

Further Evidence for the Vinyl Cyclopropylidene–Cyclopentenylidene Rearrangement

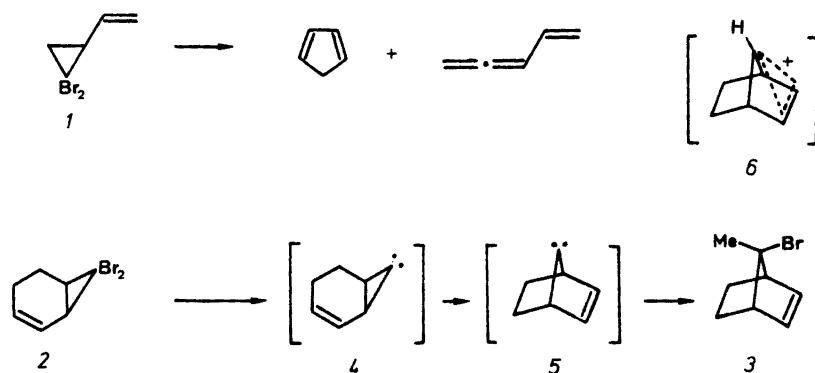
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Reactions of two intermediate vinylcyclopropylidenes, generated from the corresponding nitrosoareas by two different routes, have been studied. For one of them, a carbene–carbene rearrangement was the main reaction mode while for the other, ring opening to the allene occurred exclusively. On the other hand, dienyl ethers were the only products from ring-opening of the corresponding cyclopropane diazonium ions formed in methanol under acid conditions. The results of the former reactions relate well to those obtained from treatment of the corresponding *gem*-dibromocyclopropanes with methyllithium.

The intermediates formed from α -bromocyclopropyllithium derivatives by loss of lithium bromide exhibit reactive properties characteristic of singlet cyclopropylidenes.¹ It is also recognized that this class of carbene intermediates may well be coordinated with lithium bromide and solvated as well. Moreover, reactions of cyclopropylidenes are strongly dependent on the nature of the substituents bonded to the three-membered ring. If one of the substituents is a vinyl group, a unique rearrangement may take place.² Evidence based on reaction products,² isotope labelling³ and substituent effects⁴ as well as calculations,⁵ suggests that the vinylcyclopropylidene rearranges to a 3-cyclopentenylidene; both carbene intermediates may then give rise to the observed products. This carbene-carbene rearrangement is exemplified by the reaction of 1,1-dibromo-2-vinylcyclopropane (*1*) with methyllithium which affords a mixture of cyclopentadiene and vinylallene in a ratio of about 8:1 at -78°C (Scheme 1). In a bicyclic system, a similar rearrangement is apparent by the conversion of 7,7-dibromobicyclo[4.1.0]hept-2-ene (*2*) to the norbornene derivative *3* (Scheme 1).^{2,7} There is at present a considerable number of examples in the literature substantiating the rearrangement.^{6,8} However, it is important to seek additional evidence for the mechanisms, particularly since it has been suggested that only ionic intermediates and not carbenes are involved in the rearrangement.⁹

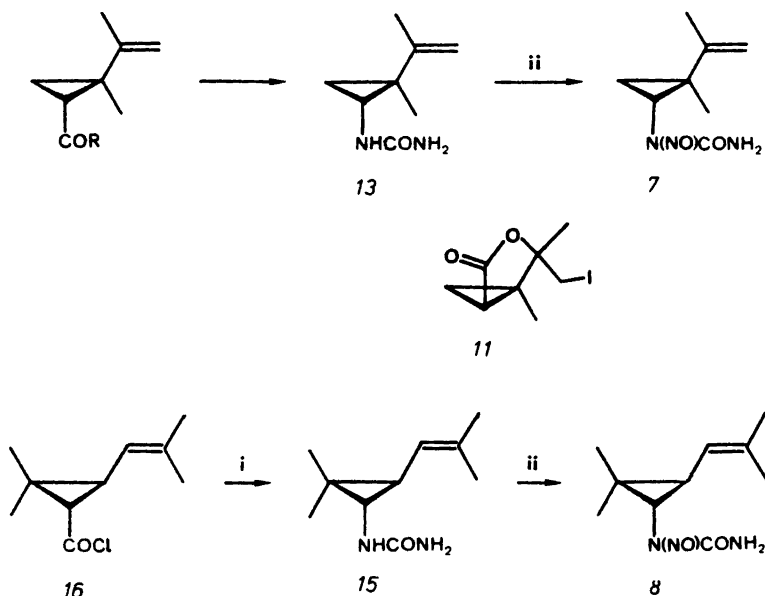
One approach to further understanding involves the generation of the cyclopropylidene by an entirely different method, and comparing the reaction products with those obtained previously. This has been done by generating the carbene, 7-norcar-2-enylidene (*4*), from the corresponding nitrosoarea and base.¹⁰ The studies confirm the rearrangement of *4* to 7-norbornenylidene *5*, although the products formed from *5* were different from those observed from the *gem*-dibromocyclopropane *2* and methyllithium due to the change in reaction conditions; protonation of the comparatively nucleophilic carbene *5* by methanol explains why the products were identical to those previously observed from the carbocation



Scheme 1.

