CATALYTIC [2 + 2]-CYCLOADDITION OF 3,3-DISUBSTITUTED CYCLOPROPENES

TO NORBORNENE AND NORBORNADIENE*

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A typical feature of the chemistry of cyclopropenes is dimerization by [2 + 2]-cycloaddition to give tricyclo $[3.1.0.0^2, 4]$ hexanes [2], which takes place with particular ease when electron-donor substituents are present in the 3-position of the cyclopropene ring [3, 4]. In contrast, the cross-[2 + 2]-cycloaddition of cyclopropene to other unsaturated compounds has received much less attention. Some of the few such reactions are the photochemical addition of phenylcyclopropenes to derivatives of fumaric and maleic acids [5], of methyl 1,2-diphenylcyclopropene-3-carboxylate to unsaturated compounds carrying electron-donor substituents [6], and intramolecular [2 + 2]-cycloaddition in 3-alkenylcyclopropenes, which takes place effectively both on photolysis [7-9] and thermolysis of the latter [9, 10]. The catalyzed [2 + 2]-cycloaddition of cyclopropenes to unsaturated compounds has not been reported.

We carried out for the first time the cross-[2 + 2]-cycloaddition of cyclopropenes, by reacting 3,3-dimethyl- (Ib) and 3-methyl-3-cyclopropylcyclopropene (Ic) with strained unsaturated hydrocarbons such as norbornene (NB) and norbornadiene (NBD), to give the corresponding bicyclo[2.1.0]pentanes, both thermally and catalytically [1]. Continuing these investigations, we have now examined in detail the catalyzed reaction of 3,3-disubstituted cyclopropenes (Ibd) and of cyclopropene itself (Ia) with NB and NBD in the presence of (PhO)₃P·CuCl or Ph₃P·CuCl. The experiments were carried out at -20°C, by adding 0.3-0.5 mole % of the catalyst to a solution of the cyclopropene and the olefin in dichloromethane (molar ratio 1:4-8:4-8). Under these conditions, reaction of (Ic) with NB in the presence of (PhO)₃P·CuCl gave ~90% of 4methyl-4-cyclopropyl-exo,trans-tetracyclo[5.2.1.0²,⁶.0³,⁵]decane (IIc) as a mixture of two isomers (~1:1) differing in the positions of the methyl and cyclopropyl groups.

Similarly, reaction of (Ic) with NBD gave 90-94% of isomeric (1.25:1) 4-methyl-4-cyclopropyltetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-enes (IVc).

It is noteworthy that both with NB and NBD, cross-[2 + 2]-cycloaddition takes place to a much greater extent than cyclodimerization of the starting material (Ic) to the isomeric 3,6-dimethyl-3,6-dicyclopropyltricyclo-[3.1.0.0²,⁴]hexanes (IIIc). The use of Ph₃P·CuCl as



*For previous communication, see [1].

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1534-1540, July, 1987. Original article submitted February 27, 1986. catalyst in the reaction of (Ic) with NB and NBD under similar conditions also gave good yields (90-95%) of the cycloadducts (IIc) or (IVc).

No separation of the isomeric hydrocarbons obtained was achieved by GC (5% SE-30, SP-2100 or Carbowax 20M on chromatone N-AW-DMCS), but their PMR spectra indicated the presence of two isomers of adducts (IIc) and (IVc), and of three isomers in the case of the dimer (IIIc).

For steric reasons, of the four possible isomers of $tetracyclo[5.2.1.0^2, 6.0^3, 5]$ decanes with substituents at C⁴, only two isomers with the exo, trans- and endo, trans-orientations of the bicyclopentane moiety are capable of existence.



In the PMR spectra of (IIc) and (IVc), the signals for the protons at C² and C⁶ appear as narrow multiplets with coupling constants $J_{1,2} \leq 1.5$ Hz, in accordance with the exo-trans isomer [11]. In order to confirm this conclusion, we reacted NBD with cyclopropene (Ia) in the presence of $(PhO)_3P$ ·CuCl to obtain the unsubstituted tetracyclo[5.2.1.0²,⁶.0³,⁵]dec-8-ene (IVa), which according to GC and its PMR spectrum was a pure compound. Comparison of its PMR spectrum with that of an authentic sample of the endo, trans-isomer of the hydrocarbon (IVa), obtained by the Diels-Alder reaction of bycyclo[2.1.0]pentane with cyclopentadiene [12], in fact showed differences in the chemical shifts of the relevant protons. In full accordance with the exo, trans-orientation of the fused bicyclopentane moiety, the signal for the H^a proton at C¹⁰ was seen at δ 2.2 ppm, due to the combined influences of the cyclobutane and cyclopropane fragments (in the endo, trans-isomer, $\delta = 1.13$ ppm for H^a [12]).

