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PHOTOCHEMISTRY OF NITROSO DERIVATIVES IN SOLUTION—XXX†

TEMPERATURE EFFECTS ON RADICAL ADDITIONS TO TERPENES AND REACTIONS OF 2-AMMONIUM NITROSOALKANES[1]

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Abstract—Temperature effects on aminium radical initiated photoaddition to three monoterpenes were investigated. Photoaddition of N-nitrosopiperidine to camphene and pinenes gave the α-piperidinium tertiary-nitrosoalkanes as the primary adducts derived from 1,2-addition; the additions to pinenes required a low temperature (−40°) to suppress the cyclobutane ring opening pathway of the C-radical intermediate. Since the functional groups of these α-piperidinium nitrosoalkanes could assume *cis*-coplanar configuration, they underwent a facile cleavage reaction to give the corresponding oximes and immonium salts. As the photolysis temperature was raised, in the addition to pinenes, the cyclobutane ring opening pathway progressively dominated the reaction giving increasing amounts of 8-nitroso-*p*-menthene derivatives which underwent solvolysis and elimination reactions. A mechanistic interpretation in favor of the homolytic ring opening process from the C-radical intermediate is presented. The results established a diagnostic rule for stepwise addition to olefins. An efficient preparation of tricyclene from a commercial camphene sample was appended.

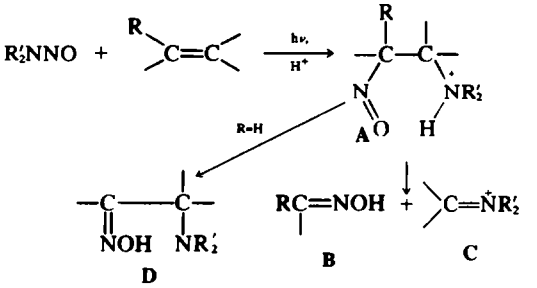
INTRODUCTION

In theory the cleavage reaction of the adduct obtained from photoaddition of a N-nitrosamine to an olefinic bond can occur if the intermediate **A**, an 2-ammonium nitrosoalkane, has a sufficiently long lifetime to allow the cyclic electron reorganization pathway, **A**→**B**+**C**, (Scheme 1) to compete efficiently against the tautomerization pathway, **A**→**D**.[2,3] Such a situation arises in one of two possible circumstances, namely (i) R is an alkyl group disallowing the tautomerization to occur[3] or (ii) the rate of the tautomerization is slow by the reasons discussed previously.[2] Furthermore, the stereoelectronic requirements for the cleavage pathway are such that the two functional groups must orient themselves in the *cis*-coplanar configuration (or nearly so) as shown in **A**.[1b] When the conditions are favorable, the photoaddition to an olefin and the cleavage of the intermediary adduct are carried out in a one step operation to give an oxime **B** and immonium species **C** and is similar to ozonolysis in its overall results.[3] The photocleavage reaction is decisively more advantageous since the products can be separated readily due to the different functional groups. We wish to describe three examples of this cleavage reaction as applied to terpene chemistry.

RESULT

Photoaddition of N-nitrosopiperidine (NNP) to *dl*-camphene (**1**) was carried out by the method previously described.[2,3] During the photoaddition, the photolysate maintained a deep blue color which, upon completion of the reaction, changed to a greenish yellow solution. The major product, obtained in the "neutral fraction", was simply recrystallized to give *dl*-camphenilone oxime[4] (**2**) in 70–85%. The higher yield was obtained, and could be improved, when the solvent of the photolysate was carefully distilled preventing the loss of volatile oxime **2**.

The second product, dipiperidinomethane, was isolated in the "basic fraction". The *anti*-configuration of **2** was decided by the chemical shift of the C-1 bridgehead proton at τ 6·54 by comparisons with those of the corresponding protons of *anti*- norbornanone oxime (τ 6·55) and *syn*-norbornanone oxime (τ 7·13). The *gem*-dimethyl protons in **2**, in spite of the fact that they are located in chemically non-equivalent environment, appeared as a singlet at τ 8·87.



Scheme 1.

All commercial camphene samples examined so far contain about 25% of tricyclene **3** and a large scale purification of camphene is difficult. In view of the large difference in the rates of hydrogen abstraction and addition to a double bond by the piperidinium radical,[5] it was anticipated that the photoinitiated addition-cleavage sequence with a commercial camphene might yield cleanly camphenilone oxime (**2**) and tricyclene (**3**) in one operation. This was realized when the photoaddition to a commercial *dl*-camphene (**1**) was carried out under the usual conditions; oxime **2** was readily crystallized from the "neutral fraction" and the recovered hydrocarbon was enriched (85–90%) in **3**.