6 in a similar environment. However, reactions of the nitrosoarene under acid conditions, favouring formation of the diazonium ion and the cyclopropyl cation did not lead to norbornenyl derivatives, *e.g.* the rearrangement did not occur. Recently, Warner and Chu have provided evidence for the carbene-carbene rearrangement of 8-bicyclo[5.1.0]oct-2-enylidene.^{11,12}

Hence, we decided to undertake a similar study with monocyclic diazocyclopropane derivatives. This paper describes the decomposition of two such diazo compounds under conditions promoting either formation of the cyclopropylidene or the corresponding cation; the latter was also generated by a silver ion assisted solvolysis of a bromocyclopropane derivative. The results* are compatible with the occurrence of the vinylcyclopropylidene



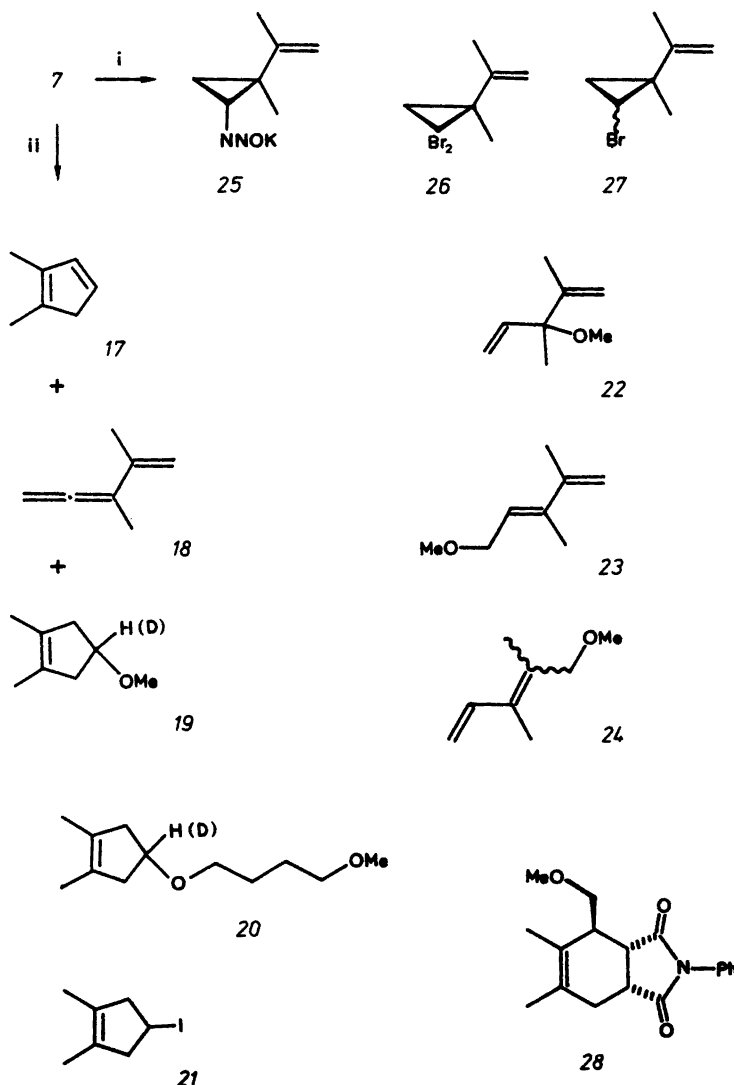
Scheme 2. 9, R=OEt; 10, R=OH; 12, R=N₃; 14, R=Cl.

i, (1) NaN₃/H₂O-acetone, (2) Δ/benzene, (3) NH₃; ii, N₂O₄/Et₂O.

* Reported in part at the EUCHEM Conference on Electron Deficient Intermediates, Geneva, Switzerland, October 9-12, 1978.

3-cyclopentenylidene rearrangement. After this work was completed Kirmse and co-workers¹³ came to the same conclusion based on a similar study.

The *N*-nitrosourea derivatives 7 and 8 were chosen as starting materials for the corresponding diazo compounds. The cupric sulfate catalyzed addition of ethyl diazoacetate to 2,3-dimethyl-1,3-butadiene furnished a 1.2:1 mixture of the *cis* and *trans* cyclopropane esters 9, respectively, in 74 % yield¹⁴ (Scheme 2). Neither the esters nor the acids 10, obtained by hydrolysis, could be separated on a practical scale by fractional distillation or column chromatography. However, treatment of the isomeric carboxylate anions with a solution of iodine in potassium iodide¹⁵ converted all of the *cis* isomer to the crystalline iodolactone 11, and *trans*-10 was obtained pure as a liquid in 55 % yield after acidification.



Scheme 3. i, *t*-BuOK/THF; ii, MeOLi · MeOH/pentane.

Table 1. Demination of the nitrosoarea 7 and the diatzoate 25.

Starting materials	Reaction conditions			Products and relative distribution / %							
	Reagents	Solvents	Temperature °C	Cyclopentadiene 17	Allene 18	Cyclopentene 19	20	21	22	23	24
15	MeOLi·MeOH	Pentane	0	51	4	44	-	-	-	-	-
25	MeOH	THF	-110-20	5	2	65	28	-	-	-	-
25	MeOD	THF	-110-20	8	2	52 ^a	38 ^a	-	-	-	-
25	MeOH, LiI	THF	-78	25	-	15	-	60	-	-	-
26	MeLi	Et ₂ O	-78	99 ²	1 ²	-	-	-	-	-	-
26	MeLi	Et ₂ O	0	97	3	-	-	-	-	-	-
25	MeOH ₂ ⁺	THF	-110-0	-	-	-	-	-	69	21	10 ^b
25	MeOD ₂ ⁺	THF	-110-0	-	-	-	-	-	75	14	10 ^b
27	Ag ⁺ , 2, 6-lutidine	MeOH	20	-	-	-	-	-	58	24	18 ^c

