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Some Reactions of Diethyl-2,3,4,6,7,8,9,10-octahydro-2,6-dioxo-4,8-diphenyl-4a,8a-anthracene Dicarboxylate with Nitrogen and Carbon Nucleophiles

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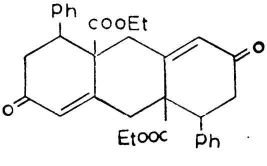
The reactions of compound(I) with nitrogen and carbon nucleophiles such as hydrazines, hydroxylamine hydrochloride, primary amines, urea, thiourea, active methylene compounds under Michael reaction conditions in the presence of sodium ethoxide, malononitrile in the presence of triethyl amine and/or ammonium acetate, Grignard reagents and with aromatic hydrocarbons under Friedel-Crafts conditions have been investigated.

INTRODUCTION

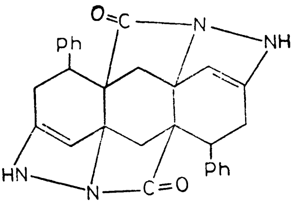
As a point of interest in this study, diethyl-2,3,4,6,7,8,9,10-octahydro-2,6-dioxo-4,8-diphenyl-4a,8a-anthracene dicarboxylate(I)[1-3] which carries two electrophilic active sites (two α, β-unsaturated ketones) has prompted us to study its chemical reactivity towards some nitrogen and carbon nucleophiles.

RESULTS AND DISCUSSION

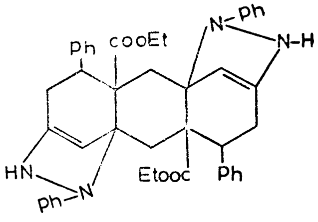
Thus, compound(I) when allowed to react with hydrazines, namely, hydrazine hydrate and/or phenylhydrazine in boiling alcohol gave 4,5,10,11-tetrahydro-5,11-diphenyl-2*H*,6*H*,8*H*,12*H*-1,11a : 5a,7-dimethano-6a,9 : 12a,3-dimethenobenzo(1,2-*c* : 4,5-*c*′) bis(1,2)diazepine-14-16dione(II) and diethyl-1,2,4,5,7,8,10,11-octahydro-1,5-7,11-tetraphenyl-6a,9 : 12a, 3-dimethenobenzo(1,2-c : 4,5-c′)bis(1,2)diazepine-5a,11a(6*H*,12*H*)dicarboxylate(III) respectively.



(I)



(II)



(III)

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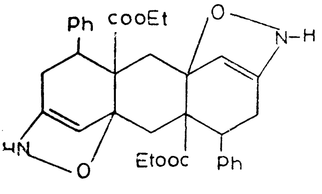
The structure of compounds (II & III) was supported by:

(i) IR spectra which showed bands at 1640 cm^{-1} due to $\nu C{=}C$ and at 1670–1735 cm^{-1} due to $\nu\ {>}C{=}O$ of compounds (II) and (III) respectively.

(ii) H^{1}NMR spectrum of compound (II) showed signals at 5.6 (s, 2H, $H{-}C{=}C$), at 1.9 (d, 4H, $\mathit{CH}_2{-}CH{-}Ph$) at 1.6 (5, 4H, $-\mathit{CH}_2-$ in the ring *b* of anthracene), at 2.6 (t, 2H, $-\mathit{CH}{-}Ph$) and at 7.1–7.7 (m, 10H, aromatic protons).

(iii) H^{1}NMR spectrum of compound (III) showed signals at 5.6 (s, 2H, $-\mathit{CH}{=}C{<}$), at 1.9 (d, 4H, $-\mathit{CH}_2{-}CH{-}Ph$), at 1.6 (s, 4H, $-\mathit{CH}_2-$ in the ring *b* of anthracene), at 2.6 (t, 2H, $-\mathit{CH}{-}Ph$), at 1.1 (t, 6H, $-COOCH_2{-}\mathit{CH}_3$), at 4.2 (q, 4H, $-COO\mathit{CH}{-}CH_3$) and at 7.1–7.8 (m, 20H, aromatic protons).

Also, the hitherto unknown reaction of hydroxylamine hydrochloride with compound (I) in boiling pyridine gave diethyl-4,5,10,11-tetrahydro-5, 11-diphenyl-2*H*,8*H*-6a,9 : 12a,3-dimethenobenzo-(1,2-f′) bis(1,2)oxazepine 5a,11a(6*H*,12*H*)-dicarboxylate(IV).



