

Oxidative Furanizations of Phenylated Unsaturated Ketones. Intermediate 5,5-Diphenyl Furanonium Salts: Phenyl Group Migrations and Reductions to 2,5-Dihydrofurans (1a)

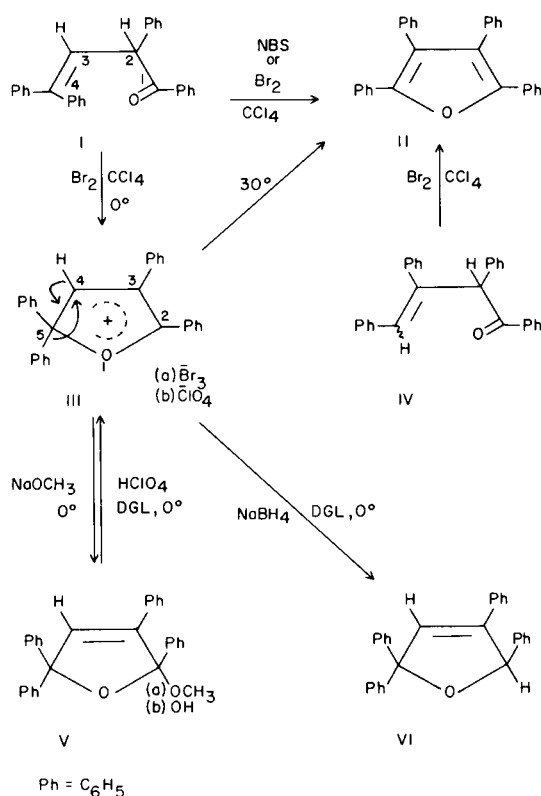
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Sir:

Investigations of brominative reactions of several phenylated β,γ -unsaturated ketones (2a) have led to new and convenient furan and dihydrofuran syntheses, and to the formation and in certain cases isolation of 5,5-diphenyl furanonium salts which are of current interest relative to recent work on furanonium ions (3).

Treatment of 1,2,4,4-tetraphenyl-3-butene-1-one (I) (2j) in carbon tetrachloride with bromine or *N*-bromosuccinimide gave tetraphenylfuran (II). The formation of II involved brominative oxidation to the furanonium ion IIIa followed by phenyl group migration and loss of a proton.



To prove the existence of the intermediate furanonium ion III compound I was brominated in diglyme at 0°. The resulting orange solution of the furanonium perbromide

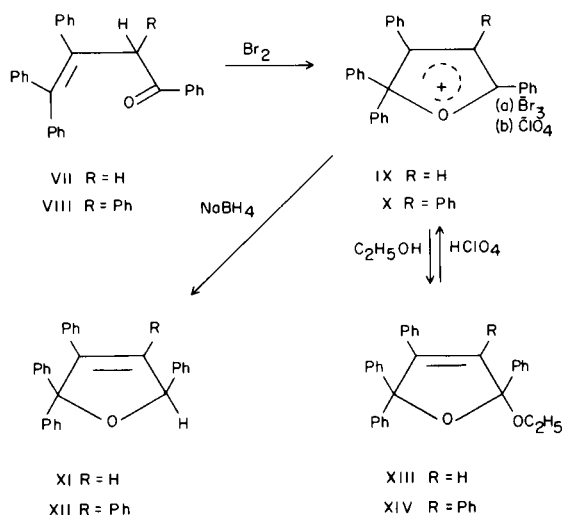
IIIa upon immediate reduction by sodium borohydride at 0° (4) produced the known 2,3,5,5-tetraphenyl-2,5-dihydrofuran (VI) (2h), and upon reaction with methanolic sodium methoxide at 0° gave 2-methoxy-2,3,5,5-tetraphenyl-2,5-dihydrofuran (Va) (2g). Acidification of the 2,3,5,5-tetraphenyl-2-hydroxy-2,5-dihydrofuran (Vb) (2g) with perchloric acid at 0° gave a yellow solution of the furanonium perchlorate IIIb which was also reduced by sodium borohydride to VI and methanolized to Va.

Nmr absorptions furnish convincing evidence for the existence of the moderately stable furanonium ion III, the salts of which have not been isolated. A freshly prepared solution of IIIb in diglyme at 0° showed a signal at δ 7.6 which is assigned to the 4-proton. It has been observed that positive charges on or near a particular carbon will cause a significant downfield displacement of the chemical shift for a proton attached to that carbon (3c). In solution the furanonium ions IIIa and IIIb upon standing for about 15 minutes at room temperature underwent spontaneous conversion to tetraphenylfuran (II) by 5-to-4 phenyl group migration and loss of the 4-proton. Support for this rearrangement of III to II is given by the change in the nmr spectrum while a solution of the furanonium ion III is warmed to room temperature. This involves gradual diminution and ultimate disappearance of the 4-proton signal at δ 7.6 while tetraphenylfuran (II) is being formed.

1,2,3,4-Tetraphenyl-3-butene-1-one (IV) (2b), a structural isomer of I, similarly underwent brominative oxidation to tetraphenylfuran (II).

Substitution of a phenyl group at carbon-3 in the β,γ -unsaturated ketones of type I, with or without a phenyl group at carbon-2, dramatically limits the reaction course by blocking phenyl group migration and, thereby, furanization; furthermore it makes possible the isolation of stable furanonium salts. Thus, 1,3,4,4-tetraphenyl-3-butene-1-one (VII) (2i) and the 1,2,3,4,4-pentaphenyl-3-butene-1-one (VIII) (2e) under the above brominative oxidation conditions gave the stable orange furanonium perbromides IXa and Xa, respectively (5).

