Reactions of Benzotriazoles with Diethyl Ethoxymethylenemalonate; Ethylation and Michael Addition. Comparison with Other Esters and *N*-Heterocycles

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Benzotriazole and its 5-methyl- and 5-nitro derivatives react with diethyl ethoxymethylenemalonate by ethylation at each of the ring *N*-atoms and through Michael addition, to give the isomeric esters ethyl (*E/Z*) 3-[5(6)-R-benzotriazol-1-yl]propenoates. Benzotriazole and its 5-nitro derivative react similarly with ethyl acetoacetate but *N*-ethyl derivatives are obtained in lower yields. Other 1,2,3-triazoles derivatives and indole were ineffective in this reaction while benzimidazole produced similar results but accompanied with a small amount of a benzimidazoline addition product, whose structure has been determined by crystallographic analysis.

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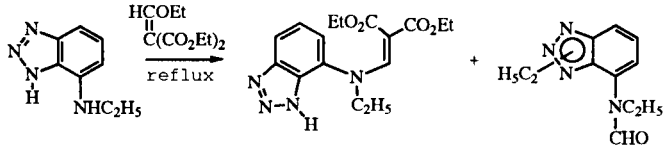
Benzotriazole is continuing to find wide application as a synthetic auxillary for it behaves as a good leaving group after reaction with a variety of carbonyl compounds [1]. However, this behaviour seems to be unique and no reactions using derivatives of the benzotriazole have been reported so far.

Recently, we have observed that when 4-ethylamino-1*H*-benzotriazole reacted with diethyl ethoxymethylenemalonate at its temperature of reflux, not only were the expected aminomethylenemalonates obtained, but also side ethylation took place at either position 1 or 2 of the triazole ring accompanied by formylation on the secondary amine (Scheme 1) [2].

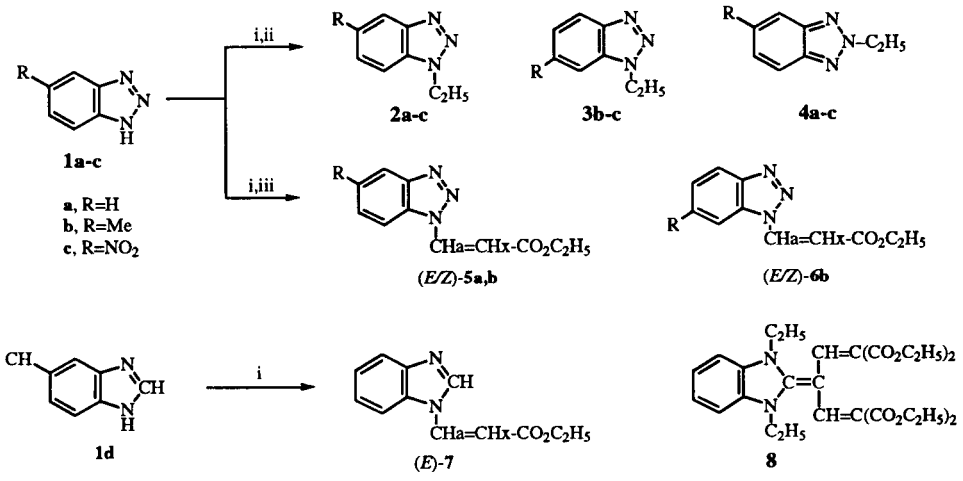
Scheme 1



This result was intriguing since it suggested a possible alkyl-oxygen fission of diethyl ethoxymethylenemalonate promoted by the nucleophile to give rise to a mixture of diethyl [benzotriazol-4-yl]ethylaminomethylenemalonate and 1(2)ethyl-1(2)*H*-4-(*N*-formyl)ethylaminobenzotriazole. This observation, in the light of the peculiar reactivity of 1*H*-benzotriazole [1], prompted us to investigate the effect of this reagent and of some of its 5-substituted derivatives on both diethyl ethoxymethylenemalonate and other esters as well as the effect of the replacement of the benzotriazole with other *N*-heterocycles.

Thus, reacting **1a-c** with diethyl ethoxymethylenemalonate at 100, 140 and 180° we obtained in all cases the *N*-ethylbenzotriazole isomers **2a-c**, **3b-c** and **4a-c** accompanied respectively by ethyl propenoates (*E*)-**5a** and a mixture of (*Z*)-**5b** and (*Z*)-**6b**, according to Scheme 2. Compounds **2a** and **4a** were known and coincident with those described [3a] but their ^{1}H-nmr spectra are now reported. Compounds **2b-c**, **3b-c** and **4b-c** are new and were identified by comparison with those obtained by direct ethylation of benzotriazoles **1b-c** with diethyl sulfate in an alkaline medium. Separation of compounds **4a-c** from the other isomers owing to their insolubility in concentrated hydrochloric acid aqueous solution, as reported in the case of *N*-methyl derivatives [3b], was only partial and the best result was obtained by flash column chromatography. Compounds **2b** and **3b** could not be separated because of no difference in both Rf and bp's. Compound (*E*)-**5a** was identified by comparison with an authentic sample obtained by a straightforward addition of ethyl propiolate upon benzotriazole (**1a**) in the absence of solvent from which compound (*Z*)-**5a** was also obtained. Similarly compound (*Z*)-**6b** was identified by comparison with an authentic sample coming from the Michael addition of ethyl propiolate upon **1b**, that gave rise to a mixture of isomeric couple of (*Z*)-**5b** and (*Z*)-**6b** along with (*E*)-**5b** and (*E*)-**6b** which were separated by flash column chromatography. Formation of the ethyl propiolate addition products on position 2 of the triazole ring seems to be precluded under the conditions examined. The nature of the products obtained (Scheme 2) clearly indicates that an oxygen-carbon fission on diethyl ethoxymethylenemalonate had taken place.