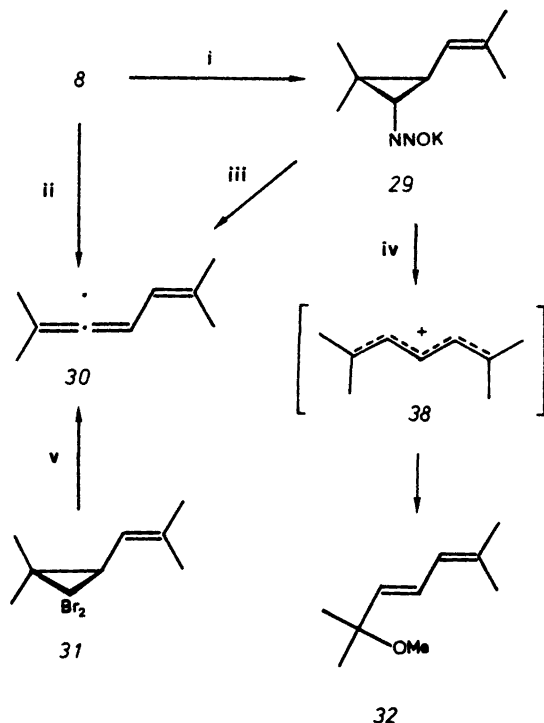
^a 100 % D-incorporation, ^b isomer ratio 4:1, ^c isomer ratio 1:1.

The corresponding acid was transformed *via* the azide 12 and isocyanate into the crystalline urea 13 in 76 % overall yield. This urea derivative was also prepared from the acid chloride 14 in 73 % overall yield. The last method was used to prepare the urea 15¹⁶ from the corresponding acid chloride 16¹⁷ in 80 % overall yield (Scheme 2).

The nitrosation of the ureas 13 and 15 was best performed with dinitrogen tetroxide in ether. In this way the *N*-nitrosoureas 7 and 8 were obtained in 50 and 62 % yields, respectively. The spectroscopic properties of the nitroso compounds were in complete agreement with the assigned structures.

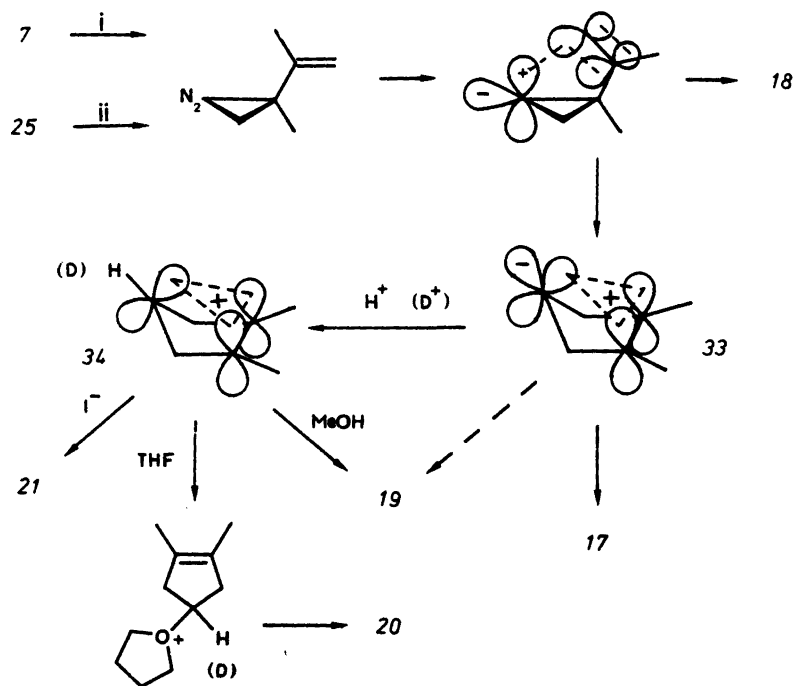
We chose to generate the carbenes in two ways: (a) treatment of pentane solutions of the nitrosoureas with lithium methoxide, containing an equimolar amount of methanol, and (b) reaction of preformed tetrahydrofuran (THF) solutions of the potassium diazotates with methanol. The diazotates were formed when the pertinent nitrosourea was treated with potassium *t*-butoxide in THF¹⁸ (Scheme 3,4). The reaction products were analyzed immediately after completion in order to diminish errors caused by formation of secondary products. The components of the product mixtures were separated by preparative GLC or column chromatography and identified by spectroscopic properties and comparison with authentic samples.

Reaction of the nitrosourea 7 according to method (a) produced a mixture of 1,2-dimethyl-1,3-cyclopentadiene (17),¹⁹ 3,4-dimethyl-1,2,4-pentatriene (18)² and 4-methoxy-1,2-dimethyl-1-cyclopentene (19) as shown in Table 1 and Scheme 3. The cyclopentadiene was converted to the Diels-Alder adduct with *N*-phenylmaleimide. An



Scheme 4. i, *t*-BuOK/THF; ii, MeOLi·MeOH/pentane; iii, MeOH; iv, MeOH₂⁺; v, MeLi/Et₂O.

authentic sample of the ether **19** was prepared from **17** by hydroboration-oxidation to 3,4-dimethyl-3-cyclopenten-1-ol followed by methylation with diazomethane. A THF solution of the diazotate **25** was cooled to $-110\text{ }^{\circ}\text{C}$ and methanol, precooled to the same temperature, added all at once. The reaction mixture turned yellow immediately, indicating the presence of the diazo compound, and gas evolution started first at about $-20\text{ }^{\circ}\text{C}$. The product consisted of four compounds; small amounts of **17** and **18** were present as shown by GLC but the two major components were separated by flash chromatography and identified spectroscopically as the ethers **19** and 4-(4-methoxy-1-butoxy)-1,2-dimethyl-1-cyclopentene (**20**). When the reaction was carried out with deuterated methanol, deuterium was incorporated selectively at C-4 in both ethers as shown by the absence of proton resonances at δ 3.75 and 4.06, respectively, in the NMR spectra; the ratio between the ethers was lower than that obtained using undeuterated reagent. In the presence of methanolic lithium iodide the diazotate **25** reacted to yield the cyclopentadiene **17**, the ether **19** and as the major product 4-iodo-1,2-dimethyl-1-cyclopentene (**21**); the allene **18** and the ether **20** were not detected. On the other hand, when a THF solution of the diazotate was subjected to methanolic sulfuric acid at $-110\text{ }^{\circ}\text{C}$, a brisk gas evolution ensued and the product consisted of the ethers **22**–**24** in the relative proportions given in Table 1. A similar mixture was obtained by silver ion assisted solvolysis of a stereoisomeric mixture of 1-bromo-2-isopropenyl-2-methylcyclopropane (**27**)²⁰ in methanol, a reaction which required several days at room temperature for completion. The isomeric ethers were difficult to separate by preparative GLC. However, treatment of the mixture with *N*-phenylmaleimide afforded the adduct **28** derived from the ether **23**. From the mother liquid the tertiary ether **22** was separated by preparative GLC, while the ether **24** was obtained as a mixture of



