Tetrahedron Letters No.21, 2293-2300, 1966. Pergamon Press Ltd.
Printed in Great Britain.

ADDITIONS OF AZODICARBONYL COMPOUNDS TO NORBORNENE AND NORBORNADIENE

Joseph J. Tufariello, Thomas F. Mich,* and Paul S. Miller**
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

(Received 3 March 1966; in revised form 22 March 1966)

The reaction of ethyl azodicarboxylate with norbornadiene has been described previously.[1,2] The observation was made[1] that two 1:1 adducts were formed in _ca._ 75% overall yield. The two adducts, formed in approximately equal amounts, were separated and assigned the structure Ia (or IVa) and IIa. The structure of IIa was further substantiated[2] by its conversion into quadricyclene.

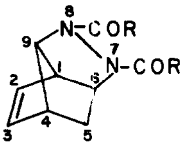
The structural assignment of the unsaturated adduct remained somewhat tentative, several alternative possibilities being considered[1] (_i.e._, IIIa, IVa and Va); however, the arguments presented against structures IIIa and Va appear convincing (_vide infra_). Although the formulation of the unsaturated adduct IVa could not be ruled out, the rearranged structure Ia appears to have been favored.[2,3]

Catalytic hydrogenation of the unsaturated adduct afforded the corresponding saturated adduct (presumably Ia → VIa, or IVa → VIIa). Recently Thaler and Franzus[3] reported this saturated adduct as a product of the

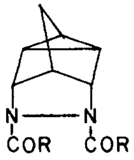
---

* Union Carbide Corporation Fellow, 1965 - 1966.

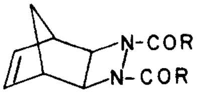
** NSF Undergraduate Research Participant, Summer, 1965.



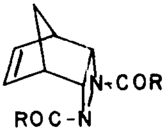
I



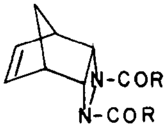
II



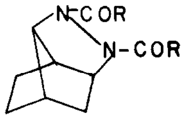
III



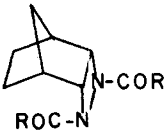
IV



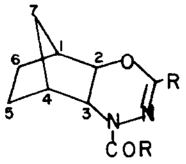
V



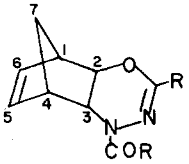
VI



VII



VIII



IX

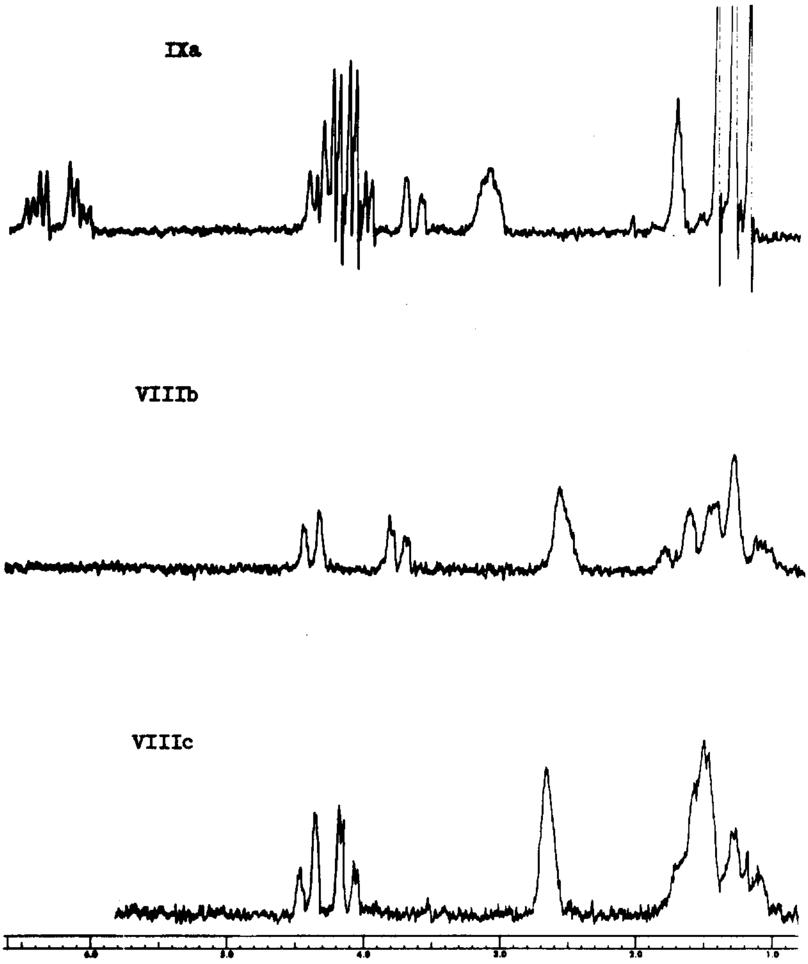
a, R = $-OC_2H_5$; b, R = $-OC_6H_5$; c, R = $-C_6H_5$

reaction of norbornene with ethyl azodicarboxylate. We established the identity of the saturated adducts formed by both routes by infrared and nuclear magnetic resonance spectral comparison.

