Decomposition and Cycloaddition Reactions of Some Bis(azodicarbonyl) Compounds

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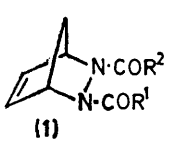
During oxidation of 1,5-dibenzoylcarbonohydrazide and 1,6-dibenzoyloxalohydrazide with *N*-bromosuccinimide and pyridine evidence was obtained for the formation of the corresponding bisazo-compounds (4a and b). Both oxidations yielded the oxadiazolone (6), which was the main product in the former. The oxalohydrazide reaction also gave minor products, perhaps attributable to the intermediacy of benzoyldi-imide. Oxidation of 1,7-dibenzoylmalonohydrazide led to intractable mixtures.

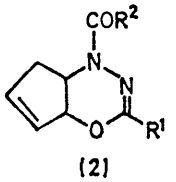
Oxidation of 1,8-dibenzoylsuccino- and 1,10-dibenzoyladipo-hydrazides and of the bisethoxycarbonyl and dipivaloyl derivatives of terephthalohydrazide gave the fairly stable bisazo-compounds (5a—d) which could be trapped as the *meso*- and racemic mixture of bisadducts with cyclopentadiene (7a—d). The stereochemical possibilities for the concerted rearrangement of such adducts to bis-1,3,4-oxadiazines are fully discussed. In the adducts (7a and b) only participation of the outer (benzoyl) group and in the ester adduct (7c) only participation of the inner (tetraphthaloyl) group was observed, a diastereomeric pair of structures being produced in each case. The dipivaloyl adduct (7d) showed all three possible modes of isomerisation, utilising both inner and outer acyl groups; one of the pair of diastereoisomers formed was isolated pure in each case.

As an extension of related work [1] we have become interested in the competition between the various isomerisation pathways which are possible with the adducts from unsymmetrical azo-compounds and cyclic dienes. Thus the cyclopentadiene adduct (1) can give either of two oxadiazines [(2) and (3)], depending on which carbonyl group participates in the isomerisation; some examples of this type have been described.[1a]

A logical extension of this kind of competition can arise with the cyclopentadiene adducts of symmetrical bisazo-compounds, and we describe here our attempts to prepare some representative examples of these by oxidation of the corresponding tetrahydro-derivatives, the bis-hydrazides. Information on bis(azodicarbonyl) compounds is scanty, and apart from a few scattered references in the chemical literature,[2-6] mainly involves patented work of special interest to the polymer industry.



(1)



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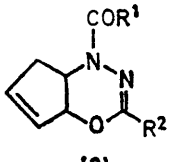


(3)

We divide our results into two sections, (*A*) dealing with the formation of the very unstable azo-compounds (4a—c) which could not be trapped with cyclopentadiene, but whose formation could be inferred from their decomposition products, and (*B*) the fairly stable azo-compounds (5a—d) which gave thermally labile bis-adducts. Our choice of end groups was governed by our experience with their ability to promote isomerisation in the adducts.[1]

$PhCO{\cdot}N{=}N{-}X{-}N{=}N{\cdot}COPh$	$RCO{\cdot}N{=}N{\cdot}CO{-}Z{-}CO{\cdot}N{=}N{\cdot}COR$
(4)	(5)
a; X = CO	a; R = Ph, Z = $[CH_2]_2$
b; X = CO·CO	b; R = Ph, Z = $[CH_2]_4$
c; X = CO·CH_2CO	c; R = EtO, Z = *p*-C_6H_4
	d; R = CMe_3, Z = *p*-C_6H_4

Of the required precursor bis-hydrazides only dibenzoylsuccinohydrazide and dipivaloylterephthalohydrazide had not been reported: they were made by routine methods. The oxidations were carried out by the usual procedures, treatment of the bismercury(II) salts with bromine,[1b] or direct reaction of the hydrazides with *N*-bromosuccinimide (NBS) and pyridine [1b] or with lead tetra-acetate.[7]

Section (*A*).—The oxidation of dibenzoyl-carbono-hydrazide, -oxalohydrazide,† and -malonohydrazide was done with NBS and pyridine. Gases were evolved and benzoic acid was a minor product in all the reactions. The neutral products are shown in Table 1.

The oxadiazolone (6), the major product from dibenzoylcarbonohydrazide, may arise by a nucleophilic decomposition of the azo-compound (Scheme 1), analogous to that proposed [5] for the oxidation with aqueous hypochlorite. NuH might be succinimide or pyridine, poor nucleophiles normally, but the azo-compound would be highly reactive since the leaving group is effectively nitrogen.

An alternative and more likely mechanism is shown in Scheme 2. The benzoyl migration and the cyclisation of the resonance-stabilised diradical could be sequential

† This hydrazide formed a dihydrate when synthesised in aqueous alkali. Both it and the anhydrous form were very insoluble in methylene chloride, but the hydrate gave a much higher yield of (6) (47, as compared with 6%). The reaction is probably heterogeneous and different sites may be exploited for dehydrogenation in the two crystalline forms. The oxidation was much faster in acetonitrile, in which the hydrazide was more soluble. In either solvent more than 2 equiv. of NBS was needed for complete oxidation.

[1] (*a*) D. Mackay, J. A. Campbell, and C. P. R. Jennison, *Canad. J. Chem.*, 1970, **48**, 81; (*b*) J. A. Campbell, D. Mackay, and T. D. Sauer, *ibid.*, 1972, **50**, 371; (*c*) C. Y.-J. Chung, D. Mackay, and T. D. Sauer, *ibid.*, 1972, **50**, 3315; (*d*) D. Mackay, C. W. Pilger, and L. L. Wong, *J. Org. Chem.*, 1973, **38**, 2043.

[2] N. Rabjohn, *J. Amer. Chem. Soc.*, 1948, **70**, 1181; P. J. Flory, N. Rabjohn, and M. C. Shaffer, *J. Polymer Sci.*, 1949, **4**, 435.

