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HOMOPYRYLIUM CATIONS

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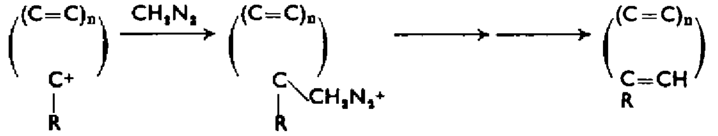
Abstract—Reactions between several pyrylium cations and diazo compounds have been investigated. It is found that the isolable products are those which retain the pyran ring system.

INTERACTIONS between centres of unsaturation and carbonium ions affording putative homoallylic and homobenzylic cations are well established.[1,2] We have previously shown that the reaction between benzylic and phenyl substituted allylic cations and diazo compounds, especially diazomethane, constitutes a convenient route to moderately complex examples of these homo-cations.[3-5] An intriguing facet of this reaction is the possibility of concurrent ring expansion and dearomatization of cyclic aromatic cations with formation of the next higher-membered ring containing $4n + 4\pi$ electrons (Eq. 1).[6] The possibility that the 8π electron heterocycle oxepin will exhibit certain properties characteristic of an "aromatic" ring system[7,8] has accordingly prompted us to investigate application of the carbonium ion–diazo compound reaction to the synthesis of some non-annulated derivatives of this heterocycle. We now wish to report that although pyrylium cations readily react with diazomethane and ethyl diazoacetate, oxepins, if formed, are not stable under the reaction conditions employed. The only product which could be isolated from the complex reaction mixtures were shown to retain the six-membered pyran ring system. Both pyrylium perchlorate[9] and 2,6-diphenylpyrylium perchlorate[10] were found to react with diazomethane to afford complex reaction mixtures. From the latter reaction there was



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[1] J. D. Roberts and R. H. Mazur, *J. Amer. Chem. Soc.* 73, 2509 (1951).

[2] D. J. Cram, *J. Amer. Chem. Soc.* 71, 3863 (1949).

[3] H. W. Whitlock, Jr., *Tetrahedron Letters* 593 (1961).

[4] H. W. Whitlock, Jr., *J. Amer. Chem. Soc.* 84, 2807 (1962).

[5] H. W. Whitlock, Jr. and M. R. Pesce, *Tetrahedron Letters* 743 (1964).

[6] e.g. The preparation of dibenz[b.f.]oxepin from xanthylium cation[3] and the conversion of triphenylcyclopropenium cation to pentaphenylcyclopentadiene, reported by R. Breslow, *Organic Chemistry Symposium*. Bloomington, Ind. (1961).

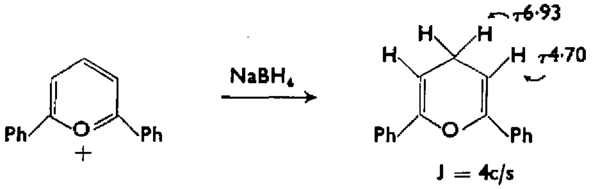
[7] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists* p. 280. J. Wiley, New York (1961).

[8] M. J. Jorgenson, *J. Org. Chem.* 27, 3224 (1962).

[9] F. Klages and H. Trager, *Chem. Ber.* 86, 1327 (1956).

[10] H. Stetter and A. Reischl, *Chem. Ber.* 93, 1253 (1960).

isolated, as the only identifiable product, a 10% yield of 2,6-diphenyl-4H-pyran. An authentic sample of this pyran was prepared by the sodium borohydride reduction of 2,6-diphenylpyrylium perchlorate according to the general procedure of Balaban *et al.*[11] (Eq. 2) and was isolated as colourless air sensitive needles, m.p. 99–100°. Its IR spectrum exhibited the now characteristic[8] twin double bond stretching bands at 5·9 and 6·1 microns.



