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PROPELLANES—XXXIX

^{13}C NMR-SPECTRA OF CONFIGURATIONALLY DIFFERENT PROPELLANE ISOMERS CONTAINING CYCLOPROPANE RINGS†

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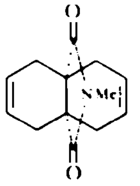
Abstract—The *mono*- and *bis*-adducts obtained in the reaction of carbethoxycarbene with 12-methyl-11,13-dioxo-12-aza[4.4.3]propella-3,8-diene have established configurations of cyclopropane rings and ester groups with respect to the hetero-ring. Thus ^{13}C NMR measurements afford data which correlates the ^{13}C absorptions of these isomers with their configurations.

Many products, 3 of 4 possible *mono*-adducts and 5 of 10 possible *bis*-adducts, obtained from the reaction of the methylimide 1 and ethyl diazoacetate in 1,2-dichloroethane at 80° in the presence of copper sulfate, have all been interrelated chemically.[1] (A sixth *bis*-isomer of unknown structure was also isolated.)[1] Since the structure including all configurational detail of an acid corresponding to one of the above 8 compounds was established unequivocally by X-ray crystallography,[2] the structures of all of these 8 products 2–9 are known in full configurational detail.

The table records the ^{13}C-chemical shift data relative to TMS for compounds **1–6**, **8** and **9**.

The spectral assignments allow comparison between



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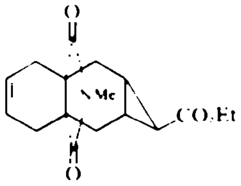

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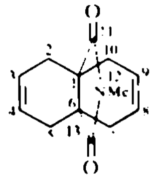

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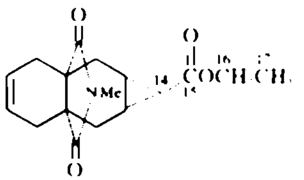

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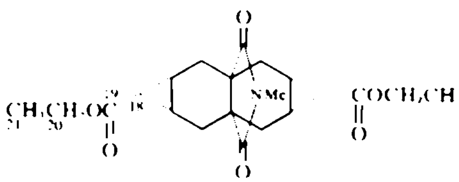

5, 6 **8, 9**

Compound	1	2	3	4	5	6	8	9
C_1; C_6	51.0	49.5	49.9	49.0	48.7	49.0	47.7	48.1
C_2; C_5	32.3	32.1	32.3	31.1	31.9	31.7	30.7	31.2
C_3; C_4	128.5	128.5	128.6	128.6	17.9	18.1	18.5	18.3
γ C_7; C_{10}	32.3	32.1	24.5	30.8	31.9	24.1	30.7	23.7
β C_8; C_9	128.5	18.0	20.2	19.3	17.9	20.1	17.6	20.1
C_{11}, C_{13}	182.5	182.5	~183	181.8	182.1	182.8	181.6	182.5
C_{12}	25.0	25.3	~25	24.7	25.5	25.3	24.9	24.9
α C_{14}	-	32.3	~29.5	32.6	30.7	28.3	30.1	28.3
C_{15}		172.5	~171	~172	172.7	171.7	172.7	171.5
C_{16}	-	60.6	~60	60.7	60.7	60.4	60.7	60.5
C_{17}	-	14.3	14.3	14.2	14.3	14.1	14.3	14.3
C_{18}	-			-	30.7	30.4	30.1	31.2
C_{19}		-	-	-	172.7	172.7	172.7	172.7
C_{20}	-				60.7	60.6	60.7	60.7
C_{21}	-	-	-	-	14.3	14.1	14.3	14.4

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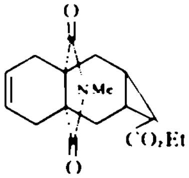
†Part XXXVIII. J. Kalo, E. Vogel and D. Ginsburg, *Tetrahedron* 33, 1183 (1977).



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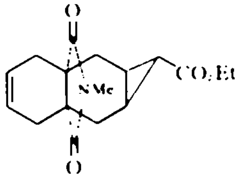

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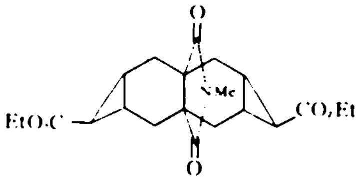

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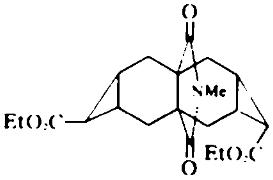

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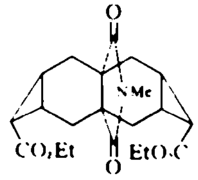

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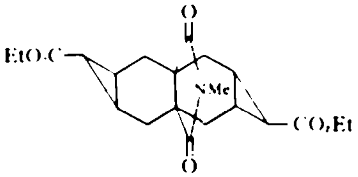

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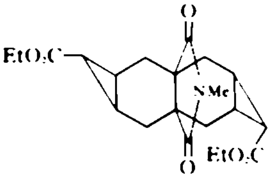

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the substrate **1**, the *mono*-adducts and the *bis*-adducts. They were checked by off resonance or gated decoupling. We observe small differences, e.g. an upfield shift of 0.5–1 ppm in **4** as compared to **2** but this can hardly be used as an unequivocal tool in assigning configuration. The more noticeable shifts (italicized in table) are associated with the cyclopropane ring which is *anti*- to the imide ring with the *endo*-ester group, i.e. a feature common to compounds **3**, **6** and **9** (as well as **7** for which we have no data).

The shifts in these compounds as compared to the isomers of other configurations are manifested particularly at the carbon atoms α, β and γ to the carbethoxy group, i.e. C_{14}, C_8 and C_9, C_7 and C_{10} in the order $\alpha > \gamma > \beta$. This may not be attributed simply to the γ-effect.[3]

EXPERIMENTAL

Measurements were conducted in $CDCl_3$ solution (50 mg in 1.5 ml). Insufficient quantity of **3** made for difficulty in accuracy. Not enough of **7** was available for measurement. A Bruker WP-60 instrument was used at 15.08 MHz.

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