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THE SYNTHESIS AND REACTIONS OF HETEROCYCLES UNDER HIGH PRESSURES[†]

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Abstract —— In this review are brought together the representative results which are presently available concerning the use of high pressures on reactions involving heterocyclic compounds.

1. Introduction.
2. Cycloadditions to heterocycles.
3. Pressure assisted N-alkylations, acid catalysed solvolyses, and polymerisations of heterocycles.
4. Synthesis of heterocycles.
5. Conclusions.

1. Introduction

It is well known that the application of pressure accelerates reactions which take place with a net contraction in volume.[1] However, the use of very high pressures in reactions involving organic, and especially heterocyclic, molecules has been little explored in spite of the expected wide applicability of the technique. This is doubtless due to the difficulty in obtaining and maintaining the necessary apparatus, but the apparatus now is only moderately expensive.[2] This review brings together results presently available concerning the use of high pressures on

$$-RT(\delta \ln k/\delta P)_T = \Delta V^{\ddagger}$$

reactions involving heterocyclic compounds. From the point of view of preparative chemistry it is assumed[§] that 1 bar $\doteq$ 1 atmosphere $\doteq$ 1 $kg \cdot cm^{-2}$ $\doteq$ 10^5 Pa.

The mechanisms of reactions taking place under high pressures have been investigated in only a few instances,[3] and it is possible that extrapolation of mechanisms, established beyond reasonable doubt for reactions proceeding at 1 bar, to structurally analogous transformations which proceed only say at 10 kbar, may lead to incorrect conclusions. Small changes in reaction conditions can cause reactions to give the same products but by very different pathways, for example, chlorobenzene with aqueous sodium hydroxide yields phenol. However, using 6 M hydroxide at 330°C 86% of the conversion proceeds by an S_N2 displacement and 14% by benzyne as an intermediate, while in 4 M hydroxide and 340°C the corresponding values are 16% and 84% respectively.[4]

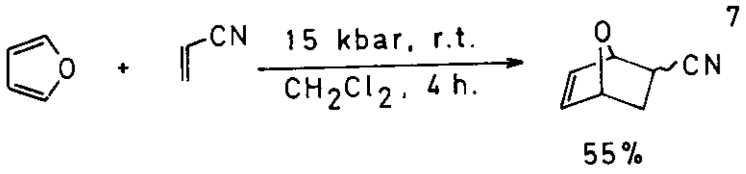
[§] 1 bar = 0.986923 atmosphere = 1.01972 $kg \cdot cm^{-2}$

2. Cycloadditions to heterocycles

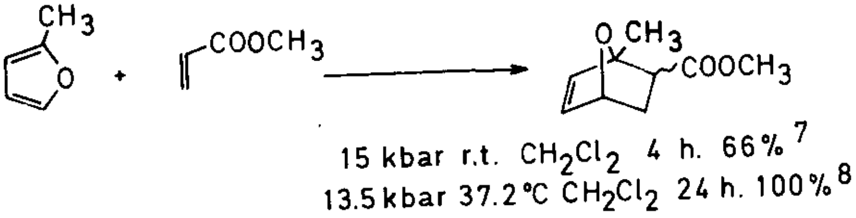
Addition reactions of the Diels-Alder type are reversible, and attempts to carry out such reactions with a number of heterocycles at atmospheric pressure have failed. This can be due to the adduct being stable only at low temperature, and being formed very slowly under these conditions. Under these circumstances the application of high pressure can be very advantageous.

2.1 Furans and thiophenes

Furans possess significant resonance stabilization (ca. 25 kcal/mole),[5] bicyclo[2.2.1]heptane systems are strained, so Diels-Alder reactions of furans are limited to reactive dienophiles such as maleic anhydride and dimethyl acetylenedicarboxylate (DMAD).[6] However, at 13.5-15 kbar, and appropriate temperatures, furan and 2-methylfuran add rapidly to monoactivated dienophiles yielding 7-oxabicyclo[2.2.1]heptanes as shown below.[7,8]

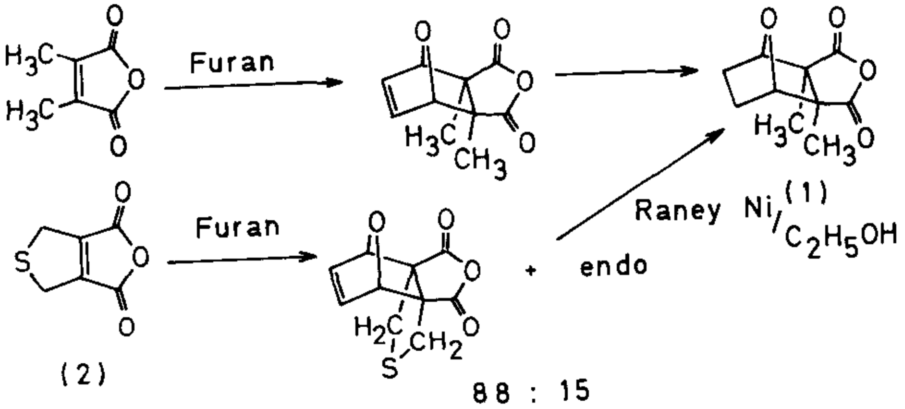


(cf. 39% after 5 weeks at atmospheric pressure)[9]