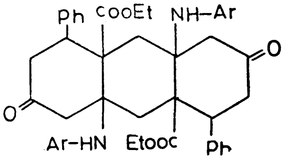
(IV)

The structure of compound (IV) was confirmed by:

(i) IR spectrum showed bands at 1640 cm^{-1} due to $\nu\ {>}C{=}C{<}$ and at 1740 cm^{-1} due to $\nu\ {>}C{=}O$ (ester) respectively.

(ii) H^{1}NMR of compound (IV) showed signals at 5.7 (s, 2H, $-\mathit{CH}{-}C{=}C{<}$), at 2.0 (d, 4H, $-\mathit{CH}_2{-}CH{-}Ph$), at 1.6 (s, 4H, $-\mathit{CH}_2-$ in the ring *b* of anthracene), at 2.6 (t, 2H, $-\mathit{CH}{-}Ph$), at 1.2 (t, 6H, $-COOCH_2{-}\mathit{CH}_3$), at 4.3 (q, 4H, $-COO\mathit{CH}_2{-}CH_3$) and at 7.1–7.7 (m, 10H, aromatic protons).

It has been found that primary amines such as aniline, p-toluidine, p-anisidine, benzylamine, methylamine and/or ethylamine react with compound (I) to give diethyl dodecahydro-2,6-dioxo-4,8-diphenyl-9a,10a-di(phenyl or p-toluidino or p-anisidino or benzylamino or methylamino or ethylamino)-4a,8a-anthracene-dicarboxylate (Va–f) respectively.



(V)

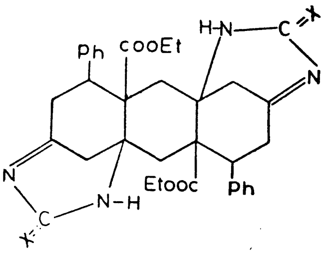
(a) Ar = C_6H_5—, (b) Ar = C_6H_4—CH_3—p,
(c) Ar = C_6H_4—OCH_3—p—, (d) Ar = C_6H_5—CH_2—,
(e) Ar = CH_3—, (f) Ar = CH_3—CH_2—.

The structure of compounds (Va–f) was cnfirmed by:

(i) IR spectra which exhibited absorption bands in the region (1620–1630 cm^{-1}) due to $\nu\ {>}C{=}C{<}$, at 1715 cm^{-1} due to $\nu\ {>}C{=}O$ (ketone), at 1735 cm^{-1} due to $\nu\ {>}C{=}O$ (ester) and in the region (3220–3250 cm^{-1}) broad band due to νNH which are consistent with the proposed structure.

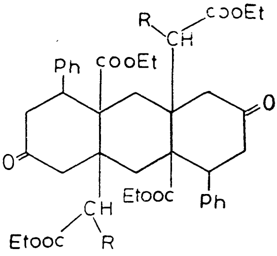
(ii) H^1NMR of compound (Va) showed signals at 2.1 (d, 4H, —CH_2—CH—Ph) at 2.3 (s, 4H, —COCH_2), at 2.6 (t, 2H, $-\overset{|}{C}H-$Ph), 1.4 (s, 4H, —CH_2— in the ring *b* of anthracene, at 1.1 (t, 6H —$COOCH_2$—CH_3), at 4.2 (q, 4H, —COOCH_2—CH_3) and at 7.1–7.7 (m, 20H, aromatic protons).

In view of the utility of 2-mercaptopyrimidines as a vulcanization accelators, the behaviour of compound (I) towards the action of thiourea was investigated; thus, the condensation of (I) with urea and/or thiourea in boiling[4] ethanolic KOH yielded diethyl 1,2,5,6,8,9,12,13-octahydro-2, 9-(dioxo or dithioxo)-6,13-diphenyl-4,14a : 7a,11-dimethanobenzo(1,2-*d*:4, 5-*d*)bis(1,3)-diazocine-6a,13a-(7*H*,14*H*)-dicarboxylate (VIa & b) respectively.



(VI a&b)
(a) X = O, (b) X = S

Also, in this study, the hitherto unknown reaction of the behaviour of the addition of active methylene compounds to the olefinic double bond activated by carbonyl moiety under Michael reaction conditions was discovered. Thus, compound (I) reacted with active methylene compounds, namely, ethylacetoacetate, ethyl cyanoacetate, ethyl bromoacetate and/or diethyl malonate under Michael reaction conditions in the presence of sodium ethoxide giving the normal Michael adducts α,α'-(diacetyl or dicyano or dibromo or dicarbethoxy)-9a,10a-dicarboxydodecahydro-3, 7-dioxo-1,5 diphenyl-4a,8a-anthracenediacetic acid, tetraethyl ester (VIIa–d) respectively.



