LITERATURVERZEICHNIS

[1] *L. Maier*, Angew. Chem. *81*, 154 (1969); Helv. *53*, 1216 (1970).
[2] *Varian Associates*, NMR.-Spectra Catalog.
[3] *Organic Syntheses*, Vol. *3*, 394.
[4] *Y. Ueno, T. Nakai & M. Okawara*, Bull. chem. Soc. Japan *43*, 168 (1970).

---

167. Further Examples of Steric Inhibition to Cyclopropyl Conjugation in α, β-Unsaturated Esters

by **Margaret J. Jorgenson**[1] and **Hans-Ulrich Gonzenbach**[2]

Department of Chemistry, University of California, Berkeley, California 94720, USA

(1. VII. 70)

Zusammenfassung: Das UV.-Absorptionsmaximum des α,β-ungesättigten Esterchromophors wird in Cyclopropylacrylsäureestern durch den Dreiring bathochrom um ca. 24 nm verschoben [2]. Durch die Substitution mit Methylgruppen in den γ-(**2a, b**), α- und γ-(**3a, b**) sowie β- und γ-Stellungen (**1a, b**) wird gezeigt, dass dieser auxochrome Effekt stark von der Konformation abhängt und sogar negativ werden kann, wenn die für die Konjugation optimale bisektrische Lage von Dreiring und Doppelbindungsebene sterisch destabilisiert wird.

In the course of continuing investigations of the photochemistry of cyclopropylacrylic esters [1], we have synthesized and examined the spectral properties of four additional prototypes (**2a, b** and **3a, b**). Steric factors which come into play in cyclopropyl conjugative interaction are prominently embodied in these examples, and they provide experimental support to previous conclusions on this point.

We have previously [2] interpreted the hypsochromic shift of the ultraviolet spectrum of ester **1a** in terms of an antagonistic orthogonal alignment of the cyclopropane vis-à-vis the enoic ester chromophore. The apparent cause for this effect is the cyclopropane methyl substituent which inhibits the requisite bisected conformation even more strongly in the geometrical isomers of esters **2** and **3**[3]. UV. spectral data of the new compounds, together with those previously reported for esters **1a** and **1b**, are listed in the Table. In the *cis* series, the previously reported auxochromic effect is paralleled by a mild bathochromic effect in ester **2a** and an even larger hypsochromic shift for ester **3a**. In the *trans* series, the bathochromic effect is pronounced for **2b**, and largely attenuated for **3b**. A more meaningful relationship between structure and spectra becomes evident upon comparison with the parent cyclopropylacrylic ester, lacking the γ-methyl substituent on the cyclopropane methine carbon. It is immediately obvious that the effect of the γ-methyl substituent is to dramatically suppress any supplementary bathochromic effects derived from the methyl group, in

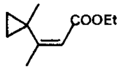
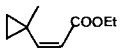
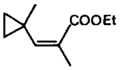
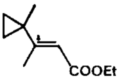
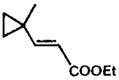
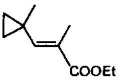
---

[1] Deceased on March 12, 1970.

[2] To whom correspondence should be addressed at the Laboratorium für Organische Chemie, Eidg. Technische Hochschule, 8006 Zürich, Switzerland.

[3] Prepared from 1-methylcyclopropylcarboxaldehyde and the appropriate phosphonate ester, and characterized spectrally and analytically. Distinction between *cis* and *trans* isomers was made on the basis of characteristic deshielding effects by the ester carbonyl on the olefinic hydrogen or β-allylic methyl group.

UV. and NMR. Spectral Data

Compound		$\lambda_{\max}^{\mathrm{EtOH}}$ [a] [nm]	log ε	Auxochromic effect ($\Delta\lambda$) of cyclopropyl group [b] [nm]	Auxochromic effect ($\Delta\lambda$) of γ-CH_3 group [c] [nm]	Proton magnetic resonance, chemical shifts [δ] α-H	β-H	α-CH_3	β-CH_3	γ-CH_3
1a[d]		217	4.17	– 3.5	– 21	5.63	–	–	1.85	1.20
2a		211	3.88	+ 3	– 21	5.63	6.04	–	–	1.25
3a		210	3.85	– 7.5	– 28	–	5.80	1.82	–	1.20
1b[d]		231	4.08	+13.5	– 5	5.70	–	–	2.05	1.22
2b		232	4.31	+24	+ 1	5.70	6.37	–	–	1.22
3b		224	4.06	+ 7	–10.5	–	6.68	1.97	–	1.27

[a] Spectra were obtained as reported in [2].

[b] Compared to non-cyclopropyl model, where the 1-methylcyclopropyl substituent is equated with either a *t*-butyl (compounds **1a**, **b**) or isopropyl group (compounds **2a**, **b** and **3a**, **b**).

