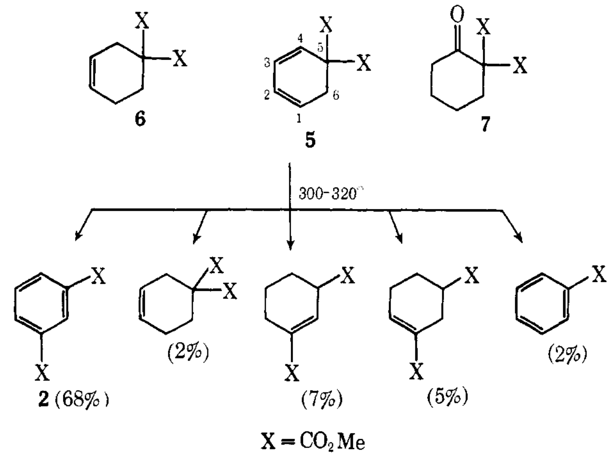
[1,3]-carbomethoxyl migration, was thus excluded. Although the data permit a mechanism with two successive [1,3] migrations, it is not obvious why the intermediate **4** in this process should not readily lose methyl formate[10] or acetic acid to give methyl acetylsalicylate or **2**-*4*-*d*, respectively, neither of which was among the products. The [1,5]-shift mechanism fits the observations without special assumptions.

The presence of the acetoxyl function is not a necessary feature for the carbomethoxyl rearrangement. Thus, pyrolysis at 300–320° for 1 hr (97.5% conversion) of 5,5-dicarbomethoxycyclohexa-1,3-diene (**5**) (prepared by straightforward transformations from either 4,4-dicarbomethoxycyclohexene (**6**)[11] or 2,2-dicarbomethoxycyclohexanone (**7**)[12]) although complicated by the formation of the disproportionation products shown (Scheme II) gave dimethyl isophthalate (**2**) as the major product (yields determined by vpc with diphenyl ether internal standard). Pyrolysis at lower temperatures permitted the isolation of unstable intermediates of the same oxidation state as **5**, which were readily converted to dimethyl isophthalate (**2**) upon further pyrolysis.

Scheme II



The rearrangement of diene **5** to dimethyl isophthalate (**2**) was shown to be intramolecular by the absence of **2**-d_3 in the products from pyrolysis of a mixture of **5**-d_6 (X = CO_2CD_3) and **5**-d_0 (X = CO_2CH_3).

Ring-labeled diene diester **5**-*4*-*d*, prepared from **7** by a sequence beginning with $NaBD_4$ reduction, gave on pyrolysis to 10% completion dimethyl isophthalate in which isomer **2**-*4*-*d* predominated over isomer **2**-*2*-*d* by a factor of 8.[13] This was again consistent with overall predominance of [1,5] (or two successive [1,3]) shifts rather than a single [1,3] shift.

Of course, the stereochemical inversion associated with concerted [1,3] migration of alkyl groups[14] (sp^3 hybridized in the reactant) cannot be observed in [1,3] migration of carbomethoxyl (sp^2 hybridized in the reactant). Nevertheless, orbital symmetry imposes an "opposite-face" type of bonding during suprafacial [1,3] migration even of carbomethoxyl because of the need to use both lobes of an antisymmetric orbital (ideally p) in the construction of the basis set for the transition state. This rehybridization forces the remaining σ bonds of the migrating carbon to have more s character in the transition state than in the ground state, a change that is opposed by electronegative substituents on the migrating carbon. The [1,5] transition state does not require this, and the energetic benefit so conferred must be a contributing factor in the [1,3] *vs.* [1,5] competition.

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[10] In model experiments, pyrolyses of dimethyl 1,4-dihydrophthalate and of 6,6-dicarbomethoxycyclohexa-1,4-diene gave methyl benzoate as a major product.

[11] (a) K. Alder and H. F. Rickert, *Chem. Ber.*, **72**, 1989 (1939); (b) G. B. Bachmann and H. A. Tanner, *J. Org. Chem.*, **4**, 493 (1939).

[12] *Cf.* J. P. Ferris, B. G. Wright, and C. C. Crawford (*ibid.*, **30**, 2367 (1965)) for the diethyl ester **7** (X = CO_2Et).

[13] Longer pyrolyses gave product **2** with lower deuterium position specificity and lower total deuterium content because of a competing degenerate rearrangement in **5**.