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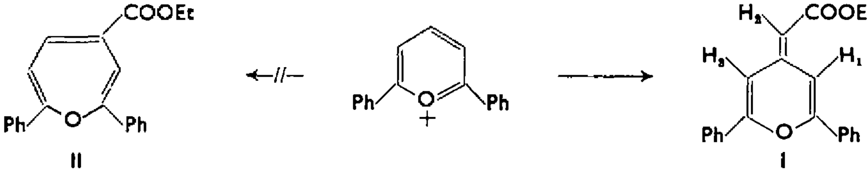
Addition of ethyl diazoacetate to a solution of 2,6-diphenylpyrylium perchlorate in acetonitrile at 0° proceeded with rapid evolution of the theoretical amount of nitrogen. TLC of the dark reaction mixture afforded 2,6-diphenyl-4H-pyran (9% yield isolated) and suggested the presence of between eleven and twenty other products, among which were small amounts of yellow oils having maximal UV absorption in the vicinity of 350 mμ. Addition of triethylamine to the reaction mixture gave similar results except that the yield of the pyran was increased to 14%. The yield of long wavelength absorbing products appeared to reach a maximum when an acetonitrile solution of the pyrylium salt was added to a solution of ethyl diazoacetate and 2,6-lutidine (1 equiv.) in acetonitrile under nitrogen at 0°. The major product isolated from the reaction mixture (eleven components by TLC), and the only one obtained in a pure state, is formulated as 2,6-diphenyl-4-carbethoxymethylene-4H-pyran (I) on the following grounds. It was isolated in 18% yield as bright yellow needles, m.p. 104·5–104°, whose elemental analysis corresponded to the formula $C_{21}H_{18}O_3$. Its IR ($\lambda_{max}^{CHCl_3}$ 5·95, 6·10, 6·32 and 6·41 u) and UV ($\lambda_{max}^{Et_2O}$ 351 mu (2·5 × 10^4)) spectra indicated the presence of a highly unsaturated system.[12] Its NMR spectrum showed the presence of three different vinyl hydrogens at τ1·71, 3·60 and 4·78, the first two being doublets (J = 2·5 c/s), plus ten phenyl and five ethyl hydrogens.



II I

These data can be interpreted in light of either the methylenepyran I with long range coupling between H_1 (τ1·71) and H_2 (τ3·60)[13] or the expected oxepin II. The large

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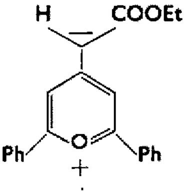
[11] A. Balaban, G. Hihai and C. Nenitzescu, *Tetrahedron* **18**, 258 (1962).

[12] Catalytic hydrogenation (PtO_2) resulted in uptake of 3 equivs H_2. The formation of 3 products (not stereoisomers) and presence of benzylic oxygens in I made the significance of this dubious.

[13] The alternate assignment, coupling between H_1 (τ 1·71) and H_3 (τ 3·60), would imply substantial contribution by the dipolar "aromatic" form *i*; an unlikely case.[14] Proton exchange experiments were not successful.

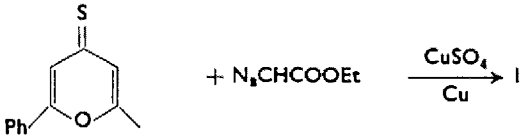
[14] G. V. Boyd and L. M. Jackson, *J. Chem. Soc.* 548 (1963); G. G. Hall, A. Hardisson and L. M. Jackman, *Tetrahedron* **19**, Supplement 2, 101 (1963).



i

downfield shift of H_1, however, is more consistent with the deshielding effect of the carbethoxy group[15] in I than in II.