(VII a-d)

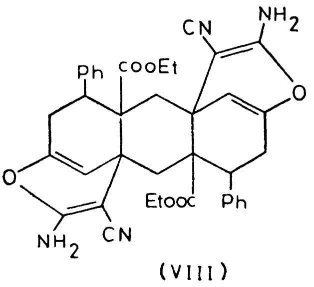
(a) R=—COCH₃, (b) R=CN
(c) R=Br, (d) R=—COOEt

The following support the structure assigned for (VIIa-d):

(i) IR spectra of (VIIa-d) showed absorption bands at (1730–1740 cm^{-1}) due to ν $>C=O$ (ester), at 1720 cm^{-1} due to ν $>C=O$ (cyclic ketone), at 1710 cm^{-1} (of compound VIIa) and at 2230 cm^{-1} due to ν $>C\equiv N$ (of compound VIIb).

(ii) H^{1}NMR spectrum of (VIIb) showed signals at 2.1 (d, 4H, —*CH*$_2$—*CH*—Ph), at 2.3 (s, 4H, —CO—*CH*$_2$—), at 2.6 (t, 2H, —*CH*—Ph), at 1.4 (s, 4H, —*CH*$_2$— in the ring *b* of anthracene), at 3.8 (s, 2H, —*CH*(CN). COOEt), at 1.2 (t, 12H, —COO—CH$_2$—*CH*$_3$), at 4.3 (q, 8H, —COO—*CH*$_2$—CH$_3$) and at 7.1–7.7 (m, 10H, aromatic protons).

On the other hand, compound (I) reacted with malononitrile in the presence of triethylamine[5] as a base in dry benzene to give diethyl-2,9-diamino-1,8-dicyano-5,6,12,13-tetrahydro-6,13-diphenyl-7a,11 : 14a,4-dimetheno-benzo-(1,2-d:4,5-d')-bis oxocin-6a,13a-(7H,14H)-dicarboxylate(VIII).



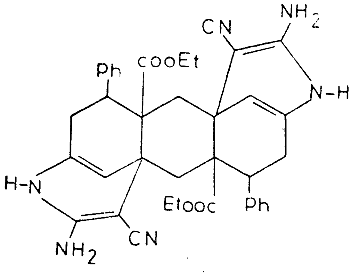
(VIII)

The structure of compound (VIII) was confirmed by:

(i) IR spectrum reveals the presence of $\nu C{\equiv}N$ at 2225 cm^{-1}, νNH_2 at 3330 cm^{-1}, $\nu C{=}C$ at 1625 cm^{-1} and $\nu C{=}O$ (ester) at 1735 cm^{-1}.

(ii) H^1NMR spectrum of (VIII) showed signals at 5.6 (s, 2H, $\overset{|}{C}H{=}C$—), at 1.9 (d, 4H, —CH_2—CH—Ph), at 2.6 (t, 2H, —*CH*—Ph), at 1.4 (s, 4H, —CH_2— in the ring *b* of anthracene), at 1.2 (t, 6H, —$COOCH_2$—CH_3), at 4.2 (q, 4H, $COOCH_2$—CH_3) and at 7.1–7.7 (m, 10H, aromatic protons).

However, the authors extended such reaction to include the reaction of compound (I) with malononitrile[6] in the presence of ammonium acetate under Michael reaction conditions to afford diethyl-2,9-diamino-1,8-dicyano-5,6,12,13-tetrahydro-6,13-diphenyl-3*H*,10*H*-7a,11 : 14a,4-dimethanobenzo-(1,2-*d*:4,5-*d*′)-bis azocine-6a,13a(7*H*,14*H*)-dicarboxylate (IX).



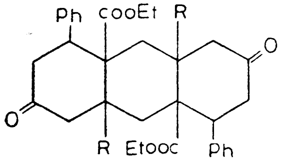
(IX)

The structure of compound (IX) was supported by:

(i) IR spectrum showed absorption bands at 2230 cm^{-1} due to $\nu C{\equiv}N$, 3300 cm^{-1} due to νNH_2, at 1735 cm^{-1} due to $\nu C{=}O$ (ester) and at 1630 cm^{-1} due to $\nu C{=}C$.