The NMR spectrum of the unsaturated adduct is complicated by the presence of non-equivalent ester methylenes centered at 4.12 p.p.m. (c.f., Fig. I). Nevertheless, a somewhat modified AB quartet is apparent in the 3.5 - 4.5 p.p.m. region. The "A" portion of the pattern lies partially beneath the ester methylene resonances, but the "B" portion is clearly visible. This "AB" pattern could conceivably be assigned to the allylic protons H_1 and H_4 in Ia. Then the broad signal at ca. 3.10 p.p.m. would be attributed to the protons adjacent to nitrogen (i.e., H_6 and H_9). Alternatively, these assignments can be reversed. The former possibility can be ruled out by observation that hydrogenation of the unsaturated adduct shifts the 3.10 p.p.m. signal upfield to 2.46 p.p.m., a feature characteristic of allylic proton signals[4], while the position of AB pattern remains relatively unaltered. The latter alternative is also cast in doubt by the realization that it requires $^4J_{6,9} = 7$ cps, a four bond coupling value unprecedented[5,6,7] in norbornyl systems! This dilema led us to consider other structural possibilities for the unsaturated adduct. We propose that the structure of the adduct is one not previously considered, namely VIIIa.

We decided to distinguish between the structures VIIIa and VIa by determining whether the norbornyl system had undergone rearrangement during adduct formation, a circumstance demanded by VIa, but obviated by VIIIa.

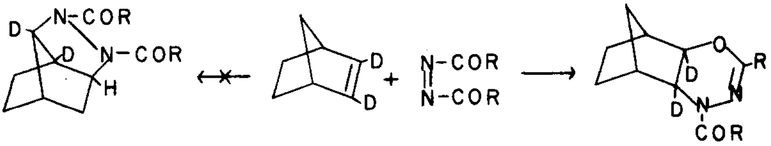
Recently, Franz and co-workers[7], through the use of 2,3-dideuterionorbornene, demonstrated that the benzenesulfonyl azide-norbornene



p.p.m.

FIGURE I

NMR SPECTRA (60 Mcs., TMS internal standard) adduct did not incorporate a rearranged norbornyl skeleton. Since the modified AB pattern in the saturated adduct was partially submerged beneath the ester methylene resonances, we decided to investigate other adducts in which the AB pattern would be clearly discernible, thereby facilitating the deuterium analyses. For this purpose, we prepared the norborene-phenyl azodicarboxylate (i.e., VIIIb) and norbornene-dibenzoyl diimide (i.e., VIIIc) adducts. That VIIIa, VIIIb and VIIIc are indeed all of a similar nature is supported by an examination of their NMR spectra (cf., Fig. I)*. Then, 2,3-dideuterionorbornene, containing 1.24



XIb
XIc

XIIb
XIIc

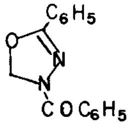
deuterium atoms/molecule, was allowed to react with phenyl azodicarboxylate[8,11] in one case and dibenzoyl diimide[12] in another to furnish the corresponding deuterated adducts (i.e., XIIb and XIIc, respectively).

The deuterium content of these materials was determined by NMR and the results indicate the adducts (i.e., XIIb and XIIc) to be unrearranged. The ratio of protons at the 1,4-, and 2,3- and the 5,6,7- positions remained relatively constant. The rearranged adducts, XIb and XIc, would demand a substantial decrease in the number of 1,4 protons and a similar increase in the number of protons adjacent to the nitrogens. Thus, we can clearly

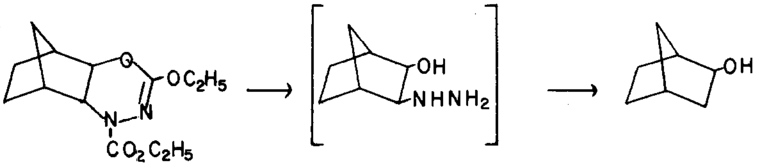
---

*The NMR spectrum for VIIIa is not shown since it has been reported previously[3]; however, it is worthwhile mentioning that the spectra of VIIIa and VIIIb are extremely similar save for the ethyl signals in VIIIa and the phenyl signals in VIIIb.

