Table VII. Intermolecular Contacts Less than 3.6 Å

Atom 1	Atom 2	Symmetry[a]	Distance, Å
C(3)	C(3)	$-x+1, -y+1, -z+1$	3.557
C(4)	C(18)	$-x+1, -y+1, -z+1$	3.406
C(9)	C(18)	$-x+1, -y+1, -z+1$	3.596
C(14)	C(16)	$-x, -y+2, -z$	3.516
C(15)	C(15)	$-x, -y+2, -z$	3.527
O(1)	C(20)	$x, y-1, z+1$	3.425
O(1)	O(1)	$-x+1, -y+2, -z+1$	3.096
O(1)	N(1)	$-x+1, -y+2, -z+1$	3.417
O(1)	C(10)	$-x+1, -y+2, -z+1$	3.194
O(2)	O(3)	$x+1, y, z$	3.262
O(2)	O(4)	$-x+1, -y+1, -z+2$	3.231
O(3)	C(13)	$x-1, y+1, z-1$	3.392
O(3)	C(16)	$-x+1, -y+1, -z+1$	3.474
O(3)	O(4)	$-x+2, -y+1, -z+2$	2.667
O(3)	C(19)	$-x+2, -y+1, -z+2$	3.515
O(4)	C(12)	$-x+1, -y+2, -z+1$	3.313
O(4)	C(13)	$-x+1, -y+2, -z+1$	3.271
O(4)	O(4)	$-x+2, -y+1, -z+2$	3.267
O(4)	C(19)	$-x+2, -y+1, -z+2$	3.356

[a] Transformation to be applied to the coordinates of atom 1 as listed in Table III. Only contacts between heavy atoms are tabulated here.

acid group about centers of inversion to form molecular dimers. The dimensions of the hydrogen bond dimer are given in Figure 5. Although it has been pointed out by Donohue[34] that the β-carbon atom of the carboxylic acid hydrogen bond dimer is usually coplanar with the carboxylate group, the β-carbon in indomethacin, C(3), is 0.76 Å out of the carboxylate plane (Figure 5). The second important feature of the crystal packing is the overlapping of the indole ring with the acetic acid group of another molecule. A view of the crystal packing normal to the indole ring is given in Figure 6, and the overall crystal packing is illustrated in Figure 7. Intermolecular distances between heavy atoms closer than 3.6 Å are collected in Table VII.

(34) J. Donohue, *Acta Crystallogr., Sect. B*, 24, 1558 (1968).

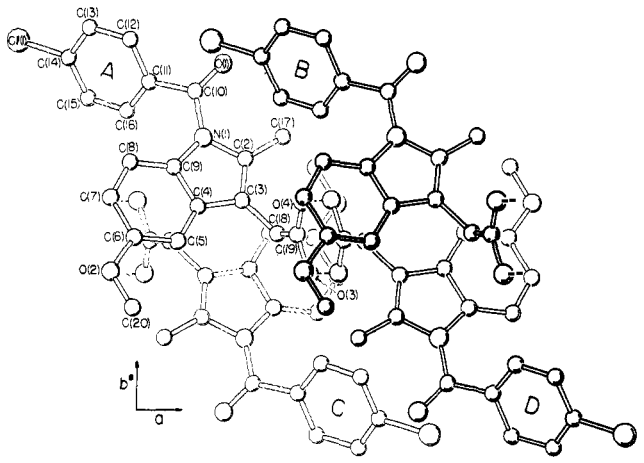


Figure 7. A view normal to the *ab** plane of the crystal packing in indomethacin. The labeled molecules and their symmetry transforms relative to the coordinates in Table III are: A: x, y, z; B: $1+x, y, 1+z$; C: $1-x, 1-y, 1-z$; D: $2-x, 1-y, 2-z$.