(ii) H^1NMR spectrum of (IX) showed signals at 5.4 (s, 2H, $\diagdown CH{=}C\langle$), at 1.8 (d, 4H, —CH_2—$\overset{|}{C}H$—Ph), at 2.6 (t,2 H, —$\overset{|}{C}H$—Ph), at 1.4 (s, 3H, CH_2— in the ring *b* of anthracene), at 1.3 (t, 6H, —$COOCH_2$—CH_3), at 4.3 (q, 4H, —$COOCH_2$—CH_3) and at 7.1–7.7 (m, 10H, aromatic protons).

Compound (I) reacted with methylmagnesium iodide and/or benzylmagnesium chloride giving diethyl dodecahydro-2,6-dioxo-4,8-diphenyl-9a-(methyl or benzyl)-10a-(methyl or benzyl)-4a,8a-anthracene dicarboxylate (Xa & b) respectively.



(X a&b)

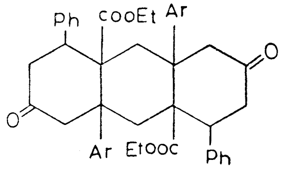
(a) R=—CH_3, (b) R=—CH_2—C_6H_5

The structure of compounds(Xa & b) was supported by:

(i) IR spectra exhibited absorptions characteristic of both νC=O (ketone) and νC=O (ester) at 1710 and 1735 cm^{-1} respectively.

(ii) H^{1}NMR spectrum of (Xa) showed signals at 2.1 (d, 4H, —CH_2—CHPh), at 2.3 (s, 4H, —CO—CH_2—), at 2.6 (t, 2H, —$\overset{|}{CH}$—Ph), at 1.4 (s, 4H, —CH_2— in the ring *b* of anthracene), at 1.1 (s, 6H, CH_3), at 1.3 (t, 6H, —COOCH$_2$—CH_3), at 4.3 (q, 4H, COOCH_2—CH$_3$) and at 7.1–7.7 (m, 10H, aromatic protons).

In the present study, the alkylation of aromatic hydrocarbons with compound (I) was studied. Thus, treatment of (I) with aromatic hydrocarbons, namely, benzene, toluene, *p*-xylene, *o*-xylene, *m*-xylene and/or cumene in the presence of anhydrous aluminium chloride under Friedel-Craft's reaction conditions, gave the corresponding diethyl dodecahydro-2,6-dioxo-4,8-diphenyl-9a,10a-di(phenyl or tolyl or *p*-xylyl or *o*-xylyl or *m*-xylyl or cumenyl)-4a,8a-anthracene dicarboxylate (XIa–f) respectively.



(XIa–f)

(a) Ar=C_6H_5—, (b) Ar=C_6H_4—CH_3—
(c) Ar=$C_6H_3(CH_3)_2$—1,4, (d) Ar=$C_6H_3(CH_3)_2$—2,3
(e) Ar=$C_6H_3(CH_3)_2$—1,3, (f) Ar=C_6H_4—$CH(CH_3)_2$—4

The structure of compounds (XIa–f) was confirmed by:

(i) IR spectra exhibited absorption bands in the region (1705–1770 cm^{-1}) due to νC=O (ketone) and in the region (1730–1740 cm^{-1}) due to νC=O (ester).

(ii) H^{1}NMR spectrum of (XIa) showed signals at 2.1 (d, 4H, —CH_2—CHPh), at 2.3 (s, 4H, —CO—CH_2—), at 2.6 (t, 2H, —CH—Ph), at 1.4 (s, 4H, —CH_2— in the ring *b* of anthracene), at 1.3 (t, 6H, —COOCH$_2$—CH_3), at 4.2 (q, 4H, —COO—CH_2—CH$_3$) and at 7.1–7.7 (m, 20H, aromatic protons).

EXPERIMENTAL

All melting points reported are uncorrected. IR spectra (KBr) were recorded on Pye-Unicam Spectrophotometer (ν_{max} in cm^{-1}). H^{1}NMR spectra in CDCl$_3$ were run on a varian VN (S 60 T) instrument using TMS as the internal reference (chemical shifts in δ scale).

