiety required rigorous proof. Fortunately, this could conveniently be established by means of NOE measurements<sup>(\*)</sup> using <sup>4</sup>H-NMR differential spectroscopy<sup>(\*)</sup>. The pertinent NOE enhancements (in %) are summarized in the Newman projection for the 1,2,4-trioxane <u>4a</u> (Eq.2).<sup>(10)</sup> The large vicinal enhancements of the 1-H (17.4%) and 6-H (15.3%) clearly speak for the <u>cis</u> ring junction. Besides the other expected vicinal enhancements between the 8-H and 9-H protons, of interest are the appreciable enhancements between 9-H. (3.9%) and 1-H (7.6%) and between 6-H (7.5%) and the <u>ortho</u>-H (4.1%) of the axial phenyl substituent. Consequently, in the conformational equilibrium of Eq.2 conformer <u>4a</u> is the energetically preferred one.



In the case of p-benzoquinone, the VIS output (454.5, 457.9, 465.8, 472.7, 476.5, 488.0, 496.5, 501.7, 514.5 nm ca. 4.5 W) of the argon ion laser was employed. After 4 h irradiation, flash chromatography on silica gel at  $-20^{\circ}$  C, eluting with a 10:15:2 mixture of dichloromethane-petroleum ether (50-70°C)-ethyl acetate afforded the 1,2,4-trioxane <u>4b</u> (20%)<sup>(11)</sup> and the ethylene glycol diformate (34%)<sup>(7)</sup>, besides 18% unreacted benzoquinone. The expected oxetane <u>3b</u> was detected by <sup>1</sup>H-NMR (400 MHz) in the crude photolysate, but did not survive the flash chromatography even on silylated silica gel at  $-20^{\circ}$ C. Besides the positive peroxide test (KI-HOAc), the structure proposed for the 1,2,4-trioxane

<u>4b</u> is consistent with the spectral and analytical data. The <u>cis</u> ring junction in 1,2,4-trioxane <u>4b</u> was ascertained by low temperature  $(-60^{\circ}\text{C} \text{ in } \text{CDCl}_3)$  <sup>1</sup>H- and <sup>13</sup>C-NMR spectra. These spectra exhibit two sets of nearly equally intense resonances for the conformers <u>4b</u> and <u>4b</u><sup>\circ</sup> (Eq.3), while for the <u>trans</u> junction only one conformer is feasible. An attempt to corroborate the <u>cis</u> ring junction by NOE <sup>1</sup>H-NMR differential spectroscopy was not possible at room temperature (cf. Eq.3)<sup>(10)</sup> due to the fast conformational equilibrium. However, at -63°C clearcut positive enhancements were observed between the 1-H (12.4%) and 6-H (11.4%) protons (cf. Eq.3, values in parentheses), confirming the <u>cis</u> junction. Unfortunately, on the basis of the NOE results an assignment of the chemical shifts for the individual conformers <u>4b</u> and <u>4b</u><sup>\circ</sup> was not possible because saturation of a given proton in one conformer brought about saturation (even at -63°C) of the corresponding proton in the other.



The present study establishes that short-lived triplet preoxetane intermediates such as  $\underline{2}$  can be trapped with molecular oxygen in the form of 1,2,4trioxanes  $\underline{4}$ , therewith providing chemical evidence for these elusive diradicals (<sup>3</sup>). It should be of interest to apply our quantitative oxygen trapping technique<sup>(4)</sup> to estimate the lifetimes of the triplet Paterno-Büchi 1,4-diradicals  $\underline{2}$ and compare them with those determined by laser flash spectroscopy<sup>(2)</sup>.

## ACKNOWLEDGEMENTS:

We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Italian Consiglio Nazionale delle Ricerche for the generous financial assistance, Discussions with Prof. R. M. Wilson (Cincinnati) were particularly helpful.