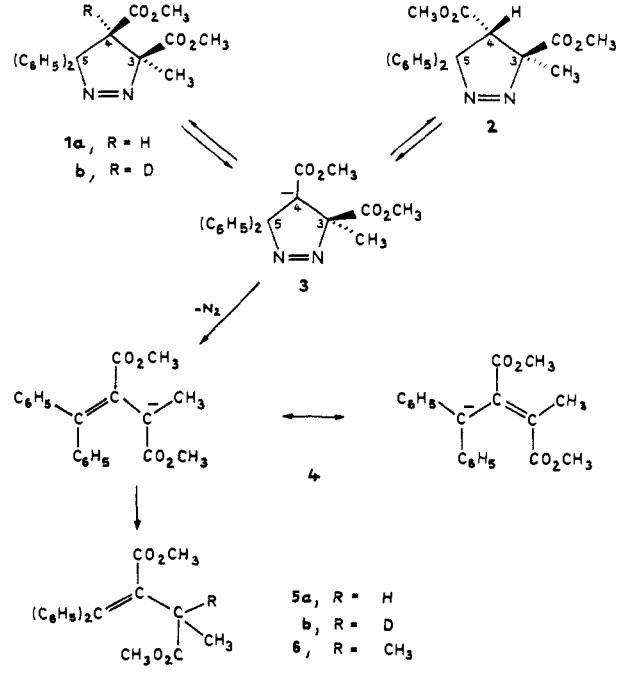
Communications to the Editor

Formation of an Allyl Anion from 1-Pyrazolin-4-yl Anion by Cycloreversion. Electronic Prototype of 1,3-Dipolar Cycloaddition

Sir:

1,3-Dipoles are heteroallyl anions[1] and their cycloadditions are symmetry-allowed concerted processes of the type $_{\pi}2_s + {}_{\pi}4_s$.[2,3] The combination of an allyl anion with ethylene to form a cyclopentyl anion[3] may be regarded as the still unknown electronic prototype of a 1,3-dipolar cycloaddition. The addition of cyclopentadienylmagnesium bromide to benzyne[4] comes perhaps closest to this prototype; however, there is no evidence about the concertedness of this reaction. We wish to report on the formation of an allyl anion by a 1,3-cycloreversion reaction, the fast rate of which suggests the absence of high-energy intermediates.

On treatment of dimethyl *cis*- or *trans*-3-methyl-5,5-diphenyl-1-pyrazoline-3,4-dicarboxylate[5] (**1a** or **2**) with



(1) R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, 2, 633, 644 (1963); *J. Org. Chem.*, 33, 2291 (1968).
(2) R. B. Woodward and R. Hoffmann, *Angew. Chem.*, 81, 797, 833 (1969).
(3) A. Eckell, R. Huisgen, R. Sustmann, G. Wallbillich, D. Grashey, and E. Spindler, *Chem. Ber.*, 100, 2192, 2212 (1967).
(4) W. T. Ford, R. Radue, and J. A. Walker, *Chem. Commun.*, 966 (1970).
(5) W. M. Jones and W.-T. Tai, *J. Org. Chem.*, 27, 1030 (1962).

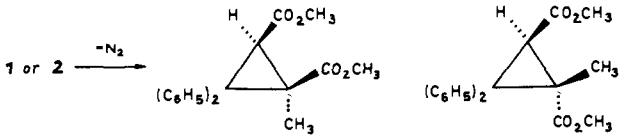
sodium hydride in dimethylformamide (DMF) or with dimsylsodium in dimethyl sulfoxide (DMSO) at room temperature, nitrogen (and H_2 in the case of the NaH reaction) was eliminated and a deep-red solution of the allyl anion **4** (configuration unknown) was obtained as its sodium salt. The solution was stable for several days if kept with the usual precautions for handling metalorganic compounds. Acidification was accompanied by immediate decolorization and gave >90% of dimethyl 1,1-diphenyl-1-butene-2,3-dicarboxylate[6] (**5a**, mp 80.5–81.5°, ν_{CO}(KBr) 1701 and 1743 cm^{-1}). The Stobbe condensation of benzophenone and dimethyl methylsuccinate produced an ester acid (94%), which furnished **5a** with diazomethane.

Deuterium exchange experiments reveal the virtually quantitative formation of the allyl anion **4**. After treatment of the pyrazoline **1a** with an excess of dimsylsodium in DMSO and quenching of the allyl anion **4** after 45 min with CH_3–CO_2D + CH_3OD, we isolated 85% of the diester **5**, containing the H and D species, **5a** and **5b**, in the ratio 8:92. The analogous reaction of the deuterated pyrazoline **1b** with dimsylsodium and acidification by CH_3–CO_2H + CH_3OH after 3 min produced 69% of diester **5a** with no detectable amount of **5b**. The red color of **4** also disappeared when methyl bromide was introduced; the product of methylation, **6** (mp 101–103°; nmr ($CDCl_3$) τ 6.58 and 6.59 (2- and 3-CO_2CH_3, s), 8.64 (2-CCH_3, s)), was formed in 95% yield.