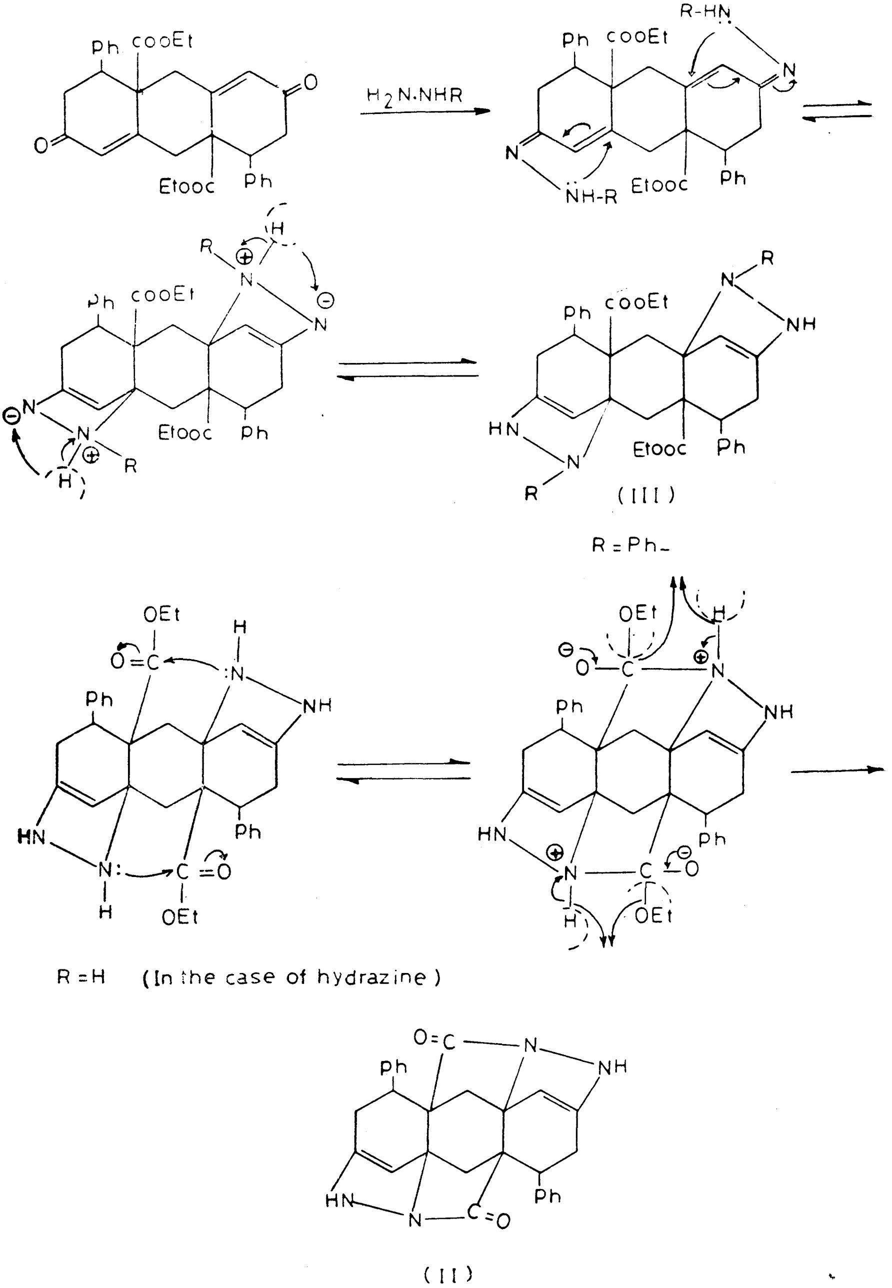
Reaction of (I) with Hydrazine Hydrate : Formation of (II)

A mixture of (I) (0.01 mole) and (0.02 mole) of hydrazine hydrate in (40 ml) butanol was heated under reflux for 6 hrs. The solid product obtained after concentration and cooling was crystallized from the suitable solvent to obtain (II)(cf.Table 1).

Reaction of (I) with Phenylhydrazine : Formation of (III)

A mixture of (I) (0.01 mole) and (0.02 mole) of phenylhydrazine in

MECHANISM OF FORMATION OF COMPOUNDS(II) AND (III)



(40 ml)ethanol was heated under reflux for 6 hrs. The solid product obtained after concentration and cooling was crystallized from the proper solvent to give(III) (cf. Table 1).

Reaction of (I) with Hydroxylamine Hydrochloride : Formation of (IV)

A mixture of (I) (0.01 mole) and hydroxylamine hydrochloride (0.02 mole) in dry pyridine (40 ml) was heated under reflux for 8 hrs. The mixture after cooling was poured into ice-cold dil. HCl. The solid obtained was crystallized from the suitable solvent to give (IV).

