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THE BROMINATION OF TETRAPHENYLCYCLOBUTADIENE-NICKEL BROMIDE COMPLEX

H. H. Freedman and G. A. Doorakian
The Dow Chemical Company, Eastern Research Laboratory, Framingham, Mass.

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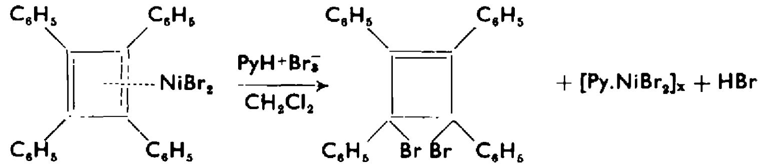
Abstract—The action of pyridinium hydrobromide perbromide on the title compound yields 3,4-dibromotetraphenylcyclobutene and 2,5-di-*p*-bromotetraphenylfuran, the relative yields of which depend on the history of the brominating agent. A derivative of the latter compound can be reduced to a new dihydrofuran system.

It has previously been reported[1] that the bromination of tetraphenylcyclobutadiene–nickel bromide (I) makes available the versatile new compound, 3,4-dibromotetraphenylcyclobutene (II). A detailed account of both the genesis of II and the formation of an unexpected by-product is now presented.

When the complex I, in methylene chloride solution, is treated with molecular bromine, extensive decomposition occurs yielding only traces of the desired cyclobutene, II. In contrast, bromination by means of excess pyridinium hydrobromide perbromide ($PyH^+Br_3^-$) in methylene chloride proceeds smoothly and leads to II in yields of up to 88%. The use of $PyH^+Br_3^-$ as a mild selective brominating agent, particularly suited for compounds prone to decomposition, needs no further documentation here. Its specific success in this instance may perhaps be attributed to the removal of the coordinated nickel as a pyridinium complex with simultaneous bromination of the exposed cyclobutadiene ring, or alternatively, the reaction may occur step-wise, with pyridine successively displaying the nickel cyclobutadiene π-bond and bromination occurring without the intermediacy of free tetraphenylcyclobutadiene. However, for the present, mechanistic interpretation must remain purely speculative.



I II

The yield of II, in the early stages of its preparation, varied erratically from 40 to 80%. Investigation disclosed that the production of II varied inversely with the formation of a by-product, which was readily separated from II, and was eventually identified as 2,5-di-*p*-bromotetraphenylfuran (III). It is of interest that though III was first prepared by Zinnin[2] in 1867, and the gross structure established by Salkind[3] in 1932, the exact position of the bromine atoms in Zinnin's "dibromolepidin" remained in doubt for almost 100 years until the correct structure was recently inferred by

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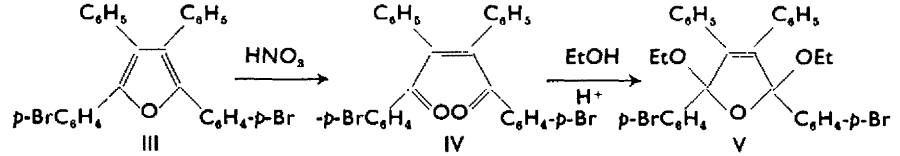
[1] H. H. Freedman and A. M. Frantz Jr., *J. Am. Chem. Soc.* **84,** 4165 (1962).

[2] N. Zinnin, *J. Pract. Chem.* **101,** 160 (1867); *Bull. Soc. Chim.* France [2], **8,** 271 (1867).

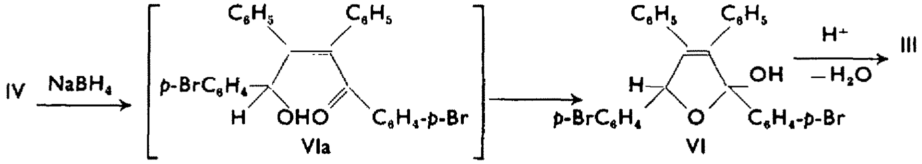
[3] J. Salkind and V. Teterin, *J. Pract. Chem.* **133,** 195 (1932).

Wilcox and Stevens[4] and substantiated through synthesis by Lutz and Welstead.[5] We



had independently arrived at this structure for III from a consideration of the NMR spectrum of the nitric acid oxidation product of III, *cis*-di-(*p*-bromobenzoyl)-stilbene (IV). The spectrum of IV consists of a single sharp peak for the two stilbene-type phenyls at 2·8 τ and a typical A_2B_2 quartet at lower field (ca. 2·4 τ) for two benzoyl phenyls containing *para*-substituents. An alternative structure for IV, and therefore for III, is ruled out by the NMR data.