eliminate Ia and VIa as possible structures for the unsaturated and saturated adducts, respectively. The lack of rearrangement is consistent with IX, as well as III, IV, and V, as the structure of the unsaturated adduct; however, as noted earlier[1] the presence of non-equivalent ester methylenes in the NMR spectrum of the unsaturated adduct argues strongly against III and V. Moreover, the norbornene dibenzoyl diimide adduct, VIIIc, shows UV absorption at 292 mμ (ϵ 15,400). This band is absent in dibenzoyl diimide, dibenzoyl hydrazine, and dibenzoyl dimethyl hydrazine, but present in the oxadiazoline XIII, λ_{max}^{EtOH} 302 mμ (ϵ 16,400).[13] This would appear to confirm the presence of the oxadiazole ring in VIIIc and therefore presumably in VIIIa, VIIIb, and IXa as well. Thus, the diazacyclobutane structure III, IV, and V would appear to be eliminated. Consistent with this conclusion is the observation that acid catalyzed hydrolysis of VIIIa, followed by neutralization and treatment with oxygen in the presence of cupric chloride, afforded <u>exo</u>-norborneol.



XIII



The NMR spectra of the saturated adducts, VIIIa, VIIIb, and VIIIc, add further support to the structural assignment. The modified AB pattern is, in each case, attributed to H_2 and H_3. The chemical shift and coupling constant data are consistent with the proposed structure.[5,6] The protons H_2 and H_3 are seen to be further coupled, although to different degrees. We believe that this additional splitting can be attributed to coupling with the anti-7-hydrogen. Couplings of the magnitude observed (cf., Fig. I) are well precendented in norbornyl systems.[5,6] Spin decoupling of the 7-hydrogens (1.7 p.p.m.) in IXa leads to a sharpened AB quartet ($J_{2,3}$ = 7 cps). Moreover, decoupling of the bridgehead protons (i.e., H_1 and H_4) does not appreciably influence the nature of the AB patterns in the spectra of compounds VIIIb, VIIIc, or IXa. These observations strongly suggest that the adducts bear the oxadiazole ring in the exo-orientation, as shown in structures VIII and IX. If the protons H_2 or H_3 were exo, they would be expected to be coupled to the bridgehead protons to an observable extent (i.e., J. ca., 3-4 cps)[5,6]. Coupling of the bridgehead protons to endo-protons in norbornyl systems does not usually lead to observable splitting.[6,7]

The evidence presented here strongly supports the structural assignment, IXa, for the unsaturated adduct formed from norbornadiene and ethyl azodicarboxylate and VIIIa, VIIIb, and VIIIc for the adducts derived from norbornene and ethyl azodicarboxylate, phenyl azodicarboxylate and dibenzoyl diimide, respectively.

ACKNOWLEDGEMENT - The authors wish to express their appreciation to the National Science Foundation for financial support (GP-3525). We would also like to thank Dr. James G. Colson of the Hooker Research Center on Grand Island, New York for performing the spin decoupling experiments.

REFERENCES

1. S. J. Cristol, E. L. Allred, and P. L. Wetzel, J. Org. Chem., 27, 4058 (1962).
2. R. M. Moriarty, ibid., 28, 2385 (1963).
3. W. A. Thaler and B. Franzus, ibid., 29, 2226 (1964).
4. R. R. Frazer, Can. J. Chem., 40, 78 (1962).
5. P. Laszlo and P. von R. Schleyer, J. Am. Chem. Soc., 86, 1171 (1964); and references cited therein.
6. J. Davis and T. V. Van Auken, ibid., 87, 3900 (1965).
7. J. E. Franz, C. Osuch and M. W. Dietrich, J. Org. Chem., 29, 2922 (1964).
8. Phenyl hydrazodicarboxylate was prepared from phenyl chloroformate and hydrazine hydrate. The hydrazo compound was oxidized to phenyl azodicarbonylate following established procedures.[10,11]
9. N. Rabjohn, Org. Syn. Coll., Vol. III, 375 (1955).
10. S. G. Cohen, R. Zand and C. Steel, J. Am. Chem. Soc., 83, 2895 (1961).
11. Satisfactory analyses were obtained for all compounds reported herein.
12. J. E. Leffler and W. B. Bond, ibid., 78, 335 (1956).
13. R. Breslow, C. Yaroslavsky and S. Yaroslavsky, Chem. and Ind., 1961 (1961).