Scheme 2

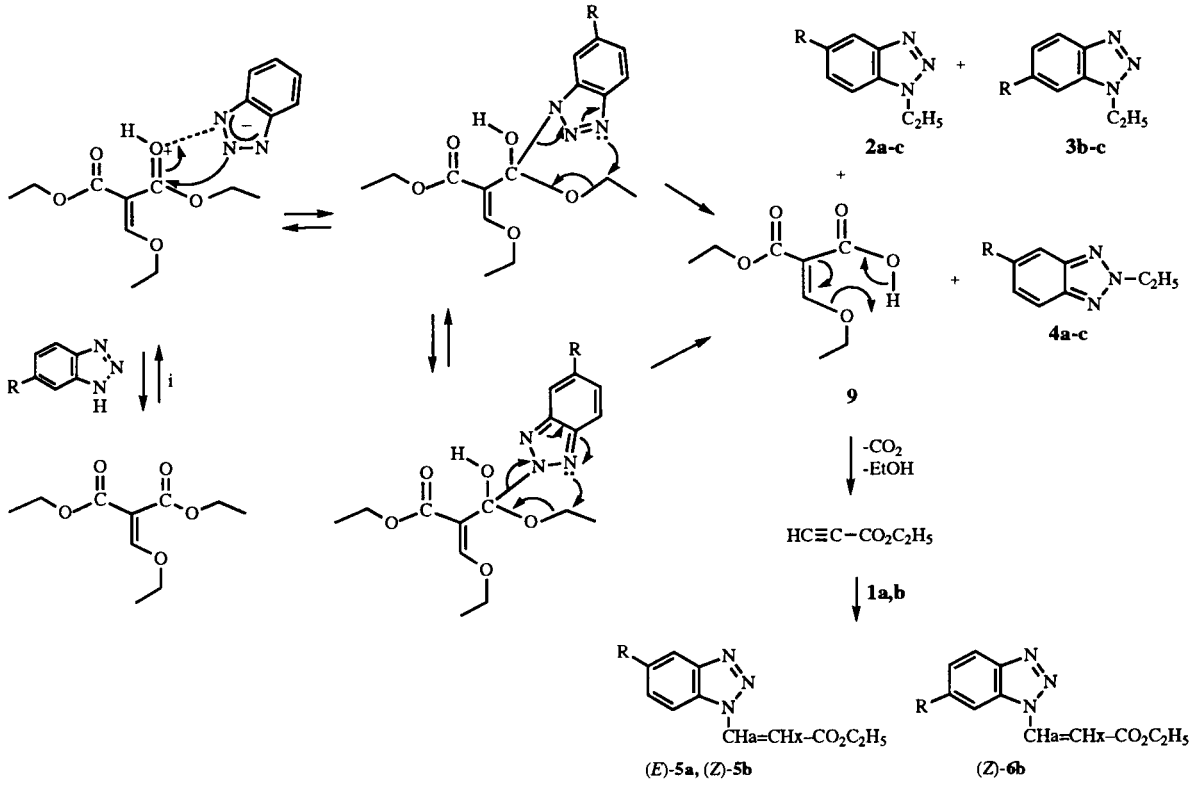


Reagents: i) with diethyl ethoxymethylenemalonate and other esters, ii) with diethyl sulfate; iii) ethyl propiolate;

It is our opinion that, according to the yields of the products formed, benzotriazole first attacks one or both carbonyls of the ester groups thus giving rise to protonation of carbonyl in a fashion observed in reaction of benzotriazole with aldehydes [1]. The mesomeric nucleophilic benzotriazole anion attacks the protonated carbonyl and, *via* a concerted process, promotes transfer of the ethyl group to positions 1-, 2- or 3- of ring (Scheme 3).

On the other hand the thus formed intermediate semiester **9** undergoes a concerted decarboxylation accompanied by a retro-Michael addition to give rise to ethyl propiolate. The latter reacts in turn with the free benzotriazole to give selectively the compound (*E*)-**5a** and a mixture (1:1 ratio) of (*Z*)-**5b** and (*Z*)-**6b** in low yield (Scheme 3). It is noteworthy that compound **1c** did not give rise to the (*Z*/*E*)-propenoates whereas the yields of the ethylated isomers **2c,**

Scheme 3



3c and **4c** were similar to those obtained by means of diethyl sulfate. This result seems to evidentiate that the effect of the nitro group favours the release of protons and as a consequence the resulting anion is not nucleophilic enough to undergo Michael addition to the intermediate propiolate. In order to discover if this type of reaction could be of general applicability we repeated the experiments using other esters such as ethyl acetoacetate, ethyl orthoformate and ethyl propionate. The results obtained so far seem to indicate that only the activated esters diethyl ethoxymethylenemalonate, ethyl acetoacetate and ethyl orthoformate are susceptible, to some extent, to an attack by the benzotriazoles **1a-c** according to a similar mechanism shown in Scheme 2, whereas ethyl propionate was unaffected and recovered unchanged after reaction.

Table 1

Bond Distances (Å) and Angles (°) with e.s.d.'s in Parentheses

O1	- C15	1.205(4)	C41	- C42		1.379(5)
O2	- C15	1.341(5)	C42	- C43		1.462(5)
O2	- C16	1.442(4)	C42	- C46		1.470(5)
O3	- C18	1.339(5)	C44	- C45		1.434(9)
O3	- C19	1.450(5)	C47	- C48		1.406(9)
O4	- C18	1.199(4)	C49	- C50		1.355(6)
O5	- C23	1.213(4)	C50	- C51		1.471(4)
O6	- C23	1.350(4)	C50	- C54		1.482(5)
O6	- C24	1.434(5)	C52	- C53		1.450(10)
O7	- C26	1.320(5)	C55	- C56		1.388(10)
O7	- C27	1.461(5)				
O8	- C26	1.193(5)	C15	-O2	-C16	117.2(3)
O9	- C46	1.199(5)	C18	-O3	-C19	117.8(3)
O10	- C46	1.341(5)	C23	-O6	-C24	116.9(3)
O10	- C47	1.452(6)	C26	-O7	-C27	115.3(3)
O11	- C43	1.208(5)	C46	-O10	-C47	116.6(4)
O12	- C43	1.339(6)	C43	-O12	-C44	117.8(4)
O12	- C44	1.439(7)	C51	-O14	-C52	117.5(3)
O13	- C51	1.206(5)	C54	-O16	-C55	117.1(4)
O14	- C51	1.350(6)	C7	-N1	-C11	126.2(3)
O14	- C52	1.438(5)	C6	-N1	-C11	108.2(3)
O15	- C54	1.202(4)	C6	-N1	-C7	125.1(3)
O16	- C54	1.322(5)	C9	-N2	-C11	126.1(3)
O16	- C55	1.464(6)	C1	-N2	-C11	109.0(3)
N1	- C6	1.390(4)	C1	-N2	-C9	124.9(3)
N1	- C7	1.458(5)	C35	-N3	-C36	125.6(3)
N1	- C11	1.350(4)	C29	-N3	-C36	124.6(3)
N2	- C1	1.393(4)	C29	-N3	-C35	109.4(3)
N2	- C9	1.460(5)	C35	-N4	-C38	125.5(4)
N2	- C11	1.334(4)	C34	-N4	-C38	125.9(4)
N3	- C29	1.388(4)	C34	-N4	-C35	108.6(3)
N3	- C35	1.337(5)	N2	-C1	-C6	106.5(3)
N3	- C36	1.477(4)	N2	-C1	-C2	131.8(3)
N4	- C34	1.386(5)	C2	-C1	-C6	121.7(3)
N4	- C35	1.347(4)	C1	-C2	-C3	116.6(4)
N4	- C38	1.480(6)	C2	-C3	-C4	122.1(5)
C1	- C2	1.387(5)	C3	-C4	-C5	122.0(4)
C1	- C6	1.386(5)	C4	-C5	-C6	115.8(4)
C2	- C3	1.364(6)	C1	-C6	-C5	121.9(3)
C3	- C4	1.395(7)	N1	-C6	-C5	131.1(3)
C4	- C5	1.381(6)	N1	-C6	-C1	107.0(3)
C5	- C6	1.393(4)	N1	-C7	-C8	112.1(3)
C7	- C8	1.515(7)	N2	-C9	-C10	112.8(4)
C9	- C10	1.505(8)	N1	-C11	-N2	109.3(3)
C11	- C12	1.466(4)	N2	-C11	-C12	126.5(3)
C12	- C13	1.416(4)	N1	-C11	-C12	124.1(3)
C12	- C21	1.409(5)	C11	-C12	-C21	119.9(3)
C13	- C14	1.364(5)	C11	-C12	-C13	122.4(3)

Table 1 (continued)