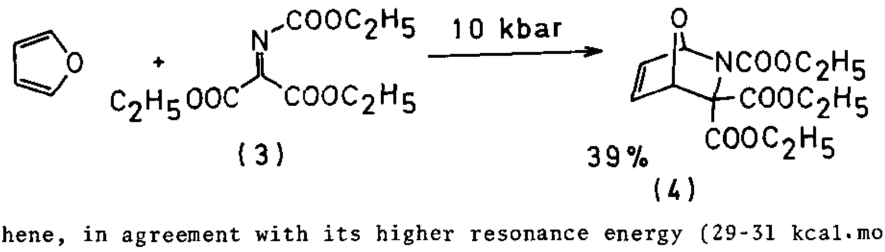


Methyl crotonate and crotononitrile gave poor yields, while mesityl oxide did not react even at 15 kbar;[7] steric hindrance may explain these observations. Electron attracting groups in the heterocycle also inhibit addition for furfural and methyl furoate failed to react with ethyl vinyl ether or DMAD at 15 kbar.[7]

A beautifully simple synthesis of cantharidin (1) would consist in the addition of furan to dimethylmaleic anhydride followed by hydrogenation, but the addition could not be effected even at 40 kbar.[10] Perhaps surprisingly the 2,5-dihydrothiophene (2) added quantitatively to furan, yielding a mixture of isomers, one of which on reductive desulphurisation yielded cantharidin.[11]



Furan also combined with the electron deficient imine (3) *at 100°C and 10 kbar* to give (4).[12]



Thiophene, in agreement with its higher resonance energy (29-31 kcal.mol^{-1}),[13] undergoes additions across the 2,5-positions only with the most reactive dienophiles, dicyanoacetylene, tetrafluorobenzyne,[14] and with DMAD[15] at 165°C. Sulphur extrusion takes place at once yielding benzene derivatives. Maleic anhydride is inert at atmospheric pressure, but at 100°C and 10 kbar in dichloromethane the adduct (5) was obtained[16] in 43% yield. The addition was very sensitive to the conditions for changing the solvent to benzene reduced the yield to 6% and no reaction occurred at room temperature at 1 bar or 15 kbar.

(5)

Under the optimum conditions for maleic anhydride, thiophene showed no sign of reacting with dimethyl maleate or fumarate, methyl acrylate or acrylonitrile.[16]

2.2 Indoles

Indole combines slowly with DMAD at room temperature to give a variety of products[17] stemming presumably from the initial production of the charged Michael-type intermediate (cf. 7). High pressure accelerates[18] this reaction and one new product (6) was identified. The results are summarized in the Table. 1-Methylindole in dichloromethane with DMAD at 10 kbar/room temperature gave[18] more of the azepine (9) than were obtained[19] in refluxing acetonitrile at atmospheric pressure. High pressures accelerate [2+2] cycloadditions of both the concerted and non-concerted types.[3, 20]

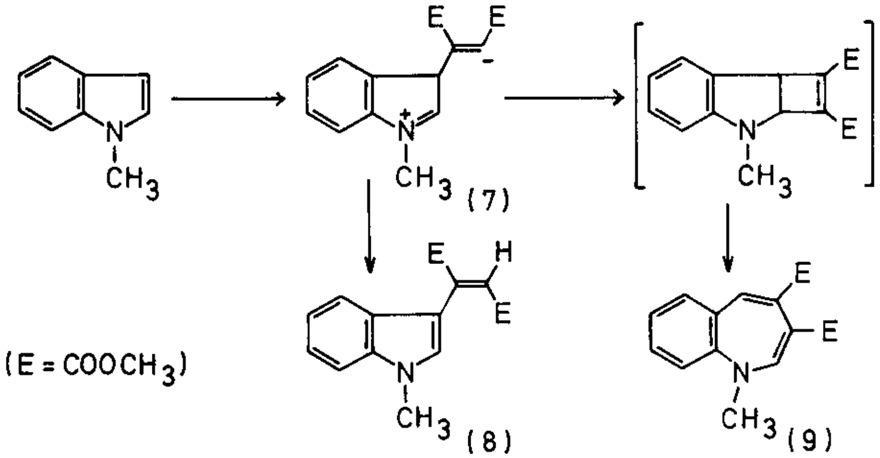
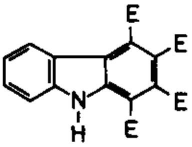
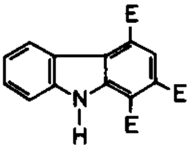
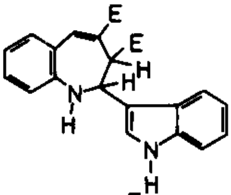
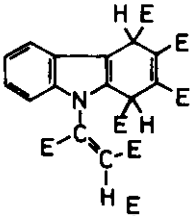
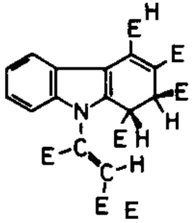
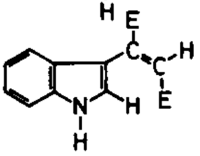
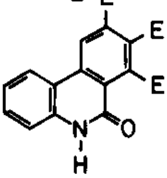


Table Products from indole and dimethyl acetylenedicarboxylate

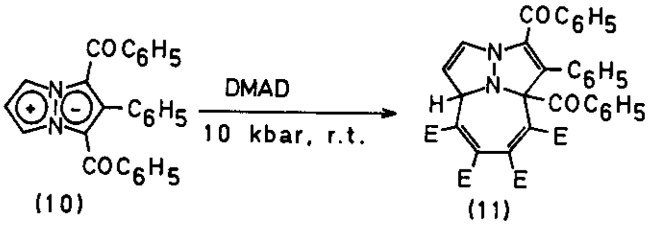
Products	Atmospheric Pressure	10 kbar		Products	Atmospheric Pressure	10 kbar	
	112 d (%)	7 d (%)	1 d (%)		112 d (%)	7 d (%)	1 d (%)
	13.4	—	0.8		1.0	—	—
	9.8	1.6	—	 (6)	—	—	1.1
	7.5	3.7	—		trace	—	0.4
	6.6	—	0.2	**recovered** indole	18.1	0.6	8.8