Strong evidence for the furanonium salt structures IXa and Xa are the infrared and nmr absorptivities. The infrared spectra in each case exhibit an intense band at

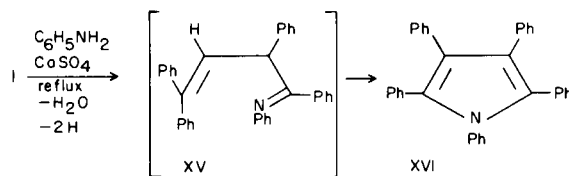


about 1540 cm^{-1} attributable to the allyl cation $\text{-C}\equiv\text{C}\equiv\text{C}\equiv\text{O}^{\pm}$. The nmr spectrum (deuteriochloroform) of IXa showed an absorption at δ 9.1 integrating 1:20 with the aromatic protons, which was assignable to the 4-proton, and its position is consistent with that observed for similar protons in other furanonium ions (3). A signal at δ 8.7 is attributable to the two *ortho* protons of the 2-phenyl group. The 8-proton multiplet centered at δ 7.9 is assigned to the three *meta* and *para* protons of the 2-phenyl group and the five protons of the 4-phenyl group. The ten-proton aromatic singlet at δ 7.5 is assigned to the protons of the two phenyl groups attached to position-5. The absorption of the two *ortho* protons of the phenyl group at position 2 at a field significantly lower than normal indicates strong localization of positive charge at the 2-carbon atom relative to carbon atoms at positions 3,4, and 5.

The perchlorates IXb(5) and Xb(5) were obtained from the 2-ethoxydihydrofurans XIII (2a) and XIV (2e) by the action of perchloric acid in diglyme. They underwent ethanolysis to the 2-ethoxy-2,5-dihydrofurans XIII and XIV. Sodium borohydride reacted with the salts only at carbon-2 and gave the 2,5-dihydrofurans XI (5) and XII (5) with no detected formation of the isomeric 2,3-dihydrofurans. All of these reactions, including those of III, indicate greater localization of positive charge at carbon-2 than at carbon-4, but they are doubtless influenced by the large steric shielding of carbon-4 due to the two phenyl groups at position 5. The reductions constitute a convenient preparative method for 2,5-dihydrofurans.

The attempt (6) by the action of refluxing aniline to convert ketone I into its anil XV for photochemical study

resulted in oxidative pyrrolization to pentaphenylpyrrole, XVI, presumably involving a pyrrolonium ion and phenyl group migration. This reaction was shown not to proceed through tetraphenylfuran (II) as intermediate.



Principles involved in the oxidative furanizations and pyrrolizations are seen in the stepwise conversions of dypnone to furans (7a) or pyrroles (7b,c) through γ -bromo and γ -morpholinyl dypnones and subsequent hydrolysis or aminolysis.

REFERENCES

- (1a) Supported in part by Grant GP-5453 from the National Science Foundation; (b) Shell Companies Fellowship, 1965-1966 (LPT); (c) P. F. duPont Fellowship, 1967-1968 (WMH).
- (2) Ph.D. Dissertations, University of Virginia: (a) L. P. Tenney, 1966; (b) D. W. Boykin, Jr., 1965; (c) J. I. Dale, 1962; (d) L. T. Slade, 1961; (e) C. L. Dickenson, 1954; (f) R. E. Lutz and C. L. Dickenson, *J. Org. Chem.*, **27**, 2024 (1962); (g) R. E. Lutz, C. L. Dickenson and W. J. Welstead, Jr., *ibid.*, **27**, 3062 (1962); (h) R. E. Lutz, J. I. Dale and D. W. Boykin, Jr., *J. Am. Chem. Soc.*, **85**, 2340 (1963); (i) D. W. Boykin, Jr. and R. E. Lutz, *ibid.*, **86**, 5046 (1964); (j) R. E. Lutz, R. G. Bass and D. W. Boykin, Jr., *J. Org. Chem.*, **29**, 3660 (1964).
- (3a) V. E. Wiersum and H. Wynberg, *Tetrahedron Letters*, 2951 (1967); (b) A. Fabrycy, *Roczniki Chem.*, **40**, 1657 (1966); *Chem. Abstr.*, **66**, 94840M (1967); (c) cf. N. C. Deno, *Prog. Phys. Org. Chem.*, **2**, 160 (1964).
- (4) cf. G. A. Reynolds and J. A. Van Allan, *J. Org. Chem.*, **32**, 3616 (1967).
- (5) The following new compounds gave correct C and H analyses: Data: IXa, m.p. $150\text{-}151^\circ$, infrared band at 1540 cm^{-1} ; IXb, m.p. 180° ; Xa (monohydrate) 152° . Xb, m.p. $181\text{-}182^\circ$; XI, m.p. 122° , λ (EtOH) $254\text{ m}\mu$ ϵ 13,170, no infrared band at 1640 cm^{-1} for C=C-O; XII, m.p. 172° , λ (EtOH) $261\text{ m}\mu$ ϵ 12,166, no infrared enol ether band at 1640 cm^{-1} [the compound m.p. 185° supposed to be XII [D. A. Hahn and R. Murray, *J. Am. Chem. Soc.*, **36**, 1484 (1914)] is in error (2e)].
- (6) A. B. Turner, unpublished results, 1968.
- (7a) R. E. Lutz, L. T. Slade and P. A. Zoretic, *J. Org. Chem.*, **28**, 1358 (1963); (b) A. Padwa, R. Gruber and D. Rashayan, *ibid.*, **33**, 1 (1968); (c) R. M. Rodenbaugh and N. A. Cromwell, *Tetrahedron Letters*, 2859 (1967).

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