[3] E. Müller and S. Petersen, *Angew. Chem.*, 1951, **63**, 18.

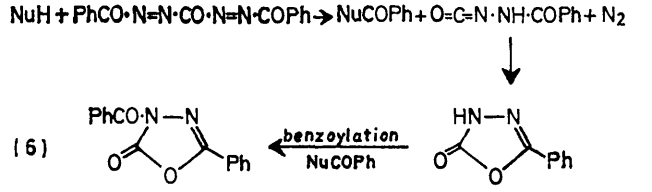
[4] S. S. Ivanov, N. A. Yuzefovich, A. V. Sidorovich, and E. F. Federova, *Kolloid Z.*, 1956, **18**, 285 (*Chem. Abs.*, 1957, **51**, 1637f).

[5] H. Minato, R. Hisada, and M. Tanaka, *Bull. Chem. Soc. Japan*, 1966, **39**, 2512.

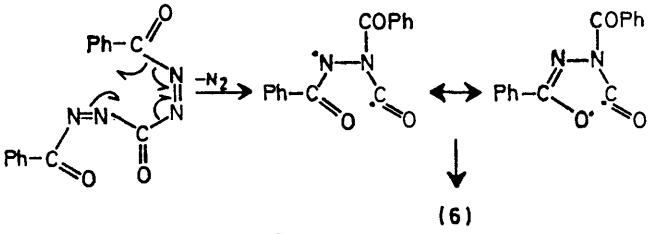
[6] B. Saville, *Chem. Comm.*, 1971, 635.

[7] R. A. Clement, *J. Org. Chem.*, 1960, **25**, 1724; R. A. Clement, *ibid.*, 1962, **27**, 1115; B. T. Yellis and J. D. Hagarty, *ibid.*, 1967, **32**, 330; B. T. Gillis and R. Weinkam, *ibid.*, p. 3321; O. L. Chapman and S. J. Dominianni, *ibid.*, 1966, **31**, 3862.

(as shown) or fully concerted. In a variant of Scheme 2 homolysis to free benzoyl radicals and attack of these on azo-nitrogen (a reaction which has precedent [8]) could also lead to (6), but the rather high yields of the latter are more consistent with the cyclic process.



SCHEME 1



SCHEME 2

In the dibenzoyloxalohydrazide oxidation, the formation of oxadiazolone (6) can be easily rationalised by a cyclisation mechanism like that of Scheme 2 [benzoyl migration in (4b) through a six-centred transition state with loss of CO + N_2]. The di- and tri-benzoylhydrazines and the diphenyloxadiazole are just the oxidation products described in earlier work on the reaction of benzoylhydrazine with silver oxide,[8] interpreted as occurring through the intermediacy of benzoyldi-imide. A logical sequence to the latter starts with 1,6-dehydrogenation:

$$(PhCO{\cdot}NH{\cdot}NH{\cdot}CO)_2 \xrightarrow{-2H\cdot} (PhCO{\cdot}\dot{N}{\cdot}NH{\cdot}CO)_2 \longrightarrow 2PhCO{\cdot}N{=}NH + 2CO$$

The anhydride may arise from reaction of benzoyloxyl radicals [8] or of an *N*-quaternised cation (*e.g.* *N*-benzoylpyridinium) with benzoic acid.

The oxidation of dibenzoylmalonohydrazide in methylene chloride or acetonitrile led to unidentified products (except for traces of dibenzoylhydrazine and diphenyloxadiazole *) lacking methylene absorption in their n.m.r. spectra. Oxidation at CH_2 is evidently faster than at NH.

The oxidation of all three hydrazides was also carried out in the presence of cyclopentadiene, either included from the start of the reaction or added immediately after the oxidising agent. No conclusive evidence of attack on either of the azo-compounds (4a and b) was found, but from the dibenzoyloxalohydrazide oxidation products, a small amount of a bisadduct of (4b) was identified by i.r., n.m.r., and (in particular) mass spectroscopy (M^+ 454; $C_{26}H_{22}N_4O_4$).

Section (*B*).—The question of structural isomerism and stereoisomerism in the formation and rearrangement of the cyclopentadiene bisadducts of a bisazo-compound like (5) requires elaboration. Considering only structural isomerism, Scheme 3 shows the results of 'in' (-Z-C(H)=O → Z-C(H)=N-) and 'out' (R-C(H)=O → R-C(H)=N-) half isomerisations to (8) and (9), which are then completed to the symmetrical 'in–in' and 'out–out' bisoxadiazines (10) and (11) and the unsymmetrical 'in–out' bisoxadiazine (12).

TABLE 1

Decomposition products of dibenzoyl-carbonohydrazide, -oxalohydrazide, and -malonohydrazide

$(PhCO{\cdot}NH{\cdot}NH)_2X$		NBS–pyridine		Time	Product yield (mol % per mol hydrazide) [a]				
X	mol	(mol)	Solvent; ml	(h)	A	B	C	D	E
CO	16·8	33·6	CCl_4; 75	1	87 [f]				
CO·CO	1·4 [c]	2·8	CH_2Cl_2; 25	48	6		+		+
	2·5	10·0	MeCN; 30	1	19	2	22	7	5 [g]
	b	10·0 [d]	CH_2Cl_2; 100	2	47				
$CO{\cdot}CH_2CO$	2·5	5·0	CH_2Cl_2; 45	48				+	
	2·5 [e]	5·0	MeCN; 45	5		+		11	

[a] The symbol + refers to the non-quantitative identification of a small amount of product; A, 3-benzoyl-5-phenyl-1,3,4-oxadiazol-2(3*H*)-one; B, 2,5-diphenyl-1,3,4-oxadiazole; C, benzoic anhydride; D, dibenzoylhydrazine; E, tribenzoylhydrazine; yield based on assumption that 2 mol produced from 3 mol of hydrazide; identification by m.p. and elemental analysis. [b] Dihydrate. [c–e] 25, 75, and 28% unchanged starting material, respectively. [f] Yield varies from 40 to 90% depending on temperature and solvent. [g] Inclusion of cyclopentadiene led to isolation by chromatography of a fraction containing the adduct $C_{26}H_{22}N_4O_4$ (*m/e* 454)