β-Pinene (**4**) contains, as in camphene, an *exo*-cyclic double bond attached to a bridged bicyclic system and is

†For Part XXIX and XXVIII see Ref. 1.

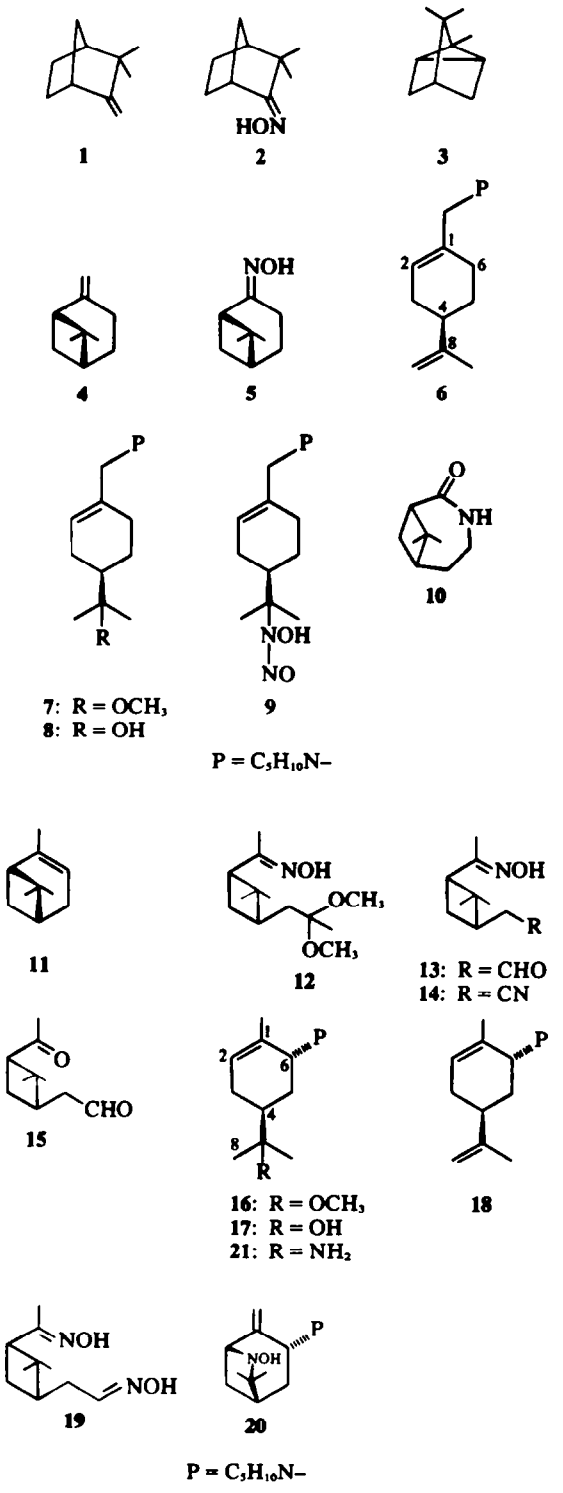
expected to add NNP in the same fashion. However, when the reaction was run at room temperature in the usual manner, the expected nopinone oxime (**5**) was formed in only a small yield; both the "neutral" and "basic fraction" were complex mixtures that required extensive chromatography. In the "neutral fraction" nopinone oxime (**5**) was isolated together with a large quantity of acid catalysed β-pinene rearrangement products such as α-terpineol, and the corresponding methyl ether and borneol.[6] These acid catalysed rearrangement products could be eliminated if the photolysate was neutralized before the work-up. The basic fraction consisted of the 8-substituted *p*-menthene derivatives **6**, **7**, **8** and **9**. Except for N-nitrosohydroxylamine **9** (m.p. 47–49°), other oily products were purified by extensive column and thin layer chromatography. On attempted acetylation (pyridine-acetic anhydride) of **9**, the N-nitrosohydroxylamino group was eliminated to give **6**. These structures were decided by their spectroscopic data as summarized in Table 3.

As the temperature during photolysis was lowered the yield of nopinone oxime **5** increased dramatically at the expense of the yields of the ring opened products **6–9** (Table 1). Indeed, in the photolysis at −40°, oxime **5** was obtained in 84% yield and some dipiperidinomethane was isolated. Crude nopinone oxime from a neutral photolysate was a mixture of *anti*-oxime **5** (τ 8·72, 9·18) and the corresponding *syn*-oxime (τ 8·66, 9·18, 6·48) in a ratio of 1:6. This mixture was rapidly converted to pure *anti*-oxime **5** in 0·1 N HCl solution or when adsorbed on a silicic acid column. Phosphorous pentachloride treatment of oxime **5** gave a lactam which was tentatively assigned as **10**. Although the migrating group is not *anti* to the departing OH group, this rule does not necessarily apply to a bridged bicyclic ketooxime since it has been shown the methylene terminal migrates preferentially over the methine terminal in norbornanone oxime.[6a] We believe that the methylene, being capable of stabilizing carbanion character of the migrating group better, should preferentially migrate over the bridgehead carbon in these cases.