[14] (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 114 ff; (b) J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **89**, 5503 (1967); **92**, 1096 (1970); (c) J. A. Berson, *Accounts Chem. Res.*, **1**, 152 (1968).

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A Thermal Shift of Carbethoxy and Carbomethoxy Groups

Sir:

Sigmatropic 1,5 shifts of species other than hydrogen have been reported for the cyano,[1a] methyl,[1b] and alkyl groups.[1c] In this communication we report evidence for an intramolecular shift of carbethoxy and carbomethoxy groups.

With the synthesis of diethyl cyclohexa-2,4-diene-1,1-dicarboxylate (**2a**) in mind, diethyl 2-acetoxycyclohex-3-ene-1,1-dicarboxylate (**1**),[2] prepared from 1-acetoxy-1,3-butadiene[3] and diethyl methylenemalonate,[4] was pyrolyzed in a flow system[5] at 420°. To our surprise, isophthalic acid was isolated, in 16% yield, after saponification of the pyrolysate. The formation of an isophthalic acid skeleton from **1** (or **2a**) intrigued us since it was unprecedented and it required a 1,3 (or

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[1] (a) E. Ciganek, *J. Amer. Chem. Soc.*, **89**, 1458 (1967); J. A. Berson, P. W. Grubb, R. A. Clark, D. R. Hartter, and M. R. Willcott, III, *ibid.*, **89**, 4076 (1967); (b) V. A. Mironov, V. S. Pashegorova, T. M. Fadeeva, and A. A. Akhrem, *Tetrahedron Lett.*, 3397 (1968); (c) R. Grigg, A. W. Johnson, K. Richardson, and K. W. Shelton, *Chem. Commun.*, 1192 (1967); V. Boekelheide and E. Sturm, *J. Amer. Chem. Soc.*, **91**, 902 (1969).

[2] Satisfactory elemental and spectral analyses were obtained for new compounds. Elemental analyses by George Robertson, Florham Park, N. J.

[3] H. J. Hagemeyer and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

[4] W. Feely and V. Boekelheide, "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 298.

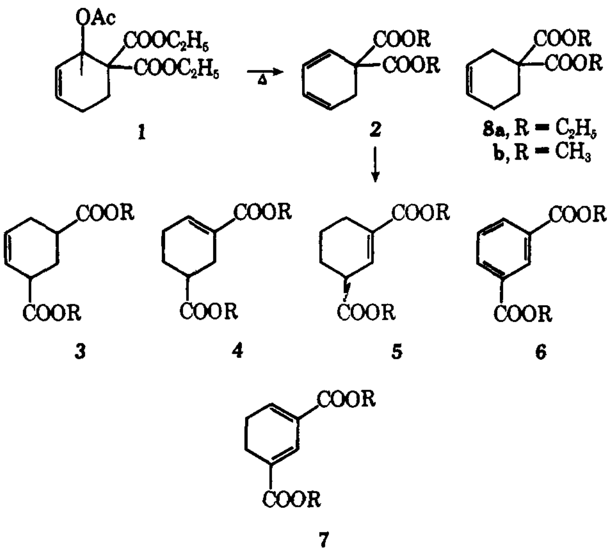
[5] For a description of the apparatus used, see: W. J. Bailey and H. R. Golden, *J. Amer. Chem. Soc.*, **75**, 4780 (1953).

1,5) shift of the carbethoxy group and a dehydrogenation step from intermediate **2a**. Several questions about this rearrangement remained unanswered and since the pyrolysis of an ester could be run under comparatively mild conditions for the formation of some thermally unstable compounds,[6] we undertook a reinvestigation of the problem.

The pyrolysis of **1** was run in methanol solution and as a pure liquid at 410 and 455°.[7] The pyrolysates were analyzed by gas chromatography[8a] after extraction of a pentane solution with water (to remove acetic acid) and after distillation. In addition to the expected three ethyl cyclohexadiene carboxylates,[9] five compounds with a ratio of 6:10:70:7:7 were present. Each one was isolated by preparative gas chromatography and analyzed by high-resolution mass spectrometry.