Thus, the [2 + 2]-cycloaddition of cyclopropenes to NB and NBD takes place exclusively at the exo-position, and the double sets of signals in the PMR spectra of (IIc) and (IVc) is due to anti,syn-isomerism of the methyl and cyclopropyl groups. Consideration of the effects of the anisotropy of the cyclopropane and cyclobutane fragments leads to the conclusion that the highfield signals with δ 0.53 ppm in (IIc) and 0.63 ppm in (IVc) most likely correspond to the protons of the methyl group in the anti-position.

The signals in the PMR spectra of the tricyclohexanes (IIIc) indicate the presence of three isomers with the a,a-, e,e-, and a,e-disposition of the methyl groups (in a ratio of ~3.5:1:4, respectively). Assignment of the signals was carried out as for (IIc) and (IVc).

We then examined the behavior of other 3,3-disubstituted cyclopropenes in their catalyzed [2 + 2]-cycloadditions to NBD. For instance, the reaction of (Ib) with NBD in the presence of (PhO)₃P·CuCl under the conditions described above also results in the formation of the corresponding [2 + 2]-cycloadduct, 4,4-dimethyltetracyclo $[5.2.1.0^2, 6.0^3, 5]$ dec-8-ene (IVb) in 60-65% yield, with the concurrent formation of the cyclodimer 3,3,6,6-tetramethyltricyclo- $[3.1.0.0^2, ^4]$ hexane (IIIb) (yield ~10%) together with higher molecular weight oligomeric products. The preferential formation of cyclotrimers and cyclotetramers from (Ib) has been noted previously with Ni(O) and Pd(O) catalysts with phosphorus-containing ligands [13].

The reaction of spiro[2,3]hex-1-ene (Id), which in the pure state cyclodimerizes to a significant extent at temperatures as low as 20°C, also gives a ~65% yield of the cross-[2 + 2]-cycloaddition product tetracyclo[5.2.1.0²,⁶.0³,⁵]dec-8-ene-4-spirocyclobutane (IVd) when reacted with an eightfold excess of NBD at -20°C in the presence of (PhO)₃P·CuCl, the yield of the cyclodimer (IIId) being ~25%.



When a twofold molar excess of NBD over (Id) was used, in addition to (IIId) and (IVd), the crystalline bis-adduct (V), formed by the addition of two molecules of (Id) to both double bonds in NBD, was also obtained.



Hence, the reaction of the cyclopropenes (I) with NB and NBD in the presence of $(PhO)_3P$. CuCl or Ph_3O ·CuCl at -20°C is primarily cross-[2+2]-cycloaddition. However, as we have shown previously [14], in the presence of the same catalyst $(PhO)_3P$ ·CuCl at -20°C, the reaction of (Ic) with a number of other unsaturated hydrocarbons such as cyclopentadiene proceeds exclusively with opening of the cyclopropene ring and the formation of the corresponding vinylcyclopropanes and trienes, which are the formal products of the addition and dimerization of vinylcarbenes. It is also interesting to note the change in the course of the reactions of cyclopropenes in the presence of other catalysts; in the presence of $(PhO)_3P$ ·CuCl in dichloromethane at -20°C the cyclopropene (Ic) is converted exothermically into the triene (VI), whereas in the presence of Ph₃P·CuCl it cyclodimerizes to the tricyclohexane (IIIc).



The different courses followed by the reactions of cyclopropenes are also apparent in the external factors during the course of the reactions. Unlike reactions involving opening of the cyclopropene ring [14], when [2 + 2]-cycloaddition takes place the reaction mixture does not become colored, or a sharp increase in temperature occurs.

It appears that the difference in the reaction pathways of cyclopropenes are controlled by the possibility of their complexing with CuCl, and are dependent on both the structure of the cyclopropene and on the nature of the ligands entering the coordination sphere of the copper ion. In this case, as a result of the differing steric hindrance and electronic factors associated with the ligands, the interaction of the copper d-electrons with the π -electrons of the cyclopropene double bond changes, resulting in both activation of the double bond with the subsequent formation of [2 + 2]-cycloaddition products, and in more extensive reaction resulting in cleavage of the less stable 1,3-bond in the cyclopropenes.