On the basis of the observations obtained in the cleavage reaction of β-pinene, similar cleavage operation of α-pinene (**11**) was carried out at −40° to give a good combined yield of acetal **12** (76%) and the corresponding aldehyde **13** (14%). These primary products were obviously sensitive to acid catalysis since on acidic work up of a photolysate or on treatment of **12** or **13** in dilute acid, a complex mixture of **13**, **14** and **15** and other unidentified compounds was obtained. Nitrile **14** was assumed to be formed from dehydration of *bis*-oxime **19** the presence of which in several chromatographic fractions could be inferred from the spectra but could not be isolated in pure form.

When the photoaddition to α-pinene was carried out in the vicinity of 0°, the *p*-menthene derivatives **16**, **17** and **18** in addition to N-hydroxylamine **20** were formed: all of which were formed via a ring opened intermediate (*vide infra*). The last mentioned compound **20** was readily oxidized by air to the corresponding stable nitroxide radical, the chemistry of which was described in the recent communication.[7] The total yield of **16–19** increased as the photolysis temperature was raised (Table 2). The structures of **16–18** were determined by their spectroscopic data (Table 3).

It should be mentioned that mass spectroscopic data of *p*-menthene derivatives **6–8**, **16–18**, and **21** indicated the preferential cleavage of C_4–C_8 bond to give the intense peaks of the respective species. This fragmentation mode is common with those of α-terpineol and its methyl either and serves to support the structural assignment. These compounds also gave common intense peaks corresponding to piperidinotropylium and tropylium ions. The NMR spectra of these *p*-menthene derivatives all exhibited unresolved and complex patterns for their olefinic protons; however, chemical shifts and shapes of these protons were remarkably similar to those of α-terpineol and its methyl ether.



DISCUSSION

As we have established previously, in acidic photoaddition of nitrosamines, aminium radicals preferentially add to the least substituted C atom of the double bond[2] (Scheme 1), addition to a 1,1-disubstituted double bond sets the stage nicely for the cleavage pathway. Efficiency of this cleavage scheme is amply demonstrated in the case of α-methylstyrene, described previously,[2] and camphene and β-pinene in the present investigation. Photocleavage reaction of α-pinene follows the same principle but involves stereochemical variations of the functional groups.

In contrast to the ready cleavage reaction of camphene under ordinary irradiation conditions, it is noteworthy that the similar operation with β-pinene results in extensive ring opening of the cyclobutane ring. The results summarized in Table 1 indicate that the intermediate radical **22** captures nitric oxide to give **23** efficiently even at −40° while at a higher temperature the ring opening process to **24** becomes the dominant process; the latter process leads to the formation of C-nitroso compound **25**, the observed blue color of the photolysate is ascribed to the presence of **25** but not that of **23** (*vide infra*).

Survey of literature show that radical additions of various reagents to β-pinene are generally accompanied by the cyclobutane ring opening giving the 1:1 adducts,[8-13] such as **25**, except in the cases of thiolacetic acid and peroxy radical additions[14,15] where the formation of unrearranged products, such as **23**, have been obtained. The present results demonstrate that the rate of the ring opening process (**22**→**24**) can be controlled by regulating the temperature during the radical addition to β-pinene and thus *the overall product pattern can be manipulated.* This process (**22**→**24**) must have a small but definite activation energy as shown by the rapid ring cleavage at −10°. At a low temperature, intermediate **22** is stabilized and its lifetime is prolonged to have more chance to engage in the bimolecular reaction with ·NO. The total lack of skeletal rearrangement in the photoaddition to camphene and the propensity of the ring cleavage of β-pinene at a higher temperature are both characteristics of *a stepwise radical addition reaction.*[16] Provided the temperature can be controlled, a similar pattern should be observable for other radical additions to these terpenes. Such methodology should be a valuable diagnostic tool for a stepwise radical addition. Similar temperature effects have been observed in a radical initiated allylic chlorination of internal olefins[16] and nitrosamine photoaddition to 2-butenes.[17]