Scheme 5. *i*, MeOLi·MeOH/pentane; *ii*, MeOH.

Table 2. Demination of nitrosoarea 8 and diazotate 29.

Starting material	Reaction conditions			Products and relative distribution / %	
	Reagents	Solvents	Temperature °C	Allene 30	Heptadienyl ether 32
28	MeOLi·MeOH	Pentane	0	100	—
29	MeOH	THF	−100 −20	100	—
30	MeLi	Et ₂ O	−20	100 ⁴	—
29	MeOH ₂ ⁺	THF	−100−0	—	100

stereoisomers. Although the ¹H NMR spectrum of the mixture at 200 MHz exhibited distinct bands for each of the isomers, we were not able to assign unambiguously the stereochemistry. This was a problem in the case of 23 as well, but the ready formation of the adduct 28 strongly suggests the *E* configuration. When the reaction was carried out using deuteriosulfuric acid in deuterated methanol, no deuterium was incorporated in the products according to the ¹H NMR spectra.

Treatment of a pentane solution of the nitrosoarea 8 with lithium methoxide as described for the analogue 7 gave 2,6-dimethyl-2,3,5-heptatriene 30²¹ as sole product, which was also the result when a THF solution of the diazotate 29 was subjected to methanol at −20 °C. In the presence of sulfuric acid, however, the allene was not present in the reaction mixture which consisted essentially of (*E*)-6-methoxy-2,6-dimethyl-2,4-heptadiene (32) and five minor unidentified compounds; the coupling constant of 14.8 Hz due to the vicinal olefinic protons are in accordance with the *E* configuration. The results are summarized in Table 2 and Scheme 4.

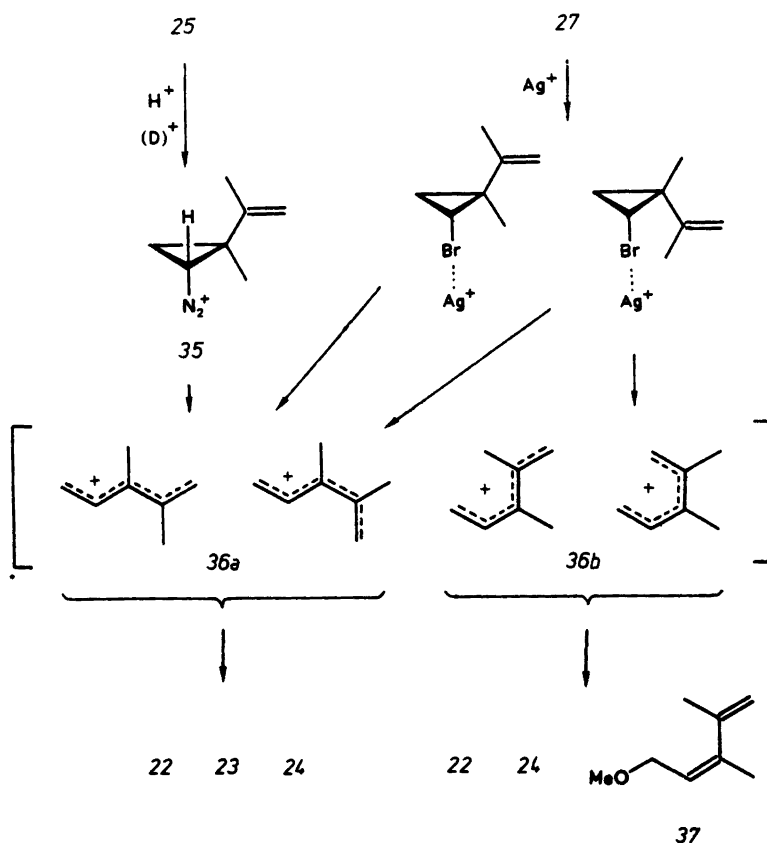
All the available evidence shows that *N*-nitrosoareas and the corresponding diazotates react under basic conditions to diazo compounds and subsequently carbenes;^{1,18} furthermore, it is equally well established that under acid conditions cationic intermediates are involved and not carbenes.^{18,22} Hence, the allenes 18 and 30 and the cyclopentadiene 17 must result from initially formed cyclopropylidenes while the ethers 22–24, and 32 derive from carbocations. It remains to explain the origin of the cyclic ethers 19 and 20.