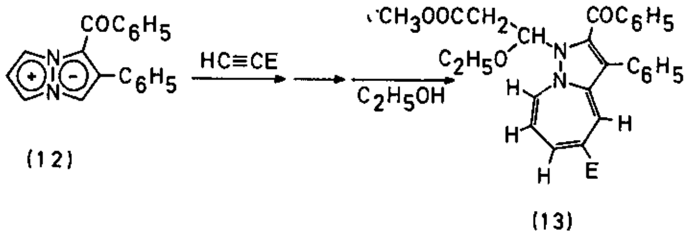
2.3 Azapentalenes

The mesoionic heteropentalenes have attracted considerable attention[21] in recent years because of their intriguing chemical properties. Many of these compounds, which are usually sensitive to heat and acids, undergo cycloadditions with electron deficient acetylenes and olefines to give novel structures such as cyclazines.[22]

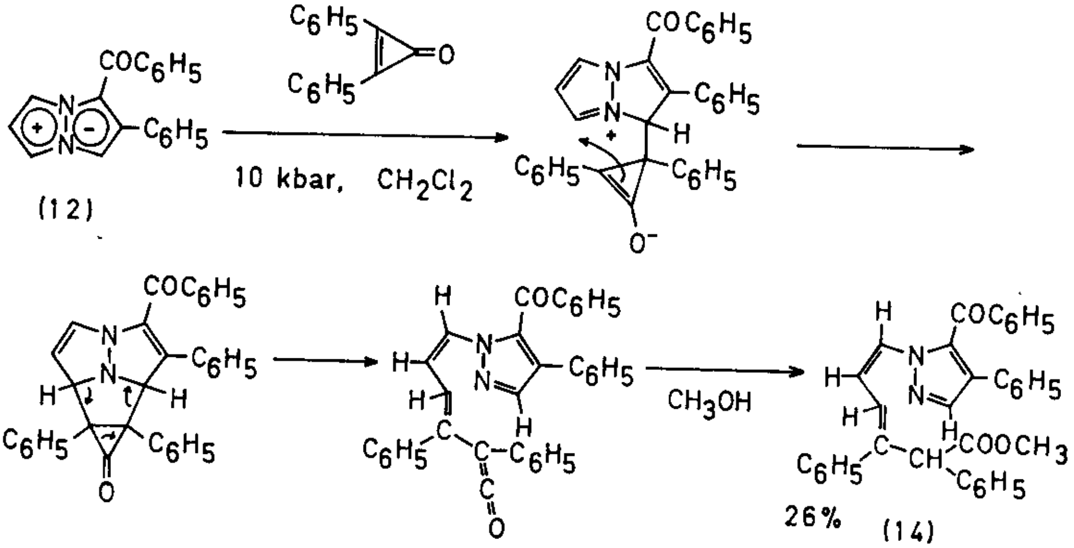
1,3-Dibenzoyl-2-phenyl-3a,6a-diazapentalene (10) reacts slowly with DMAD at 1 bar but after 12 h at 10 bar and room temperature a 1:2 molar adduct (11) was obtained almost quantitatively.[23]

1-Benzoyl-2-phenyl-3a,6a-diazapentalene (12), was hardly affected by methyl propiolate at atmospheric pressure but at 10 kbar a new product was formed. Crystallisation was initiated by ethanol, which was incorporated yielding (13).[23]



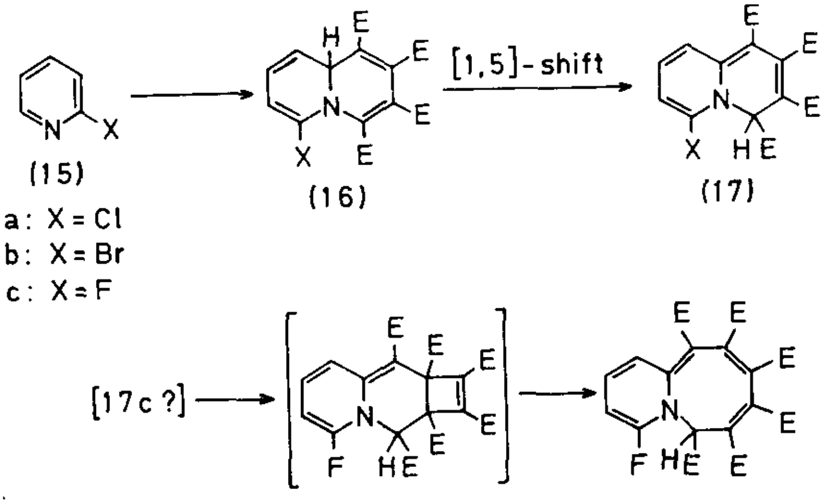


Diphenylcyclopropenone (DPP) possesses a highly electrophilic double bond, can behave as an activated diphenylacetylene,[24] and combines with iminonium, sulfonium and phosphonium ylids.[24, 25] With the diazapentalene (12) at 10 kbar, followed by methanol treatment, it gave the pyrazole (14).[23]