It is assumed that *p*-menthene derivatives **6**, **7** and **8** are derived from **25** by acid catalysed elimination and solvolysis while **9** by the addition of HNO (*vide infra*). Certainly they are not derived directly from radical intermediate **24** since mechanistically such radical processes would be unreasonably endothermic and are scarcely known. The mechanism of these C-nitroso compound reactions are obscure. However, there are some precedents for these types of reactions.[2,18]

During the cleavage reaction of α-pinene (Table 2) the similar ring opening pathway as shown in Scheme 3 is also operating but to a lesser extent than that of β-pinene. There is only limited information available on radical addition to α-pinene;[15,18] additions of mercapto derivatives are shown to give the 1:1 adducts without ring openings.[14,15] Although products in other additions were not identified in most of the cases, the ring opening pathway was indicated by the detection of a double bond in the adducts.[15] Our results demonstrate that such rearrangement of the intermediate, i.e. **27**→**29**→**30**, becomes important at room temperature and above, but suppressed at a low temperature.

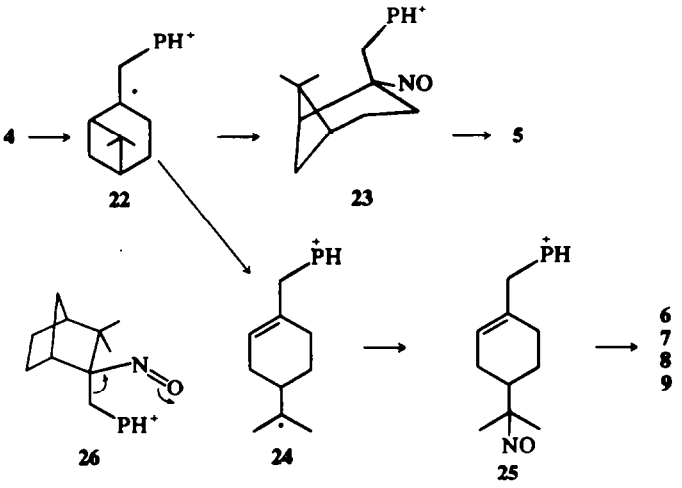
As established previously a *cis*-coplanar orientation of the functional groups in the C-nitroso intermediates **23**, **26** and **28** controls the probability of cleavage pathway.[1b] The expected intermediates derived from camphene and β-pinene can rotate the functional groups to assume a *cis*-coplanar arrangement as shown in **26** and **23** and can undergo the cyclic cleavage reaction in so far as the total conformational energy of the transition state is not prohibitive. This is the case as demonstrated by the facile cleavage of both of the olefins. Whereas NNP photoaddition to cyclohexene proceeds by the *anti*-diaxial approach to the double bond to give *trans*-α-amino–nitrosocyclohexane,[17] the same photoaddition to α-pinene is expected to give *cis*-configuration **28** from steric hindrance considerations.† It is most likely the stepwise addition of both piperidinium radical and nitric oxide approaches from the side opposite to the CMe_2 bridge to give **28**. The efficient cleavage reaction of this double bond substantiates the validity of *cis*-configuration in **28**. The same steric argument leads us to conclude that all *p*-menthene derivatives **16**, **17**, **18** and **21** have the *trans* - 1,3 - configuration of the piperidino and isopropyl units, maintaining the stereochemistry of the precursor **29** unless an unlikely isomerization intervenes.‡ It is clear that this configuration, but not alternative *cis*-1,3, allows the intermediate to undergo efficient cyclization to give hydroxylamine **20** as observed.

From these discussions the scope and limitation of this photocleavage reaction can be expanded further from those conditions described in the Introduction. In principle, a NNP adduct which are flexible enough to assume a *cis*-coplanar configuration (or nearly so) will be able to undergo the cleavage pathway; for example, the adducts from acyclic and exocyclic double bonds belong to this category. A NNP photoaddition to a double bond located in a rigid framework will result in a *trans*-diaxial adduct which should fail to undergo the cleavage reaction.

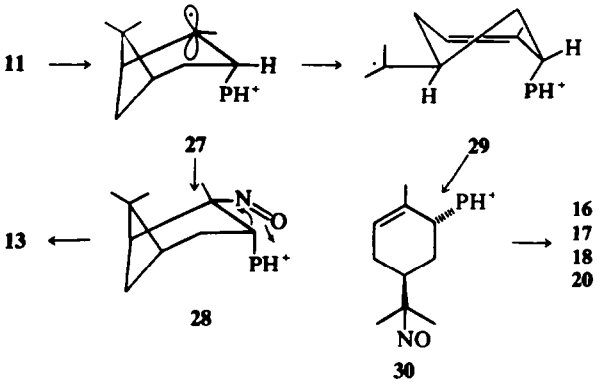
While discussions on the temperature effects presented above is self consistent and the most likely one, it is not the exclusive mechanism at this stage. The obvious alternative of assuming **23** and **28** as the direct or indirect (via **25** and **30**) intermediates common to all the products in the respective cleavage reaction (Schemes 2 and 3) runs into serious contradictions in several ways. First of all the cleavage pathway (**23**→**5** and **28**→**13**) is an efficient intramolecular process[16] very little affected by a change in temperature as shown in photoaddition to camphene and others.[3] Secondly the persisting blue color observed at the end of photoaddition to α-pinene is now shown to be that of **30**, but not that of **28**, since immediate reduction of this blue photolysate gives diamine **21** and not diamine corresponding to **28**. Indirectly this also infers that **28** and