The cyclopentadiene 17, the product of the proposed vinylcyclopropylidene rearrangement, is formed almost exclusively from 1,1-dibromo-2-isopropenyl-2-methylcyclopropane (26) and methyllithium; even at 0 °C the ratio to the allene 18 is 97:3, which is considerably higher than that observed from reactions of 7 and 25 (Table 1). At first sight a serious discrepancy between the results from the two cyclopropylidene generating reactions seems apparent; however, if the cyclic ethers were to arise from the rearranged carbene, *e.g.* 3,4-dimethyl-3-cyclopentenylidene (33), excellent correspondance between the two modes would actually exist. Calculations⁵ indicate that the empty *p*-orbital of the carbene 33 (Scheme 5) interacts significantly with the π -electrons of the double bond resulting in a delocalized positive charge which renders the carbene comparatively nucleophilic. This promotes protonation to the carbocation 34 and probably suppresses the normally very facile C–H insertion to the cyclopentadiene; thus, the cyclic ethers 19 and 20 derive from reactions of 34, and hence 33, with the solvents. The observed selective deuterium incorporation, fully supports this mechanism which strongly resembles that proposed for reactions of the related 7-norbornenylidene.^{4,10} The formation of 20 was surprising. There is

precedent in the literature for ring opening of THF caused by carbocations,²³ but our results do not exclude a mechanism involving initial ylide formation between the carbene and the oxygen atom. Delocalization of the positive charge in both carbene and carbocation demands bent structures for these species, and evidence for a bent structure of the unsubstituted carbocation has recently been provided by Kirmse and co-workers¹³ in elegant experiments.

We have recently reported on a pronounced effect of methyl substituents on the vinylcyclopropylidene 3-cyclopentenyldiene rearrangement⁴ based on reactions of differently substituted vinyl-1,1-dibromocyclopropanes with methyllithium. In view of these results the exclusive formation of the allene **30** from the nitrosoarene **8** and the diazotate **29** was actually expected.

Protonation of **25** leads to the diazonium ion *trans*-**35** (Scheme 6). Concerted ring opening affords the pentadienyl cations **36a** which react with methanol to the observed ethers **22**, **23** and **24**. The same ethers should result from concerted ring opening of the bromide *trans*-**27** which is in accordance with observation. On the other hand, concerted ring opening of the *cis*-**27** should preferably give rise to the cations **36b** which with methanol should afford the ethers **22**, **24** and **37**. The latter is not part of the product mixture, suggesting that the cations **36b** are not formed. The fact that both isomers of **27** were



Scheme 6.

consumed at similar rates indicates that *cis*-27 undergoes solvolytic ring opening to 36a, an unfavourable mode which nevertheless has precedence.²⁴ There is no evidence for any significant isomerization of either the bromides 27 or the ether 23 under the reaction conditions.²⁵

In conclusion the present study provides clear evidence for the occurrence of the rearrangement of vinylcyclopropylidene to 3-cyclopentenylidene in monocyclic systems and furthermore, strongly suggests that the same rearrangement is operating in reactions of *gem*-dibromocyclopropanes with methyllithium.

EXPERIMENTAL

The NMR shift data are given in δ values and were recorded on Varian 360 A or Bruker CXP 200 instruments. The mass spectra were obtained on a MM 7070 GLC/MS instrument.

trans-2-Isopropenyl-2-methyl-1-cyclopropanecarboxylic acid (10). The ester 9¹⁴ was hydrolyzed with KOH/70 % EtOH, furnishing in 87 % yield the corresponding mixture of stereoisomeric acids 10, b.p. 69.5–70 °C/0.4 mmHg (lit.¹⁴ 122–123 °C/15 mmHg). To a stirred solution of the acid mixture (22.84 g, 0.163 mol) in 50 ml of 1.6 M Na₂CO₃ and 50 ml of saturated NaHCO₃ at 0 °C was added 150 ml of a 0.7 M solution of iodine (1.05 mol) in 2.5 M KI over a 3 h period.¹⁵ After an additional 30 min, the solution was filtered, and the filtrate extracted twice with CHCl₃. Work-up of the acidic fraction in the usual way afforded 12.67 g (55 %) of *trans*-10 as a liquid.

IR (film): 3000 (m), 1700 (s), 890 (m) cm⁻¹. ¹H NMR (CCl₄): 1.21 (1 H, d, *J* 8.2 Hz), 1.32 (1 H, d, *J* 6.5 Hz), 1.55 (3 H, s), 1.72 (1 H, dd partly hidden, *J* 6.5, 8.0 Hz), 1.80 (3 H, d, *J* 1.0 Hz), 4.77 (1 H, m), 4.83 (1 H, s), 12.25 (1 H, s). The acid was used in the next step without further purification. In addition 18.01 g (42 %) of 4-iodomethyl-4,5-dimethyl-3-oxabicyclo[3.1.0]-hexan-2-one (11) was obtained as a cream-coloured solid, m.p. 84–85 °C (hexane). IR (KBr) 1760 (s), 490 (m) cm⁻¹. ¹H NMR (CCl₄): 1.11 (1 H, d, *J* 7.3 Hz), 1.14 (1 H, d, *J* 4.5 Hz), 1.43 (3 H, s), 1.63 (3 H, s), 1.89 (1 H, dd, *J* 4.5, 7.5 Hz), 3.31 (2H, s).

trans-2-Isopropenyl-2-methyl-1-cyclopropanecarbonyl chloride (14). Thionyl chloride (1.44 ml, 20 mmol) was added over a 10 min period to a stirred solution of 2.10 g (15 mmol) of *trans*-10 and 2.78 ml (20 mmol) of triethylamine in 15 ml of CHCl₃ kept at 0 °C. After 21 h at the same temperature, volatile material was removed at reduced pressure on a rotary evaporator and 30 ml dry pentane was added. The mixture was filtered and the precipitated salt washed with additional pentane. Evaporation of the solvent and distillation afforded 1.10 g (46 %) of the pure acid chloride, b.p. 56 °C/8 mmHg. IR (film): 3090 (m), 3000 (s), 1790 (s), 910 (s) cm⁻¹. ¹H NMR (CCl₄): 1.34 (3 H, s), 1.39 (1 H, d, *J* 8.0 Hz), 1.40 (1 H, d, *J* 7.0 Hz), 1.83 (H, d, *J* 1.0 Hz), 2.24 (1 H, dd, *J* 7.0, 8.0 Hz), 4.74–4.92 (2H, m).

