cyclopropyl ring, the product is very largely unrearranged.

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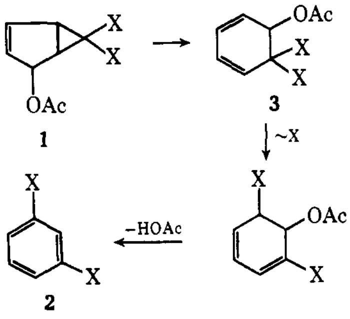
Thermal Sigmatropic Migration of the Carbomethoxyl Group

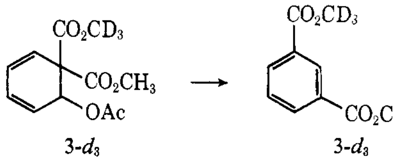
Sir:

Although there are scattered reports of photochemical[1] and thermal[2-4] carbomethoxyl group migrations, one of the few previous examples of a thermal process, the rearrangement of 5-carbomethoxy-1,5-dimethylbicyclo[2.1.0]pentane to 3-carbomethoxy-1,2-dimethylcyclopentene, has been interpreted[3] as a 1,2 shift in a diradical intermediate. Our observation that gas-phase pyrolysis at 295° of 6,6-dicarbomethoxybicyclo[3.1.0]hex-3-en-2-yl acetate (**1**, X = CO_2Me) gave a quantitative yield of acetic acid and *dimethyl isophthalate* (**2**, X = CO_2Me) therefore assumed special significance, because the 1,2-shift mechanism would have led to dimethyl phthalate instead. The present work elucidates the mechanism of the **1** → **2** rearrangement and establishes the occurrence of intramolecular thermal sigmatropic rearrangements of carbomethoxyl groups in this and related systems.

As a working hypothesis, we assumed that the rearrangement might occur by preliminary isomerization of **1** to the acetoxydiene diester **3**, which then might undergo [1,5] (or [1,3]) carbomethoxyl migration and elimination to **2**. A necessary condition for this mechanism was satisfied by the observation that pyrolysis of independently synthesized **3**[5,6] gave acetic acid and **2** quantitatively. Rough kinetic measurements indicated that the **3** → **2** rearrangement was not very much faster than the overall **1** → **2** process. Acetoxydiene **3** thus accumulated during incomplete pyrolysis of **1** and could be isolated (in addition to **2**) by thin-layer chromatography of the mixture obtained from pyrolysis of **1** to 38% conversion.

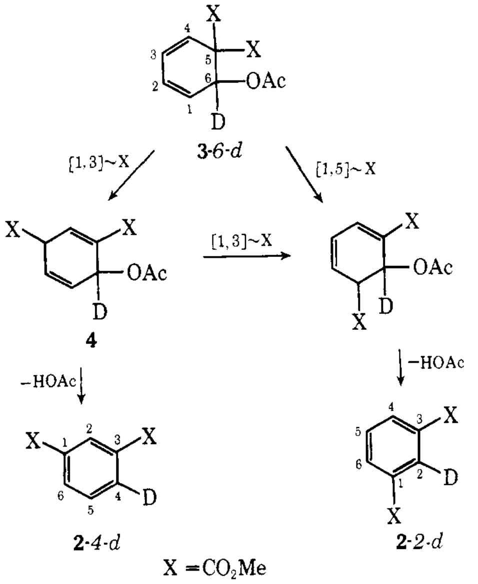


Pyrolysis of acetoxydiene **3**-d_3 (prepared by the synthesis already described[5] with the modification that the esterification was carried out with methyl-d_3 *p*-toluenesulfonate) gave **2**-d_3 containing no **2**-d_0 or **2**-d_6 (analysis by mass spectrometry). This excluded a radical-chain mechanism and demonstrated the complete intramolecularity of the **3** → **2** rearrangement.