It is appropriate to mention here a novel chemical transformation of the diketone IV, discovered while in the process of proving its structure. Reduction of IV with excess sodium borohydride, followed by isolation under non-acid conditions, led to a new reduction product in 85% yield. This compound, $C_{28}H_{20}O_2Br_2$, displayed an hydroxyl but no carbonyl band in its IR spectrum and its NMR spectrum contained six discrete lines; four lines in the phenyl region (2·5–3 τ), and two singlets representing one proton each at 3·65 τ and at 6·6 τ. Its UV spectrum in ethanol was very similar to that of the cyclic ketal V (obtained by the ketalization of IV with acidified ethanol),[6] suggesting that both compounds possess similar chromophoric systems. The reduction product was quite stable to base but on exposure to acid was rapidly and quantitatively converted to the original furan, III. These data are readily accommodated by the 2,5-dihydrofuran structure VI arising by internal ketalization of the



intermediary hydroxy-ketone (VIa). Facile acid catalized dehydration of VI is therefore not an unexpected reaction, generating as it does a stable aromatic system, and in fact, it is quite surprising that VI is capable of more than a transitory existence. The stereochemistry of VI is not known at present, but it appears that this is the first known example of the 2-hydroxy-2,5-dihydrofuran system containing a proton in the 5-position.[7]

One final point is worthy of attention: the origin of the dibromofuran III from the action of $PYH^+Br_3^-$ on I. It has been mentioned previously that the bromine atoms of II are extraordinarily labile[1] and are instantly hydrolysed when exposed to

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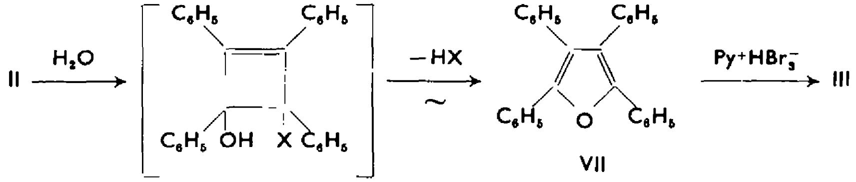
[4] C. F. Wilcox Jr. and M. P. Stevens *J. Am. Chem. Soc.*, **84**, 1258 (1962).

[5] R. E. Lutz and W. J. Welstead *Ibid*, **85**, 755 (1963).

[6] The preparation of this ketal (V) is implied by Lutz, Dickerson, Welstead and Bass (*J. Org. Chem.*, **28**, 711 (1963)), but is not substantiated in their experimental section.

[7] The data of R. E. Lutz, Bauer, R. G. Lutz and Gillespie (*J. Org. Chem.* **20**, 218 (1955)) suggested to us that an intermediate analogous to III could be obtained from the $NaBH_4$ reduction of *cis*-dibenzoylstilbene using non-acidic conditions of isolation. The resulting product proved to be exceedingly unstable and could not be purified without reverting to tetraphenylfuran. The exact nature of the stabilizing influence of the *p*-bromo substituents on VI is not understood.

water. The resulting hypothetical glycol or bromohydrin, IIa, is evidently too unstable to tolerate isolation and internally eliminates water or hydrogen bromide with rearrangement to the stable product of isolation, tetraphenylfuran.[8] Bromination of VII in anhydrous medium is known to produce III[5] and we have ascertained that $PYH^+Br_3^-$ acts similarly. Thus, it is clear that the presence of water will eventually lead to the dibromofuran III at the expense of the dibromocyclobutene II.



IIa X = OH or Br

The source of the water necessary to produce VII was eventually traced to the brominating agent. When this reagent was freshly prepared according to the method of Fieser,[9] the yield of II was 60% and that of III was 20%. When this material was allowed to age while unprotected from atmospheric moisture, the yield of II dropped to 10% and that of III increased to 65%. All these difficulties were obviated when pure, anhydrous $PYH^+Br_3^-$ was prepared *in situ* from pyridine hydrobromide and an equivalent of bromine in methylene chloride. Using this anhydrous reagent, the dibromocyclobutene II was obtained consistently in yields of 85% or better and little or no dibromofuran III was observed.

EXPERIMENTAL[10]

Bromination of tetraphenylcyclobutadiene-nickel bromide complex

(a) *With "ordinary"* $PYH^+Br_3^-$. To 4·3 g (7·5 mmol) I, partly dissolved in 125 ml dry methylene chloride, was added 4·8 g (15 mmol) $PYH^+Br_3^-$, freshly prepared according to the method of Fieser.[9] The deep-purple solution was stirred magnetically under a N_2 atm at room temp for ~15 hrs (conveniently, overnight). During the time, the color gradually changed to orange-yellow, HBr fumes were evolved, and a tan solid was deposited. The solution was separated from amorphous, water-soluble complex which was not further investigated other than to show that it qualitatively contained pyridine, Ni and ionic bromide. Removal of the solvent left a mixture of II, III, and excess $PYH^+Br_3^-$. Trituration with 25 ml dry acetone dissolved the latter two components leaving a white solid which was washed with a small amount of acetone and air-dried to yield 2·3 g. (66%) substantially pure II, m.p. 173–74°. Recrystallization of this material from ligroin, with the help of methylene chloride, did not significantly change the m.p., but yielded well-formed crystals of analytical purity. (Found: C, 64·9; H, 3·9; Br, 31·0. $C_{28}H_{20}Br_2$ requires: C, 65·1; H, 3·9; Br, 31·0%). The spectroscopic and chemical properties of II supported its proposed structure and will be reported in detail in a subsequent publication.