N-(*trans*-2-Isopropenyl-2-methyl-1-cyclopropylurea) (13). The procedure is essentially that of Weinstock.²⁶ To a stirred solution of (*E*)-10 (12.62 g, 90 mmol) in 80 ml of acetone at 0 °C was added successively 14.0 ml (0.1 mol) of triethylamine in 120 ml of acetone, 11.5 ml (0.12 mol) of freshly distilled ethyl chloroformate in 40 ml of acetone, and a solution of 11.7 g (0.18 mol) sodium azide in 40 ml of water. After 5 h, the reaction mixture was poured into 400 ml of ice-water and the azide extracted with a total of 1000 ml toluene and dried (MgSO₄). The azide solution was added to a flask kept at 100 °C during 90 min. After an additional 1 h at this temperature, the solution of the isocyanate was cooled to 0 °C. A vigorous stream of dry ammonia was bubbled through the stirred solution for 2 h, until no absorption at 2250 cm⁻¹, due to the isocyanate, was visible in the IR. Evaporation and recrystallization of the residue from hexane/ethyl acetate 1:1 gave 10.55 g (76 %) of the urea 13, m.p. 86–87 °C. IR (KBr): 3500 (m), 1670 (s), 1610 (s), 900 (m) cm⁻¹. ¹H NMR (CCl₄): δ 0.53 (1 H, dd, *J* 2.8, 4.8 Hz), 1.09 (1 H, dd, *J* 2.8, 7.8 Hz), 1.22 (3 H, s), 1.73 (3 H, s), 2.37–2.65 (1 H, m), 4.65–4.85 (2 H, m), 5.33 (2 H, broad s), 5.88 (1 H, broad s).

The azide 12 was also prepared from the acid chloride 14, which was subsequently converted to the urea 13 in 73 % yield as previously described for similar compounds.²⁷

*Preparation of nitrosoureas 7 and 8. General procedure.*²⁸ A solution of 4.13 g (45 mmol) N₂O₄ in 200 ml of dry ether was added to a stirred mixture of 40 mmol urea, 13.12 g (160

mmol) finely powdered anhydrous sodium acetate, and 300 ml of ether at -25°C (bath) within 1 h. After an additional 30 min, the mixture was allowed to reach 0°C and filtered. The filtered solid was washed with a total of 100 ml of ether. The combined ether solution was washed successively with 1 M phosphate buffer pH 6 and brine, and dried (MgSO_4) for 2 h at 0°C . The crude nitrosoarea was recrystallized from ether-pentane 1:2 and used without further purifications in the deamination reactions.

N-(trans-2-Isopropenyl-2-methyl-1-cyclopropyl-*N*-nitrosoarea (7), was obtained in 50 % yield, m.p. 95°C (decomp.). IR (KBr): 3400 (m), 1700 (s), 1510 (s), 1000 (s), 900 (m) cm^{-1} . ^1H NMR (CCl_4): 0.89 (3 H, s), 1.02 (1 H, dd, J 5.1, 5.8 Hz), 1.50 (1 H, dd, J 5.8, 8.2 Hz), 1.89 (3 H, d, J 0.7 Hz), 2.38 (1H, dd, J 5.1, 8.2 Hz), 4.85 (1 H, m) 4.92, (1 H, s) 5.49 (1 H, br.s) 6.86 (1 H, br.s.).

N-trans-3,3-Dimethyl-2-(2-methyl-1-propenyl)-cyclopropyl-*N*-nitrosoarea (8), was obtained in 62 % yield, m.p. $97-98^{\circ}\text{C}$ (decomp.). IR (KBr): 3450 (m), 1700 (s), 1510 (s), 1030 (m) cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz): 0.90 (3 H, s), 1.02 (1 H, dd, J 5.1, 5.8 Hz), 1.50 (1 H, dd, J 5.8, 8.2 Hz), 1.89 (3 H, d, J 0.7 Hz), 2.38 (1 H, dd, J 5.1, 8.2 Hz), 4.85 (1 H, sharp m), 4.92 (1 H, s), 5.49 (1 H, broad s), 6.86 (1 H, broad s).

Deamination of nitrosoarea 7 with lithium methoxide. $\text{MeOLi} \cdot \text{MeOH}$ (0.231 g, 3.3 mmol, prepared as described for the ethyl homologue²⁷) was added in one portion to a vigorously stirred suspension of 3.0 mmol nitrosoarea 7 in 15 ml of pentane at 0°C . A brisk evolution of nitrogen took place for about 5 min. After 1 h, the mixture was filtered through a small amount of celite and the filtrate analyzed by GLC. (10 % SE-30, 10 % PEG-4000, and 5 % SP-2100). A solution of 0.52 g (3.0 mmol) *N*-phenylmaleimide in 20 ml of ether was added to the filtrate. After 16 h at ambient temperature, the solvents were distilled through an efficient column, and the residue purified by column chromatography (SiO_2 /pentane, CH_2Cl_2 /pentane 1:1, and CH_2Cl_2) giving 125 mg (33 %) of 4-methoxy-1,2-dimethyl-1-cyclopentene (19), and 237 mg (30 %) of the Diels-Alder adduct² of 1,2-dimethyl-1,3-cyclopentadiene (17). A third component was identified as 3,4-dimethyl-1,2,4-pentatriene (18) by comparing GLC retention times with those of an authentic sample.² A small amount (~1 %) of unidentified products was also present.

An ethereal solution of 3,4-dimethyl-3-cyclopenten-1-ol²⁹ reacted with diazomethane in the presence of cat. amounts of AlCl_3 ³⁰ to give crude 19 in practically quantitative yield. A pure sample was obtained by prep. GLC (10 % OV-17, 120°C). IR (film): 1080 (s) cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz), 1.61 (6 H, broad s), 2.30 (2 H, broad d, J 16.0 Hz), 2.53 (2 H, broad dd, J 6.7, 16.0 Hz), 3.30 (3 H, s), 3.69-3.81 (1 H, m). MS: 126 (M^+ , 58), 111 (63), 94 (100), 79 (69).