C14	- C15	1.477(4)	C13	-C12	-C21	117.6(3)
C14	- C18	1.475(5)	C12	-C13	-C14	135.6(3)
C16	- C17	1.497(8)	C13	-C14	-C18	123.7(3)
C19	- C20	1.491(6)	C13	-C14	-C15	116.6(3)
C21	- C22	1.364(5)	C15	-C14	-C18	119.6(3)
C22	- C23	1.457(5)	O2	-C15	-C14	112.5(3)
C22	- C26	1.497(4)	O1	-C15	-C14	125.0(3)
C24	- C25	1.452(6)	O1	-C15	-O2	122.4(4)
C27	- C28	1.464(9)	O2	-C16	-C17	107.3(3)
C29	- C30	1.378(6)	O4	-C18	-C14	125.4(3)
C29	- C34	1.391(6)	O3	-C18	-C14	112.2(3)
C30	- C31	1.388(7)	O3	-C18	-O4	122.4(4)
C31	- C32	1.389(9)	O3	-C19	-C20	106.0(4)
C32	- C33	1.338(9)	C12	-C21	-C22	133.9(3)
C33	- C34	1.394(5)	C21	-C22	-C26	123.9(3)
C35	- C40	1.456(5)	C21	-C22	-C23	122.0(3)
C36	- C37	1.503(7)	C23	-C22	-C26	113.9(3)
C38	- C39	1.452(11)	O6	-C23	-C22	113.5(3)
C40	- C41	1.400(5)	O5	-C23	-C22	125.0(3)
C40	- C49	1.423(5)	O5	-C23	-O6	121.5(3)
O6	-C24	-C25	109.8(4)	C41	-C42	-C46	124.3(3)
O8	-C26	-C22	124.2(3)	C41	-C42	-C43	116.8(3)
O7	-C26	-C22	112.9(3)	C43	-C42	-C46	118.9(3)
O7	-C26	-O8	122.8(4)	O12	-C43	-C42	112.1(3)
O7	-C27	-C28	107.9(4)	O11	-C43	-C42	126.2(4)
N3	-C29	-C34	106.1(3)	O11	-C43	-O12	121.7(4)
N3	-C29	-C30	132.0(4)	O12	-C44	-C45	110.0(5)
C30	-C29	-C34	121.9(4)	O10	-C46	-C42	111.1(3)
C29	-C30	-C31	115.9(5)	O9	-C46	-C42	126.7(4)
C30	-C31	-C32	121.8(6)	O9	-C46	-O10	122.1(4)
C31	-C32	-C33	122.1(6)	O10	-C47	-C48	109.0(5)
C32	-C33	-C34	117.5(5)	C40	-C49	-C50	134.0(3)
C29	-C34	-C33	120.7(4)	C49	-C50	-C54	124.6(4)
N4	-C34	-C33	132.2(4)	C49	-C50	-C51	116.4(3)
N4	-C34	-C29	107.1(4)	C51	-C50	-C54	118.6(3)
N3	-C35	-N4	108.8(3)	O14	-C51	-C50	112.0(3)
N4	-C35	-C40	125.6(3)	O13	-C51	-C50	125.4(4)
N3	-C35	-C40	125.5(3)	O13	-C51	-O14	122.5(4)
N3	-C36	-C37	112.0(3)	O14	-C52	-C53	111.9(4)
N4	-C38	-C39	112.5(5)	O16	-C54	-C50	113.5(4)
C35	-C40	-C49	119.9(3)	O15	-C54	-C50	124.1(4)
C35	-C40	-C41	122.5(3)	O15	-C54	-O16	122.3(4)
C41	-C40	-C49	117.6(3)	O16	-C55	-C56	111.7(5)
C40	-C41	-C42	135.4(3)				

The attempted reaction of diethyl ethoxymethylenemalonate with the *N*-heterocycles, as 1*H*-1,2,3-triazole (**1e**), 1*H*-1,2,4-triazole (**1f**), 1*H*-naphtho[1,2-*d*]-triazole (**1g**), 1*H*-triazolo[4,5-*b*]pyridine (**1h**) and indole (**1i**), was absolutely negative and starting material was recovered unchanged. In contrast, the reaction of diethyl ethoxymethylenemalonate with the 1*H*-benzimidazole (**1d**) gave rise to almost identical amounts of (*E*)-**7** (8% yield) and **8** (10%) only at high temperature.

Formation of (*E*)-**7** may be ascribed to a similar mechanism claimed in the Scheme 3 for the other propenoates, whereas the assignment of **8** was based upon both X-ray crystallographic analysis, that confirmed a benzimidazoline

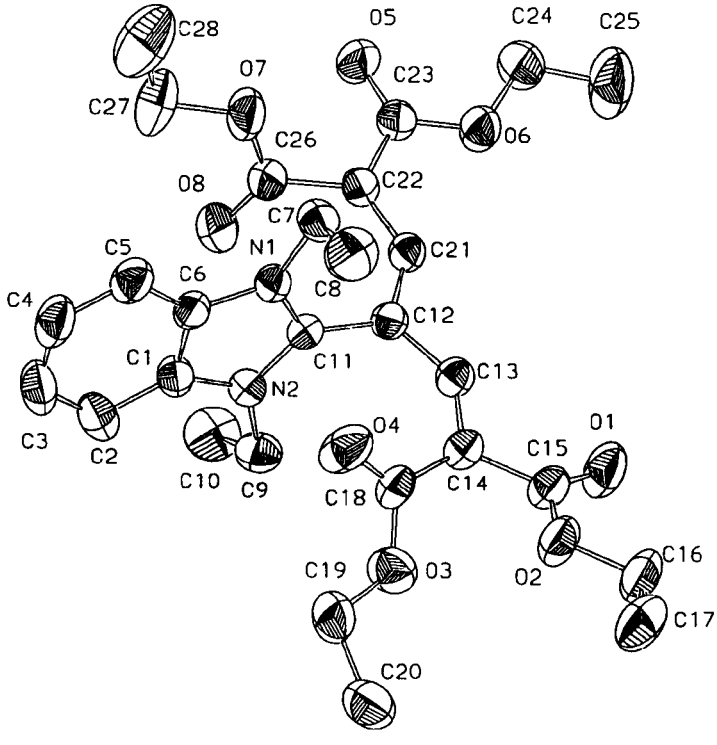


Figure 1. Perspective view and atom labeling of the crystal structure of **8**.

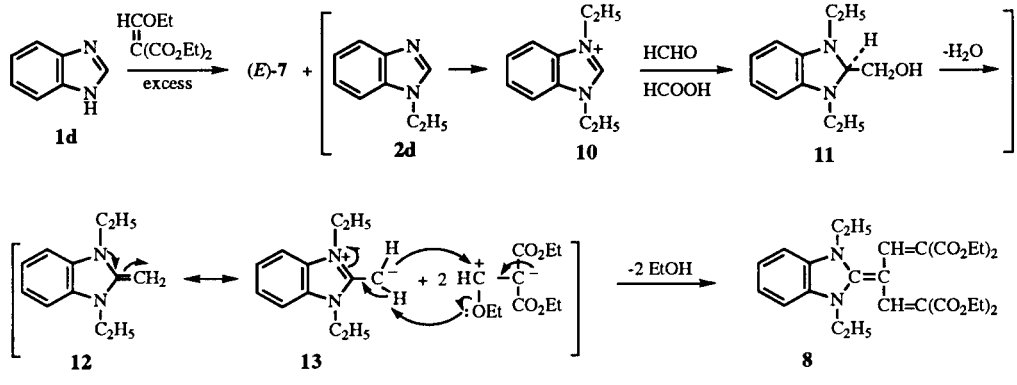
amine and, on its zwitterionic form **13**, undergoes two successive electrophilic attacks by one mole of diethyl ethoxymethylenemalonate on its dipolar form strongly stabilised by the ester groups [5] to give **8** (Scheme 4).