A final decision between structures I and II was arrived at by a consideration of the consequences of protonation. The methylenepyran I should accept a proton on the exocyclic methylene group to afford a pyrylium cation.[14,16] This cation should, to a considerable extent, *revert to* I on treatment with base. While the oxepin II could accept a proton with rearrangement[17] to afford a pyrylium cation, this should be a relatively slow process. More important, however, if this did occur (barring accidental congruence of the absorption curves of I and II) basification of an acidified solution of II would not regenerate the original spectrum. In the event, addition of perchloric acid to an acetonitrile solution of the yellow compound caused an immediate change of the spectrum to one closely resembling that of 2,6-diphenylpyrylium perchlorate. Addition of base then caused an immediate reversion of the spectrum to that of the yellow compound. When carried out on a preparative scale the acidification afforded a high melting yellow solid whose elemental analysis was consistent with the formulation of its structure as 2,6-diphenyl-4-carbethoxymethylpyrylium perchlorate. This suggests that the major isolable product formed in the reaction between 2,6-diphenylpyrylium perchlorate and ethyl diazoacetate is the methylenepyran I. It was found that I could be prepared in an alternate manner (although in very poor yield) by the addition of ethyl diazoacetate to 2,6-diphenylpyran-4-thione[18] in the presence of copper powder and copper sulphate (Eq. 3). Identity of the two



(3)

samples was established by comparison of TLC R_f values and UV spectra.

Extensive chromatography of the pyrylium salt–ethyl diazoacetate reaction mixture revealed the presence of several other long wavelength absorbing compounds. While they are generally present to the extent of 1% or less and could not be isolated in a completely pure state, application of the "acid test" described above showed that they were reversibly transformed into pyrylium salts on addition of acid and are, on the basis of their UV spectra, methylenepyrans more highly substituted than I. Significantly perhaps, one of these could be shown to arise from the room temperature reaction between I and ethyl diazoacetate.

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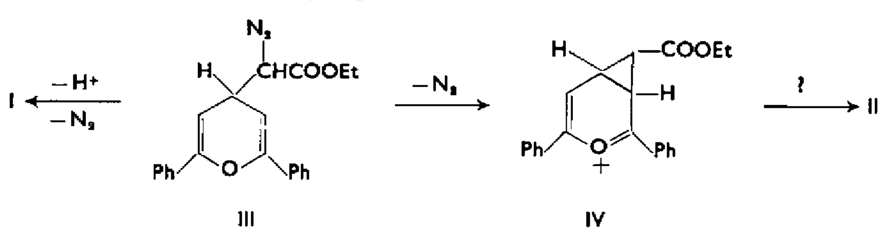
[15] L. M. Jackman and R. H. Wiley, *J. Chem. Soc.* 2886 (1960).

[16] K. Dimroth, *Angew. Chem.* **72**, 331 (1960).

[17] P. Rumpf and R. Reynaud, *Bull. Soc. Chim., Fr.* 2241 (1962).

[18] F. Arndt, E. Schloz and P. Nachtwey, *Chem. Ber.* **57**, 1903 (1924).

The nonobservance of products arising from the initially formed bridged ion IV is surprising. This most likely explanation would seem to be a combination of (a) instability of products derived from IV to the reaction conditions, (b) the effect of added 2,6-lutidine[19] in keeping I in its unprotonated form (the conjugate acid of I, 2,6-diphenyl-4-carbethoxymethylpyrylium cation, reacts rapidly with ethyl diazoacetate), and (c) a non-selective partitioning of diazonium ion III between proton loss and bridging[20] into the pyran system.



EXPERIMENTAL[21]