Deaminations of potassium trans-2-isopropenyl-2-methyl-1-cyclopropanediazotate (25). A. *With methanol.* A solution of nitrosoarea 7 (257 mg, 1.4 mmol) in 4.0 ml dry THF was added to a stirred solution of 474 mg (4.2 mmol) *t*-BuOK in 9.0 ml THF at -50°C (bath) during 10 min. The reaction mixture was kept at this temperature for 2 h before use. The solution of the diazotate 25 was cooled to -110°C (methanol/ N_2 liq.). Methanol (11.4 ml, 280 mmol), cooled to just above the freezing point, was added all at once. The mixture, which changed its colour immediately from slightly turbid brown to clear light yellow, was allowed to reach room temperature over a 6 h period. Gas evolution started at about -20°C (bath). A phosphate buffer solution, pH 7, (100 ml of a 0.25 M) was added, and the aqueous layer extracted with ether. The extract was analyzed by GLC. The solvents were distilled under reduced pressure through an efficient column. The residue, 225 mg of a brown oil, consisted of 19 and 4-(4-methoxy-1-butoxy)-1,2-dimethyl-1-cyclopentene (20) in the ratio 2.3:1, besides small amounts of 17, 18, and several unidentified components ranging from 0.1-5 % as determined by GLC. The major products were separated by flash chromatography (SiO_2). Pure 20 was eluted with 3 % ether/ CH_2Cl_2 . IR (film): 2850 (s), 1110 (s) cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz): 1.56-1.67 (10 H, m), 2.30 (2 H, broad d, J 16.0 Hz), 2.53 (2 H, broad dd, J 6.8, 16.0 Hz), 3.33 (3 H, s), 3.36-3.45 (4 H, m), 4.06 (1 H, m).

The reaction was repeated with CH_3OD on a 2 mmol scale, giving 252 mg of crude product, consisting mainly of 4-methoxy-1,2-dimethyl[4- $^2\text{H}_1$]-1-cyclopentene and 4-(4-methoxy-1-butoxy)-1,2-dimethyl[4- $^2\text{H}_1$]-1-cyclopentene in a ratio 1.4:1. The ethers were isolated as above. In the ^1H NMR spectra the absorptions at δ 3.75 and 4.06 respectively were absent as compared to those of the undeuterated ones. In both cases, the dd at 2.53 had collapsed to a d (J 16.0 Hz).

B. *With methanol in the presence of lithium iodide.* To a stirred solution of the diazotate 25 (0.75 mmol) in 7 ml of THF, kept at -78°C , was added a saturated solution of 6.69 g (50 mmol) of lithium iodide in 2.60 g (81 mmol) of methanol. The mixture solidified immediately, and was allowed to reach 0°C during 2.5 h. Water (50 ml) was added, the aqueous layer extracted with pentane and the organic layer analyzed by GLC (PEG-4000, 80°C). Work-up afforded 91 mg of a dark brown oil consisting mainly ($>90\%$) of 17, 19 and 4-iodo-1,2-dimethyl-1-cyclopentene (21) in the ratio 1.7:1:4. A pure sample of 21 was obtained by preparative GLC (PEG-4000, 80°C). IR (film): 1420 (s), 1180 (s), 880 (m), 740 (m) cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 200 MHz): 1.64 (6 H, s), 2.70–3.03 (4 H, m), 4.45 (1 H, m). MS: 221 (2), 111 (54), 95 (36), 43 (100), 51 (52). The compound decomposed on standing.

C. *With methanolic sulphuric acid.* To 3.0 mmol of the diazotate solution, kept at -110°C (bath), was added in one portion a solution of 1.60 ml (30 mmol) of conc. sulphuric acid in 20 ml (0.5 mol) of methanol (cooled to just above the freezing point). In this case the mixture spontaneously turned very viscous accompanied by a brisk evolution of nitrogen. The reaction mixture was allowed to reach room temperature during 4 h. Work-up as described under A gave 359 mg (95 %) of a mixture of the isomeric ethers 3-methoxy-2,3-dimethyl-1,4-pentadiene (22), (*E*)-5-methoxy-2,3-dimethyl-1,3-pentadiene (23), and (*E*) and (*Z*)-5-methoxy-3,4-dimethyl-1,3-pentadiene (24), in the ratio 6.9:2.1:1 as determined by $^1\text{H NMR}$ and GLC. Capillary GLC (12 m Cross-linked methyl silicone, 80 – 200°C) and $^1\text{H NMR}$ showed that 24 consisted of a 4:1 mixture of stereoisomers. The tertiary ether 22 was separated from the primary ethers 23 and 24 by prep. GLC (10 % PEG-4000, 40°C). IR(film) 1640 (m), 1120 (s), 900 (s) cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 200 MHz), 1.37 (3 H, s), 1.70 (3 H, dd, J 0.7, 1.1 Hz), 3.15 (3 H, s), 4.97 (1 H, m), 5.00 (1 H, m), 5.11–5.27 (2 H, m), 5.81 (1 H, dd, 10.7, 17.5 Hz). MS: 126 (M^+ 12) 111 (100), 85 (99), 55 (72). The primary ethers 23 and 24 were identified by comparison (GLC, $^1\text{H NMR}$) with samples obtained from solvolysis of the bromocyclopropane derivative 27 (see below).

In a similar way, 2.0 mmol of the diazotate 25 in 21 ml of THF was treated with 2.00 g (20 mmol) of D_2SO_4 dissolved in 10 ml (0.25 mol) of CH_3OD . Work-up gave 246 mg (97 %) of a crude mixture containing $>85\%$ of the ethers 22, 23 and 24 in the ratio 6.8:1.3:1. The remaining product consisted of several minor unidentified compounds.