Reaction of (I) with Primary Amines : Formation of (Va–f)

A mixture of (I) (0.01 mole) and (0.02 mole) of primary amines, namely, aniline, *p*-toluidine, *p*-ansidine, benzylamine, methylamine and/or ethylamine in ethanol (50 ml) was heated under reflux for 5 hrs. The products separated after cooling were crystallized from the suitable solvent to give (Va–f) (cf. Table 1).

Condensation of (I) with Urea and/or Thiourea: Formation of (VIa & b)

A mixture of (I) (0.01 mole) and urea or thiourea (0.02 mole) was dissolved in ethanol (60 ml). To this solution alcoholic KOH (4 ml, 25%) was added and the reaction mixture was refluxed for 5 hours. The reaction mixture, after cooling, was dissolved in cold water and then neutralized by dil. HCl. The solid filtered off, washed with water and crystallized from the proper solvent to give compounds (VIa & b) (cf. Table 1).

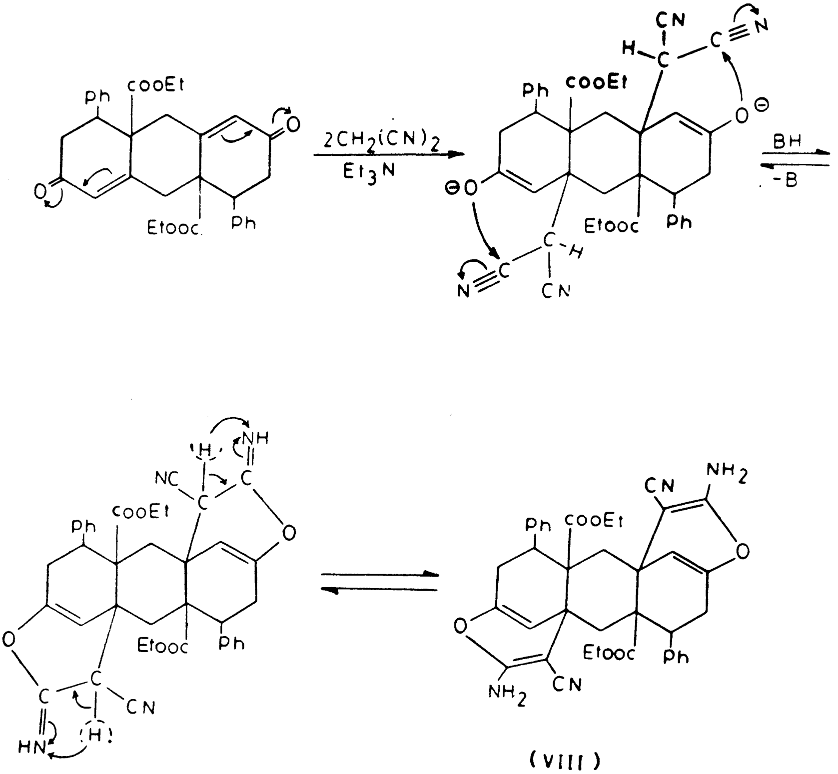
Reaction of (I) with Active Methylene Compounds: Formation of (VIIa–d)

A mixture of (I) (0.01 mole), an active methylene compound (0.02 mole) such as ethyl acetoacetate, ethyl cyanoacetate, ethyl bromoacetate and/or diethyl malonate, and sodium ethoxide solution (prepared from 0.35 g. of metallic sodium in 15 ml. absolute ethanol; 0.15 mole), was heated for 8 hrs. at 120–130°C. The reaction mixture was poured into water and extracted with ether to get rid of any unreacted organic material. The aqueous layer was acidified with ice-cold dil. HCl and solid product so formed was crystallized from the proper solvent to the corresponding Michael products (VIIa–d). The results are given in Table (I).

Reaction of (I) with Malononitrile in the Presence of Triethyl-Amine: Formation of (VIII)

Triethylamine (1 ml) was added dropwise with stirring to a mixture of (I) (0.01 mole) and malononitrile (0.02 mole) in dry benzene (50 ml). Stirring was continued in cold for 5 hrs., during which the sticky compound formed at the beginning of the reaction. The reaction mixture was then evaporated and crystallized from the proper solvent to give compound (VIII) (cf. Table 1).