All evidence shows that only a *cis*-ring junction is formed in the rearrangements.[1] With this restriction the stereochemical consequences are shown in Scheme 4. The configurationally opposite pyridazine rings in (7) are symbolised by *pyr* and $\overline{pyr}$, as exemplified by the *meso* form *pyr*-$\overline{pyr}$ (reading from left to right). An oxadiazine ring generated by 'out' participation is designated *ox* if derived from *pyr* (and $\overline{ox}$ from $\overline{pyr}$) and one generated by 'in' participation is designated *ox'* if derived from *pyr* (and $\overline{ox'}$ from $\overline{pyr}$).† The stereospecificity of the isomerisation then demands the complete set of pathways shown in Scheme 4 in (i), (ii), and the reflection of (ii).

Thus *meso*-(7) gives *rac*-(8), (9), and (12) and *meso*-(10) and (11), while *rac*-(7) gives a different set of *rac*-(8), (9), and (12) and *rac*-(10) and (11), *i.e.* each of (8)—(12) can be expected in two diastereoisomeric forms.

* The formation of these two products again points to the intermediacy of benzoyldi-imide.

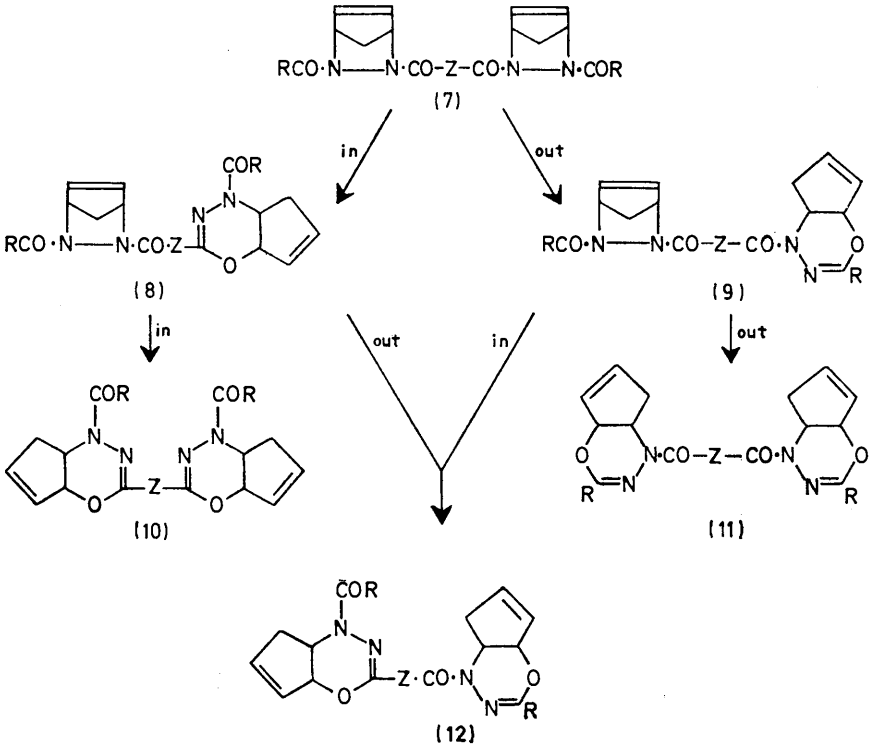
† As an example the absolute configuration of the 'in–in' isomer *ox'–ox'* is shown in Scheme 4. The specifications for the chiral carbons in *pyr* are: outer carbon *S*; inner carbon *R*; in *ox* *R*, *R*; and in *ox'* *S*, *S*.

[8] D. Mackay, U. F. Marx, and W. A. Waters, *J. Chem. Soc.*, 1964, 4793.

The azo-compound (5a) was unstable, but could be trapped in solution with cyclopentadiene as its bisadduct in *ca.* 25% yield. Compounds (5b and c) were orange-yellow crystalline solids, stable indefinitely at 0°; no effort was made to isolate (5d) but it was stable in solution. The reactions of (5b—d) with cyclopentadiene proceeded in good to quantitative yields.

None of the bisadduct mixtures could be separated by fractional crystallisation, but enrichment of one isomer of (7c) was achieved by silica gel chromatography, monitored by the lanthanide (Figure 1b; early fractions shown †).

The double isomerisation of (7a—d) was accomplished by refluxing in a suitable inert solvent, typically benzene



a; R=Ph, Z=$[CH_2]_2$
b; R=Ph, Z=$[CH_2]_4$
c; R=EtO, Z=*p*-C_6H_4
d; R=CMe_3, Z=*p*-C_6H_4

SCHEME 3

As expected the diastereoisomeric forms of the adducts (7) proved spectroscopically indistinguishable under normal conditions. Thus the n.m.r. spectrum of (7c) showed one aromatic singlet and one ethyl pattern, and that of (7d) one aromatic singlet and one Bu- singlet * in the normal range of solvents. By using the shift reagent Eu(fod)$_3$, however, in carbon tetrachloride a clear separation was obtained between the terephthaloyl singlets of the diastereoisomers of both (7c and d) (Figure 1a) and showed the diastereoisomeric yields to be about equal in each case.

* Since these signals are all sharp very small shift differences would have been detected. Assuming rapid rotation round all acyl groups the patterns generated for the *meso*-forms are two enantiotopic pairs of terephthaloyl protons (A_4) and two enantiotopic Et or Bu^t patterns, and for the *rac*-forms four equivalent terephthaloyl protons (A_4) and two equivalent Et or Bu^t patterns. The CH_2·CH_2 group in each diastereoisomer of (7a) is AA'BB' even under conditions of rapid rotation. The absorption appeared as a rather broad singlet.

or toluene. In each of the first three isomerisations one bisoxadiazine structure was the major or exclusive product. The dipivaloyl adduct (7d) gave all three structural isomers. The properties of all these products are listed in Table 2.

