Similar results were obtained with rabbit anti-SE serum (Table III). Both in rat and rabbit, at the peak of primary response, haemolysin is due to IgM, and agglutination is exhibited by both IgG and IgM. These results indicate that 2–ME affects IgM both in free and complexed states.

TABLE III

Effect of 2–ME on various components of haemolysin titration of rabit anti-SE serum

	Material treated	% activity of haemolysin activity of antiserum	
		+2-ME	−2-ME
(*a*)	Anti-SE serum	10	100
(*b*)	SE	100	100
(*c*)	Antibody-SE complex	25	100
(*d*)	Complement	40–45	100

a, *b*, *c* and *d* are same as in Table I.

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DIELS-ALDER REACTION OF TETRACYCLONE WITH SOME MALEIMIDES

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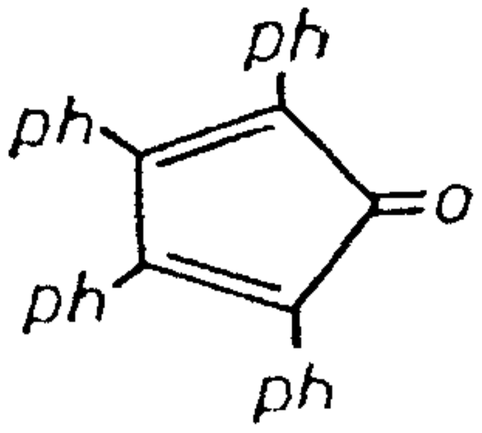
ABSTRACT

Tetracyclone I reacts with N-substituted maleimides II to give the adducts III *a–f*. Dehydrogenation of III *c*, *e*, *f* gave IV *a–c*. In a similar manner III adds another molecule of either maleic anhydride or N-substituted maleimide to give V *a–b* and VI *a–e* respectively. On the other hand, VI *b* dehydrogenates readily to VII.

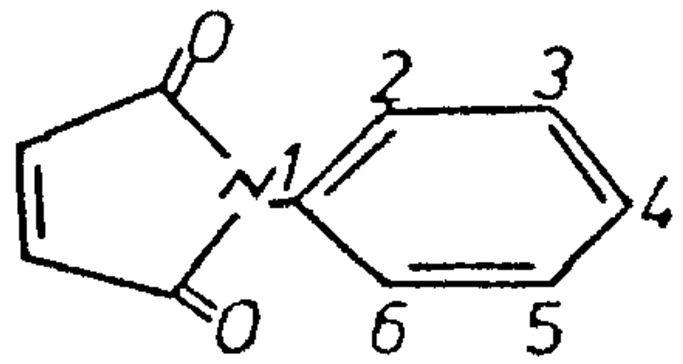
TETRAPHENYLCYCLOPENTADIENONE (tetracyclone) I and its analogues were reported to undergo Diels-Alder reaction with ethylenic dienophils[1–13].

We now succeeded to isolate the adducts III *a–f* from the reaction of one molecule of N-substituted maleimides II *a–f* with one molecule of tetracyclone in bromobenzene or in dry toluene. III *c–e* are dehydrogenated readily with bromine to give IV *a–c*.



I

The structure assigned for the addition products III *a–f* has been supported by analytical and spectral (U.V., I.R. and N.M.R.) data. III *e*, for example, shows a carbonyl two bands widely separated at 1770 cm^{-1} and 1690 cm^{-1} (for $-CO\cdot NH\cdot CO-$)[15]. The U.V. spectrum of III *c* showed an absorption band at 340 mμ.[16] The structure of the adducts obtained has been further evidenced by the N.M.R. spectrum. For example the N.M.R. spectrum of III *a* showed