MECHANISM OF FORMATION OF COMPOUND (VIII)



(VIII)

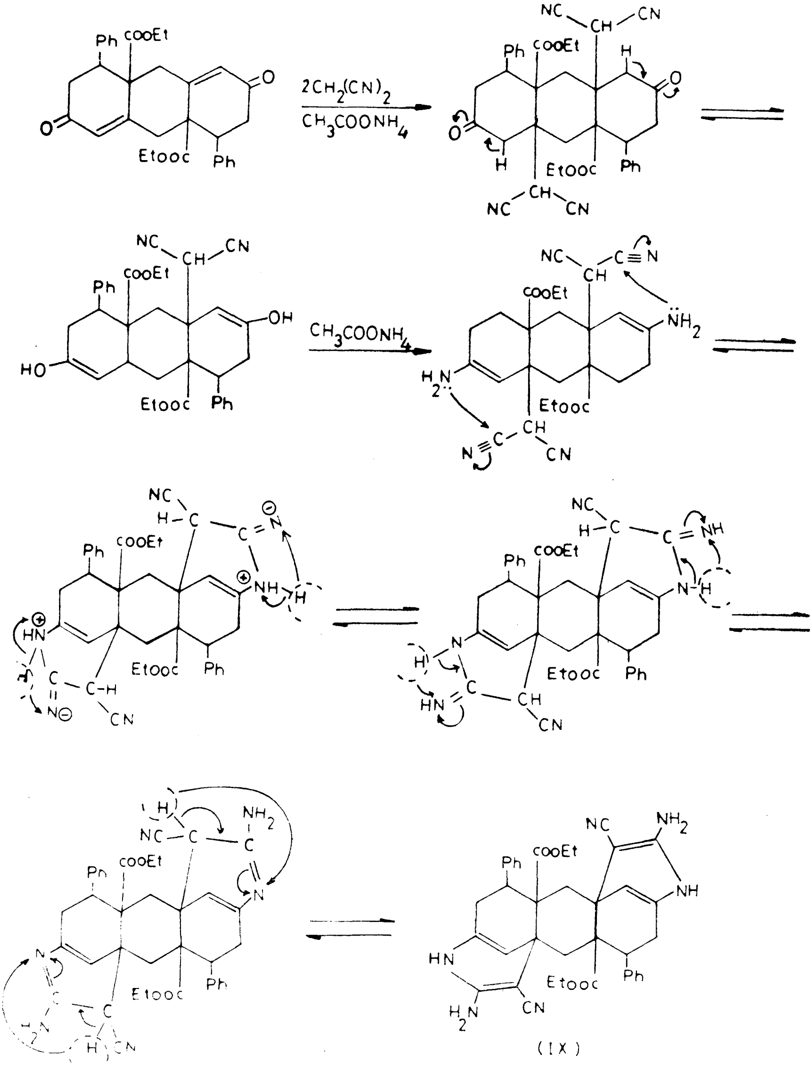
Reaction of (I) with Malononitrile in the Presence of Ammonium Acetate: Formation of (IX)

A mixture of malononitrile (0.02 mole), (I) (0.01 mole) and ammonium acetate (0.03 mole) was heated at 140–150°C for 8 hrs., then allowed to cool. The organic residue product was evaporated and crystallized from the suitable solvent to give compound (IX) (cf. Table 1).

Reaction of (I) with Grignard Reagent: Formation of (Xa & b)

A solution of (I) (0.01 mole) in dry benzene (200 ml) was added to an ethereal solution of methyl magnesium iodide and/or benzyl magnesium chloride (0.04 mole) during one hour. The reaction mixture was refluxed for 6 hrs., during which ether was allowed to evaporate, left overnight, hydrolysed with ice-cold saturated ammonium chloride and extracted with ether. The ethereal layer was dried (anhydrous sodium sulphate) and evaporated to give an oil which triturated with light petrol (40–60°C). The crude solid so obtained was crystallized from the suitable solvent to give (Xa & b) (cf. Table 1).

MECHANISM OF FORMATION OF COMPOUND(IX)



Reaction of (I) with Aromatic Hydrocarbons : Formation of (XIa–f)

To a solution of (I) (0.01 mole) in benzene, toluene, *p*-xylene, *o*-xylene, *m*-xylene and/or cumene (60 ml), anhydrous $AlCl_3$ (0.04 mole) was added with stirring; a vigorous evolution of HCl gas took place, stirring was continued for an additional 8 hrs. at room temperature, then added to ice-cold HCl. The organic layer washed with water and excess solvent removed by steam distillation, the solid obtained was crystallized from the proper solvent to give (XIa–f) (cf. Table 1).