[c] Compared to parent system, cyclopropylacrylic esters lacking γ-methyl group [2].

[d] Data from reference [2].

contrast to the effects found for methyl groups located on cyclopropane methylene carbons. In almost every case large attenuation of the overall effectiveness of the cyclopropane in extending the chromophore is evident.

From consideration of the inductive contribution on the *p*-components of the cyclopropane bonds, the bathochromic effect of the methine methyl group should be pronounced; this has been born out experimentally in a number of ketones [3]. The large hypsochromic effect in **3a** is particularly startling, since the maximum seems to be indicative of the operation of an electron withdrawing effect, relative to an isopropyl group, by the cyclopropane substituent[4]. It is worth noting that the methyl group in **3** is more accomodating sterically than the carbethoxy group, since in contrast to **3a**, the *trans* isomer **3b** still exhibits a bathochromic shift. SM. interference to coplanarity of the enoic ester chromophore in **3a** might be a contributing factor to this difference.

The NMR. spectra (data listed in the Table) of esters **2** and **3** corroborate the conformational interpretation of these auxochromic effects. The reference model,

---

[4] Electron withdrawing effects, relative to isopropyl, have been noted in a number of examples, where the favorable bisected conformation is structurally precluded: see references [4].

trans ethyl 4,4-dimethyl-2-pentenoate, exhibits a doublet for the α- and β-hydrogens, respectively, at 5.56 and 6.75 δ. The cyclopropyl analog **2b**, which possesses an almost normal UV. spectrum, exhibits chemical shifts for the corresponding α- and β-hydrogens at 5.70 and 6.37 δ. The upfield shift of the β-hydrogen by 0.38 is consonant with the expected appreciable population by this ester of the favorable bisected conformation which leads to substantial shielding effects on the β-proton. By contrast, this *cis* isomer **2a** lacks this shielding phenomenon; the β-hydrogen is virtually indistinguishable in its chemical shift (6.04 δ) from that in the acyclic model, *cis* ethyl 4,4-dimethyl-2-pentenoate. For the isomeric pair **3a–3b**, for which a precise acyclic model is not available, downfield shifts of the β-hydrogen can be recognized in comparison with *cis* and *trans* ethyl 2,4-dimethyl-2-pentenoates.

Financial support by the *National Science Foundation* (USA) is gratefully acknowledged.

BIBLIOGRAPHY

[1] *M.J.Jorgenson*, J. Amer. chem. Soc. *91*, 6432 (1969).
[2] *M.J.Jorgenson & T.Leung*, J. Amer. chem. Soc. *90*, 3769 (1968).
[3] *W.G.Dauben & G.H.Berezin*, J. Amer. chem. Soc. *89*, 3449 (1967); *J.Pete*, Bull. Soc. chim. France *1967*, 357.
[4] *T.L.Brown, J.M.Sandri & H.Hart*, J. phys. Chemistry *61*, 698 (1957); *J.C.Martin & B.R. Ree*, J. Amer. chem. Soc. *91*, 5882 (1969); *P.v.R.Schleyer & V.Buss*, *ibid.* *91*, 5880 (1969); *H.C.Brown & J.D.Cleveland*, *ibid.* *88*, 2051 (1966).

---

168. Dünnschichtchromatographie anorganischer Ionen

11. Mitteilung

Trennung verschiedener Oxydationsstufen von Vanadium

von **H. Seiler**

Institut für Anorganische Chemie, Universität Basel

(8. VII. 70)

Summary. The separation of V^{III}, V^{IV} and V^{V} by thin-layer chromatography is described.

Wie wir schon früher [1] zeigen konnten, beruht die chromatographische Trennung von Ionen an Kieselgel-Dünnschichten auf Ionenaustausch, gekoppelt mit Komplexbildung. Durch geeignete Wahl des Fliessmittels können auch die aus den verschiedenen Oxydationsstufen eines Elements resultierenden Ionen voneinander getrennt werden, falls sie sich in ihrer Ladung bzw. in der Stabilität ihrer Komplexe unterscheiden.

Die vorliegende Arbeit beschreibt die Trennung von V^{III}, V^{IV} und V^{V} mittels stark saurer Fliessmittel; es kann also angenommen werden, dass V^{III-V} jeweils als Kation vorlag, d.h. als V^{3+}, VO^{2+} bzw. VO_2^+. Untersucht wurden frisch hergestellte Lösungen von $NH_4V(SO_4)_2 \cdot 12H_2O$, $VOSO_4$ und NH_4VO_3. Als Fliessmittel dienten *n*-Butanol ges. mit 1N HCl, mit 1N H_2SO_4 oder mit 1N $HClO_4$, wobei nur mit *n*-Butanol ges. mit 1N HCl alle drei Oxydationsstufen verschiedene Steighöhen auf-