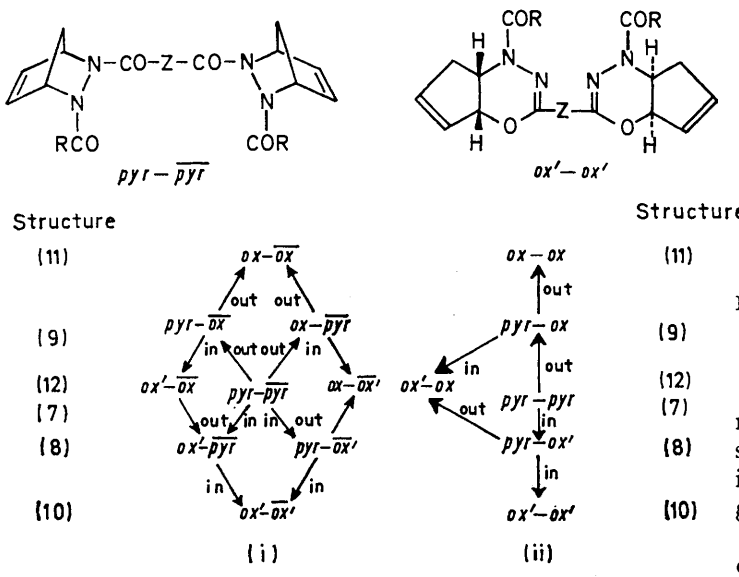
The product mixture from (7a) gave a single isomer, m.p. 193—194·5°, on repeated crystallisation. Its identification as an 'out–out' isomer (11a) followed from the sharp methylene singlet,‡ and the intense u.v. absorption maximum at 283·5 nm (ε 2·8 × 10^4) diagnostic

† This also confirms the interpretation of the equal intensities of the peaks in Figure 1a. An alternative explanation might have been that terephthaloyl rotation *is* slow on the n.m.r. time scale and that the difference in chemical shift ($\Delta\nu_{\infty}$) between the non-equivalent *meta*-related protons was made visible by the shift reagent.[9]

‡ More consistent with the symmetrical AA'BB' system in (10) or (11a) than the ABCD system in (12a).

[9] S. R. Tanny, M. Pickering, and C. S. Springer, jun., *J. Amer. Chem. Soc.*, 1973, **95**, 6227.

of its two PhC=N chromophores [*cf.* the PhC=N band in (2; R^1 = Ph, R^2 = CMe_3) with $\lambda_{max.}$ 281 nm (ε 1·25 × 10^4); the alkyl-C=N chromophore absorbs around 240 nm [1b]].



SCHEME 4 Stereospecificity of the isomerisation of (i) the *meso*-form and (ii) one enantiomeric form of the bisadduct (7)

Isomerisation of (7b) likewise gave (11b) as an amorphous mixture, the structure again being that required by the u.v. spectrum.

clusive participation of the terephthaloyl group to give (10c). Fractional crystallisation gave both isomers,*

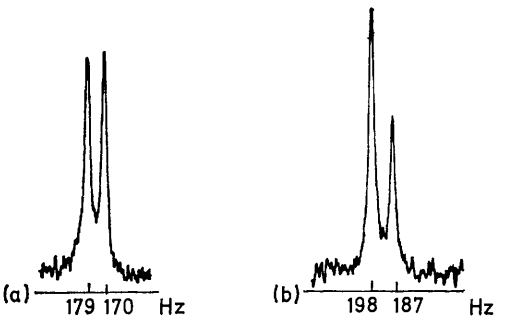


FIGURE 1

Effect of Eu(fod)$_3$ on aromatic singlets of a diastereoisomeric mixture of (7c) in CCl_4 solution (a) before and (b) after partial separation by column chromatography. Peak positions are downfield from benzene as internal standard

m.p.s 246—248° and 200·5—202·5°. These were spectroscopically indistinguishable except for slight differences in the i.r. absorption maxima of their C=O and C=N groups.

Hydrolysis of each isomer (1N-KOH in MeOH) gave different dibases (13). The dibase from the higher melting isomer was converted back into its parent bisoxadiazine with ethyl chloroformate in pyridine and each dibase gave a different dibenzoyl derivative. The hydrolysis and reconversion reactions provide unambiguous proof of the bisoxadiazine structure.

TABLE 2

Bisadducts of cyclopentadiene and bis(azodicarbonyl) compounds (5a—d)