TABLE 1

PHYSICAL DATA OF VARIOUS COMPOUNDS PREPARED

Cmpd.	M.pt.(°C)	Solvent for crystn.*	Mol. formula (M.Wt.)	Analysis (%)		
					Calcd.	Found
II	240	Bu	$C_{28}H_{24}O_2N_4$	C	74.89	74.79
			(448.52)	H	5.39	5.38
				N	12.49	12.48
III	100	P	$C_{44}H_{44}O_4N_4$	C	76.27	76.26
			(692.86)	H	6.40	6.42
				N	8.09	8.12
IV	235	M	$C_{32}H_{34}O_6N_6$	C	70.83	70.79
			(242.63)	H	6.32	6.32
				N	5.16	5.23
Va	140	B+P	$C_{44}H_{46}O_6N_2$	C	75.62	75.30
			(698.86)	H	6.63	6.62
				N	4.01	4.12
Vb	135	B+P	$C_{46}H_{50}O_6N_2$	C	76.01	76.12
			(726.91)	H	6.93	6.82
				N	3.85	3.83
Vc	170	E	$C_{46}H_{49}O_8N_2$	C	72.80	72.79
			(757.91)	H	6.91	6.89
				N	3.69	3.65
Vd	115	E	$C_{46}H_{50}O_6N_2$	C	76.01	76.12
			(726.91)	H	6.93	6.88
				N	3.85	3.86
Ve	122	E	$C_{34}H_{42}O_6N_2$	C	71.06	71.12
			(574.72)	H	7.37	7.36
				N	4.87	4.86
Vf	105	E	$C_{36}H_{46}O_6N_2$	C	79.71	79.71
			(602.77)	H	7.69	7.68
				N	4.65	4.65
VIa	220	E	$C_{34}H_{36}O_6N_4$	C	68.44	68.39
			(596.68)	H	6.08	6.12
				N	9.38	9.29
VIb	235	E	$C_{34}H_{36}O_4N_4S_2$	C	64.94	64.89
			(628.81)	H	5.77	5.76
				N	8.91	8.92
VIIa	200	E	$C_{44}H_{52}O_{12}$	C	68.38	68.36
			(772.89)	H	6.78	6.78
VIIb	210	M	$C_{42}H_{46}O_{10}N_2$	C	68.28	68.31
			(738.84)	H	6.28	6.30
				N	3.79	3.78
VIIc	160	M	$C_{40}H_{46}O_{10}Br_2$	C	56.74	56.72
			(846.81)	H	5.48	5.43

*Bu = Butanol, B = Benzene, E = Ethanol, P = Light petrol (80–100), M = Methanol A = Acetic acid.

TABLE 1 (Contd.)

Cmpd.	M.pt.(°C)	Solvent for crystn.*	Mol. formula (M.Wt.)	Analysis (%)		
					Calcd.	Found
VIId	215	Bu	$C_{46}H_{56}O_{14}$	C	66.45	66.51
			(835.94)	H	6.75	6.76
VIII	100	B+P	$C_{38}H_{36}O_6N_4$	C	70.79	70.75
			(644.73)	H	5.63	5.63
				N	8.69	8.59
IX	>240	A	$C_{38}H_{38}O_4N_6$	C	72.41	72.41
			(642.76)	H	5.96	5.96
				N	13.08	13.07
Xa	>240	P	$C_{34}H_{40}O_6$	C	79.97	79.89
			(544.69)	H	7.40	7.50
Xb	140	P	$C_{46}H_{48}O_6$	C	79.28	79.31
			(696.88)	H	6.94	6.93
XIa	145	P	$C_{44}H_{44}O_6$	C	79.02	79.02
			(668.83)	H	6.63	6.62
XIb	130	P	$C_{46}H_{48}O_6$	C	79.28	79.27
			(696.88)	H	6.94	6.93
XIc	170	P	$C_{48}H_{52}O_6$	C	79.53	79.53
			(724.94)	H	7.23	7.24
XId	160	B+P	$C_{48}H_{52}O_6$	C	79.53	79.53
			(724.94)	H	7.23	7.23
XIe	150	B+P	$C_{48}H_{52}O_5$	C	79.53	79.53
			(724.94)	H	7.23	7.24
XIf	120	B+P	$C_{50}H_{56}O_6$	C	79.76	79.74
			(752.99)	H	7.50	7.49

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