II

a, 2-COOH
b, 3-COOH
c, 4-COOH
d, 2-Me, 3-Cl
e, 2-Me, 5 Cl
f, 4-Me, 3-Cl

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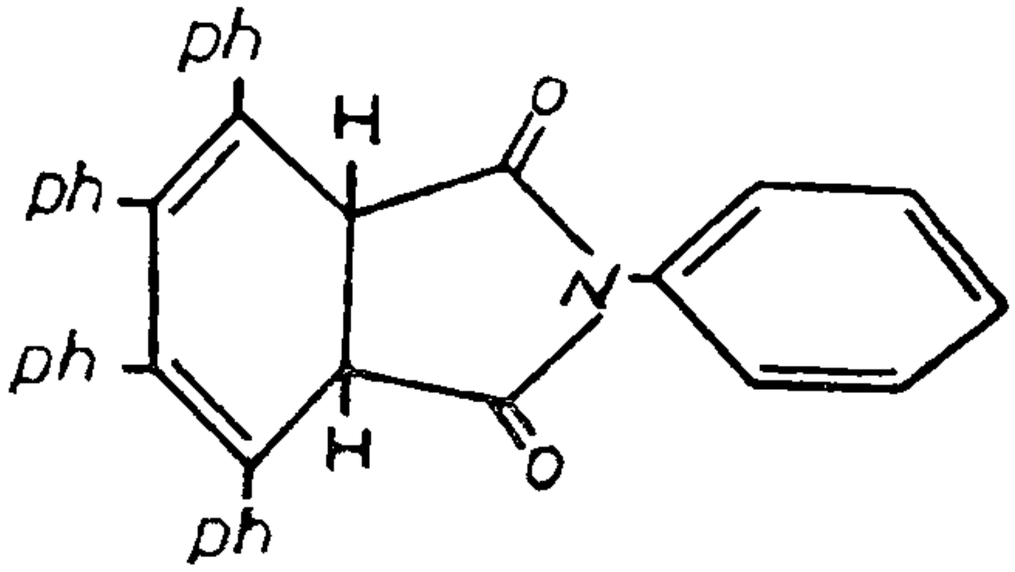
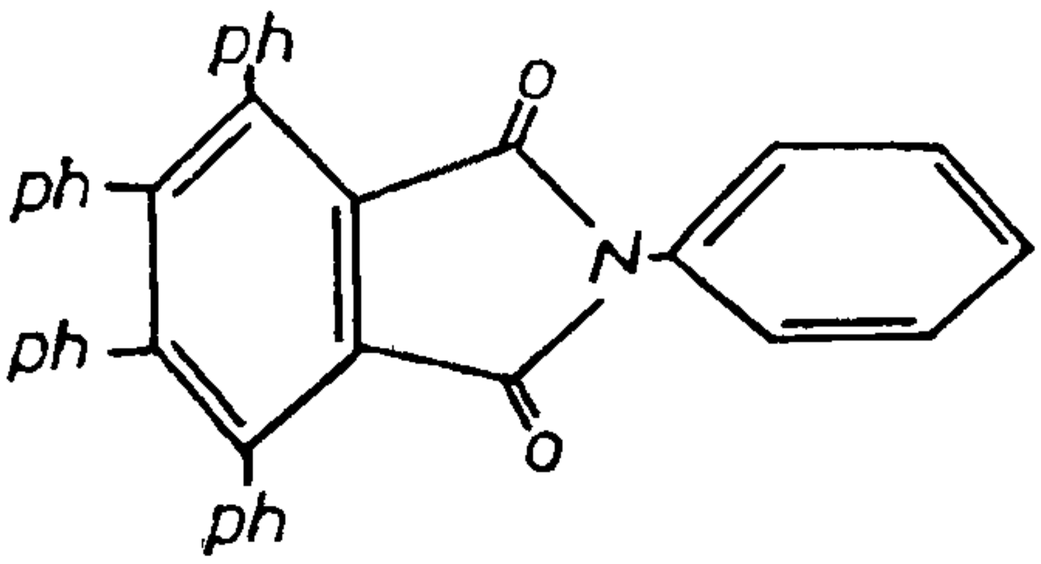
a two singlet at *d* 4·4, 4·45 for the two hydrogen protons and a singlet at *d* 2·15 for the methyl group. Moreover two multiplets at 6·8 *d* and 7·1 *d* has appeared for the aromatic protons.

