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CIS ADDITION OF BROMINE TO DIAROYLETHYLENES

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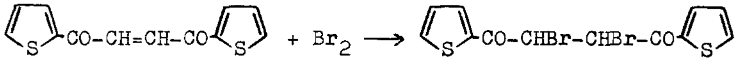
Structure of brominated dithenoylethene.

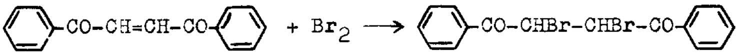
In the course of investigations aimed at synthetic routes for the preparation of terthienyls (1) bromine was added to trans dithenoylethene (I) in both acetic acid and chloroform as solvents. Two products were isolated in each case with melting points 177-178° and 156-157°. Both compounds proved by elementary analysis and NMR spectra to be the bromine addition product (II). The high-melting form (IIa) showed in the NMR spectrum apart from the thiophene absorption one singlet at τ = 4.24 (relative to TMS), the low-melting form (IIb) a singlet at τ = 4.40. The obvious conclusion is that one compound is the meso dibromide and the other the dl dibromide II.



I II

By NMR analysis it appeared that the products IIa and IIb were formed in the ratio 3 : 2 in acetic acid and 1 : 3 in chloroform.

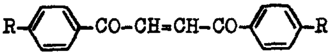
This observation is related to the results of Lutz and coworkers in the nineteen twenties who likewise found cis-addition products when bromine was added to cis dibenzoylethene (III) or trans dibenzoylethene (2-6) (IV).


III cis (R = H)
IV trans (R = H)
V (R = H)

Lutz (4) proved that the high melting product (Va) represented the *meso* dibromide (m.p. 179°) and the low melting compound the *dl* product (m.p. 168°). When starting from trans dibenzoylethene the amount of the *dl* product (Vb) was lower in acetic acid than in chloroform. We found NMR singlets for the CHBr group to be situated at $\tau = 4.07$ for (Va) and at 4.26 for (Vb). Thus the melting points, product distribution and NMR absorptions all point to the *meso* configuration for (IIa) and the *dl* configuration for (IIb).

Stereochemistry.

Because of the uncommon nature of cis-halogen additions we investigated the mechanistic aspects of this reaction in some detail. Since trans dibenzoylethene is easily transformed into the cis isomer photochemically (a reaction which we were not yet able to perform with trans dithenoylethylene), most experiments were done with the dibenzoylethenes. In addition some experiments were done with two substituted dibenzoylethenes: trans bis(p-methoxybenzoyl)-ethene (VI) and trans bis(p-chlorobenzoyl)ethene (VII).



VI trans (R = OCH_3)

VII trans (R = Cl)

The following observations of Lutz were confirmed and extended.

1. The product distribution is independent on whether the cis or trans dibenzoylethene is used in the bromination reaction.
2. Lower solvent polarity favours the formation of the <u>dl</u> dibromide.

The data given in the table illustrate these rules. They were obtained by reacting in darkness equimolar quantities of the ethylene and bromine till the colour had disappeared. After evaporating the solvent, the residue was dissolved in $CDCl_3$ and the integrated values of the NMR absorptions at τ around 4 were used to determine the ratio of both isomers.

From a comparison of the dibenzoylethenes a third rule appears to be followed:

3. The electron attracting substituent favours the formation of the <u>meso</u> isomer and vice versa. The results of Lutz in this respect are inconclusive (3,5).

Kinetics.

More insight into the mechanism was obtained from kinetic experiments in carbon tetrachloride solution. Reasonably reproducible results were obtained when polyethylene bottles were used as reaction vessels. The reactions were performed in the dark at 25.0°. At fixed times samples were

TABLE

Isomer Distribution of the Bromine Adducts of trans Dithenoylethene (I) and Dibenzoylethenes (% meso compound given, 25°).

Solvent	Starting compound trans dithenoyl-ethene (I)	trans dibenzoyl-ethene (IV)	cis dibenzoyl-ethene (III)	trans bis(p-methoxy-benzoyl)ethene (VI)	trans bis(p-chloro-benzoyl)ethene (VII)
DMF	100	51	48		
CH_3OH	100				
CH_3COOH	62				
$CHCl_3$ a)	26	45	40	30	75
$CHCl_3$ + 9% CH_3OH	75	90	75	65	90
CCl_4	15	10	15	7	29

a) Stabilizer (1% ethanol) not removed.

taken, quenched with aqueous KI and the iodine titrated with $Na_2S_2O_3$. No addition of I_2 to the ethylenes occurs.