2,6-Diphenylpyrylium perchlorate and ethyl diazoacetate. To a stirred solution of 0·950 g (2·9 mmoles) 2,6-diphenylpyrylium perchlorate in 20 ml dry acetonitrile maintained at 0° under a N_2 atm. in a 2-necked 100 ml flask fitted with magnetic stirrer, dropping funnel, and condenser with attached gas burette was added over a period of 0·5 hr a solution of 0·325 g (3 mmoles) ethyl diazoacetate in 5 ml acetonitrile. By completion of the addition, 68 ml gas had been evolved. The bulk of the acetonitrile was removed *in vacuo* and replaced with ethyl acetate. The dark green ethyl acetate solution was washed with sat $NaHCO_3$ aq, water and saturated salt solution, dried over Na_2SO_4 and evaporated to afford 0·849 g dark brown oil, $\lambda_{max}^{Et_2O}$ 248 mu ($E_{1cm}^{1\%}$ = 460); 365 mu ($E_{1cm}^{1\%}$ = 132). TLC (Alumina G, hexane, 1:1 chloroform–hexane) showed at least 8 constituents. The reaction mixture (200 mg) was chromatographed on a 20 cm preparative TLC plate (Alumina G, 1·25 mm, 1:9 chloroform–hexane), to afford, among other products, 15 mg (9% yield) of 2,6-diphenyl-4H-pyran, R_f 0·76, identified by comparison of its IR and UV spectra with an authentic sample, and 80 mg of a viscous yellow oil R_f 0·43, $\lambda_{max}^{Et_2O}$ 247 mu ($E_{1cm}^{1\%}$ = 455), 357 mu ($E_{1cm}^{1\%}$ = 305), TLC of which indicated 6 constituents. Rechromatography of this second fraction (Silica gel G, 1·25 mm not activated, 6:4 chloroform–hexane) afforded 3 mg 2,6-diphenyl-4H-pyran and 5 mg tacky yellow crystals R_f 0·58, $\lambda_{max}^{Et_2O}$ 252 mu ($E_{1cm}^{1\%}$ = 600), 267 mu ($E_{1cm}^{1\%}$ = 600), 298 mu ($E_{1cm}^{1\%}$ = 700), and 365 mu ($E_{1cm}^{1\%}$ = 900) later identified as impure 2,6-diphenyl-4-carbethoxymethylene-4H-pyran by comparison of its IR and UV with a pure sample.

2,6-Diphenyl-4H-pyran. To a solution of 4·0 g (12·0 mmoles) 2,6-diphenylpyrylium perchlorate in 25 ml water and 15 ml ether which was rapidly stirred at 0° under N_2 was added 0·1 g solid $NaHB_4$ in several portions (gas evolution). After stirring at 0° for 1 hr, the ether layer was separated and washed with water, dried over Na_2SO_4 and evaporated to afford 2·72 g (97% crude yield) gummy yellow crystals. Seven recrystallizations from diisopropyl ether at −70° afforded 1·0 g (36% yield) of 2,6-diphenyl-4H-pyran, m.p. 99–100°. (Found: C, 86·94; H, 6·14. Calc. for $C_{17}H_{14}O$: C, 87·15; H, 6·02%).

The NMR spectrum exhibited a triplet centered around τ 6·93 (J = 4 c/s), a triplet centered around τ 4·70 (J = 4 c/s) and a complex multiplet centered around τ 2·6 in the relative areas of 2:2:10. The IR spectrum exhibited $\lambda_{max}^{CHCl_3}$ 3·29 u (m), 3·52 u (m), 5·92 u (s), 6·09 u (s), 6·26 u (m), 6·34 u (m), 6·72 u (s), 6·95 u (s), 7·40 u (s), and 7·89 u (v.s.).

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[19] Complication of the reaction mixture on substituting triethylamine for 2,6-lutidine probably arises from hydride donations from triethylamine to pyrylium cations.

[20] For related participation in a solvolysis reaction, see O. L. Chapman and P. Fitton, *J. Amer. Chem. Soc.* **85**, 41 (1963).

[21] TLC was performed on commercially available adsorbent. Unless stated to the contrary the plates were activated at 120° for 1–3 hr. NMR spectra were determined in carbon tetrachloride solutions on a Varian A-60 instrument and are referred to tetramethylsilane as 10.