In conclusion, we can say that the type of the reactivity observed in the case of benzotriazoles and benzimidazole as shown in Scheme 3 may be ascribed to an addition-elimination mechanism as postulated by Katritzky *et al* [1c] in the case of reaction of benzotriazole with aldehydes. In addition, benzimidazole not only promotes similar reaction to give propenoate (*E*)-**7** but once ethylated shows the reactivity of an enamine system.

The results obtained with our experiments seem to indicate that among the *N*-heterocycles only the benzotriazoles and benzimidazole show different degrees of reactivity and this could be due to the difference in the acidity towards the other considered *N*-heterocycles which show very high values of pK_a.

The structures of the obtained compounds were confirmed by the whole of analytical and spectroscopic data. In particular the stereochemistry of ethyl propiolate addition upon the benzotriazoles **1a,b** was determined by both their δ values of the olefinic protons [6] and the values of the coupling constant in the ^{1}H-nmr spectra, as previously reported [7,8] for similar cases. In those cases where an

Scheme 4



skeleton (Figure 1), and ^{1}H/^{13}C-nmr mono and bi-dimensional experiments (*vide infra*). At the present stage a plausible mechanism for the formation of **8** is depicted in Scheme 4, where the main intermediate is supposed to be the non-isolated *N*-ethylbenzimidazole (**2d**), formed in a similar manner to ethyl benzotriazoles, which underwent successive ethylation to give the cation **10**. At this point, owing to both formaldehyde and formic acid coming from the decomposition of diethyl ethoxymethylenemalonate as observed in Scheme 1 [2], a reductive hydroxymethylation is highly possible, as reported for similar cases [4] leading to **11** soon followed by dehydratation to enamine derivative **12** under the examined conditions. This last intermediate acts as dien-

Table 2

Atomic Coordinates (x10^4) and Equivalent Isotropic Displacement Parameters (Å^{2}x10^4) (one third trace of the diagonalized matrix), with es.d.'s in Parentheses

Atom	X/a	Y/b	Z/c	Ueq
O1	3793.8(7)	-4974(3)	-3027.3(10)	746(12)
O2	4185.0(7)	-6504(3)	-3068.1(8)	603(10)
O3	4512.6(7)	-7600(3)	-2199.8(11)	647(12)
O4	4936.0(7)	-6032(3)	-1902.1(11)	749(13)
O5	4364.9(7)	713(3)	-963.1(9)	606(11)
O6	4023.2(7)	157(3)	-1706.8(9)	556(10)
O7	5042.8(7)	-869(3)	-686.2(9)	635(11)
O8	4747.6(9)	-2562(3)	-539 0(10)	802(14)
O9	2957.3(9)	1243(3)	-1586.9(10)	711(13)
O10	2751.8(9)	3300(3)	-1848.3(11)	822(13)

Table 2 (continued)

Atom	X/a	Y/b	Z/c	Ueq
O11	3474.4(8)	5367(3)	-887.7(10)	687(12)
O12	3399.9(9)	4529(3)	-1586.9(10)	746(14)
O13	3870.3(8)	1591(4)	1001.5(10)	811(14)
O14	3511.7(8)	137(3)	1165.5(9)	706(12)
O15	2787.4(7)	-307(3)	69.3(12)	810(14)
O16	3244.0(7)	-1719(3)	379.5(12)	733(13)
N1	5148.2(7)	-3626(3)	-1225.4(9)	402(9)
N2	4822.8(7)	-5180(3)	-1077.2(9)	409(10)
N3	3043.9(7)	-710(3)	-765.4(10)	442(10)
N4	2612.7(7)	781(3)	-943.2(11)	531(11)
C1	5176.6(9)	-5406(3)	-767.5(11)	452(12)
C2	5329(1)	-6362(4)	-417(1)	574(15)
C3	5691(1)	-6275(5)	-167(1)	678(17)
C4	5899(1)	-5288(5)	-261(1)	661(16)
C5	5751.6(9)	-4335(4)	-610.7(13)	557(14)
C6	5382.0(8)	-4423(3)	-863.5(11)	419(11)
C7	5256.5(9)	-2566(4)	-1469.3(13)	498(13)
C8	5391(1)	-3139(5)	-1823(2)	769(21)
C9	4516(1)	-6000(4)	-1103(1)	517(14)
C10	4404(1)	-5731(5)	-702(2)	740(21)
C11	4812.9(8)	-4118(3)	-1347.7(10)	375(11)
C12	4491.9(8)	-3520(3)	-1710.7(11)	388(11)
C13	4303.0(8)	-4157(3)	-2149.3(11)	422(12)
C14	4336.1(8)	-5339(3)	-2355.9(11)	440(12)
C15	4072.2(9)	-5580(4)	-2840.2(12)	508(13)
C16	3966(1)	-6713(5)	-3560(1)	681(17)
C17	4173(1)	-7608(5)	-3753(2)	778(20)
C18	4629.4(9)	-6319(4)	-2134.2(11)	465(12)
C19	4779(1)	-8669(4)	-2038(2)	720(18)
C20	4615(1)	-9868(5)	-2339(2)	773(22)
C21	4364.8(8)	-2255(3)	-1632.0(11)	403(11)
C22	4472.4(8)	-1373(3)	-1263.0(11)	409(11)
C23	4290.9(9)	-87(3)	-1284.8(12)	442(12)

Table 2 (continued)

Atom	X/a	Y/b	Z/c	Ueq
C24	3830(1)	1402(4)	-1756(2)	651(17)
C25	3556(2)	1513(7)	-2229(2)	1145(28)
C26	4761.9(9)	-1674(3)	-791.9(12)	467(13)
C27	5330(1)	-1094(6)	-224(2)	879(21)
C28	5647(1)	-351(8)	-208(2)	1259(33)
C29	2730.1(9)	-1381(4)	-1040.0(13)	522(14)
C30	2665(1)	-2699(5)	-1197(2)	769(21)
C31	2310(2)	-3015(7)	-1473(2)	1021(29)
C32	2039(1)	-2055(7)	-1586(2)	997(26)
C33	2103(1)	-776(6)	-1433(2)	792(20)
C34	2457(1)	-426(4)	-1154(1)	570(14)
C35	2968.3(9)	582(4)	-711.7(11)	445(12)
C36	3407.2(9)	-1300(4)	-605.9(13)	525(14)
C37	3584(1)	-991(5)	-940(2)	700(19)
C38	2422(1)	2069(5)	-962(2)	797(21)
C39	2210(2)	2034(8)	-679(3)	1241(38)
C40	3227.5(9)	1601(3)	-443.2(11)	456(12)
C41	3313.9(9)	2722(4)	-655.1(12)	485(13)
C42	3215.2(9)	3177(3)	-1109.9(12)	474(13)
C43	3371(1)	4461(4)	-1172(1)	508(14)
C44	3500(2)	5806(6)	-1722(2)	984(29)
C45	3397(2)	5844(8)	-2222(2)	1228(35)
C46	2973(1)	2445(4)	-1528(1)	522(14)
C47	2519(2)	2716(6)	-2296(2)	1071(26)
C48	2324(2)	3759(8)	-2597(2)	1542(41)
C49	3405.6(9)	1472(4)	53.3(12)	474(13)
C50	3378.8(9)	590(4)	372.6(12)	487(13)
C51	3616(1)	838(4)	867(1)	568(15)
C52	3717(1)	317(6)	1661(1)	845(22)
C53	3558(2)	1326(7)	1860(2)	1196(34)
C54	3105.1(9)	-495(4)	263.9(12)	513(14)
C55	2992(1)	-2852(5)	283(3)	980(30)
C56	3135(2)	-4034(7)	187(3)	1345(46)