Similarly the structures of IV *a, b* have been proved by analytical data and I.R. spectra. Thus the I.R. spectrum of IV *b* shows absorption at 1750 cm $^{-1}$ and 1690 cm^{-1} (for –CO–NH–CO–)[15]. In addition, the structure of IV *c* has been confirmed by m.p. and mixed m.p. with an authentic sample obtained from the reaction of tetraphenylphthalic anhydride[14] with 4-methyl-3-chloroaniline followed by cyclization.

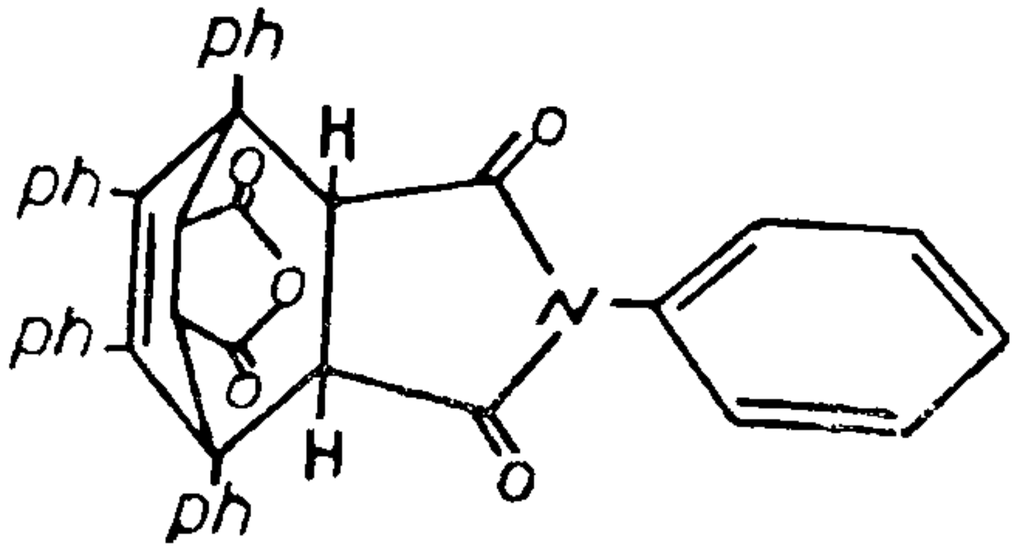


III
a, 2-COOH
b, 3-COOH
c, 4-COOH
d, 2-Me, 3-Cl
e, 2-Me, 5-Cl
f, 4-Me, 3,Cl

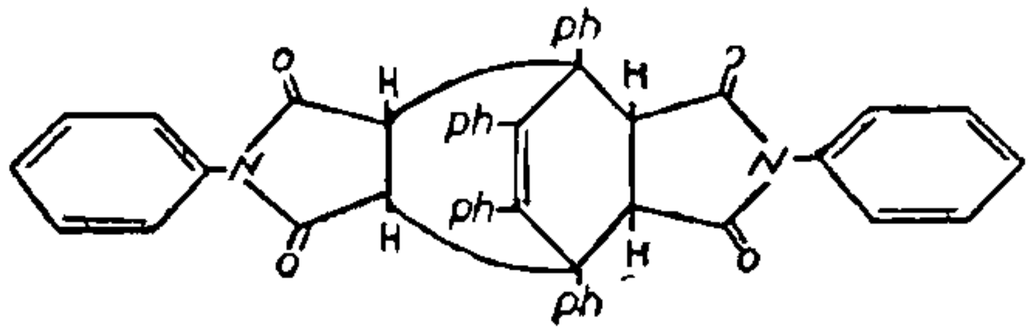


IV
a, 4 COOH
b, 2 Me, 5-Cl
c, 4 Me, 3-Cl

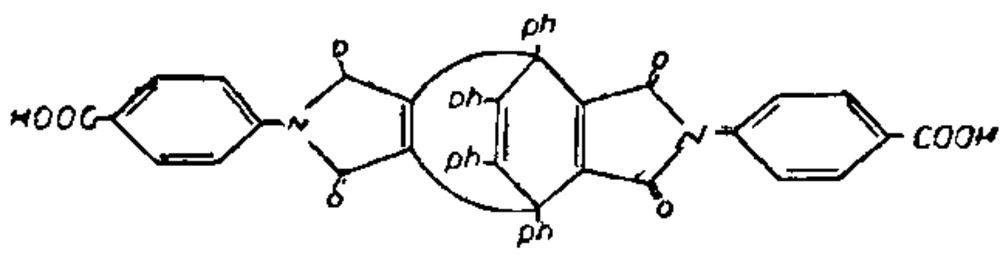
The appearance of an absorption band at 340 mμ in the U.V. spectrum[16]. of III *c*, has been established chemically by the addition of another molecule of dienophile on the created diene. So III adds one molecule of maleic anhydride to give the endo-adducts V *a, b*. The structure of V has been proved from the analytical data, I.R. spectrum of V *a*, which shows absorption at 1740 cm^{-1} and 1700 cm^{-1}. On the other hand, III *a–f* add another molecule of N-substituted maleimides to give an exo-adduct VI *a–e* on the diene formed. VI *b* is readily dehydrogenated to give VII.



V
a, 3-COOH
b, 2-Me, 3-Cl



VI
a, 3-COOH
b, 4-COOH
c, 2-Me, 3-Cl
d, 2-Me, 5-Cl
e, 4-Me, 3-Cl



VII

The structure of VI *a–e* and VII are established from the analytical data and I.R. spectra. The I.R. spectrum of VI *e* shows absorption band at 1760 cm^{-1} and 1690 cm^{-1}, and that of VII at 1790 cm^{-1}, and 1670 cm^{-1}[15]. Also the m.p. and mixed m.p. of VI *b* obtained from one or two steps confirms the above structure.