Adduct	M.p. (°C)	$\nu_{max.}$ (Nujol)/ cm^{-1} (C=O and/ or C=N)	$\lambda_{max.}$ (EtOH)/ nm(ε)	τ ($CDCl_3$) [c] Aryl	Vinyl	Tert.	Ring CH_2	Other	Analysis Reqd. / Found	C	H	N
(7a)	*a*	1660	250—260sh	2·0—2·8	3·47, 3·67	4·43, 4·94	8·23	6·4—7·6 (CO·CH_2)	$C_{28}H_{26}N_4O_4$	69·7	5·45	11·6
										69·6	5·5	11·55
(11a)	193—194·5	1660, 1633	283·5 (28,000)	1·7—2·7	3·4—3·9	4·8—5·3	6·95, 7·68 (*J* 18·5 Hz)	6·68 (CO·CH_2)		69·75	5·4	11·8
(7b)	*b*	1678, 1660	240—280sh	1·8—2·7	3·30, 3·55	4·40, 4·85	7·9—8·8 [d]		$C_{30}H_{30}N_4O_4$	70·55	5·9	10·95
										e	*e*	*e*
(11b)	*b*	1668, 1634	283 (27,000)	1·8—2·8	3·6—4·1	4·9—5·4	6·7—8·6 [d]			70·85	6·05	10·8
(7c)	*a*	1728, 1660	280 (22,800)	2·22 (s)	3·44	4·80	8·08, 8·25 (*J* 8 Hz)	5·83, 8·78 (Et, *J* 7·5 Hz)	$C_{24}H_{26}N_4O_6$	61·8	5·6	12·02
										61·65	5·75	12·0
(10c)	200·5—202·5	1735, 1693, 1628	320, 310sh, 334sh	2·04 (s)	3·5—4·0	5·0—5·4	7·07, 7·61 (*J* 18·5 Hz)	5·60, 8·58 (Et, *J* 7·3 Hz)		61·55	5·6	11·85
	246—248	1690, 1630	320 310sh, 334sh	2·04 (s)	3·5—4·0	5·0—5·4	7·07, 7·61 (*J* 18·5 Hz)	5·60, 8·58 (Et, *J* 7·3 Hz)		61·75	5·85	11·9
(7d)	*a*	1676, 1640	270—290sh	2·17 (s)	3·47	7·51, 4·85	8·04, 8·20 (*J* 9 Hz)	8·69 (CMe_3)	$C_{28}H_{34}N_4O_4$	68·55	7·0	11·4
										e	*e*	*e*
(10d)	251—252	1660, 1628	274 (19,900)	2·08	3·4—4·1	4·7—5·4	6·93, 7·65 (*J* 17 Hz)	8·50 (CMe_3)		68·85	6·85	11·35
(11d)	200—201	1644, 1630	327, 314sh, 342sh (38,000)	2·13	3·4—4·1	4·7—5·4	6·93, 7·65 (J 17 Hz)	8·87 (CMe_3)		67·95	6·8	11·25
(12d)	151·5—153	1646, 1630sh	303 (22,000)	2·08	3·4—4·1	4·7—5·4	6·93, 7·65 (*J* 17 Hz)	8·50, 8·83 (CMe_3)		68·4	6·85	11·25

[a] Crystalline mixture of diastereoisomers. [b] Amorphous mixture of diastereoisomers. [c] Values separated by dashes are the outer limits of the absorptions. [d] Total CH_2 absorption. [e] Occluded solvent prevented a good analysis.

The isomerisation of (7a and b) thus proceeds by reaction at benzoyl only, in each step, as expected in a choice between benzoyl and a sterically uncrowded acyl group.[1b]

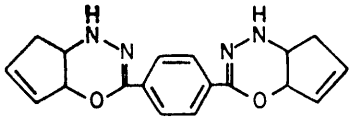
Predictably [1b] the diester (7c) isomerised with exclusive participation of the terephthaloyl group to give (10c). Fractional crystallisation gave both isomers,* m.p.s 246—248° and 200·5—202·5°. These were spectroscopically indistinguishable except for slight differences in the i.r. absorption maxima of their C=O and C=N groups.

Hydrolysis of each isomer (1N-KOH in MeOH) gave different dibases (13). The dibase from the higher melting isomer was converted back into its parent bisoxadiazine with ethyl chloroformate in pyridine and each dibase gave a different dibenzoyl derivative. The hydrolysis and reconversion reactions provide unambiguous proof of the bisoxadiazine structure.

Both pivaloyl (τ 8·50) and pivalimidoyl (τ 8·87) groups were observable in the n.m.r. spectrum of the products of isomerisation of (7d) in toluene (Figure 2a). The

* The stereoisomeric identity of these (*meso* and *rac*) is being determined by *X*-ray analysis.

presence and yields of all three structural isomers, (10d), (11d), and (12d), were readily determined by using Eu(fod)$_3$ (Figure 2b).



(13)

The relative yields of (10d)—(12d) in the isomerisation were found to be solvent (and perhaps temperature) dependent; polar solvents enhanced both the overall

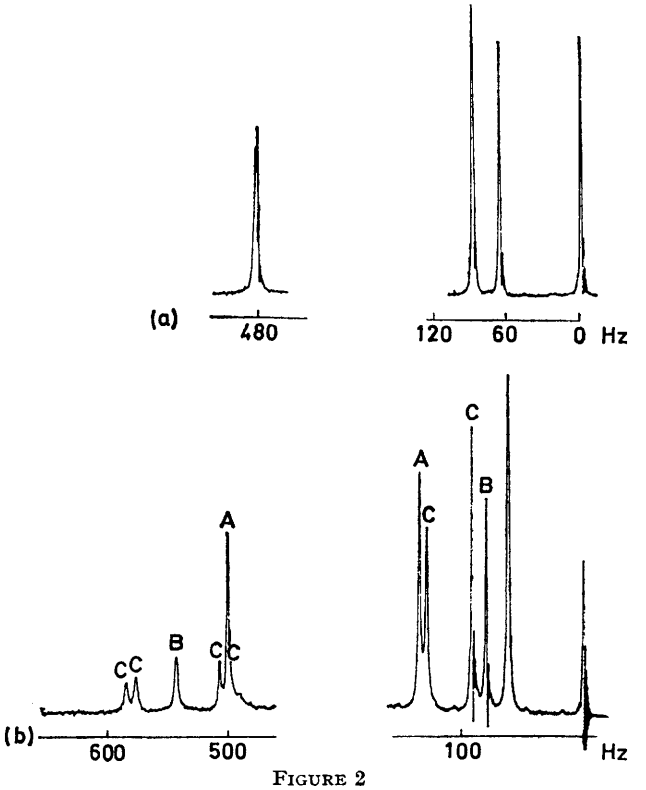


FIGURE 2

Aromatic and t-butyl absorptions (60 MHz) of the isomer mixture (10d)—(12d) from isomerisation of (7d) (a) before and (b) after addition of Eu(fod)$_3$ (0.3 mol. equiv.) to a solution in $CDCl_3$: A, (10d); (B), (11d); and (C), (12d). The peak positions are downfield from Me_4Si.

rate and the degree of participation of the pivaloyl group, as shown in Table 3.