†In both Refs 14 and 15, additions of mercapto derivatives have been claimed to give both *cis* and *trans* stereoisomers but neither have provided compelling evidence nor isolated the isomers.

‡In Ref. 15, while the same stereochemical argument was used in the CCl_4 addition to α-pinene, the authors proposed the adduct having *cis*-1,3-substitution. This configuration is not likely unless the authors imply there is a secondary isomerization at the C-2 position, e.g. ionization and recombination of the C–CCl_3 bond.



Scheme 2.



Scheme 3.

Table 1. Product distributions in the NNP photoaddition to β-pinene

Reaction No.	Duration of photolysis (hr)	Temp. (°C)	Products (%) 5	6	7	8	9
1	1·5	15	8	8	15	12	[a]
2	1·5	10	17		47[b]		20
3	2	−15	32	6	5	8	[a]
4	4·5	−40	84		4[b]	0	

[a] Not determined.
[b] The total % of combined **6**, **7** and **8**.

Table 2. Product distributions in the NNP photoaddition to α-pinene

Reaction No.	Duration of photolysis (hr)	Temp. (°C)	Products 12 + 13	16	17	18	20
1	2	10	45[a]	8	7	4	~5
2	2	0	57	[b]	[b]	[b]	18
3	2·5	−40	89	~2	2	0	0

[a] The yield of **13** is generally less than 15% depending on working up.
[b] The presence of these compounds were demonstrated by NMR but were not determined quantitatively.

23 undergo rapid cleavage reaction and would not survive long to undergo a solvolysis. Finally if any solvolytic rearrangement occurs at all, the deep seated skeletal change might lead to other bicyclic derivative corresponding to borneol and isoborneol in addition to the observed ring cleavage products, e.g. **6**–**9**. To our knowledge ionic reaction of tertiary-nitrosoalkanes have not been investigated to any extent and the probability of heterolysis of the C–NO bond is obscure. Intuitively we believe that the heterolysis by a SN1 or SN2 mechanism is energetically a much less favored process than the cleavage pathway.

EXPERIMENTAL

For the general conditions of photoreaction and of recording spectroscopic data, see our previous publication.[2,3] Irradiation was carried out with a Hanovia medium pressure lamp (654A36, 200 W) with a suitable filter; a Pyrex filter cut off the light source below 290 nm and a Norex filter below 350 nm. The progress of a reaction was followed with the disappearance of the 340 nm absorption band of NNP.

β-Pinene supplied by Columbia Chemical Co. was distilled in a Vigreaux column equipped still to give a colorless oil; b.p. 56·5°/25 mm Hg; $[\alpha]_D$ −19·9° (lit.[6] −18·2°). The sample of α-pinene purchased from Aldrich Chemical Co. was utilized without purification; $[\alpha]_D$ −53° (lit.[6] −48·3°). *dl*-Camphene supplied from Eastman Kodak or BDH was taken up in ether and purified by preparative VPC with a 30% SE-30 column (20 × ¾in., N_2 flow rate 1 ml/sec) attached to an Aerograph Model 700 at 175°. Pure camphene had retention time of 13·3 min and m.p. 48–49°.[6] The purity of these monoterpenes and the oily products were further

Table 3. Physical data of the products[a]

2 —
153 (M^+, 0·5), 136 (100), 109 (39), 79 (39). 1·76 (b, 1H), 6·54 (b, 1H), 8·05 (m, 1H), 8·87 (s, 6H) 3240, 3160, 1692, 955–920

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5 Calc. for $C_9H_{15}NO$: 153·1154. Found: 153·1148 154 (19), 153 (M^+, 95), 138 (73), 136 (68), 124 (32), 111 (84), 110 (100), 94 (59), 82 (54), 69 (51) 1·93 (b, 1H), 7·10 ~ 7·74 (3H), 8·70 (s, 3H), 9·16 (s, 3H) 3350, 1655, 1380, 1365, 1000, 940, 895 (neat) −294 (300), −205 (400), −107 (500), −74 (589), −57 (600)