Table 3

Anisotropic Displacement Parameters U_{ij} ($x10^4$ Å^2) $\exp(-2*\pi^2(U_{11}*h^2*(a^*)^2+...2*U_{12}*h*k*(a^*)*(b^*)+...)$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	508(15)	887(21)	608(17)	-144(15)	-27(13)	134(15)
O2	617(15)	698(17)	388(13)	-133(12)	86(11)	27(13)
O3	534(15)	495(15)	818(19)	20(14)	169(14)	51(12)
O4	444(15)	706(19)	879(21)	-239(16)	31(14)	43(13)
O5	693(17)	497(15)	512(14)	-111(12)	116(13)	71(13)
O6	535(14)	520(14)	492(13)	-42(11)	74(11)	139(11)
O7	460(14)	765(18)	513(15)	114(13)	16(11)	-66(13)
O8	1055(24)	711(19)	487(16)	152(15)	142(16)	-157(18)
O9	958(22)	550(17)	516(16)	-29(13)	178(15)	-37(15)
O10	804(20)	625(18)	667(19)	76(15)	-104(15)	-50(15)
O11	818(20)	485(15)	667(17)	-33(14)	198(15)	-87(14)
O12	997(23)	660(18)	657(18)	26(15)	410(17)	-198(17)
O13	657(18)	1123(26)	528(16)	-97(17)	103(14)	-349(18)
O14	656(17)	1038(23)	394(13)	50(14)	176(12)	-103(16)
O15	401(14)	974(24)	899(22)	190(19)	90(14)	-69(15)
O16	442(14)	665(18)	1034(24)	110(17)	232(15)	-67(13)
N1	357(13)	419(14)	382(13)	22(11)	94(11)	-20(11)
N2	431(14)	387(14)	396(14)	14(11)	150(11)	-9(11)
N3	368(14)	456(16)	459(15)	2(12)	118(12)	-13(12)
N4	378(15)	638(19)	511(17)	16(15)	106(13)	44(14)
C1	478(18)	457(18)	380(16)	21(14)	126(14)	64(15)
C2	665(24)	549(22)	498(20)	145(17)	219(18)	135(18)
C3	740(28)	725(27)	443(20)	130(19)	99(19)	270(23)
C4	485(21)	787(29)	520(22)	-43(21)	-4(17)	119(20)
C5	419(18)	613(23)	536(21)	-47(18)	82(16)	3(16)

Table 3 (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	405(16)	420(17)	376(16)	-35(14)	96(13)	11(14)
C7	412(17)	497(20)	549(20)	92(16)	152(15)	-39(15)
C8	906(32)	864(32)	647(26)	7(24)	425(25)	-174(27)
C9	511(20)	463(19)	605(22)	15(17)	252(17)	-80(16)
C10	731(28)	848(32)	795(29)	1(25)	465(24)	-112(24)
C11	393(16)	358(16)	349(15)	-22(13)	120(13)	-11(13)
C12	347(15)	389(16)	409(16)	0(13)	129(13)	-2(13)
C13	347(15)	456(18)	426(17)	9(14)	115(13)	-3(13)
C14	392(16)	478(19)	412(17)	-48(14)	120(14)	-29(14)
C15	441(18)	552(21)	459(19)	-80(16)	101(15)	-36(16)
C16	654(24)	827(30)	414(20)	-124(20)	55(18)	-120(22)
C17	836(30)	986(36)	520(23)	-232(24)	277(22)	-197(27)
C18	443(18)	551(20)	364(16)	-106(15)	122(14)	1(15)
C19	730(27)	633(26)	620(25)	44(21)	77(21)	203(22)
C20	973(35)	562(25)	782(30)	85(22)	346(27)	102(24)
C21	332(15)	429(17)	410(16)	25(14)	108(13)	-12(13)
C22	405(16)	395(17)	404(16)	34(13)	134(13)	3(13)
C23	437(17)	440(18)	435(17)	20(15)	156(14)	-28(14)
C24	632(24)	551(23)	669(25)	-13(19)	150(20)	202(19)
C25	1127(44)	1145(46)	724(33)	-93(31)	-100(30)	636(38)
C26	535(19)	453(19)	380(17)	-11(15)	145(15)	12(15)
C27	579(26)	1251(44)	554(25)	-30(28)	-42(20)	29(28)
C28	601(31)	1672(67)	1128(48)	-201(47)	-57(31)	-203(38)
C29	437(18)	617(22)	479(19)	-75(17)	146(15)	-129(17)
C30	714(28)	703(29)	874(32)	-243(25)	298(25)	-211(23)
C31	868(37)	999(42)	1086(44)	-461(36)	270(33)	-415(34)
C32	611(29)	1275(51)	884(37)	-324(36)	63(26)	-348(33)
C33	438(21)	1131(40)	672(27)	-136(27)	76(19)	-144(24)
C34	443(19)	711(25)	469(19)	-57(18)	87(16)	-86(18)
C35	403(16)	529(20)	384(16)	25(15)	135(14)	-12(15)
C36	424(18)	533(21)	579(21)	28(17)	158(16)	51(16)
C37	551(23)	881(32)	731(27)	84(24)	320(21)	70(22)
C38	539(24)	773(31)	1015(37)	31(27)	240(24)	139(22)
C39	1325(54)	1421(60)	1175(50)	166(45)	706(45)	536(48)
C40	431(17)	497(19)	394(17)	13(14)	115(14)	-24(15)
C41	457(18)	471(19)	475(19)	-19(15)	129(15)	-20(15)
C42	466(18)	439(18)	479(18)	17(15)	147(15)	-18(15)
C43	501(19)	465(20)	516(20)	28(17)	157(16)	19(16)
C44	1279(47)	845(36)	927(38)	125(30)	543(36)	-298(34)
C45	927(41)	1490(60)	1224(52)	662(47)	381(38)	-80(40)
C46	567(21)	461(21)	476(19)	60(16)	142(16)	-20(16)
C47	1137(43)	894(38)	657(30)	64(28)	-201(29)	-182(33)
C48	1670(71)	1194(55)	918(45)	270(41)	-384(46)	-18(51)
C49	419(17)	520(20)	442(18)	-17(15)	128(14)	-62(15)
C50	402(17)	629(22)	394(17)	4(16)	119(14)	-29(16)
C51	449(19)	783(27)	421(19)	-29(18)	120(15)	-39(19)
C52	868(33)	1169(42)	397(21)	0(25)	144(21)	-2(31)
C53	1503(59)	1220(52)	718(35)	-222(35)	284(37)	160(45)
C54	390(18)	709(25)	428(18)	62(17)	148(15)	-32(17)
C55	674(29)	739(33)	1597(57)	58(35)	523(34)	-212(26)
C56	1335(58)	946(48)	1982(82)	-316(50)	900(58)	-419(44)

inseparable mixture of isomers was obtained the exact assignment of the proton resonances was determined by decoupling experiments.

Uv spectra of compounds **2, 3** and **4a-c** match well with previously described data of 1-, or 2-methylbenzotriazoles [9]. On the other hand, the uv absorptions of the benzotriazolylpropenoates were very similar, with a batochromic shift of the maximum at the highest wavelength possibly due to the conjugation of the heterocycle with the carbonyl group in both the series of (*E/Z*)-**5a-b** and (*E/Z*)-**6b**.