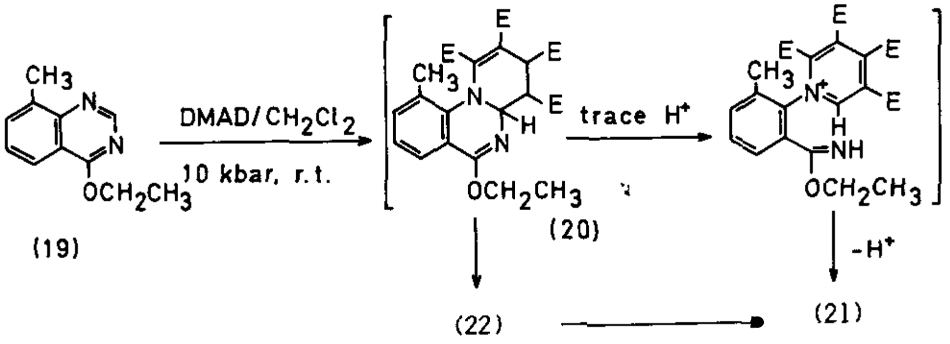
2.4 Pyridines and related aza-aromatic compounds

Various types of products have been obtained from reactions of DMAD with aza-aromatic compounds.[26] For example, pyridine, and its alkyl, methoxy, and 3- and 4-cyano derivatives react with DMAD at room temperature to give quinolizines and/or indolizines, whereas lower nucleophilicity accounts for no combination taking place when 2-chloro-, 2-bromo-, 2-fluoro-, and 2-cyanopyridines were employed. These reactions appear to proceed via dipolar intermediates and therefore were expected to be accelerated by pressure. 2-Chloropyridine (15a) did in fact react with DMAD at 10 kbar to give the 4aH-quinolizine (17a), while 2-bromopyridine (15b) gave both the 4aH- (17b) and the 9aH-quinolizine (16b);[27] the 5-substituent inhibits the [1,5] hydrogen shift.[28] *The 10 kbar treatment of 2-fluoropyridine (15c) with* DMAD gave a 1:3 molar adduct to which structure (18) is tentatively assigned.[29]

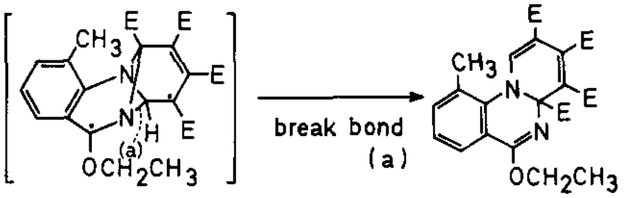


(15) (16) (17) (18)

8-Methyl-4-ethoxyquinazoline (19), in contrast to the 6-methyl isomer,[30] did not react with DMAD at atmospheric pressure because of steric hindrance to attack at the 1-nitrogen atom. At 10 kbar, however, addition occurred, giving (21).[18] The first product expected would be (20) and could undergo an acid catalysed rearrangement *[30]* from traces of hydrogen chloride in the solvent, or another type of rearrangement (via 22) recently suggested.[31]

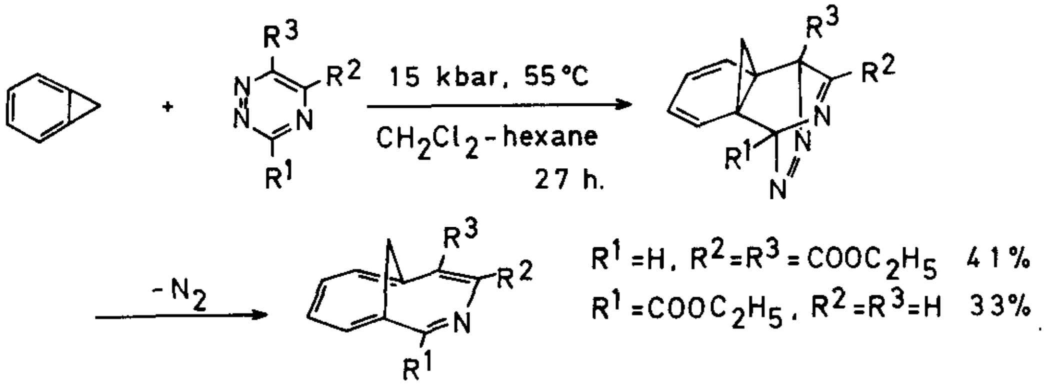


(19) (20) (22) (21)



(22) (21)

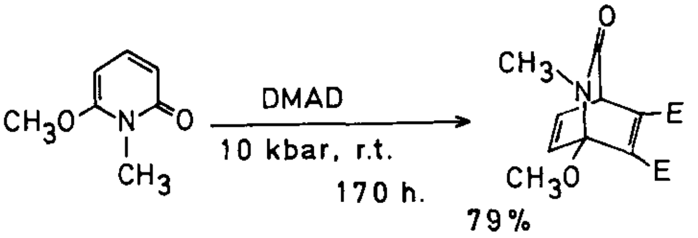
At one step synthesis of some 3,8-methanoaza[10]annulene derivatives (23) has been achieved by the high pressure cycloaddition of 1,2,4-triazines with benzocyclopropene.[32] These reactions also proceed under thermal conditions, when $R^1 = R^2 = R^3 = CO_2Et$ and $R^1 = CN$, $R^2 = R^3 = CO_2Et$, as sufficient activation of the diene is now present.