The incomplete participation of pivaloyl, especially evident in the non-polar solvents, implies that the pivaloyl and the substituted terephthaloyl group, $Me_3CO(C_5H_6N_2)CO{\cdot}C_6H_4{\cdot}CO-$, are sterically competitive in their ability to achieve the local pyramidal geometry at nitrogen necessary for the reaction. The increasing participation of pivaloyl with solvent polarity suggests that it is the more effectively solvated of the two acyl types, probably because of its exterior position in the molecule.

* Determined by using large amounts of Eu(fod)$_3$ which caused the separation of two aromatic singlets, as for (7c and d).

† Each k is in fact the sum of contributions from two diastereoisomeric pathways.

Pivaloyl participation was quantitative and rapid in the presence of trifluoroacetic acid as catalyst [1c] (again the greater accessibility of the pivaloyl groups for complexation may be the key factor). Work-up gave an equimolar mixture of diastereoisomeric (11d),* from which one pure isomer, m.p. 200—201°, was isolated.

TABLE 3

Isomerisation products from (7d) in various refluxing solvents

Solvent	Bisoxadiazines (%) (10d)	(11d)	(12d)	Total $COCMe_3$ participation (%)
PhH	42	19	39	29
PhMe	32	25	43	47
$CDCl_3$	21	34	45	57
MeOH	4	66	30	81
$CDCl_3$–$CF_3{\cdot}CO_2H$ [a]	0	100	0	100

[a] 1% acid at 35°.

The products from the toluene reaction were similarly fractionally crystallised giving, in order, the diastereoisomeric mixtures of (11d), (10d), and (the most soluble product) (12d). From the (10d) mixture one isomer was obtained, m.p. 251—252°, identical with the product of dipivaloylation of the dibase (13), obtained from the hydrolysis of (10c) of m.p. 246—248°. Chromatographic purification of (12d) followed by crystallisation gave one of the 'in–out' isomers, with m.p. 151·5—153°. The u.v. spectrum of this unsymmetrical compound showed the expected additive effect of possessing both the major chromophores found individually in the symmetrical (10d) and (11d).

The spectra of each of the three pure dipivaloyl isomers were identical with those of the appropriate unseparated diastereoisomeric mixture, showing that stereochemical differences in the series were not recognisable by conventional spectroscopy. No attempt was made to work up any of the second isomers.

A comment about the half-isomerised products (8) and (9) is in order. Monitoring the isomerisation of (7c or d) by n.m.r. spectroscopy gave clear evidence for these species from the complexity created in the aromatic region by their AA'BB' spin systems. Their other absorptions were coincident with those of either the starting material or the product.

We chose the kinetically simplest system (7c) $\xrightarrow{k_1}$ (8c) $\xrightarrow{k_2}$ (10c) † for examination since only one intermediate structural isomer was involved. We used the rate of appearance of the new vinylic proton signals to obtain approximate rate data from which a value of k_2/k_1 between 0·35 and 0·45 was determined.[10] On a statistical basis alone a value of 0·5 would be required since (7c) has two participating carbonyl groups and (8c) only one. The observed value suggests that the steric and electronic effects are of comparable importance at both steps of the isomerisation.

[10] A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1961, p. 170.

EXPERIMENTAL

The following spectrometers were used: for i.r. a Beckman IR 10, for u.v. a Coleman EPS-3T Hitachi; for n.m.r. a Varian T-60; for mass spectrometry an A.E.I. MS-30. For g.l.c. a Beckman GC4 instrument with a flame ionisation detector was used (column 6 ft × 1/8 in 3% SE30 on Chromosorb W). Silica gel was used for column chromatography.

Magnesium sulphate was used to dry solutions in organic solvents.

ω,ω'-Diacylbishydrazides.— Dibenzoyl-carbonohydrazide, -oxalohydrazide, -succinohydrazide, and -adipohydrazide were all made under Schotten–Baumann conditions, carbon dioxide being used to precipitate the alkali-soluble products.

1,8-*Dibenzoylsuccinohydrazide* gave a monohydrate (from aqueous acetic acid), m.p. 211·5—212·5°; $\nu_{max.}$ (Nujol) 3400—3200s (OH and NH), 1690, and 1643 cm^{-1} (C=O) (Found: C, 58·4; H, 5·2; N, 15·05. $C_{18}H_{18}N_4O_4,H_2O$ requires C, 58·05; H, 5·4; N, 15·05%). Heating at 120° for 12 h gave the anhydrous *hydrazide*, m.p. 196—199° (with previous shrinkage); $\nu_{max.}$ (Nujol) 3190 (NH), 1597, and 1570 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 1·9—2·6 (2 × Ph) and 6·92 (s, 2 × CH_2) (Found: C, 61·2; H, 5·0; N, 15·55. $C_{18}H_{18}N_4O_4$ requires C, 61·0; H, 5·1; N, 15·8%).

1,5-Dibenzoylcarbonohydrazide had m.p. 204—205° (lit.,[11] 205°), the oxalohydrazide, m.p. 285—287° (lit.,[12] 278°) (obtained by heating at 180° the dihydrate formed from aqueous dimethylformamide), and the adipohydrazide, m.p. 248·5—249·5° (lit.,[13] 240°).

1,7-Dibenzoylmalonohydrazide, made by refluxing diethyl malonate and 2 equiv. of benzohydrazide in xylene, gave prisms, m.p. 235—237° (lit.,[14] 242°) (from acetic acid–toluene). The sodium ethoxide-catalysed reaction in xylene [14] gave erratic results.

Bisethoxycarbonylterephthalohydrazide gave plates, m.p. 224—225° (lit.,[15] 223°) (from aqueous acetic acid).

