Thermal Cycloadditions and Isomerisation of Tetramethylallene

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RECENT preliminary reports[1,2] claim that photocycloadditions of carbonyl compounds to tetramethylallene proceed by simple 1,2-addition to give 2-alkylideneoxetans as the sole monoadducts. In sharp contrast, we find that thermal cycloadditions to tetramethylallene produce 1 : 1 adducts which arise exclusively by a preliminary isomerisation of the allene to 2,4-dimethylpenta-1,3-diene.

Thus, when tetramethylallene is kept under autogenous pressure in the dark with an equimolar proportion of an electron-deficient olefin ($CF_2{:}CF_2$, $CF_2{:}CFCl$, or $CH_2{:}CH{\cdot}CN$) or ketone ($CF_3{\cdot}CO{\cdot}CF_3$), the major products are 1 : 1 adducts (I—III) which are identical (by i.r., g.l.c., and n.m.r.) to those obtained by similar treatment of 2,4-dimethylpenta-1,3-diene. Reaction conditions and product yields are shown in Table 1; the main by-products proved to be fluoro-olefin dimers and the dimer of tetramethylallene (IV). The fluoro-olefins react by 1,2-addition to the 1,3-diene, giving the isobutenylcyclobutanes (Ia, Ib) which were readily identified by ^1H n.m.r. (at 60 mc./sec., τ 4·6, 1*H*; τ 7·5—7·6, 2*H*; τ 8·3—8·4, 6*H*; τ 8·7, 3*H*) and ^{19}F n.m.r. analysis. With acrylonitrile and hexafluoroacetone, 1,4-additions to the 1,3-diene lead, respectively, to the known trimethylcyclohexene (II) (b.p. 90—92°/10 mm., n_D^{20} 1·4690; lit.[3] b.p. 105—108°/18 mm., n_D^{20} 1·4705) and to the trimethyl-5,6-dihydro-1,2-pyran (III), identified by comparison of its ^1H n.m.r. spectrum (at 60 Mc./sec., τ 4·4, 1*H*; τ 7·7, 2*H*; τ 8·2, 3*H*; τ 8·7, 6*H*) with data for related dihydropyrans.[4]

To resolve conflicting reports concerning the thermal stability of tetramethylallene,[5,6] the dimerisation of the allene at 150° was carefully re-examined. In our hands, tetramethylallene dimerised without rearrangement to give, quantitatively, the previously reported dimer, tetramethyl-1,2-di-isopropylidenecyclobutane (IV),[6] provided that the glass reaction vessel was pretreated by rinsing with alcoholic potassium hydroxide, repeatedly rinsing with dry ethanol, and finally drying *in vacuo*. The use of unwashed or acid-rinsed tubes (see Table 2) led to rapid isomerisation of the allene to 2,4-dimethylpenta-1,3-diene, from which a complex mixture of dimers was obtained. An extension of this technique provides an alternative to the usual synthesis of the 1,3-diene (from mesityl oxide and methylmagnesium iodide[7]): a simple procedure is to heat tetramethylallene under pressure in a polar solvent which has no tendency to co-dimerise

TABLE 1

Products of cycloadditions to tetramethylallene (*TMA*) *and* 2,4-*dimethylpenta*-1,3-*diene* (*DMP*)

Diene	Addend	Time (hr.)	Temp. (°c)	Product	Yield (%)[a]	B.p.
TMA	$CF_2{:}CF_2$	72	150	Ia	86	38°/12 mm.
	$CF_2{:}CFCl$	72	150	Ib	81[b]	58°/12 mm.
	$CH_2{:}CH{\cdot}CN$	24	150	II	75	90—92°/10 mm.
	$(CF_3)_2CO$	72	25	III	64	90—95°/115 mm.
		24	170	III	95	
DMP	$CF_2{:}CFCl$	72	150	Ib	75[b]	
	$CH_2{:}CH{\cdot}CN$	24	150	II	88	
	$(CF_3)_2CO$	24	170	III	85	

[a] Moles % based on addend consumed, estimated by g.l.c. on Apiezon L–Celite at 65—150°, before distillation.

[b] G.l.c. and n.m.r. analysis of (Ib) show the presence of two geometrical isomers in the approximate ratio 55 : 45.

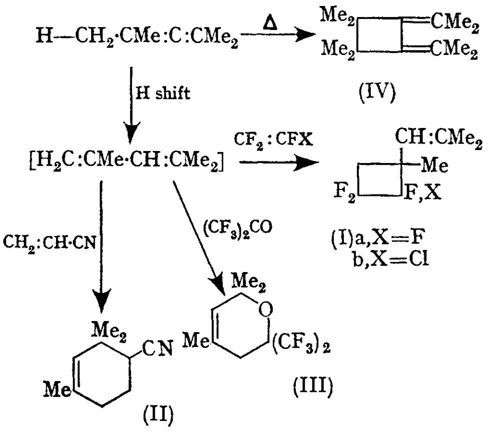
TABLE 2

Thermal dimerisation of tetramethylallene

Pretreatment of reactor	Time (hr.)	Temp. (°c)	% Conversion	Product comp. (%) DMP	(IV)	Mixed dimers
Rinsed with EtOH–KOH,EtOH	72	150	85	—	99	—
None	24	150	100	55	—	45
Rinsed with chromic acid, water	24	150	100	74	—	26

thermally with the 1,3-diene. The conjugated diene is prevented from dimerising by dilution, and is obtained in excellent yield (*e.g.*, 70% from dimethyl sulphoxide, 5 hr., 110°; 90% from acetone, 20 hr., 170°; 100% from acetonitrile, 24 hr., 170°). Whereas this isomerisation goes to completion in a polar environment, preliminary studies show that the flow pyrolysis of tetramethylallene or its precursor, the lactone dimer of dimethylketen,[8] over active charcoal at 250—450° leads to equilibrium mixtures of the allene ($\leqslant 30\%$) and the 1,3-diene ($\geqslant 70\%$).[9]

The thermal co-dimerisations of tetramethylallene with electron deficient olefins and hexafluoroacetone were performed under conditions (base-rinsed glass reactors) which would, in the absence of the olefin or ketone, have led to recovery of the allene or its dimer (IV) without rearrangement. The role of the addends in these cases seems to be to enhance electromerically the polarisation of the allene (for which 12 contributing forms of the type $H^+CH_2{:}CMe{\cdot}\bar{C}{:}CMe_2$ may be written) when it is in close proximity to their electron-deficient π-bonds, thus weakening the C–H bond sufficiently for proton migration to occur. The possibility that they might serve to sensitise the allene to thermal excitation to a diradical appears to be excluded by the failure to detect rearrangement of the allene after irradiation at 2537 Å for 2 days in the presence of mercury, although tetramethylallene quenches the fluorescence emission of mercury vapour.



(*Received, December 28th*, 1967; *Com.* 1383.)

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