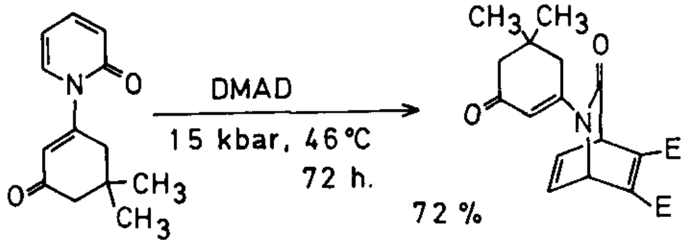
(23)

2.5 2(1H)-Pyridones

2(1H)-Pyridones have some resonance stabilisation (25-26 kcal/mol[33]), but the possibility of addition reactions taking place across the 3,6-positions has been of interest for some years. A little success has been obtained with such reactive dienophiles as DMAD, maleic anhydride and imide, and benzyne,[34] but the thermal instability of some of the desired initial adducts has led to retro-Diels-Alder reactions taking place at atmospheric pressure. These difficulties have been overcome in some cases, exemplified below, by the use of high pressure.[35]



(cf. ref. 34d)

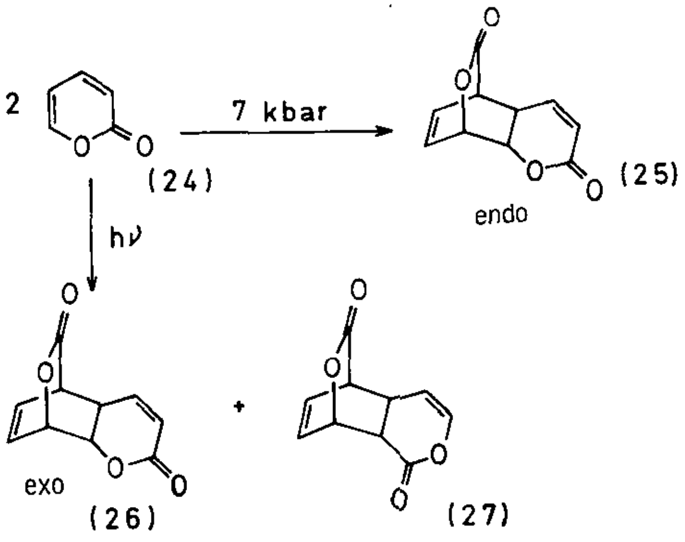


+ 1 : 3 adduct
(cf. ref. 34c)

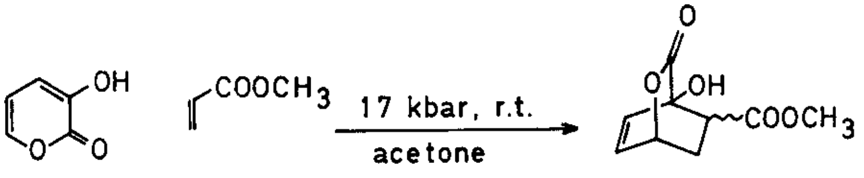
(1 : 1)

2.6 2-Pyrones

2-Pyrone behaves usually as an unsaturated[36] lactone (cf. 24) so the pyrylium 2-oxide structure contributes minimally to a resonance hybrid. Thermal dimerisation of this compound at atmospheric pressure does not occur, but in toluene or nitromethane at 70°C and 5 kbar the endo-dimer (25) is formed in low yield.[37] In contrast photosensitised dimerisation gives two other dimers, (26) and (27).



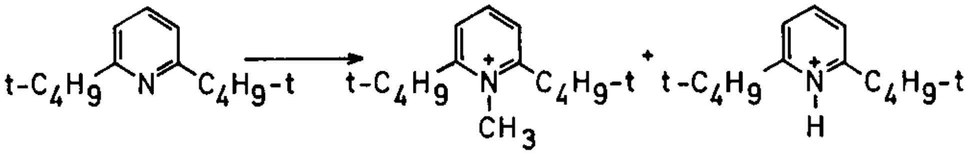
With both electron rich and deficient dienophiles 2-pyrones give Diels-Alder type adducts, but loss of carbon dioxide can take place if temperatures of 100-200°C are needed for the addition.[38, 39] One such example is 3-hydroxy-2-pyrone but simple Diels-Alder additions occur at 17-40 kbar and room temperature with methyl acrylate and crotonate, α-chloroacrylonitrile, or methyl vinyl ketone giving for example (28).[40]



(28)

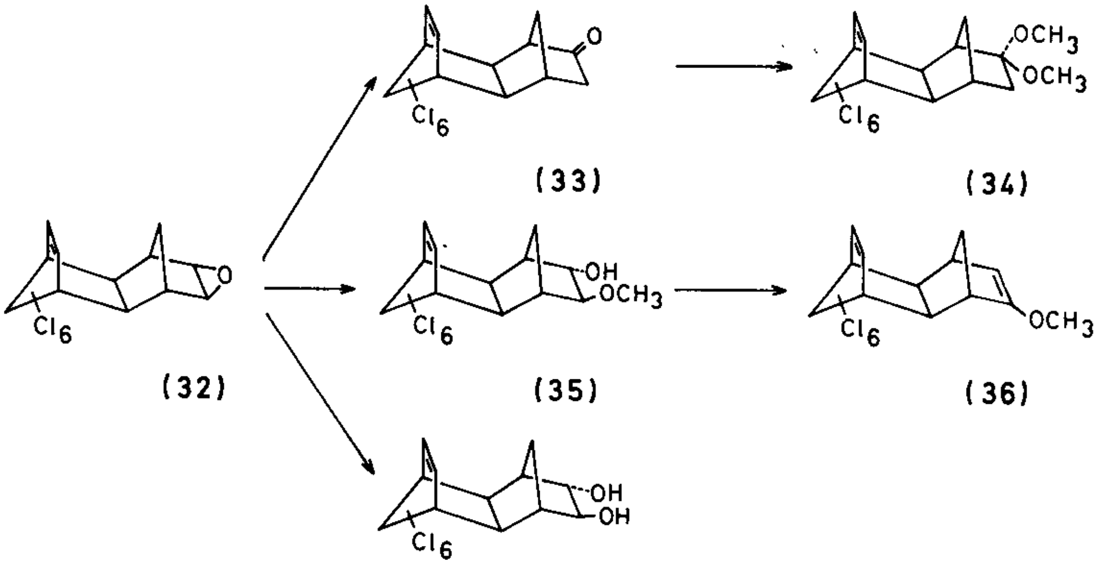
3. Pressure assisted N-alkylations, acid catalysed solvolyses, and polymerisations

2,6-Di-t-butylpyridine (29) is very sterically hindered round the nitrogen atom and does not react with methyl iodide at atmospheric pressure. At 6 kbar/90 °C attack at the nitrogen atom takes place to give (30) and (31) in 2:8 ratio, but with methyl fluorosulfonate methylation was more effective, the ratio being 8:2.[41] The latter reagent under similar conditions N-methylated 2,4,6-tri-t-butylpyridine and 4,5-dimethylacridine in good yields.[41] In contrast no reaction took place[42] between pyridine and triphenylmethyl chloride at 6 kbar/90°C.