6 Calc. for $C_{15}H_{25}N$: 219·1987. Found: 219·1980 219 (M^+, 40), 204 (8), 176 (5), 150 (50), 134 (10), 98 (100), 84 (100). 4·45 (m, 1H), 5·32 (m, 2H), 7·22 (m, 2H), 8·28 (d, J = 1, 3H) 2800, 2760, 1680, 1645, 1370, 1345, 1305, 1115, 890, 755. −279 (300), −193 (400), −114 (500), −78 (589), −60 (600), −74 (700)

7 Calc. for $C_{16}H_{29}NO$: 251, 2249. Found: 251·2242 251 (M^+, 28), 236 (6), 220 (14), 218 (8), 178 (13), 150 (8), 135 (8), 108 (8), 98 (73), 93 (17), 91 (11), 84 (100), 73 (55) 4·45 (m, 1H), 6·84 (s, 3H), 7·21 (s, 2H), 8·90 (s, 6H) 3340, 2880, 2800, 1685, 1375, 1365, 1150, 1080, 865 −535 (300), −325 (400), −189 (500), −127 (589), −114 (600), −121 (700)

8 Calc. for $C_{15}H_{27}NO$: 237·2093. Found: 237·2108 237 (M^+, 30), 221 (11), 178 (18), 150 (7), 136 (7), 122 (5), 98 (75), 93 (9), 91 (11), 84 (28) 4·41 (m, 1H), 7·23 (m, 2H), 8·81 (s, 6H) 3400, 1645, 1340, 1365, 1115, 755

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9[b] Calc. for $C_{15}H_{27}N_3O_2$: 281·2103. Found: 281·2111. 281 (M^+), 264, 251, 220, 178, 166, 118 1·5 (b 1H), 4·48 (m, 1H), 7·12 (s, 2H), 8·40 (s, 3H), 8·42 (s, 3H) 2860, 1650, 1235, 1150, 1065, 1045, 935, 760 510 (300), 52 (400), 16 (500), 5·4 (589), 5·4 (600)

12 —
229 (M^+), 214 (1), 198 (5), 182 (8), 112 (9), 86 (10), 75 (100) 0·8 (b, 1H), 5·72 (dd, J = 5·5 and 7, 1H), 6·72 (s, 6H), 8·20 (s, 3H), 8·80 (s, 3H), 9·13 (s, 3H) 3220, 1650, 1370, 1130, 1050, 960, 870

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13 —
184, 183 (M^+), 166 (1·2), 155 (2·1), 140 (7), 138 (8), 126 (11), 98 (27), 86 (100) 0·33 (b, 1H), 7·60 (m, 2H), 8·22 (s, 3H), 8·78 (s, 3H), 9·16 (s, 3H) 3265, 2980, 2720, 1740, 1370, 1230, 1120, 870

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14 —
181 (M^+), 162, 140, 122, 113, 112, 98, 85 (100) 1·72 (b, 1H), 8·19 (s, 3H), 8·77 (s, 3H), 9·10 (s, 3H) 3250, 2250, 1655, 1370, 1235

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15 —
168 (M^+), 153, 138, 136, 125, 124, 103, 98, 83, 81 0·3 (t, J = 1·5), 7·1 (m, 2H), 7·93 (s, 3H), 8·68 (s, 3H), 9·11 (s, 3H) 2730, 1725, 1710

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16 Calc. for $C_{16}H_{29}NO$: 251·2249. Found: 251·2239. 251 (M^+, 19), 236 (4), 220 (25), 178 (54), 150 (15), 135 (46), 119 (13), 108 (19), 86 (100) 4·43 (m, 1H), 6·84 (s, 3H), 7·04 (bd, 1H), 8·30 (d, J = 1, 3H), 8·91 (s, 6H) 1640, 1550, 1390, 1385, 1100, 870 (neat) −920 (300), −370 (400), −200 (500), −127 (589), −119 (600)

17 Calc. for $C_{15}H_{27}NO$: 237·2093. Found: 237·2108 237 (M^+), 219 (4), 204 (3), 178 (11), 151 (10), 136 (42), 119 (30), 86 (100), 84 (47). 4·40 (m, 1H), 6·96 (bd, 1H), 8·28 (d, 1·5, 3H), 8·52 (b, 6H), 8·82 (s, 6H) 3380, 1650, 1370, 1250, 1160, 1120, 1040, 920, 870 (neat) −605 (300), −307 (400), −151 (500), −100 (589), −92 (600), −99 (700)

18 Calc. for $C_{15}H_{25}N$: 219·1987. Found: 219·1980 219 (M^+, 10), 204 (7), 1767 (7), 164 (14), 151 (20), 136 (67), 134 (29), 119 (70), 105 (18), 92 (25), 86 (100) 4·45 (m, 1H), 5·33 (m, 2H), 6·98 (dd, 1H), 8·26 (s, 6H) 2950, 1645, 1115, 1105, 900 −279 (300), −193 (400), −114 (500), −60 (600)

[a] The physical data were given in the order of exact mass determination for the M^+, mass spectra (*m/e* and %), NMR (coupling pattern, coupling constant and number of proton), ir (cm^{-1}), and ORD data (wavelength and ϕ). The NMR spectra were taken in $CDCl_3$, the ir in $CHCl_3$ unless specified otherwise, and the ORD in methanol.