Experimental Procedure

All the melting points are uncorrected. I.R. spectra are obtained on potassium bromide pellets, on a Perkin-Elmer spectrophotometer. U.V. spectra are obtained fn ethanol, on a Beckman DK-2 spectrophotometer. The N.M.R. are obtained in $CDCl_3$ solution using a tetramethylsilane as internal standard, on a Varian A-60.

Action of tetracyclone on N–substituted maleimides.— A mixture of I (1·9 g) and the appropriate N-substituted maleimide II (0·9 g) are refluxed in 20 ml of either bromobenzene or dry toluene for three hours,

TABLE I

Analytical data of the adducts III a–f

Adducts*	m.p. °C	Mol. Formula	C% Found (Calc.)	H% Found (Calc.)	N% Found (Calc.)	Cl% Found (Calc.)
III *a*	261	$C_{39}H_{27}NO_4$	81·32 (81·66)	4·72 (4·74)	2·39 (2·44)	..
III *b*	140	$C_{39}H_{27}NO_4$	81·51 (81·66)	4·70 (4·74)	2·36 (2·44)	..
III *c*	252	$C_{39}H_{27}NO_4$	81·49 (81·66)	4·75 (4·74)	2·39 (2·44)	..
III *d*	234	$C_{39}H_{28}NO_2Cl$	81·02 (81·04)	4·81 (4·85)	2·38 (2·42)	6·16 (6·15)
III *e*	356	$C_{39}H_{28}NO_2Cl$	80·91 (81·04)	4·82 (4·85)	2·43 (2·42)	6·01 (6·15)
III *f*	328	$C_{39}H_{28}NO_2Cl$	81·12 (81·04)	4·79 (4·85)	2·40 (2·42)	6·11 (6·15)

* III *a*, *b*, *d* are crystallized from ethanol ; III *c* crystallized from benzene/benzine; III *e* crystallized from chloroform/benzine ; III *f* crystallized from benzene/alcohol ; the compounds are obtained in 58–70% yields