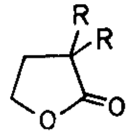
(29) (30) (31)

The oxiran ring of dieldrin (32) is unusually stable. Acid catalysed solvolysis at 1 atmosphere and 140°C gave some (37), while at 12 kbar/110°C/8 h (33) - (37) were formed.[43]

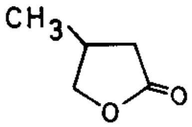


(37)

The lactones (38) at 23-24 kbar gave polyesters, but (39) under similar conditions gave water, carbon dioxide and highly branched hydrocarbons.[44] In contrast the thiolactone (40) at 17 kbar/170°C gave (41), (42), and (43), the last being fully aromatised by chloranil.[45] Similar products were obtained from γ-thiovalerolactone, δ-thiovalerolactone, indoline-2-thione and chroman-4-thione.



(38) R=H or CH_3



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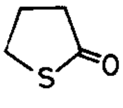

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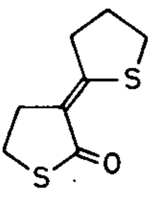

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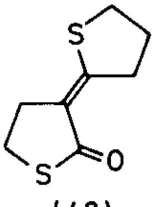

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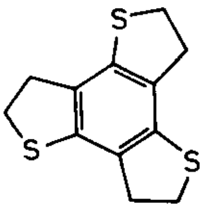
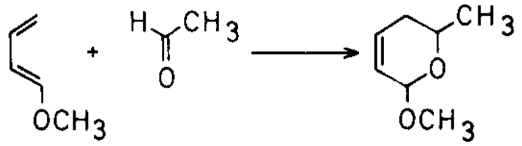


(43)

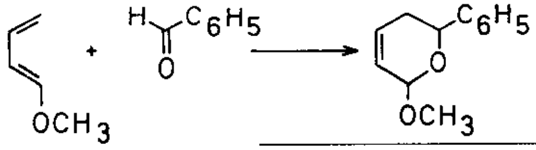
4. The synthesis of heterocycles

4.1 Pyrans

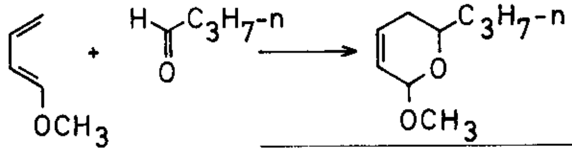
The synthesis of 5,6-dihydro-2-pyrans, valuable intermediates in the preparation of sugars and lactones, from 1-alkoxy-1,3-dienes and carbonyl compounds[47] is limited in practice to formaldehyde and other aldehydes such as chloral or glyoxylic esters where the carbonyl is attached to an electron withdrawing group. Polish[48] and Russian workers[49] have recently shown that at 14-20 kbar lower temperatures give satisfactory yields with benzaldehyde and aliphatic aldehydes. Higher



pressure (kbar)	temp. (°C)	time (h.)	yield (%)	(cis/trans)	lit. no.
20	65	5	62	(70/30)	48
14	80	6	50	(70/30)	49a,b,d
1.0 x 10^{-3}	160-180	6	2	(31/69)	49b

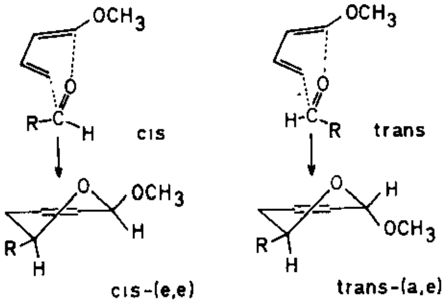


19.5	50	5	80	(75/25)	48
14	80	6	61	(70/30)	49a,b
1.0 x 10^{-3}	170	6	17	(26/74)	49b

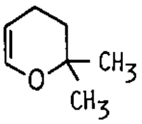


14	80	6	41	(56/44)	48b,d
1.0 x 10^{-3}	160-180	6	0		49b

pressures give an increase in the proportion of the cis isomer suggesting that there is more crowding in the intermediate transition state compared with that yielding the trans isomer.[49c]



High pressures facilitate[50, 51, 52] the complementary synthesis of 3,4-dihydro-2H-pyrans. Acrolein and isobutylene at 10 kbar/80°C give the adduct (44) in 35% yield, while only 8% is obtained[50] at 1 bar/230°C, mesityl oxide and ethyl vinyl ether at 20 kbar/110°C yield 50% of (45), but none is formed[51] in a tube sealed at 1 atmosphere and heated to 200°C.