EXPERIMENTAL

Melting points are uncorrected and were taken on a Kofler apparatus. Rf were determined on tlc silica gel plates (Whatman K6F-60) using a mixture (6:4) of diethyl ether-hexane. The uv

spectra were recorded in nm for ethanolic solutions with a Perkin-Elmer Lambda 5 spectrophotometer. The ir spectra were made by a Perkin-Elmer 781 infrared spectrophotometer. The ^1H- and ^{13}C-nmr spectra were respectively recorded at 200 MHz and 50 MHz on a Varian XL-200 instrument using tetramethylsilane as internal standard. Chemical shifts are reported in ppm downfield (δ) from tetramethylsilane and coupling constants (J) in Hertz. The mass spectrum was performed by a Finningan Mat-TSQ-700 spectrometer. Light petroleum refers to the fraction bp 40-60°. Elemental analyses were performed at the Laboratorio di Microanalisi, Dipartimento di Scienze Farmaceutiche, University of Padua, Italy.

Reaction of 1*H*-Benzotriazole (**1a**) with Diethyl Ethoxymethylenemalonate.

A mixture of **1a** (2 g, 16.8 mmoles) and diethyl ethoxymetylenemalonate (7.27 g, 33.6 mmoles) was stirred at 180° for 68 hours. After cooling, the reaction mixture was flash chromatographed through silica gel, using as eluent a mixture (1:1) of diethyl ether-light petroleum, to afford in the order the following products:

(*E*)-Ethyl 3-(Benzotriazol-1-yl)propenoate (*E*-**5a**).

This compound was obtained as colorless crystals in 5% yield, mp 108-110° (light petroleum); R_f = 0.77; ir (nujol): ν 1710, 1650 cm^{-1}; uv (ethanol): λ_{max} 311, 254, 202 nm; ^1H nmr (deuteriochloroform): δ 8.52 (1H, d, $J_{a,x}$ = 14.3, H_a), 8.14 (1H, dd, $J_{4,5}$ = 8.4 and $J_{4,6}$ = 1, H-4), 7.73 (1H, dd, $J_{6,7}$ = 8.4 and $J_{5,7}$ = 1, H-7), 7.65 (1H, ddd, $J_{6,7}$ = 8.4, $J_{5,6}$ = 7 and $J_{4,6}$ = 1, H-6), 7.49 (1H, ddd, $J_{5,6}$ = 7, $J_{4,5}$ = 8.4 and $J_{5,7}$ = 1, H-5), 6.76 (1H, d, $J_{a,x}$ = 14.3, H_x), 4.33 (2H, q, J = 7.1, CH_2-CH_3), 1.38 (3H, t, J = 7.1, CH_3-CH_2).

Anal. Calcd. for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.10; N, 19.35. Found: C, 60.64; H, 5.26; N, 19.20.

2-Ethyl-2*H*-benzotriazole (**4a**).

This compound was obtained as an oil in 14% yield; R_f = 0.69; n^{20} = 1.5623 (lit 1.5612 [3]); ir (neat): ν 1615, 1595 cm^{-1}; uv (ethanol): λ_{max} 282, 262, 256, 208 nm; ^1H nmr (deuteriochloroform): δ 7.87 (2H, m, H-4 and H-7), 7.38 (2H, m, H-5 and H-6), 4.75 (2H, q, J = 7.4, CH_2-CH_3), 1.72 (3H, t, J = 7.4, CH_3-CH_2).

1-Ethyl-1*H*-benzotriazole (**2a**).

This compound was obtained as an oil in 28% yield, bp 75-77°/2 mbar; R_f = 0.54; n^{20} = 1.5575 (lit 1.5580 [3]); ir (neat): ν 1620, 1590 cm^{-1}; uv (ethanol): λ_{max} 280, 262, 256, 207 nm; ^1H nmr (deuteriochloroform): δ 8.07 (1H, dd, $J_{4,5}$ = 8.2 and $J_{4,6}$ = 1, H-4), 7.52-7.33 (3H, m, H-5, H-6 and H-7), 4.70 (2H, q, J = 7.4, CH_2-CH_3), 1.64 (3H, t, J = 7.4, CH_3-CH_2).

Reaction of 5-Methyl-1*H*-benzotriazole (**1b**) with Diethyl Ethoxymethylenemalonate.

Following the procedure described above, from compound **1b** (2 g, 15 mmoles) and diethyl ethoxymethylenemalonate (6.49 g, 30 mmoles) after 42 hours at 180° and chromatography of the resulting mixture, we obtained a major fraction (0.55 g, 23% yield) of a mixture of 1-ethyl-5-methyl-1*H*-benzotriazole (**2b**) and 1-ethyl-6-methyl-1*H*-benzotriazole (**3b**), in a 1:1 molar ratio based on the integral ratio of methyl resonance at ^1H nmr, bp 80-82°/2 mbar; R_f = 0.54; ir (neat): ν 1630, 1590 cm^{-1}; uv (ethanol): λ_{max} 280, 264, 258, 209 nm; from the data of the ^1H nmr spectrum (deuteriochloroform) of the mixture we were able to assign the appropriate resonances to each isomer, as indicated:

Compound **2b** had δ 7.80 (1H, d, $J_{4,6}$ = 1.4, H-4), 7.42 (1H, d, $J_{6,7}$ = 8.4, H-7), 7.29 (1H, dd, $J_{6,7}$ = 8.4 and $J_{4,6}$ = 1.4, H-6), 4.67 (2H, q, J = 7.4, CH_2-CH_3), 2.50 (3H, s, 5-CH_3), 1.63 (3H, t, J = 7.4, CH_3-CH_2).

Compound **3b** had δ 7.91 (1H, d, $J_{4,5}$ = 8.6, H-4), 7.32 (1H, d, $J_{5,7}$ = 1.4, H-7), 7.18 (1H, dd, $J_{4,5}$ = 8.6 and $J_{5,7}$ = 1.4, H-5), 4.65 (2H, q, J = 7.4, CH_2-CH_3), 2.53 (3H, s, 6-CH_3), 1.63 (3H, t, J = 7.4, CH_3-CH_2).

Anal. Calcd. for $C_9H_{11}N_3$: C, 67.05; H, 6.88; N, 26.07. Found: C, 66.98; H, 6.91; N, 26.13.

A minor fraction (0.25 g, 7.2% yield) corresponded to a 1:1 mixture of ethyl 3-[(5-methyl)-1*H*-benzotriazol-1-yl]propenoate (*Z*-**5b**) and ethyl 3-[(6-methyl)-1*H*-benzotriazol-1-yl]propenoate (*Z*-**6b**). Repeated attempts at separating the single isomers by flash chromatography or distillation *in vacuo* failed.

Reaction of 5-Nitro-1*H*-benzotriazole (**1c**) with Diethyl Ethoxymethylenemalonate.

Following the same procedure described above, from a mixture of **1c** (1 g, 6.1 mmoles) an diethyl ethoxymethylenemalonate (2.63 g, 12.2 mmoles), after 68 hours at 180° and chromatography of the reaction mixture, were obtained in order of elution:

2-Ethyl-2*H*-5-nitrobenzotriazole (**4c**).