Silver assisted methanolysis of 1-bromo-2-isopropenyl-2-methyl-cyclopropane (27). A 1:1 stereoisomeric mixture of 27²⁰ (1.40 g, 8.0 mmol) was stirred with a suspension of 2.04 g (12 mmol) finely ground silver nitrate in 40 ml of dry methanol, containing 0.98 ml (8.4 mmol) of redistilled 2,6-lutidine, in the dark at room temperature for 27 days. After this time no starting material was detected by GLC. The reaction was quenched by addition of 10 ml of brine. Work-up gave 941 mg (93 %) of the ethers 22, 23 and 24 in the ratio 3.2:1.3:1 as determined by $^1\text{H NMR}$ and GLC. The tertiary ester 22 was separated by flash chromatography (SiO_2 , CH_2Cl_2 /pentane 1:1). A solution of 231 mg (1.83 mmol) of the ether mixture in 6.0 ml of CH_2Cl_2 was stirred with 346 mg (2.0 mmol) of *N*-phenylmaleimid for 56 h at room temperature. Flash chromatography (SiO_2 , CH_2Cl_2 /pentane 1:1 followed by CHCl_3) of the crude mixture gave 87 mg (38 %) of 22, 22 mg (9.5 %) of a 1:1 mixture of stereoisomers 24 and 92 mg (17 %) of the unstable Diels-Alder adduct 28, mp. 100°C (hexane/ CHCl_3). IR(KBr): 1710 (s), 1380 (m), 1180 (m), 1110 (m) cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 200 MHz): 1.73 (3 H, s), 1.76 (3 H, s), 2.34 (1 H, dd, J 7.9, 15.3 Hz), 2.5–2.7 (2 H, m), 3.1–3.4 (2 H, m), 3.33 (3 H, s), 3.74 (2 H, d, J 6.0 Hz), 7.2–7.5 (5 H, m).

By comparing the spectroscopic data of the primary ether mixtures with and without the presence of 23, the following spectroscopic properties are assigned to 23: IR (film): 3395 (m), 1600 (m), 1100 (s), 890 (m) cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 200 MHz): 1.83 (3 H, s), 1.93 (3 H, d, J 0.8 Hz), 3.37 (3 H, s), 4.10 (2 H, d, J 6.2 Hz), 4.97 (1 H, s), 5.08 (1 H, s), 5.72 (1 H, t, J 6.2 Hz).

It was not possible to separate the stereoisomers of 24 by chromatography, but their respective spectroscopic properties were obtained from those of the mixtures.

24a. IR(film): 1260 (m), 1100 (s), 1020 (m), 900 (m), 800 (m) cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 200 MHz): 1.83 (3 H, s), 1.85 (3 H, s), 3.30 (3 H, s), 4.06 (2 H, s), 5.06 (1 H, d, J 10.9 Hz), 5.21 (1 H, d, J 17.1 Hz), 6.88 (1 H, dd, J 10.9, 17.1 Hz).

24b. IR(film): same as for 23a. $^1\text{H NMR}$ (CDCl_3 , 200 MHz): 1.83 (3 H, s), 1.84 (3 H, s), 3.31 (3 H, s), 4.03 (2 H, s), 5.11 (1 H, d, J 10.6 Hz), 5.24 (1 H, d, J 17.0 Hz), 6.84 (1 H, dd, J 10.6, 17.0 Hz).

Deamination of nitrosoarea 8 with lithium methoxide. A suspension of 1.056 g (5.0 mmol) of the nitrosoarea 8 in 90 ml dry pentane, kept at 0 °C, was treated with 0.735 g (10.5 mmol) of MeOLi · MeOH as described earlier for the deamination of the nitrosoarea 7. Work-up gave 579 mg (95 %) of 2,6-dimethyl-2,3,5-heptatriene (30)²¹ as the only product (>99 % pure by GLC on 10 % SE-30). The compound was identical to that prepared from the corresponding dibromide 31 and methylolithium.⁴

Deamination of potassium trans-3,3-dimethyl-2-(2-methyl-1-propenyl)-1-cyclopropanediazotate (29). To a solution of 470 mg (4.2 mmol) of *t*-BuOK in 14 ml THF was added 422 mg (2.0 mmol) of the nitrosoarea 8 in 7 ml THF in the same way as in the preparation of the diazotate 25. The diazotate solution was kept at -50 °C for 1 h before use.

A. *Deamination with methanol.* The reaction was carried out as for 25 by addition of 14 ml of methanol, giving 237 mg (97 %) of the triene 30 as the only product (>99 %, GLC).

B. *With methanolic sulfuric acid.* The reaction was carried out as for 25 by adding a solution of 0.53 ml (10 mmol) conc. sulfuric acid in 7 ml (0.18 mol) of methanol to a solution of 1.0 mmol diazotate 28 in 11 ml of THF, kept at -110 °C. Work-up gave 147 mg (96 %) of (*E*)-6-methoxy-2,6-dimethyl-2,4-heptadiene (32) as the major (>90 %) product isolated by prep. GLC (10 % SE 30, 65 °C). IR (film): 1650 (m), 1070 (s), 780 (m) cm⁻¹. ¹H NMR (CDCl₃): 1.28 (6 H, s), 1.74 (6 H, broad s), 3.13 (3 H, s), 5.44 (1 H, d, *J* 14.8 Hz), 5.75 (1 H, d, *J* 10.0 Hz), 6.27 (1 H, dd, *J* 10.0, 14.8 Hz). MS: 154 (M⁺, 37), 139 (100), 107 (89), 91 (66), 59 (69).

Five minor products were not identified.

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