TABLE II

Analytical data of the adducts VI a–e

Adducts*	M.P. °C	Mol. Formula	C% Found (Calc,)	H% Found (Cal.)	N% Found (Calc.)	Cl% Found (Cal.)
VI *a*	301	$C_{50}H_{34}N_2O_8$	76·01 (75·94)	4·31 (4·33)	3·51 (3·54)	..
VI *b*	343	$C_{50}H_{34}N_2O_8$	75·86 (75·94)	4·30 (4·33)	3·53 (3·54)	..
VI *c*	265	$C_{50}H_{36}N_2O_4Cl_2$	75·00 (75·10)	4·46 (4·50)	3·49 (3·50)	8·92 (8·90)
VI *d*	233	$C_{50}H_{36}N_2O_4Cl_2$	75·06 (75·10)	4·48 (4·50)	3·51 (3·50)	8·81 (8·90)
VI *e*	248	$C_{50}H_{36}N_2O_4Cl_2$	74·98 (75·10)	4·46 (4·50)	3·47 (3·50)	8·86 (8·90)

* VI *a* crystalized from ethanol ; VI *b* crystallized from dil. ethanol ; VI *d* and VI *e* crystallized from benzene/alcohol ; VI *c* crystallized from benzene/benzine. Compounds are obtained in 70–80% yields.

then allowed to cool. The solid products so formed are filtered and crystallized from the suitable solvent (*cf.* Table I) and identified as III *a–f*.

Action of maleic anhydride on III b, d.—A mixture of III *b* or III *d* (1·1 g) and maleic anhydride (0·2 g) are heated in 20 ml of either bromobenzene or dry toluene, the reaction mixture is refluxed for three hours, then allowed to cool. The solid products so obtained are filtered and crystallized from the suitable solvent and identified as V *a*, *b*.

V *a* crystallized from ethanol, mp. 175°C ; yield 70% (Found: C, 77·01 ; H, 4·28; N, 2·03. Calcd. for $C_{13}H_{29}NO_{713}$: C, 76·90 ; H, 4·32 ; N, 2·08).

V *b* crystallized frnm benzene/benzine ; m.p. 244°C, yield 63% (Found : C, 76·28 ; H, 4·41 ; N, 2·06 ; Cl, 5·19. Calcd. for $C_{43}H_{30}NO_5Cl$; C, 76·38 ; H, 4·44 ; N, 2·07 ; Cl, 5·26).

Action of N-substituted maleimides on III a–f— A mixture of III *b–f* (1·1 g) and the appropriate N-substituted maleimide (0·9 g) are heated together in dry toluene (20 ml), the reaction mixture is refluxed for three hours and allowed to cool. The solid products are filtered and crystallized from the suitable solvent (*cf.* Table II) and identified as VI *a e*.

Dehydrogenation. The same procedure used for the synthesis of tetraphenylphthalic anhydride[14] has

been applied for the dehydrogenation of III *c*, *e*, *f* and VI *b* to give IV *a–c* and VII respectively.

IV *a* crystallized from ethanol, m.p. 359° C ; yield 70% (Found : C, 81·92 ; H, 4·32 ; N, 2·41, Calcd. for $C_{39}H_{25}NO_4$: C, 81·96 ; H, 4·38 ; N, 2·45).

IV *b* crystallized from benzene/alcohol, m.p. 342° C; yield 70% (Found : C, 81·33 ; H, 4·49 ; N, 2·45 ; Cl, 6·13. Calcd. for $C_{39}H_{26}NO_3Cl$: C, 81·32; H, 4·52 ; N, 2·43 ; Cl, 6·17).

IV *c* crystallized from ethanol, m.p. 260° C ; yield 73% (Found : C, 81·29 ; H, 4·51 ; N, 2·44 ; Cl, 6·15 . Calcd. for $C_{39}H_{26}NO_2Cl$: C, 81·32 ; H, 4·52 ; N, 2·43 ; Cl, 6·17).

VII crystallized from dil. ethanol, m.p. 353° C ; yield 70% (Found : C, 76·25 ; H, 3·76 ; N, 3·52. Calcd. for $C_{50}H_{30}N_2O_8$; C, 76·33 ; H, 3·84 ; N, 3·56).

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