The presence of Ph_3P or $(PhO)_3P$ in the coordination sphere of the copper, in conjunction with NB and NBD, which are more capable of forming complexes with CuCl than any other unsaturated hydrocarbons, modifies the steric and electronic environment of the active site in such a way that the cyclopropene reacts with the CuCl complex at the π -olefin only. The use of CuCl or $(PhO)_3P$ ·CuCl in the absence or presence of weakly complexing olefins results in greater deformation of the electron density in the cyclopropenes, favoring their isomerization.

EXPERIMENTAL

GC analyses were carried out on an LKhM-8MD chromatograph with a flame ionization detector and an I-02 integrator (300×0.3 cm column with 5% SE-30, SP-2100 or Carbowax 20M on chromaton N-AW-DMCS, 0.16-0.20 mm, carrier gas helium, 30 ml/min). PMR spectra were obtained using 5-10% solutions in CDCl₃ on a Bruker WM-250 instrument (250 MHz) relative to TMS as internal standard, and mass spectra on a Varian MAT CH-6, ionizing electron energy 70 eV.

The starting cyclopropenes (I) were obtained by the selective monoreduction of gem-dibromocyclopropanes as described in [15], followed by dehydrobromination of the resulting 2-bromo-1,1-dialkylcyclopropanes as in [16].

 $\frac{4-\text{Methyl}-4-\text{cyclopropyl}-\text{exo,trans-tetracyclo}[5.2.1.0^2, ^6.0^3, ^5]\text{decane (IIc)}.$ To a solution of 0.94 g (10 mmole) of 3-methyl-3-cyclopropylpropene (Ic) and 6 g (63 mmole) of norbornene (NB) in 5 ml of dichloromethane was added, under argon at -20°C, 0.02 g (0.05 mmole) of (PhO)₃P·

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. PMR Spectra of Tetracyclo[5.2.1.0. ^{2,5} .0 ^{3,3}]decane (IIc) and Decenes (IV) (in CDCl ₃ , ö, ppm; J,	Other protons		0.79 t,t and 1.15 m (CH in cyclo- $C_{3}H_{5}$, $J_{cis} = 8.1$, $J_{trans} = 5.5$), 0.41 m, 0.21 m and -0.02 m (CH ₂ CH ₂)	0.90 d.t (anti-H ⁴) and 0.65 d.t (syn-H ⁴), Jgem = 3.9, Jcis = 5.6. Jtrans = 1.3		0.99 t.t and 0.87 t.t (CH in cyclo-C ₃ H ₅ , J _{Ci} s ⁼ 8.3, J _{Irans} ⁼ 5.2), 0.26 m and 0.04 m (CH ₅ CH ₅)	2,15-1,9 m (CH ₂) ₈
	Me	syn	1,21 s		1,18s	1,21s	
		anti	0,53 s		0,95 \$	0,63 s	
	H ¹⁰	uks	2,24 m 2,29 m = 9.6	2,21 br.d .m ≠ 8.6	2,21 m = 8,6 m	2,21 br.d 2,27 br.d m = 8.2	2,19 m m = 8.5
		anti	1,16 m 1,14 m gen	1,27 br. d Jge	1,23 m J Be	1,27 br.d 1,24 br.d	1,23 m /ge
	H ⁸ , H ⁹		1,48 m 1,02 m	5,98 br. t $J = \sim 1,6$	5,99 br. t $J = \sim 1,8$	6,03 br. t 6,05 br. t $J = \sim 1,7$	$J = \sim 1,5$
	$\mathrm{H}^3,~\mathrm{H}^5$		0,97 m 0,83 m	1,31 d.d.d. $J_{cis=5,6}$ $J_{trans=1,3}$ $J_{2,3}=2,0$	1,05 br.d $J = \sim 1,2$	1,03 br.d 1,16 br.d J=~1,8	1,20 br. d. $J=\sim 1,8$
	H ² , H ⁴		1,82 m 1,58 m	1,53 m	1,47 m	1,48 m 1,73 m	1,41 m
	H', H'		2,05m 2,01 m	2,68 m	2,61m	2,63 m 2,67 m	2,63 m
TABLE 1	Com- pound		(11c)	(IVa)	(I V b)	(1Vc)	(IVd)