2955

REFERENCES

1071. 2, Freilich, S, C.; Peters, K, S, J, Am, Chem, Soc. 1981, 103, 55. 3. Wilson, R. M. In "Organic Photochemistry", Padwa, A., Ed., Marcel Dekker: New York, 1985; Vol. 7, p. 339. 4. Adam, W.; Hannemann, K.; Wilson, R. M. J. Am. Chem. Soc., in press. 5. Schmid G.; Hofheinz W. <u>J. Am. Chem. Soc.</u> 1983, <u>105</u>, 624. 6. <u>cis</u>-2,3,5,7,10-Pentaoxa-4,4-diphenylbicyclo[4,4,0]dodecane (<u>4a</u>): Colorless needles. m.p. 105-107°C (2-propanol). IR (CDC)<sub>3</sub>): 3060, 3040, 2950, 2870, 1490, 1450, 1275, 1245, 1205, 1165, 1075, 1020, 1010, 855 cm<sup>-1</sup>.- $^{1}$ H-NMR (CDC)<sub>3</sub>, 400 MHz):  $\delta = 3.62$  (m; 1H, 8-H, ), 4.02 (m; 1H, 9-H, ), 4.15 (m; 1H, 9-H<sub>e</sub>), 4.45 (m; 1H, 8-H<sub>e</sub>), 4.88 (d,  $J_{1,6}$  = 2.2 Hz; 1H, 1-H), 4.99 (d,  $J_{4,1} = 2.2 \text{ Hz}; 1\text{H}, 6\text{-H}), 7.2\text{-}7.5 \text{ (m; 10H, phenyl)}$  $^{13}$  C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 59.59$  (t), 65.41 (t), 86.16 (d), 94.59 (d), 106.78 (5), 126.83, 127.59, 128.16, 128.60, 129.45, 130.02, 132.33, 138.16 (s), 139.15 (s).-MS (70 eV): m/e = 284 (0.02%, M⁺-0), 268 (0.5%) 182 (79%), 105 (100%), 86 (14%), 77 (100%), 60 (25%).-C17H1605 (300.3): Calcd. C 67.99, H 5.37; Found C 67.68, H 5.63.-7. Formed from 1,4-dioxene by cleavage with singlet oxygen, the latter being produced in situ by molecular oxygen quenching of triplet ketone. 8. Noggle J. H.; Schirmer R. E. "The Nuclear Overhauser Effect", Academic Press, New York, 1971. 9. The usual procedure for gated decoupling was adopted; as only modification, a multiplet was uniformly irradiated with the least saturating power by a 8-sec cyclic perturbation of all multiplet lines. 10. The values give the enhancements in % upon saturation of the connected nucleus measured at ca. 30°C. those in parentheses at -63°C; error ±0.2%. 11.Spiro[2.3.5.7.10-pentagxabicyclo[4.4.0]decane-4,1'-cyclohexa-2',5'-dien-4'-one] (<u>4b</u>): Colorless needles, m.p. 80-81°C (1:1 CH₂Cl₂- petroleum ether).--IR(CDC1<sub>3</sub>): 3000, 2960, 2880, 1695, 1680, 1645, 1455, 1380, 1320, 1280, 1250, 1180, 1135, 1115, 1080, 1010, 980, 870, 860 cm<sup>-1</sup>.-<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 90 MHz, ca. 35°C): S = 3.72-3.87 (m; 2H, 8-H, 9-H), 4.06-4.16 (m; 2H, 8-H, 9-H), 5.16 (d,  $J_{1,6}$  = 2.3 Hz; 1H, 1-H), 5.26 (d,  $J_{6,1}$  = 2.3 Hz; 1H, 6-H), 6.28 (m; 1H, 5'-H), 6.30 (m; 1H, 3'-H), 6.92 (m; 1H, 6'-H), 7.30 (m; 1H, 2'-H).-<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz, ca, 35°C): 8 = 62.15 (t), 63.00 (t), 88.05 (d), 93.99 (s), 94.04 (d), 129.61 (d), 131.14 (d), 138.90 (d), 140.97 (d), 184.34 (5).-MS (70 eV): m/e = 226 (2.4%, M<sup>+</sup>), 108 (92%), 86 (63%), 82 (52%), 60 (59%), 54 (100%), 44 (65%).-C10H10O4 (226.1): Calcd. C 53.12, H 4.46; Found C 53.05, H 4.39.-(Received in Germany 14 March 1986)

1. Adam, W.; Hannemann, K.; Wilson, R. M. Angew. Chem. Int. Ed. Engl. 1985 , 24,