This compound was obtained as crystals in 21% yield, mp 108-110° (diethyl ether); R_f = 0.81; ir (nujol): ν 1620, 1580 cm^{-1}; uv (ethanol): λ_{max} 275, 239 sh, 232 nm; ^1H nmr (deuteriochloroform): δ 8.87 (1H, d, $J_{4,6}$ = 2, H-4), 8.23 (1H, dd, $J_{6,7}$ = 9.3 and $J_{4,6}$ = 2, H-6), 7.98 (1H, d, $J_{6,7}$ = 9.3, H-7), 4.86 (2H, q, J = 7.4, CH_2-CH_3), 1.77 (3H, t, J = 7.4, CH_3-CH_2).

Anal. Calcd. for $C_8H_8N_4O_2$: C, 49.99; H, 4.20; N, 29.16. Found: C, 49.79; H, 4.24; N, 29.08.

1-Ethyl-1*H*-6-nitrobenzotriazole (**3c**).

This compound was obtained as crystals in 24% yield, mp 112-113° (diethyl ether); R_f = 0.58; ir (nujol): ν 1600, 1595 cm^{-1}; uv (ethanol): λ_{max} 292 sh, 264, 225 nm; ^1H nmr (deuteriochloroform): δ 8.55 (1H, d, $J_{5,7}$ = 1.9, H-7), 8.28 (1H, dd, $J_{4,5}$ = 9 and $J_{5,7}$ = 1.9, H-5), 8.17 (1H, d, $J_{4,5}$ = 9, H-4), 4.82 (2H, q, J = 7.3, CH_2-CH_3), 1.73 (3H, t, J = 7.3, CH_3-CH_2).

Anal. Calcd. for $C_8H_8N_4O_2$: C, 49.99; H, 4.20; N, 29.16. Found: C, 49.91; H, 4.30; N, 28.90.

1-Ethyl-1*H*-5-nitrobenzotriazole (**2c**).

This compound was obtained as crystals in 26% yield, mp 103-104° (diethyl ether); R_f = 0.38; ir (nujol): ν 1615, 1590 cm^{-1}; uv (ethanol): λ_{max} 277, 229, 222 nm; ^1H nmr (deuteriochloroform): δ 9.02 (1H, d, $J_{4,6}$ = 2, H-4), 8.41 (1H, dd, $J_{6,7}$ = 9 and $J_{4,6}$ = 2, H-6), 7.69 (1H, d, $J_{6,7}$ = 9, H-7), 4.80 (2H, q, J = 7.3, CH_2-CH_3), 1.70 (3H, t, J = 7.3, CH_3-CH_2).

Anal. Calcd. for $C_8H_8N_4O_2$: C, 49.99; H, 4.20; N, 29.16. Found: C, 50.21; H, 4.36; N, 28.88.

Reaction of 1*H*-Benzimidazole (**1d**) with Diethyl Ethoxymethylenemalonate.

Following the same procedure as reported for **1a**, from **1d** (2 g, 17 mmoles) and diethyl ethoxymethylenemalonate (7.4 g, 34 mmoles) after 42 hours at 180° and chromatography of the reaction mixture, were obtained in order of elution:

Ethyl 3-(Benzimidazol-1-yl)propenoate (*E*-**7**).

This compound was obtained as crystals in a 8% yield, mp 95-96°; R_f = 0.58; ir (nujol): ν 1705, 1660, 1640, 1610, 1590 cm^{-1}; uv (ethanol): λ_{max} 299, 293 infl, 261, 234, 218 nm; ^1H nmr (deuteriochloroform): δ 8.20 (1H, s, H-2), 8.16 (1H, d, $J_{a,x}$ = 14.4, H_a), 7.85 (1H, m, H-4), 7.65 (1H, dd, $J_{6,7}$ = 6 and $J_{5,7}$ = 3.6, H-7), 7.41 (2H, m, H-5 and H-6), 6.32 (1H, d, $J_{a,x}$ = 14.4, H_x), 4.31 (2H, q, J = 7.2, CH_2-CH_3), 1.37 (3H, t, J = 7.2, CH_3-CH_2).

Anal. Calcd. for $C_{12}H_{12}N_2O_2$: C, 66.65; H, 5.59; N, 12.96. Found: C, 66.67; H, 5.64; N, 13.10.

1,3-Diethyl-2-[2',2'-(bis diethoxycarbonyl)vinyl]methylenebenzimidazoline (**8**).

This compound was obtained as crystals in a 10% yield, mp 119-120° (diethyl ether); R_f = 0.53; ir (nujol): ν 1705, 1670, 1580 cm^{-1}; uv (ethanol): λ_{max} 412, 282 infl, 272, 250, 222 nm; ^1H nmr (deuteriochloroform): δ 7.92 (2H, s, H-3 and H-3'), 7.62-7.49 (4H, m, aromatic H), 4.16 (8H, q, J = 7.2, OCH_2-CH_3), 3.44 (4H, q, J = 7.2, NCH_2-CH_3), 1.48 (6H, t, J = 7.2, OCH_2-CH_3), 1.27 (6H, t, J = 7.2, OCH_2-CH_3), 0.98 (6H, t, J = 7.2, NCH_2-CH_3); ^{13}C nmr: δ 167.5 (s, C=O), 166.9 (s, C=O), 152.9 (s, C-2), 150.6 (d, C-3'and C-5'), 130.9 (s, C-4'), 125.1 (d, C-4 and C-7), 111.8 (d, C-5 and C-6), 100.6 (s, C-3a and C-7a), 87.3 (s, C-2'and C-6'), 59.6 (t, OCH_2-CH_3), 59.4 (t, N CH_2-CH_3), 41.2 (t, OCH_2-CH_3), 14.1 (q, OCH_2-CH_3), 13.8 (q, NCH_2-CH_3), 13.0 (q, OCH_2-CH_3); ms: m/z (%) 528 (M^+, 100), 483 (20), 369 (16), 323 (29), 199 (39).

Anal. Calcd. for $C_{28}H_{36}N_2O_8$: C, 63.52; H, 6.87; N, 5.30. Found: C, 63.34; H, 6.81; N, 5.33.

General Procedure for the Reactions of 1*H*-1,2,3-Triazole (**1e**), 1*H*-1,2,4-Triazole (**1f**), 1*H*-Naphtho[1,2-*d*]triazole (**1g**), 1*H*-1,2,3-Triazolo[4,5-*b*]pyridine (**1h**) and Indole (**1i**) with Diethyl ethoxymethylenemalonate.

A 1:2 molar ratio mixture of the appropriate heterocyclic compound **1e-i** (2 g, 12-29 mmoles) and diethyl ethoxymethylenemalonate was stirred at 75° for 24 hours, 120° for 24 hours and 180° for 72 hours. After chromatography of the reaction mixture the unchanged *N*-heterocycles **1e-i** were exclusively recovered.

Reaction of 1*H*-Benzotriazole (**1a**) with Diethyl Sulfate.

To a solution of the compound **1a** (1 g, 8.40 mmoles) in 15 ml of 2*M* sodium hydroxide aqueous solution, diethyl sulfate (1.59 g, 10 mmoles) was slowly added and the resulting mixture stirred for 4 hours at 110°. After cooling the solution was repeatedly extracted with chloroform. The combined extracts, dried on sodium sulfate, after evaporation of the solvent afforded an oily residue. Flash chromatography on silica gel, eluting with a mixture of diethyl ether-light petroleum in 1:1 ratio, yielded in succession **4a** (0.58 g, 47% yield) and **2a** (0.62 g, 50% yield), which were identical to the samples previously described in the reaction of **1a** with diethyl ethoxymethylenemalonate.

