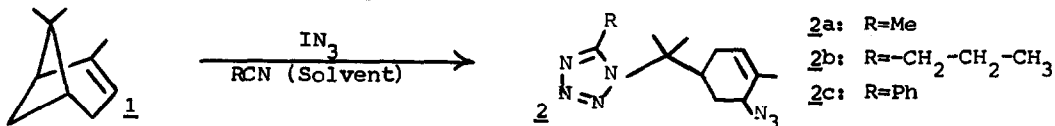


THE "HASSNER-RITTER" REACTION
 IN IODINE AZIDE ADDITIONS TO PINENES WITH SOLVENT PARTICIPATION

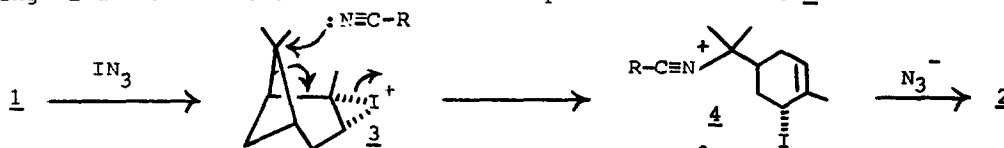
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This communication reports, *inter alia*, the following remarkable transformation:



Thus, the reaction of α -pinene (**1**) with iodine azide in acetonitrile gave a 95% yield of the tetrazole **2a**^{1*} (mp 125-126°; ν_{\max} (KBr) 2100 (azide) cm^{-1} ; nmr: $\delta_{(\text{CDCl}_3)}$: 1.76, 1.78 (gem dimethyl, olefinic methyl), 2.75 (tetrazolyl methyl), 3.87 (br, t-proton), 5.62 (br, olefinic proton); ms: 218 ($\text{M}^+ - \text{HN}_3$); mw (osmometry): 277). The formation of the tetrazole is rationalized on the basis of the solvent assisted opening of the initially formed iodonium ion **3**, to yield the Ritter reaction intermediate **4**, which by sequence involving azide ion addition and azide ion displacement leads to **2a**:**



Amongst the innumerable olefins subjected to IN_3 addition² which are invariably conducted in acetonitrile, no such participation has been thus far observed. Indeed, a study of IN_3 additions to α -pinene (**1**), β -pinene (**5**), camphene (**6**) and Δ^3 -carene (**7**)^{***}, has demonstrated that the tetrazoles are formed only with pinenes, thus highlighting the pronounced tendency that is present in these systems for the opening of the iodonium-ion intermediate by rupture of the weak cyclobutane σ -bond. The novel "Hassner-

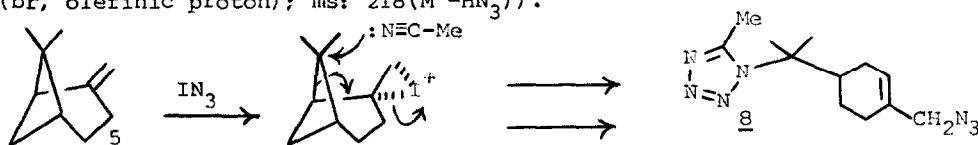
* A solution of α -pinene (1.36 g) in acetonitrile (5ml) was gradually added to IN_3 - produced *in situ*, at -10°, by addition of ICl (1.8 g) to a stirred slurry of NaN_3 (1.62 g) in acetonitrile (10 ml) - and after overnight stirring poured onto 5% thio-sulfate (100 ml). The precipitated solid was collected, dried and crystallized from benzene-petrol to yield 2.5 g (96%) of **2a**, mp 125-126°.

**The reaction of α -pinene with IN_3 in ether gave a complex mixture.

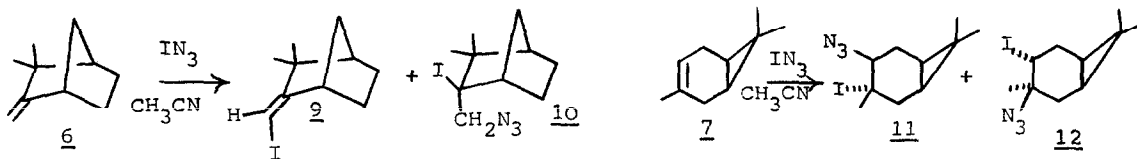
***The genesis for this work is related to the possibility of preparing *exo* azido pinanes and bornanes, which could be used to functionalize the bridgehead methyls by trans annular insertion followed by fragmentation.

Ritter" reaction illustrated here should be perfectly generally applicable wherever possibility for a solvent assisted intra-molecular opening of the initially formed iodonium ion exists. The reaction of α -pinene with IN_3 in butyronitrile and benzonitrile media gave, respectively, the expected azidotetrazoles 2b¹ and 2c¹ (2b: (40%), mp 95-97°; $\text{ir:} \nu_{\text{max}}$ (KBr) 2100 cm^{-1} ; $\text{nmr:} \delta_{(\text{CDCl}_3)}$ 1.12(t, propyl methyl, $J=7\text{Hz}$), 1.78, 1.85(gem dimethyl, olefinic methyl), 2.96(t, tetrazolyl methylene, $J=7\text{Hz}$), 3.84(br, t-proton), 5.62(br, olefinic proton); 2c(30%), gum(tlc pure); $\text{ir:} \nu_{\text{max}}$ (neat) 2100 cm^{-1} ; $\text{nmr:} \delta_{(\text{CDCl}_3)}$ 1.55(gem dimethyl, 1.75(olefinic methyl), 3.72(br, t-proton), 5.55 (br, olefinic proton), 7.45 (aromatic protons)).

The reaction of β -pinene(5) with IN_3 proceeded precisely as anticipated to give, in 90% yields, the crystalline azidotetrazole 8¹. (mp: 72-73°; $\text{ir:} \nu_{\text{max}}$ (KBr) 2100 cm^{-1} ; $\text{nmr:} \delta_{(\text{CDCl}_3)}$ 1.75, 1.78(gem dimethyl), 2.75(tetrazolyl methyl), 3.75(azidomethylene), 5.75(br, olefinic proton); $\text{ms: } 218(\text{M}^+ - \text{HN}_3)$).



Interestingly, the camphene(6) and Δ^3 -carene(7) frameworks showed no tendency for rearrangement in IN_3 additions. The reaction yielded ω -iodocamphene(9, 20%)¹ and the adduct 10(60%)¹ from 6 and the regioisomeric mixture (1:1) 11 and 12 (90%)¹ from 7. (9: oil; $\text{ir:} \nu_{\text{max}}$ (neat) 1640(C=C). cm^{-1} ; $\text{nmr:} \delta_{(\text{CDCl}_3)}$ 1.15(gem dimethyls), 2.22, 3.08 (br, br, bridgehead protons), 5.6(s, olefinic proton); 10: oil; $\text{ir:} \nu_{\text{max}}$ (neat) 2100 cm^{-1} ; $\text{nmr:} \delta_{(\text{CDCl}_3)}$ 1.03, 1.16(methyls), 2.1, 2.5(br, br, bridgehead protons), 3.5(d, d; $J=12\text{Hz}$, azidomethylene); 11 and 12: oil; $\text{ir:} \nu_{\text{max}}$ (neat) 2100 cm^{-1} ; $\text{nmr:} \delta_{(\text{CDCl}_3)}$ 1.03 (methyls), 3.85(m, non-bridgehead t-proton)).



REFERENCES

1. Analysis in excellent accord with that calculated has been obtained for this substance
2. A. Hassner, Acc. Chem. Res., **4**, 10 (1971).