Hz) ppm: .I. Ś (TTc) and Decenes (TV) (in CDC). ç 0 2,6 03,51dara c 3015 E 4 ΰ aMa E

CuCl. The resulting almost colorless mixture was stirred for 30 min at -20 °C. The excess NB and solvent were then distilled off, and the residue treated with pentane and filtered through silica gel. Fractional distillation gave 1.76 g (94%) of a colorless liquid, bp 73-76 °C (1 mm) containing ~95% (IIc) and ~5% of the cyclodimer (IIIc). For the PMR spectrum of (IIc) see Table 1).

 $\frac{4-\text{Methyl}-4-\text{cyclopropyl}-\text{exo,trans-tetracyclo}[5.2.1.0^{2}, {}^{6}.0^{3}, {}^{5}]\text{dec}-8-\text{ene} (IVc)}{\text{IVc}}.$ We obtained, similarly, from 4.7 g (50 mmole) of the cyclopropene (Ic) and 19 g (0.2 mole) of norbornadiene (NBD), 8.8 g of (IVc), 94% yield, 98% purity, bp 78-79°C (1 mm). Mass spectrum (m/z): 186 (2%) M⁺, 171 (5%) [M - CH₃]⁺, 120 (62%)[M - C₅H₆]⁺, 117 (33%) C₉H₉⁺, 105 (100%) C₈H₉⁺, 91 (85%) C₇H₇⁺.

Similarly, from 0.94 g (10 mmole) of (Ic) and 6.5 g (70 mmole) of NBD in the presence of 0.02 g of Ph_3P ·CuCl there was obtained 1.73 g (93%) of (IVc).

<u>exc,trans-Tetracyclo[5.2.1.0²,⁶.0³,⁵]dec-8-ene (IVc)</u>. The cyclopropene (Ia), obtained as in [17] from 2 g of allyl chloride and 1 g of NaNH₂, was treated with a solution of 0.5 g of NBD and 5 mg of $(PhO)_3P$ ·CuCl in 3 ml of dichloromethane at -30°C while a stream of argon was passed through. After 1 h, the solvent was evaporated, the residue treated with pentane, filtered through a layer of silica gel, and the pentane and NBD distilled off. The residue (0.11 g) was a colorless liquid, which according to GC and its PMR spectrum was practically pure (IVa), yield ~50% on the cyclopropene formed.

 $\frac{4,4-\text{Dimethyl-exo,trans-tetracyclo}[5.2.1.0^{2,6}.0^{3,5}]\text{dec-8-ene (IVb)}.$ To a solution of 0.81 g (12 mmole) of dimethylcyclopropene (Ib) and 6.5 g (70 mmole) of NBD in 5 ml of dichloromethane was added at -20°C 0.2 g of (PhO)₃P·CuCl, and the mixture stirred for 1 h. The solvent and excess NBD were then distilled off, and the residue treated with 10 ml of pentane and filtered through silica gel. Fractionation gave 1.24 g (65%) of (IVb), bp 92-93°C (20 mm), purity 98.5%, $n_D^{2^0}$ 1.4977, and 0.08 g (~10%) of 3,3,6,6-tetramethyltricyclo[3.1.0^{2,4}]hexane (IIIb), the PMR spectrum of which was identical to that given in [18]. Mass spectrum of (IVb) (m/z): 160 (2%) M⁺, 145 (20%) [M - CH₃]⁺, 117 (50%) [M - C₃H₇]⁺, 105 (40%) [M - C₄H₇]⁺, 94 (100%) [M - C₅H₆]⁺. For the PMR spectrum of (IV), see Table 1.