[b] This compound has λ_{max} 230 nm (ϵ, 4300).

checked with VPC and TLC and their NMR and IR spectra were recorded.

Photocleavage of camphene

A soln containing NNP (836 mg), *dl*-camphene (1 g), conc HCl (0·7 ml) and MeOH (130 ml) was irradiated for 1 hr. The photolysate was adjusted to pH 7 with a satd Na_2CO_3 aq soln. The aqueous soln was acidified with 1 N HCl (20 ml) and was extracted with ether. On evaporation of ether, it gave a crystalline solid (m.p. 98–102°, 83 mg, 75%). One recrystallization from pentane gave **2**: 106–107° (lit.[4] m.p. 105–107°). (Found: C, 70·21; H, 9·78; N, 9·03. Calcd. for $C_9H_{15}NO$: C, 70·55; H, 9·87; N, 9·14%).

The aqueous soln was basified and was extracted with ether to give a basic fraction which was distilled to afford dipiperidinomethane (543 mg): b.p. 48°/0·2 mm;[3] the IR and the NMR spectra were superimposable with those of an authentic sample prepared from CH_2Cl_2 and piperidine.

Photocleavage of β-pinene

A soln containing β-pinene (0·048 mole), NNP (0·03 mole) and HCl (0·048 mole) in MeOH (300 ml) was irradiated in the photolysis apparatus described before. Light was filtered through a Norex filter and photocell was immersed in a proper coolant. The photolysate was neutralized with solid Na_2CO_3 and worked up as described before. If the photolysate was worked up without neutralization, a large quantity of the neutral fraction was obtained and was chromatographed on alumina to give α-terpineol methyl ether, borneol,[6] α-terpineol and oxime **5** in this order of elution. The sample of oxime **5** obtained from the chromatograph showed a complex NMR pattern with 4 Me singlets (τ 8·72, 8·66, 9·16 and 9·18; the signal ratio 85 : 14) which on chromatography on silicic acid or upon treatment with 0·1 N methanolic HCl soln gave a sample showing two distinct Me singlets at τ 8·70 and 9·16. The sample was further purified by preparative TLC and was distilled under vacuum to give a liquid. (Found: C, 70·33; H, 9·92; H, 9·08. Calcd. for $C_9H_{15}NO$: C, 70·55; H, 9·87; N, 9·14%).

The basic aqueous soln after removal of other compounds was extracted continuously for 24 hr with ether and the ether extract was worked up in the usual manner to give a solid. The solid was recrystallized from a mixture of acetone and light petroleum to give a white crystal: m.p. 47–49°. (Found: C, 64·25; H, 9·72, N, 14·80. Calcd. for $C_{15}H_{27}N_3O_2$: C, 64·03; H, 9·67; N, 14·93%).

The basic fraction was chromatographed on a silicic acid column using chloroform and increasing amount of MeOH in chloroform as eluents. The semipure fractions were combined together and further chromatographed in the similar manner to afford respective compounds in reasonably pure states. The order of elution was **6**, **7** and **8** and the % yields were calculated from the result of the chromatography and checked by the integration curve of the NMR spectra. The oily products **6**, **7** and **8** were further purified by preparative TLC and distilled under vacuum to give pure samples.

Photocleavage of α-pinene

The reaction was carried out in the similar manner to that of β-pinene. In the acidic work up, i.e. without neutralization with solid Na_2CO_3, the neutral fraction was chromatographed on alumina using light petroleum as the eluent. α-Terpineol and its methyl ether were the first crop of compounds to be eluted followed by **15**, **13**, **14** and **19** in that order of elution. The oily

fraction of **19** showed complex IR bands at 900–700 cm^{-1} and was decomposed on attempted distillation at 120°/0·5 mm.

Ketoaldehyde **15** was transformed, on storage for several months, to the corresponding keto acid: I.R. 2800–3300, 1720, 1710 cm^{-1}; τ 1·50 (b, D_2O exchangeable), τ 12(t, J = 8 Hz, 1H) 7·98 (s, 3H), 8·69 (s,3H) and 9·13 (s, 3H). The same keto acid was also obtained when **15** was taken up in EtOH containing a trace of KOH aq and was aerated overnight.