Compounds a, b, and c had identical molecular ion values, *m/e* 226.1204 (calcd for $C_{12}H_{18}O_4$: 226.1216), and similar fragmentation patterns, loss of OC_2H_5 and $COOC_2H_5$. Compound a had no uv absorption, while b and c showed absorptions at 232 and 229 nm, respectively. We conclude, therefore, that a, b, and c are the three diethyl cyclohexenedicarboxylates **3**, **4** and **5**.[10] Compound d proved to be diethyl isophthalate (**6**), identified by its spectral properties and retention time compared to an authentic sample. The final compound, e, was one of the cyclohexadiene diesters herein depicted as **7**: *m/e* 224.1048 (calcd for $C_{12}H_{16}O_4$: 224.1040); λ_{max} 288, 279, and 236 nm. At this point it was evident that a 1,3- or 1,5-carbethoxy shift occurred, with **2** as a key intermediate. Diethyl isophthalate (**6**) and the three cyclohexene diesters, **3**, **4**, and **5**, arise by a disproportionation of cyclohexadiene diesters.[11]

Since the intermediacy of **2a** was implied for the formation of **3** to **7**, it was considered necessary to synthesize it by an unequivocal route and subject it to the same pyrolytic conditions. Accordingly, **2a** (bp 80° (0.4 mm); nmr δ 2.77 (d, 2, J = 2.0 Hz, CH_2), 5.83 (m, 4, CH=CHCH=CH); uv $\lambda_{max}^{CH_3OH}$ 258 nm (ϵ 3100)) was synthesized from diethyl cyclohex-3-ene-1,1-dicarboxylate (**8a**)[12] by interaction with *N*-bromosuccinimide and dehydrobromination of the resulting allylic bromide. Identical results were obtained when **2a** was pyrolyzed at 455°.



1 2 8a, R = C_2H_5 b, R = CH_3

3 4 5 6

7

It was conceivable that the rearrangement could occur either by an intramolecular shift or an intermolecular shift, the latter involving homolytic cleavage and recombination of a carboethoxy group. We chose to establish this aspect of the mechanism by subjecting a mixture of diethyl and dimethyl esters, **2a** and **2b**, to pyrolysis. Dimethyl cyclohexa-2,4-diene-1,1-dicarboxylate (**2b**), bp 70° (0.35 mm) (nmr and uv spectra similar to **2a**), was prepared similarly to **2a**, after diazomethane esterification of the diacid (**8**, R = H). An equimolar mixture of **2a** and **2b** was pyrolyzed at 455°, and the pyrolysate was analyzed by mass spectrometry. In addition to the molecular ions derived from rearrangement and disproportionation reactions described above for **2a**, those corresponding to **2b** were present. However, the mixed ester (methyl ethyl isophthalate), having a molecular weight of 208, did not appear in the spectrum. It must be concluded, therefore, that a 1,3- or 1,5-carbethoxy and -carbomethoxy shift occurred intramolecularly.

Both 1,3- and 1,5-carbalkoxy shifts are allowable on the basis of orbital symmetry rules.[13] Experiments are under way to tell us whether either or both shifts can occur.

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[6] W. J. Bailey and R. A. Baylouny, *J. Org. Chem.*, **27**, 3476 (1962).

[7] Glass helices in the pyrolysis tube were examined after each run. They were found to be as clean as they were before pyrolysis except for a small area at the top and bottom of the helices. Carbonization of helices has been considered as a possible cause for rearrangements of acid-sensitive compounds [*cf.* W. J. Bailey, J. Rosenberg, and L. J. Young, *J. Amer. Chem. Soc.*, 77, 1163 (1955)].

[8] (a) Analytical gas chromatograms were obtained with a 6 ft × 0.25 in., SE-30 column at 190°, a 10 ft × 0.25 in., 25% XF-1150 column at 185°, and a 6 ft × 0.125 in., 8% SF-96 column at 190°. (b) Preparative runs were obtained with a 10 ft × 0.375 in., 10% Carbowax 20M column at 190° and a 6 ft × 0.275 in., 25% Carbowax 1540 column at 190°.

[9] These compounds were formed by an elimination of acetic acid and decarbethoxylation of **1**. The isomers originate from 1,5-hydrogen shifts of the corresponding diene [*cf.* W. J. Bailey, R. Barclay, and R. A. Baylouny, *J. Org. Chem.*, **27**, 185 (1962)].

[10] Our data do not allow a distinction between the two conjugated unsaturated esters, **4** and **5**.

[11] The 1,2- and 1,4-positional isomers can be further ruled out since they would be expected to give only one conjugated unsaturated diester with the same uv absorption.

[12] G. B. Bachmann and H. A. Tanner, *J. Org. Chem.*, **4**, 493 (1939).

[13] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).