The acetone filtrate was evaporated to dryness and the excess brominating agent removed from the resulting orange gum by slurrying with 15 ml ethanol. The residual white solid, after drying, consisted of 0·8 g. (20%) III, m.p. 194–96° (lit.,[4] 192°).

(b) *With dry brominating agent*. To 4·3 g (7·5 mmol) I in 125 ml dry methylene chloride was added 2·4 g (15 mmol) anhydrous pyridinium hydrobromide and then 2·4 g (15 mmol) bromine in 10 ml methylene chloride. After stirring overnight, no HBr was observed, but the reaction mixture was substantially the same as previously described. Evaporation to dryness and trituration with acetone yielded 3·3 g (85%) II, m.p. 173–4°. The acetone filtrate was not investigated.

[8] Details of the various solvolytic reactions of II will be described in a future publication.

[9] L. F. Fieser, *Experiments in Organic Chemistry*, p. 65. D.C. Heath and Co., Boston (1955).

[10] All m.ps are uncorrected. Analyses are by Dr. C. K. Fitz, Needham Heights, Mass. The NMR spectra were obtained on the Varian Model A-60 and the UV spectra on the Cary Model-14.

(c) *With moist brominating agent.* The identical procedure as given under (b) was followed, except that the pyridinium hydrobromide prior to use was allowed to come in contact with atmospheric moisture. After 15 hrs of stirring, considerable HBr evolution was observed, and the yield of II, after acetone treatment, was 0·35 g (9%). The acetone filtrate yielded 2·9 g (75%) III, m.p. 193–4°.

Bromination of tetraphenylfuran. To 200 mg (0·54 mmol) of tetraphenylfuran (m.p. 173–4°) in 10 ml of methylene chloride was added 344 mg (1·1 mmol) of $PYH^+Br_3^-$, prepared according to the method of Fieser.[9] The red solution was stirred for 24 hrs and the evolution of HBr was evident. Evaporation of the solvent and trituration of the resulting gum with ethanol, yielded 195 mg (70%) III, m.p. 193–5°.

2,5-*Di*-p-*bromophenyl*-2,5-*diethoxydihydrofuran* (V). A mixture of 0·5 g. (0·91 mmol) IV (m.p. 224–5°, lit.[4] 225°) in 25 ml ethanol containing 5 drops conc. HCl was refluxed until all of the solid had dissolved (about 2 hrs). Cooling afforded colorless rosettes of product (0·45 g, 80%), m.p. 238–40°. λ_{max}^{EtOH} 229mμ (ε 17,800), 260 mμ (ε 8,250). (Found: C, 62·0; H, 4·9; Br. 25·7; OEt, 14·6. $C_{32}H_{28}Br_2O_3$ requires: C, 61·9; H, 4·6 Br, 25·7; OEt, 14·5%).

2-*Hydroxy*-1,2,3,4-*tetraphenyl*-2,5-*dihydrofuran* (*VI*). To a solution of 0·9 g $NaBH_4$ dissolved in 90 ml anhydrous methanol was added 0·8 g. (1·46 mmol) IV. The mixture was warmed briefly and then stirred until all the solid ketone had dissolved (~1 hr). The solution was poured into a large excess of water, extracted with ether and the ether layer separated and washed with water until neutral. The dried ether extract was evaporated under vacuum and the residual oil crystallized from methylene chloride–ligroin, to yield 0·7 g (86%) white crystals, m.p. 153–58°. (Further recrystallization did not improve the m.p., and care must be taken to avoid prolonged heating since this leads to its conversion to III). λ_{max}^{EtOH} 227 mμ (ε 17,500), 255 mμ (ε 6,800). Its NMR spectrum in $DCCl_3$ displayed four sharp peaks in the phenyl region between 2·5–2·9τ of total relative area = 18 protons, and two singlets at 3·5τ and 6·4τ of relative area one each for the proton at the 2-position and the hydroxyl proton, respectively. (Acidification of this solution resulted in instantaneous change to the spectrum typical of III). (Found: C, 61·0; H, 3·8; Br, 28·8. $C_{28}H_{20}O_2Br_2$ requires: C, 61·3; H, 3·7; Br, 29·2%).

Attempted preparation of VI (Br = H). A mixture of 0·7 g *cis*-dibenzoylstilbene (m.p. 214–15°) and 0·6 g $NaBH_4$ in 25 ml ethanol was warmed until all the solid dissolved. The product was then isolated as for the preceding experiment. The yellow, crystalline solid (0·4 g.) displayed an hydroxyl peak in its IR spectrum, but was obviously contaminated with tetraphenylfuran. Attempted purification by recrystallization resulted only in the isolation of VII.