When the photolysate was neutralized with Na_2CO_3 and worked up in the usual manner, the neutral fraction could be separated by silicic acid chromatography eluted with $CHCl_3$ to give the excess α-pinene, **12** and a small quantity of **13**. The amount of **13** became less if the temp of working up was kept low and the photolysate was neutralized immediately. Oxime **12** was further purified by preparative TLC and was vacuum distilled to give an oil. (Found: C, 62·96; H, 10·20; N, 5·78. Calc. for $C_{12}H_{23}NO_3$: C, 62·85; H, 10·11; N, 6·11%).

Treatment of oxime **12** (slightly contaminated with **13**) or a mixture of **12**, **13** and **15** with a Brady's reagent gave the *bis* - 2,4 - dinitrophenylhydrazone which was recrystallized from EtOAc to give yellow crystals; m.p. 225–260° dec. (Found: C, 50·22; H, 4·31; N, 21·05. Calc. for $C_{22}H_{24}N_8O_8$: C, 50·00; H, 4·58; N, 21·20%).

The basic fraction was treated with light petroleum to give the crystalline ppt of **20** which was recrystallized from light petroleum to give white crystals; m.p. 134–135°, IR 3190, 3100, 1642, 1110 and 910 cm^{-1}; UV, λ_{max} 240 nm (CH_3OH); MS *m/e* (%) 250 (M^+), 249 (12), 234 (26), 133 (100), 177 (29), 176 (69), 150 (48), 96 (83), 91 (29) and 84 (75); NMR τ 1·70 (OH), 4·92 (broad s), 5·14 (broad s) 6·09 (broad d, J = 4 Hz), 8·78 (6H, s). (Found: C, 71·97; H, 10·44; N, 11·36. Calc. for $C_{15}H_{26}N_2O$: C, 71·95; H, 10·47, N, 11·19%).

The mother liquor was chromatographed on a silicic acid column using $CHCl_3$ as the eluent to give the following compound in the order of elution; **18**, **16**, **17** and **20**. Compound **18** and **16** were further purified by preparative TLC and the recovered oil were distilled under vacuum.

Acetylation of **9**

N-nitrosohydroxylamine **9** (180 mg) was dissolved in a pyridine-Ac_2O mixture for 24 hr at room temp. The product was isolated in the usual manner and was chromatographed on a silicic acid column to give **6** as shown by IR and NMR spectra.

Beckmann rearrangement of oxime **5**

Oxime **5** (179 mg) was treated with PCl_5 (200 mg) in ether for 2 hr at room temp. After evaporating ether, the residue was heated with water (20 ml) and was extracted to give the organic fraction (130 mg). Preparative TLC gave a solid which was recrystallized from MeOH to give fine needles; m.p. 110–112°; Calc. for $C_9H_{15}NO$. 153·1160, found = 153·1154; IR 3250, 1645, 1325, 1310, 1210, 1140, 965 and 875; NMR τ 2·0 (b, 1H), 6·82 (m, 1H), 8·75 (s, 3H); *m/e* (%) 153 (M^+, 23), 138 (17), 125 (20), 110 (33), 95 (37), 85 (100), 83 (75). (Found: C, 70·62; H, 9·90; N, 9·08. Calc. for $C_9H_{15}NO$: C, 70·55; H, 9·87; N, 9·14%).

Hydrogenation of the photolysate derived from α-pinene cleavage reaction

An acidic photolysate obtained from photoaddition of NNP (2·2 g) to α-pinene (2·7 g) was hydrogenated in the presence of PtO_2 (300 mg) for 40 hr at 50 lb pressure. The basic fraction (1·5 g) was chromatographed repeatedly to give **21**; IR 3340, 3260, 1660, 1340, 1310, 1240, 1150, 1120, 1035; NMR τ 4·4 (m, 1H), 7·0 (m of d, J = 6 Hz, 1H), 8·30 (d, J = 1 Hz, 3H), 8·92 (s, 6H); *m/e* (%) 286 (M^+, 1·5), 219 (1), 204 (2), 179 (3), 178 (100), 162 (1), 136 (4), 84 (60), 58 (100).

Amine **21** was further reduced in the similar manner to give dihydro-**21**; *m/e* (%) 238 (M^+, 2), 195 (5), 180 (96), 138 (12), 124 (16), 110 (7), 98 (78), 84 (25), 58 (100); IR 3360, 3280, 2180, 1600, 1365, 1380, 1155, 1115, 1105.

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