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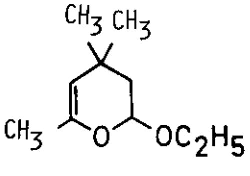
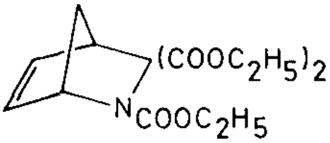


(45)

4.2 Pyridines

Triethyl azomethinetricarboxylate adds to cyclopentadiene to give the azabornene (46) at 1 bar, while 2,3-dimethylbutadiene, isoprene and 1-phenylbutadiene add only at high pressure (10 kbar) to yield 1,2,3,6-tetrahydropyridines (e.g. 47).[53]



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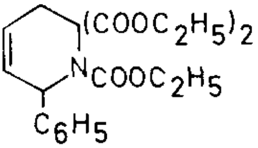
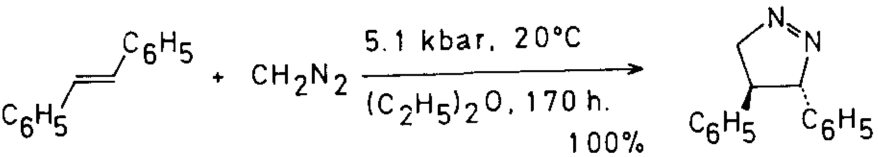


(47)

4.3 Pyrazoles

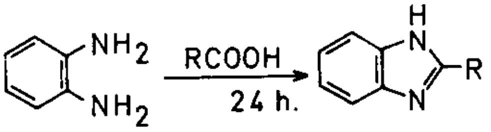
Diazomethane is almost inert to E-stilbene at room temperature, but at 5.1 kbar it yields the 1-pyrazoline (48) quantitatively.[54] Very few applications of high pressure to '1,3-dipolar' additions have been made (see 4.5).



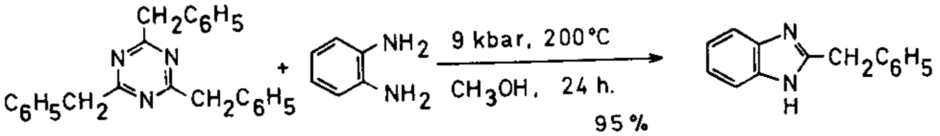
(48)

4.4 Benzimidazoles

Adamantan-1-carboxylic acid and 2,2-dimethylpropionic acid either do not react with o-phenylenediamine, or give very low yields of benzimidazoles under conditions successful for less sterically hindered carboxylic acids. At 8 kbar/110°C these acids gave 66% and 48% of the corresponding benzimidazole respectively.[55]

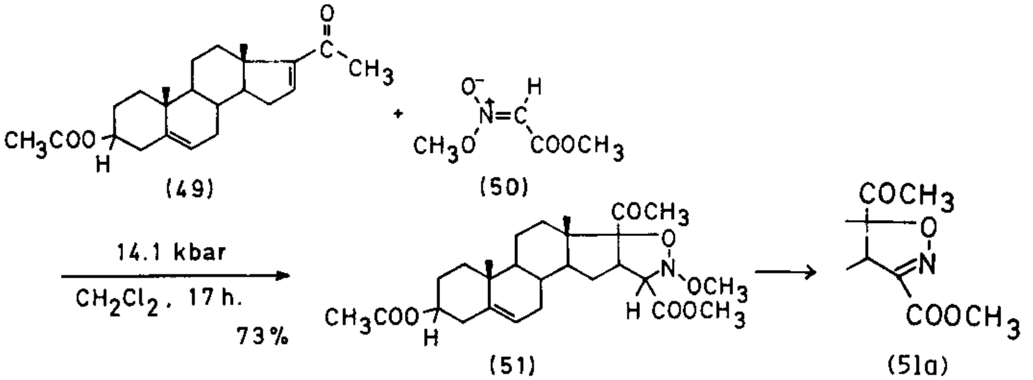


Triazines, which may be converted in situ to nitriles (see 4.7), also yield benzimidazoles with 1,2-phenylenediamine under high pressure.[56]



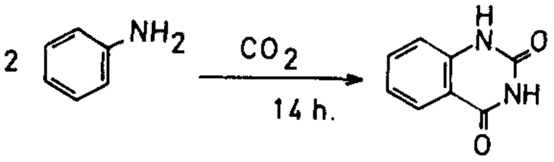
4.5 Isoxazolines

The nitronic ester (50) undergoes a 1,3-dipolar addition to the steroidal dipolarophile (49) affording a new type of the pentacyclic steroid (51) with an additional isoxazoline ring. A practical yield of (51) is only obtained at high pressure; under atmospheric conditions only 2% of the adduct forms, and Lewis acid catalysed addition of (50) to (49) yields the isoxazoline (51a) through loss of methanol.[49]



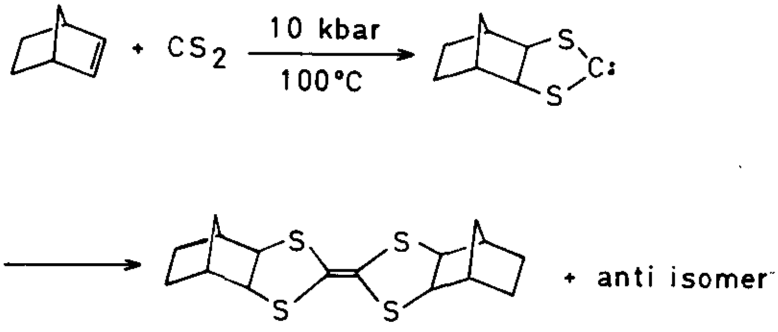
4.6 Heterocycles from carbon dioxide and disulphide

Aniline, carbon dioxide, and a base at 8.5 kbar/200°C produce 3-phenyl-2,3(1H, 3H)-quinazolidinedione (52) in 70% yield; none is formed below 3.3 kbar.[58]



(52)