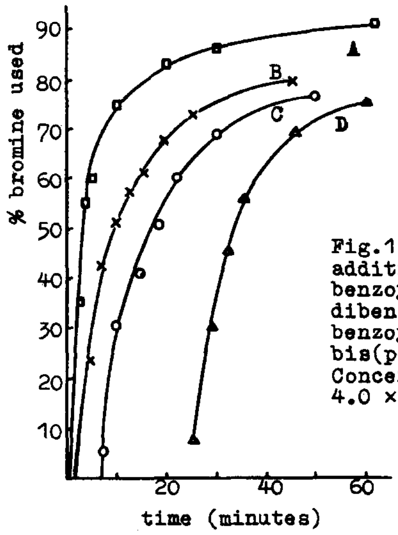


Fig.1. Velocity of bromine addition to trans bis(p-methoxybenzoyl)ethene (curve A), cis dibenzoylethene (B), trans dibenzoylethene (C) and trans bis(p-chlorobenzoyl)ethene (D). Concentration of both reagents 4.0×10^{-3}.

A number of results are illustrated in the figure. Three aspects of the reactions are immediately apparent:

a) trans dibenzoylethene shows an induction time during which no bromine is absorbed, but the cis isomer does not;

b) an electron attracting substituent increases the induction time and slows down bromine absorption and v.v.;

c) When the induction time is finished the rate of bromine absorption for cis and trans isomers is very nearly the same.

The obvious conclusion is that the trans isomer is first transformed into the cis isomer. Only when a reasonable amount of the cis isomer is formed, bromine absorption starts. The isomerization does not occur in the dark without bromine.

A detailed evaluation of the kinetics is severely hampered by the fact that in a concentration range convenient for analysis and reaction times both reactions - isomerisation and bromination - occur with comparable speed. Nevertheless we were able to collect fairly strong evidence for two more points:

d) the isomerisation reaction is either of order 1/2 or 1 (but no higher) in bromine;

e) the bromination reaction is either of second or third order in bromine (or between?).

It is clear that the two reactions proceed along different mechanisms and not via a common intermediate as the brominium ion or a radical species, which reacts further either through elimination to the (isomerised) olefin or through addition to the dibromo adduct (7). The question whether the addition involves only trans addition on the mixture of cis and trans ethylenes or whether partial cis addition occurs as well, cannot be answered until further experiments have been carried out. These will be published at a later date together with full details of the present work.

Experimental.

Trans dithenoylethene (I) was prepared from thiophene by the reaction sequence described earlier (1,8). The product (I) after crystallisation from acetone melted at 188-189° (lit. 189° (8)).

Trans dibenzoylethene (III) was prepared from benzene and fumaroyl chloride (9) (m.p. 110-111°, lit. 111° (10)). In the same way we obtained trans bis(p-methoxybenzoyl)-ethene (VI) (m.p. 172-173°, lit. 172° (11)) and trans bis-(p-chlorobenzoyl)ethene (VII) (m.p. 166-167°, lit. 165.5° (12)). Cis dibenzoylethene (III) was prepared from the trans isomer by irradiating an ethereal solution of (II) for six hours in a Rayonet photochemical reactor equipped with RPR-2537 Å lamps (m.p. 134°, lit. 134° (13)). Solvents were of pro analysi grade and used as such.

NMR spectra were taken in a Varian A 60 spectrometer with tetramethylsilane as an internal standard.

References

(1) H.J. Kooreman, Ph.D.Thesis Groningen, 1966.
H.J. Kooreman and Hans Wynberg, in the press.
(2) J.B. Conant and R.E. Lutz, J.Am.Chem.Soc.**47**,881(1925).
(3) R.E. Lutz, ibid.**48**,4905(1926).
(4) " " **49**,1106(1927).
(5) " " **51**,3008(1929).
(6) " " **52**,3423(1930).
(7) Cf. P.B.D.de la Mare and R. Bolton, Electrophilic additions to unsaturated systems, p.136 (Elsevier, Amsterdam 1966).
(8) W. Heffe and F. Kröhnke, Chem.Ber.**89**,822(1956).
(9) Organic Syntheses, Collective Volume **3**, p.248 (John Wiley and Sons, Inc., New York 1955).
(10) C. Paal and H. Schulze, Ber.**33**,3795(1900).
(11) F.I. Crowell, G.C. Halsley, R.E. Lutz and W.L. Scott, J.Am.Chem.Soc.**85**,446(1963).
(12) J.B. Conant and R.E. Lutz, J.Am.Chem.Soc.**45**,1305(1923).
(13) C. Paal and H. Schulze, Ber.**35**,168(1902).