Refluxing of a suspension of terephthalohydrazide with 2 equiv. of pivaloyl chloride in pyridine gave the *dipivaloyl derivative* (90%), which crystallised in fine prisms as a monohydrate, m.p. 302—304° (from aqueous acetic acid); $\nu_{max.}$ (Nujol) 3265 (NH), 1685, and 1650 cm^{-1} (Bu^tC=O, $-C_6H_4C$=O); τ ($CF_3{\cdot}CO_2H$) 1·86 (4 aromatic H, s) and 8·57 (s, 2 × Bu^t) (Found: C, 56·75; H, 7·0; N, 14·35. $C_{18}H_{28}N_4O_5$ requires C, 56·85; H, 7·4; N, 14·75%).

Oxidation of the Hydrazides (4a—c) *with NBS–Pyridine.*— The scale, solvent, and reaction time are given in Table 1. Sodium sulphate was included to absorb water in the reactions in methylene chloride or carbon tetrachloride. Gases were evolved in the early stages of the oxidation. After filtration and a water washing the solution was extracted with aqueous sodium hydrogen carbonate to give benzoic acid. Acetonitrile reaction mixtures were evaporated and the residues worked up with methylene chloride and aqueous sodium hydrogen carbonate.

Neutral components were isolated by direct crystallisation of the material from the organic phase or by chromatography on silica gel (see Table 1) in benzene containing increasing amounts of ether. Products were identified by comparison with authentic samples. Compound (6) was prepared as described by Stolle.[16]

* Owing to the insolubility of the bis-hydrazides in ethanol, suspensions were used in the mercury salt preparation.

[11] R. Stollé and K. Krauch, *Ber.*, 1914, **47**, 727.
[12] R. Stollé and K. Kind, *J. prakt. Chem.*, 1904, [2] **70**, 430.
[13] T. Curtius and E. Darmstaedter, *J. prakt. Chem.*, 1915, [2] **91**, 1.

αα'-Adipoylbisazobenzaldehyde (5b) *and Diethyl Terephthaloylbisazoformate* (5c).—The dimercury(II) salt formation and the oxidation with bromine were carried out by suitable modification of methods described earlier.* [16]

The oxidation to αα'-adipoylbisazobenzaldehyde was done in methylene chloride; the filtered solution was evaporated to a small volume and carbon tetrachloride was added (n.m.r. analysis of a sample with methyl benzoate as internal standard showed the yield to be 60%). Further evaporation and addition of hexane gave a yellow solid which was twice crystallised from carbon tetrachloride–cyclohexane to give prisms, m.p. 73—75° (decomp.) (orange-red melt); $\nu_{max.}$ (CCl_4) 1765 and 1728 cm^{-1} (C=O); $\lambda_{max.}$ (CCl_4) 455 nm (ε 78); τ (CCl_4) 1·7—2·9 (2 × Ph), 7·27 (m, 2 × CH_2), and 8·13 (m, 2 × CH_2) (Found: C, 63·3; H, 5·15. $C_{20}H_{18}N_4O_4$ requires C, 63·5; H, 4·8%) (N analyses were erratic).

Diethyl terephthaloylbisazoformate was isolated similarly (85%). Two crystallisations from carbon tetrachloride–hexane gave the orange-yellow azo-compound, m.p. 89—90°; $\nu_{max.}$ (CCl_4) 1·90 (4 aromatic H, s), 5·47 (2 × CH_2, q, *J* 7·5 Hz), and 8·37 (2 × Me, t) (Found: C, 50·95; H, 4·7. $C_{14}H_{14}N_4O_6$ requires C, 50·3; H, 4·2%).

Cyclopentadiene Bisadducts (7) (*see also Table* 2).— (i) *Compounds* (7a *and* d) *through* in situ *preparation of azo-compound.*—Lead tetra-acetate (8·9 g, 20 mmol) was added during 0·5 h to a suspension at −10° of the hydrazide (10 mmol) and sodium sulphate (10 g) in methylene chloride (100 ml). Cyclopentadiene (10 ml) was then added to the orange mixture, which became nearly colourless in 1 h. The organic solution was washed with water and aqueous sodium hydrogen carbonate, and evaporated. Addition of carbon tetrachloride (50 ml) to the first reaction residue gave 2,2'-*succinoylbis*-(3-*benzoyl*-2,3-*diazabicyclo*[2.2.1]*hept*-5-*ene*) (7a) (25%), and of a large volume of pentane to the second gave the *terephthaloyl compound* (7d) (60%), both crystalline solids.

(ii) *Compounds* (7b *and* c). The colour of a solution of the azo-compound (12 mmol) in benzene or carbon tetrachloride (50 ml) was discharged within 15 min by addition of cyclopentadiene (3 ml). Evaporation gave the *adipoyl compound* (7b) as a sticky solid (80%), which became an amorphous powder on adding hexane to a solution in chloroform and chilling. The yield of the *diester* (7c) was quantitative; it slowly crystallised from benzene–hexane.

Isomerisation of Compounds (7a—d) *to Bisoxadiazines.*— Solutions in toluene (typically 1%) were refluxed till n.m.r. analysis of the residue from a sample showed no further change [(7a), 12 h; (7b), 1 h; (7c), 6 h; (7d), 1·5 h, for other solvents see Table 3].

Compound (7d) (0·32 g, 0·65 mmol) was also isomerised in chloroform (5 ml) by the action of trifluoroacetic acid (50 μl); the reaction was separately monitored by n.m.r. analysis, which showed it to be complete in <30 s. The solution was neutralised with dilute aqueous ammonia and the chloroform layer evaporated. The final products were worked up as follows (see also Table 2).

(i) 1,1'-*Succinoylbis*-(1,4a,7,7a-*tetrahydro*-3-*phenylcyclopent*[e][1,3,4]*oxadiazine*) (11a) *from* (7a). Three crystallisations from ethanol gave a single *isomer* of (11a), m.p. 193—194·5°.