Scheme I shows how examination of the dimethyl phthalate (**2**) obtained from pyrolysis of ring-labeled acetoxydiene (**3**-*6*-*d*) provides the basis for a distinction between two mechanistic categories: (i) direct [1,3]-carbomethoxyl migration and (ii) direct [1,5] or two successive [1,3] shifts. The 100-MHz nmr spectrum of ordinary dimethyl isophthalate (**2**) had absorptions at δ 7.5, H_5 (1 H, t, J = 8 Hz), 8.2, H_4, H_6 (2 H, d of d, J = 8, 2 Hz), and 8.7, H_2 (1 H, t, J = 2 Hz). The dimethyl isophthalate recovered from pyrolysis of **3**-*6*-*d*[7] to 15% conversion showed the complete absence of the absorption at δ 8.7 (H_2) and was therefore at least 95% **2**-*2*-*d*.[8] Mechanistic category i, involving a single

Scheme I



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(1) See, for example, D. M. Madigan and J. S. Swenton, *J. Amer. Chem. Soc.*, **92**, 7513 (1970).

(2) M. J. Jorgenson and T. J. Clark, *ibid.*, **90**, 2188 (1968).

(3) A thermal acetyl group migration has been observed (H. Monti and M. Bertrand, *Tetrahedron Lett.*, 1235 (1969)] and briefly discussed theoretically [N. Trong Anh, "Les Regles de Woodward-Hoffmann," Ediscience, Paris, 1970, p 50] although formal proof of its intramolecularity remains to be supplied.

(4) Thermal cyano group rearrangements also have been observed [E. Ciganek, *J. Amer. Chem.Soc.*, **89**, 1458 (1967)].

(5) Sodium-ammonia-ethanol reduction of anisic acid followed by esterification (CH_2N_2) and carbomethoxylation [$LiN(i\text{-}Pr)_2$, $ClCO_2Me$] gave 1-methoxy-6,6-dicarbomethoxycyclohexa-1,4-diene, which upon hydrolysis to the ketone and $NaBH_4$ reduction was converted to 3,3-dicarbomethoxy-4-hydroxycyclohexene. Acetylation, allylic bromination (*N*-bromosuccinimide), and dehydrobromination (diazabicycloundecane) gave **3**.

(6) New substances were characterized by elemental analyses and spectroscopic properties.

(7) Prepared by the synthesis described in ref 5 with the exception that $NaBD_4$ was used in place of $NaBH_4$.

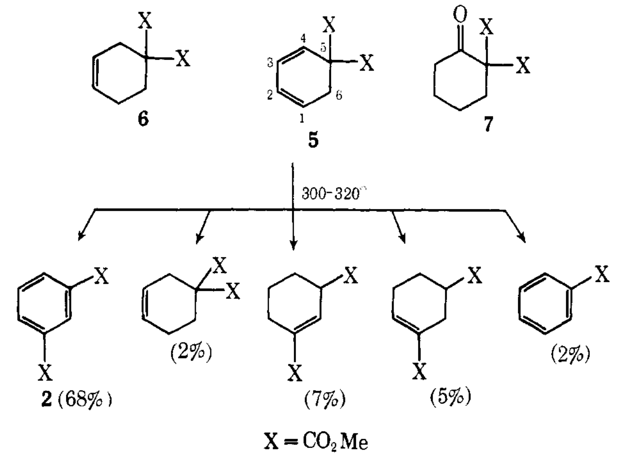
(8) The product isolated from higher conversion showed some absorption at δ 8.7, but this was ascribable to a competing degenerate rearrangement (of H or OAc?) of the starting material **3**-*6*-*d* which mixed protium at C_4 and deuterium at C_6, as was demonstrated by the nmr spectra of trisdipivaloylmethanatoeuropium [$(DPM)_3Eu$] treated[9] samples of ring-labeled **3** isolated from partial pyrolyses.

(9) (a) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969); (b) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

[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.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are also grateful to the National Institute of General Medical Sciences (GM-16962) and the National Science Foundation (GP-11017X) for research grants and to the latter agency for an institutional grant (GU-3282).

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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).

[15] Supported by National Institute of General Medical Sciences Predoctoral Fellowship No. GM-37,991.

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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).