2,6-*Diphenylpyrylium perchlorate and ethyl diazoacetate in the presence of lutidine.* To a solution of 0·34 g (3·0 mmoles) ethyl diazoacetate and 0·32 g (3·0 mmoles) 2,6-lutidine in 10 ml dry acetonitrile maintained at 0° under a N_2 atm. in a 100 ml 2-necked flask fitted with a dropping funnel, magnetic stirrer and condenser attached to a gas burette was added over 1·5 hr with stirring a solution of 1·0 g (3·0 mmoles) 2,6-diphenylpyrylium perchlorate in 30 ml acetonitrile. After addition of the salt was complete the reaction mixture was stirred at 25° for 1·5 hr and then poured into 100 ml 3% $NaHCO_3$ aq. The aqueous layer was extracted with pentane until the extracts were colourless. The combined extracts were washed with water and saturated salt solution, dried over Na_2SO_4, and evaporated to afford 0·80 g viscous brown oil, $\lambda_{max}^{Et_2O}$ 247 mu ($E_{1cm}^{1\%}$ = 490), 353 mu ($E_{1cm}^{1\%}$ = 210) TLC indicated the presence of 11 components. Chromatography of 93·3 mg of this crude product (Silica Gel G, 1·25 mm, 6:4 chloroform–hexane) gave 20 mg (18% yield) 2,6-diphenyl-4-carbethoxymethylene-4H-pyran (I), as bright yellow needles, R_f 0·26, m.p. 104·5–105° after recrystallization from pentane, $\lambda_{max}^{Et_2O}$ 255 mu ($1·8 \times 10^4$), 262 mu ($1·8 \times 10^4$), 288 mu ($1·9 \times 10^4$) and 351 mu ($2·5 \times 10^4$), $\lambda_{max}^{CHCl_3}$ 5·95 u (s), 6·10 u (v.s.), 6·33 u (s), 6·42 u (s), 6·72 u (m) and 6·93 u (m). Its NMR spectrum exhibited a doublet at τ 1·71 (J = 2·5 c/s, 1H), a complex τ 2·2–2·6 (10H), a doublet at τ 3·60 (J = 2·5 c/s, 1H), a singlet at τ 4·78 (1H) and the ethoxy group as a quartet at τ 5·8 (2H) and triplet at τ 8·7 (3H). (Found: C, 79·01, 79·20; H, 5·80, 5·68. Calc. for $C_{21}H_{18}O_3$: C, 79·22; H, 5·70%).

Addition of perchloric acid to an acetonitrile solution of I afforded a yellow-green fluorescing solution, $\lambda_{max}^{CH_3CN}$ 395 mu ($2·8 \times 10^4$) and 278 mu (23×10^4) which reverted to that of I on addition of base.

2,6-*Diphenyl-4-carbethoxymethylpyrylium perchlorate.* Dropwise addition of 60% $HClO_4$ to an ether solution of 2,6-diphenyl-4-carbethoxymethylene-4H-pyran precipitated in 35% yield the pyrylium salt. It was purified by dissolving in acetonitrile followed by precipitation with ether. It forms fine bright yellow needles which slowly decompose from 200–250°, λ_{max}^{KBr} 5·88 u. (Found C, 60·39; H, 4·65; Cl, 9·57. Calc. for $C_{21}H_{19}O_7Cl$: C, 60·22; H, 4·57; Cl, 8·47%).

2,6-*Diphenylpyran-4-thione and ethyl diazoacetate.* Under an atm. of N_2 a mixture of 31 mg (0·12 mmole) 2,6-diphenylpyran-4-thione,[18] 26 mg Cu powder, 22 mg $CuSO_4$ and 100 mg ethyl diazoacetate in 25 ml heptane was heated under reflux with stirring for 5·5 hr and stirred at 25° for 12 hr. The reaction mixture was filtered and evaporated to afford an oily reaction mixture, TLC of which indicated 19 coloured components. Chromatography (Silica Gel, G 0·75 mm, 1:1 chloroform–pentane) with isolation of the band (R_f 0·4) corresponding to the methylenepyran I afforded 1·7 mg (4% yield) of slightly impure I. Its identity was established by comparison of its UV spectrum with the product from ethyl diazoacetate and 2,6-diphenylpyrylium perchlorate, both in the presence and absence of perchloric acid, and by comparison of R_f values on TLC on alumia G and Silica Gel G in five different solvent systems.

Acknowledgement—Partial support by the National Science Foundation is gratefully acknowledged.