(ii) *The adipoyl compound* (11b) *from* (7b). Benzene–

[14] R. Quelet and R. Milcent, *Ann. Chim.* (*France*), 1967, **2**, 159.
[15] F. Eloy and C. Moussebois, *Bull. Soc. chim. belges*, 1959, **68**, 423 (*Chem. Abs.*, 1960, **54**, 7625g).
[16] R. Stollé and K. Krauch, *Ber.*, 1913, **45**, 3307; R. Stollé and K. O. Leverkus, *ibid.*, 1913, **46**, 4076.

hexane or benzene–ethanol treatment gave an amorphous mixture of the two diastereoisomers of (11b).

(iii) *Diethyl* 3,3′-p-*Phenylenebis*-(1,4a,7,7a-*tetrahydrocyclopent*[e][1,3,4]*oxadiazine*-1-*carboxylate*) (10c) *from* (7c). Two crystallisations from benzene–cyclohexane (1 : 1) gave *compound* (10c), m.p. 246—248°. Both mother liquor residues were combined and crystallised from acetone and twice from aqueous ethanol yielding the other *isomer* of (10c), m.p. 200·5—202·5°. Each isomer had *m/e* 466 (M^+) and 299 (base peak).

(iv) *Compounds* (10d), (11d), *and* (12d) *from* (7d). The diastereoisomers of 1,1′-*terephthaloylbis*-(1,4a,7,7a-*tetrahydro*-3-*t*-*butylcyclopent*[e][1,3,4]*oxadiazine*) (11d) were the sole products of the isomerisation in trifluoroacetic acid. Four crystallisations from ethanol gave one isomer as rosettes, m.p. 200—201°.

The mixture from the toluene reaction was crystallised from methanol to remove most of the (11d) isomers. The mother liquor residue was crystallised from ethanol to give substantially pure (10d) and then from benzene–cyclohexane to give one isomer as prisms, m.p. 251—252° (decomp.).

The most soluble fractions from these purifications were combined and chromatographed on silica gel from benzene–light petroleum (2 : 1), and eluted with benzene containing 3% ether to give the mixture of the unsymmetrical isomers (12d), a glass which crystallised on boiling with hexane. Slow evaporation from hexane solution gave a pure component as long needles, m.p. 151·5—153°.

The Dibases 3,3′-p-*Phenylenebis*-(1,4a,7,7a-*tetrahydrocyclopent*[e][1,3,4]*oxadiazine*) (13).—Each isomer of (10c) (250 mg, 0·5 mmol) was refluxed for 36 h in N-potassium hydroxide in methanol (10 ml). Evaporation, and addition of water gave the product (70—80%) as a yellow crystalline solid. Both compounds decomposed without melting above 200°.

The *dibase* from (10c) of m.p. 246—248° gave long needles from n-propanol, $\nu_{max.}$ (Nujol) 3240 (NH) and 1635 cm^{-1} (C=N); $\lambda_{max.}$ (EtOH) 232 and 331 nm; *m/e* 322 (M^+) and 227 (base peak) (Found: C, 67·4; H, 5·8; N, 17·65. $C_{18}H_{18}N_4O_2$ requires C, 67·05; H, 5·65; N, 17·4%). The *dibase* from (10c) of m.p. 200·5—202·5° crystallised from aqueous ethanol as prisms, $\nu_{max.}$ (Nujol) 3287 (NH) and 1630 cm^{-1} (C=N); $\lambda_{max.}$ (EtOH) 231 and 330 nm (Found: C, 66·9; H, 5·6; N, 17·6%).

Acylation Reactions of the Dibases (13).—A solution of the dibase (0·25 mmol) and the acyl chloride (0·6 mmol) was refluxed in pyridine (1 ml) for 0·5 h and poured into water.

The bisethoxycarbonyl derivative of the base from (10c) of m.p. 246—248° was identical with the latter (m.p. and mixed m.p.) after crystallisation from ethanol.

The dipivaloyl derivative of the same base was crystallised from ethanol and then benzene–cyclohexane; m.p. 250—252° (decomp.). It was identical (mixed m.p. and spectra) with the isomer of (10d) of the same m.p.

The related *dibenzoyl derivative* crystallised from aqueous acetone and then benzene as prisms, m.p. 270·5—271° (decomp.); $\nu_{max.}$ (Nujol) 1635 and 1620 cm^{-1} (C=O, C=N); $\lambda_{max.}$ (EtOH) 332, 319sh, and 345sh nm; *m/e* 530 (M^+) and 105 (base peak, $PhCO^+$); τ ($CDCl_3$) 1·9—2·8 (15 aromatic H, including C_6H_4, s), 3·5—4·1 (4 vinyl H), 4·7—5·2 (4 tert. H), and 6·83 and 7·64 (2 × CH_2, ABq, *J* 18 Hz) (Found: C, 72·3; H, 5·15; N, 10·55. $C_{32}H_{26}N_4O_4$ requires C, 72·45; H, 4·9; N, 10·55%).

The other dibenzoyl derivative gave *needles* (from aqueous acetone), m.p. 237—238° (decomp.); $\nu_{max.}$ (Nujol) 1658, 1637, and 1626 cm^{-1} (C=O, C=N) (Found: C, 72·6; H, 4·95; N, 10·55%).

Kinetic Analysis of Isomerisation of (7c) [$\xrightarrow{k_1}$ (8c) $\xrightarrow{k_2}$ (10c)].—The n.m.r. absorptions of the vinylic protons in (7c) and in the pyridazine ring of (8c) occurred between τ 3·55 and 4·12 (C_6D_6); those of (10c) and the oxadiazine ring of (8c) occurred between τ 4·12 and 4·55. If the mole fractions of (8c) and (10c) are β and γ, then the progress of the reaction as defined by $\beta + 2\gamma$ is the ratio of the growing to the total vinylic absorption and, by using the time-ratio method,[10] leads to values of k_1 and k_2. Peak area measurements could not be made with great accuracy but for the reaction in [$^2H_6$]benzene at 97° the value of k_2/k_1 lay between 0·35 and 0·45, k_1 being *ca.* 0·3 h^{-1}.

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