<u>exo,trans-Tetracyclo[5.2.1.0²,⁶.0³,⁵]dec-8-ene-4-spirocyclobutane (IVd)</u>. To a solution of 4.8 g (60 mmole) of spiro[2,3]hex-1-ene (Id), and 17 g (0.18 mole) of NBD in 10 ml of dichloromethane at -20°C was added 0.15 g of (PhO)₃P·CuCl, and the mixture stirred for 40 min. After working up in the usual way by vacuum distillation, there was obtained 1 g (23%) of cyclobutane-spiro-3-tricyclo[3.1.0.0²,⁴]hexane-6-spirocyclobutane (IIId), bp 80-83°C (7 mm), PMR spectrum: 1.25 s (4H, CH), 1.9-2.05 m (12H, CH₂), and 6.9 g (67%) of (IVd), purity 98%, bp 62-63°C (1 mm), np²⁰ 1.5213. For PMR spectrum, see Table 1. Mass spectrum (m/z): 172 (2%) M⁴, 143 (10%) [M - C₂H₅]⁺, 129 (15%) [M - C₃H₇]⁺, 106 (100%) [M - C₅H₆]⁺, 91 (80%) C₇H₇⁺.

Preparative GLC (silica gel, eluent hexane-ether, 7:1) of the still residue gave ~0.3 g (4%) of cyclobutanespiro-4-hexacyclo[5.5.1.0^{2,6}.0^{3,5}.0^{6,12}.0^{9,11}]tridecane-10-spirocyclobutane (V) as colorless crystals, mp 114-115°C (from acetone). PMR spectrum: 2.24 t (2H, H¹³, J = 1.1 Hz), 2.0 m (12H, cyclobutane CH₂), 1.40 br. s (4H, H², H⁶, H⁸, H¹²), 1.26 br. s (2H, H¹, H⁷), 1.05 br. s (4H, H³, H⁵, H⁹, H¹¹).

<u>3,6-Dimethyl-3,6-dicyclopropyltricyclo[3.1.0.0²,⁴]hexane (IIIc)</u>. To a solution of 0.94 g (10 mmole) of 3-methyl-3-cyclopropylcyclopropene (Ic) in 8 ml of dichloromethane at -20°C was added 0.018 g (0.05 mmole) of Ph₃P·CuCl, and the mixture was stirred for 1 h. After the usual workup, fractionation gave 0.87 g (92%) of (IIIc) as a mixture of three isomers (according to the PMR spectrum) in proportions e,e:a,a:a,e \approx 3.5:1:4, bp 93-95°C (7 mm), np²⁰ 1.5087. PMR spectrum: 1.37 s (CH of polycycle in the a,a-isomer), 1.27 m and 1.16 m (CH of polycycle in a,e-isomer), 1.25 s (a-CH₃ in the a,e-isomer), 1.23 s (a-CH₃ in the e,e-isomer), 1.2 m (cyclo-C₃C₅ CH), 1.07 s (CH of polycycle in e,e-isomer), 0.76 t.t (cyclo-C₃H₅ CH in the a,e-isomer, J_{cis} = 8.2 Hz, J_{trans} = 5.4 Hz), 0.72 t.t (cyclo-C₃H₅ CH in the e,e-isomer), 0.57 s (e-CH₃ in the a,e-isomer), 0.41 m, 0.25 m and 0.07 m (cyclo-C₃H₅ CH₂). Mass spectrum (m/z): 188 (2%) M⁺, 172 (10%) [M - CH₃]⁺, 159 (12%) [M - C₂H₅]⁺, 145 (20%) [M - C₃H₇]⁺, 131 (24%) [M - C₄H₉]⁺, 105 (65%) C₈H₉⁺, 91 (100%) C₇H₇⁺.

CONCLUSIONS

3,3-Dialkyl(cycloalkyl)cyclopropenes react with norbornene and norbornadiene at -20° C in the presence of complexes of CuCl with (PhO)₃P or Ph₃P exclusively by [2 + 2]-cycloaddition, giving the corresponding exo,trans-tetracyclo $[5.2.1.0^2, 6.0^3, 5]$ decanes (or decenes) in yields of 60-94%, the tricyclohexane cyclodimers being obtained in yields of 5-25%.

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CONTROL OF DIASTEREOSELECTIVITY IN THE CYCLIZATION OF DIPROPENYL KETONE TO 2,6-DIMETHYL-1-HETEROCYCLO-HEXAN-4-ONE

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On cyclization of symmetrical dienones of type (I), two isomeric cyclic products can be formed, namely meso-ee-(III) and ea-(III) racemate. In the meso-form, the asymmetric centers at C^2 and C^6 possess opposite symmetry, but in the racemate they have the same configuration (for each of the ea-(III) antipodes).

We have now examined the dependence of the cyclization $(I) \rightarrow (III)$ and the diastereoisomeric composition of (III) on the reaction conditions.



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