Corresponding experiments were carried out with **1a**, **1b**, and sodium hydride in DMF. Under these heterogenous conditions, H,D and D,H exchanges in the conversion **1** → **5** were less complete, *i.e.*, deuteration after 45 min gave **5a** and **5b** in a 25:75 ratio (100% yield), whereas protonation yielded **5a** and **5b** in a 73:27 ratio. Evidently, the allyl anion **4** competes with NaH in the deprotonation of **1**. This phenomenon was further illustrated by treatment of **1a** with NaH in dioxane, which gave **5a** without generation of a red color. Here the NaH, which acts as a catalyst, produces the allyl anion **4** in a small stationary concentration and induces an anion chain reaction: **1a** + **4** → **3** + **5a**; **3** → N_2 + **4**.

Is the 1-pyrazolin-4-yl anion **3** an intermediate in the process **1** → **4** or does the loss of N_2 occur simultaneously with the deprotonation of **1**? Sodium methoxide in methanol established a 79:21 equilibrium of the *cis*-pyrazoline **1a** and the trans isomer **2** without any evolution of N_2. Also, H,D exchange in position 4 of the pyrazolines **1a** and **2** by $NaOCH_3$–CH_3OD occurred readily (90–98% D). As expected, protonation and deuteration of the anion **3** are faster than its cycloreversion. The assumption is plausible that **3** is also an intermediate in the nitrogen elimination in the aprotic solvents DMSO and DMF.

What makes it probable that the pyrazolin-4-yl anion **3** suffers a *one-step concerted* nitrogen loss to form the allyl anion **4** in a reaction that corresponds to a 1,3-dipolar cycloreversion? The anion **4** eliminates nitrogen >10^{12} times faster than does the neutral pyrazoline **1a**. The thermolysis of the pyrazolines **1a** and **2** produced the cis,trans isomeric cyclopropanes **7** without admixture of the olefinic diester **5**; **7a** and **7b** were obtained in a 32:68 ratio from **1a** and in a 3:97 ratio from **2** in benzonitrile at 120°. Kinetic measurements of N_2 evolution from **1a** at four temperatures led to $\Delta H^{\ddagger}$ = 29.2 kcal mol^{-1} and $\Delta S^{\ddagger}$ = +2 eu. At −40°, $\Delta G^{\ddagger}$ would be 28.7 kcal mol^{-1}.



7a **7b**

Sodium triphenylmethide in tetrahydrofuran induced N_2 evolution from **1a** at −40° in a pseudo-first-order reaction[7] with k_1 = 2.5 × 10^{-4} sec^{-1}. Provisional rate comparison of the pyrazolines **1a** and **1b** revealed $k_H/k_D \approx 6$ at −20°. This isotope effect suggests the deprotonation of the pyrazoline to be rate determining.

$$\mathbf{1a} + (C_6H_5)_3C^- \underset{}{\overset{k_1}{\rightleftharpoons}} \mathbf{3} + (C_6H_5)_3CH$$

$$\mathbf{3} \xrightarrow{k_2} \mathbf{4} + N_2$$

The absence of an induction period in the nitrogen evolution allows the estimate $k_2 > 10k_1$. Thus, the process **3** → **4** must have an activation barrier $\Delta G^{\ddagger}$ < 16.3 kcal mol^{-1} at −40°. Therefore, *the 1,3 cycloreversion of the pyrazolin-4-yl anion* **3** *to the allyl anion* **4** + N_2 *has an activation energy more than 12 kcal* mol^{-1} *lower than that of the conversion of the pyrazoline* **1a** *to the cyclopropanes* **7** *via the trimethylene species.*[8] This marked difference is in agreement with a concerted N_2 elimination from **3** without formation of reactive intermediates. Rate differences for nitrogen elimination have been used earlier to distinguish between orbital symmetry-allowed and symmetry-forbidden processes.[9]

Do not solvation phenomena devaluate the mechanistic significance of a rate comparison between the breakdown of the neutral pyrazoline and the fragmentation of its anion **4**? THF solvates anions less than cations. The anionic charge is more highly dispersed in the product **4** than in the reactant **3**. Therefore, an enhancement in solvation forces would probably retard the process **3** → **4** and decrease the $\Delta\Delta G^{\ddagger}$ of the two reactions.

(6) All new compounds gave satisfactory elementary analyses and were spectroscopically characterized.

(7) The zero order in base, which was used in nearly stoichiometric amount, shows its catalytic activity. That the allyl anion is as active as the triphenylmethide anion in the deprotonation of **1a** seems to offer the simplest explanation.

(8) R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, **88**, 3963 (1966).

(9) N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *ibid.*, **91**, 5668 (1969).

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Electrocyclic Ring Opening of a Cyclopropyl Anion to an Allyl Anion

Sir:

Woodward and Hoffmann[1] predicted conrotation for the thermal ring opening of the cyclopropyl anion to the

(1) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).