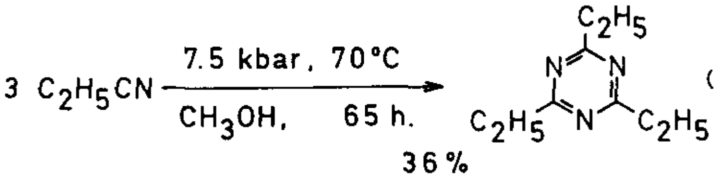
Strained olefines with carbon disulphide at 10 kbar/100°C give 2:2 molar adducts in high yield (e.g. **53**, 83%) as mixtures of isomers.[59]



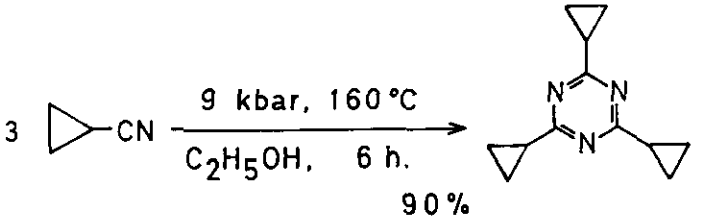
(53)

4.7 Synthesis from nitriles

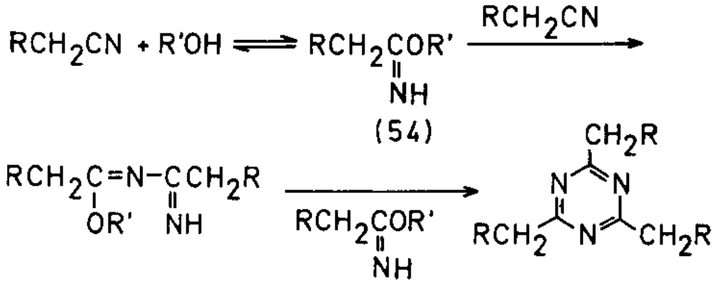
The most important contemporary general method for the synthesis of triazines is by the cyclo-trimerisation of nitriles.[60, 61] The reaction is catalysed by alcohols, *and bases such as ammonia and piperidine*[62, 63] and detailed studies have shown that alcohol catalysis proceeds by an imino-ether intermediate (**54**)[64] as outlined below.



(ref. 62)

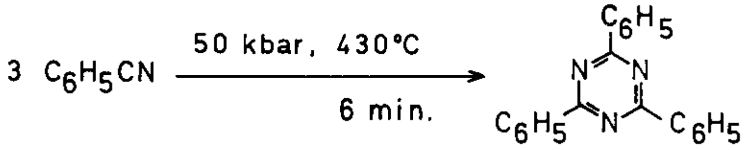


(ref. 63)



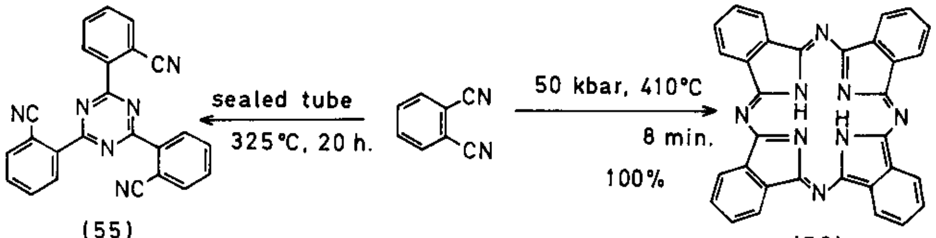
(54)

Aromatic and aliphatic nitriles undergo the trimerisation, but when an α-hydrogen atom is present a useful yield of triazine is only obtained when high pressure is applied. Under extreme conditions, 35-50 kbar/350-500°C, aromatic nitriles trimerize without a catalyst.[65]



(cf. ref. 62)

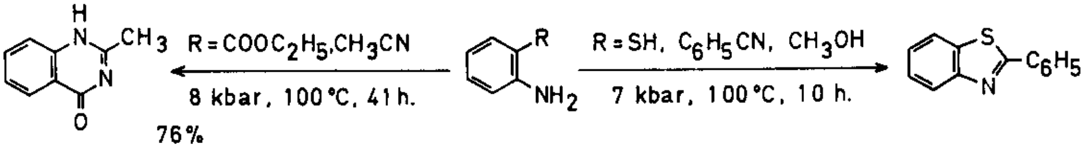
Intriguingly, phthalonitrile yields either (56) in the absence of water,[65] or (55) in its presence[66] under rather different conditions of pressure.



(55)

(56)

Benzimidazoles, benzoxazoles, and benzothiazoles have all been prepared from the appropriate aniline and nitrile in methanol as exemplified below, and a quinazolinone has been obtained similarly.[56]



5. Conclusions

The use of high pressures, which usually need to be greater than 5 kbar, to assist organic synthesis, is in its infancy. Any reaction in which bonds are formed, whether by ionic, radical, or concerted processes could be assisted by high pressures. Polymerisation of the reactants can be a problem. It is extremely difficult, at present, to predict the effect of high pressure on a reaction which fails at normal pressures, for success can depend greatly on the solvent, pressure, and temperature. High pressures strongly encourage reactions normally inhibited by steric factors, but small changes in the structures of the reactants, which do not appear to alter the steric position much, can bring success or failure. However, there seems no doubt that the use of high pressures in effecting the synthesis of heterocyclic structures otherwise very difficult, or impossible to obtain will slowly increase, as will studies of mechanism under high pressures, when the apparatus becomes more readily available. There is clearly an area of heterocyclic synthesis which it will be possible to develop only by the use of very high pressures.[67]

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[†] Molecular and Reaction Design Based on High Pressure Organic Reactions. Part 4. This work was supported by Research Grants from the Japanese Ministry of Education (Grant-in-Aid, No.284921 and 554146).--Part 3: K. Matsumoto, submitted.

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