Reaction of 5-Methyl-1*H*-benzotriazole (**1b**) with Diethyl Sulfate.

Using the same procedure as indicated for **1a**, from **1b** (1.5 g, 11.3 mmoles) and diethyl sulfate (2.12 g, 13.5 mmoles), the following reactions occurred:

2-Ethyl-5-methyl-2*H*-benzotriazole (**4b**).

This compound was obtained as an oil (0.87 g, 48% yield), bp 76-78/5 mbar; R_f = 0.87; ir (neat): ν 1630, 1560 cm^{-1}; uv (ethanol): λ_{max} 288 sh, 280, 209 nm; ^1H nmr (deuteriochloroform): δ 7.74 (1H, d, $J_{6,7}$ = 8.6, H-7), 7.60 (1H, d, $J_{4,6}$ = 1.6, H-4), 7.20 (1H, dd, $J_{6,7}$ = 8.6 and $J_{4,6}$ = 1.6, H-6), 4.74 (2H, q, J = 7.2, CH_2-CH_3), 2.48 (3H, s, 5-CH_3), 1.70 (3H, t, J = 7.2, CH_3-CH_2).

Anal. Calcd. for $C_9H_{11}N_3$: C, 67.05; H, 6.88; N, 26.07. Found: C, 67.29; H, 6.93; N, 25.90.

1-Ethyl-5-methyl-1*H*-benzotriazole (**2b**) and 1-Ethyl-6-methyl-1*H*-benzotriazole (**3b**).

A 1:1 mixture of 1-ethyl-5-methyl-1*H*-benzotriazole (**2b**) and 1-ethyl-6-methyl-1*H*-benzotriazole (**3b**), (0.90 g, 50% yield) identical to those isolated in the reaction with diethyl ethoxymethylenemalonate was obtained.

Reaction of 5-Nitro-1*H*-benzotriazole (**1c**) with Diethyl Sulfate.

In a run identical as above, from **1c** (1 g, 6.10 mmoles) and diethyl sulfate (1.18 g, 7.60 mmoles) after cooling was obtained 0.23 g of a solid precipitate, containing a mixture of three isomers **2c**, **3c** and **4c**. An additional amount (0.21 g) of the same mixture was then obtained by extraction of the mother liquors with chloroform. Flash chromatography on silica gel of the mixture eluting with diethyl ether afforded, in the order of elution, 2-ethyl-5-nitro-2*H*-benzotriazole (**4c**) (0.13 g, 11%), 1-ethyl-6-nitro-1*H*-benzotriazole (**3c**) (0.11 g, 9.4%) and 1-ethyl-5-nitro-1*H*-benzotriazole (**2c**) (0.15 g, 13%), the analytical and spectroscopic data of which were coincident with those of the samples isolated in the reaction with diethyl ethoxymethylenemalonate.

Reaction of 1*H*-1,2,3-Benzotriazole (**1a**) with Ethyl Propiolate.

A mixture of **1a** (1 g, 8.40 mmoles) and ethyl propiolate (1.65 g, 16.8 mmoles) was stirred at 60° for 12 hours. After cooling, the reaction mixture was flash chromatographed on silica gel, using as eluent a mixture 1:1 diethyl ether-light petroleum, to yield in succession (*E*)-**5a** (0.78 g, 43%), identical to a sample previously isolated in the reaction of **1a** with diethyl ethoxymethylenemalonate, and (*Z*)-**5a** (0.78, 43%) as an oil, bp 155-160°/3 mbar; R_f = 0.57; n^{20} = 1.5750; ir (neat): ν 1725, 1660, 1610, 1590 cm^{-1}; uv (ethanol): λ_{max} 301, 255, 218 sh, 206 nm; ^1H nmr (deuteriochloroform): δ 8.10 (1H, dd, $J_{4,5}$ = 8.4 and $J_{4,6}$ = 1, H-4), 7.65-7.27 (3H, m, H-5, H-6 and H-7), 7.58 (1H, d, $J_{a,x}$ = 9.6, H_a), 6.08 (1H, d, $J_{a,x}$ = 9.6, H_x), 4.18 (2H, q, J = 7.2, CH_2-CH_3), 1.12 (3H, t, J = 7.2, CH_3-CH_2).

Anal. Calcd. for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.10; N, 19.35. Found: C, 61.02; H, 5.27; N, 19.27.

Reaction of 5-Methyl-1*H*-benzotriazole (**1b**) with Ethyl Propiolate.

Using the same procedure as described for **1a**, a mixture of **1b** (3.18 g, 23.9 mmoles) and ethyl propiolate (4.70 g, 47.9 mmoles) yielded after chromatography, in the order of elution, 2.51 g (51%) of a solid formed by 1:1 mixture of the isomers (*E*)-**5b** and (*E*)-**6b** and 2.38 g (48%) of a mixture of (*Z*)-**5b** and (*Z*)-**6b**. The ratio was determined by the ratio of the integral of the 5-methyl resonances in its ^1H nmr spectra.

i.

Repeated crystallizations from diethyl ether of the mixture (*E*)-**5b** and (*E*)-**6b** gave 0.14 g (5.6%) of pure ethyl 3-(5-methybenzotriazol-1-yl)propenoate (*E*-**5b**), as crystals,

mp 88-90°; R_f = 0.83; ir (nujol): ν 1710, 1700, 1650, 1620, 1590 cm^{-1}; uv (ethanol): λ_{max} 318, 260, 232, 204 nm; ^1H nmr (deuteriochloroform): δ 8.50 (1H, d, $J_{a,x}$ = 14.4, H_a), 7.90 (1H, d, $J_{4,6}$ = 1.4, H-4), 7.63 (1H, d, $J_{6,7}$ = 8.4, H-7), 7.47 (1H, dd, $J_{6,7}$ = 8.4 and $J_{4,6}$ = 1.4, H-6), 6.69 (1H, d, $J_{a,x}$ = 14.4, H_x), 4.33 (2H, q, J = 7, CH_2-CH_3), 2.56 (3H, s, 5-CH_3), 1.38 (3H, t, J = 7, CH_3-CH_2).

Anal. Calcd. for $C_{12}H_{13}N_3O_2$: C, 62.32; H, 5.67; N, 18.17. Found: C, 62.30; H, 5.70; N, 18.30.

Characterization of compound (*E*)-**5b** by its ^1H nmr data allowed us to assign unambigously the remaining resonances to the isomer, ethyl 3-(6-methylbenzotriazol-1-yl)propenoate (*E*-**6b**); ^1H nmr (deuteriochloroform): δ 8.50 (1H, d, $J_{a,x}$ = 14.4, H_a), 7.99 (1H, d, $J_{4,5}$ = 8.6, H-4), 7.51 (1H, d, $J_{5,7}$ = 1.4, H-7), 7.25 (1H, dd, $J_{4,5}$ = 8.6 and $J_{5,7}$ = 1.4, H-5), 6.70 (1H, d, $J_{a,x}$ = 14.4, H_x), 4.33 (2H, q, J = 7, CH_2-CH_3), 2.58 (3H, s, 6-CH_3), 1.37 (3H, t, J = 7, CH_3-CH_2).

ii.

Similarly as under 1) from the mixture of (*Z*)-**5b** and (*Z*)-**6b**, 3-(6-methylbenzotriazol-1-yl)propenoate (*Z*-**6b**) was obtained pure (0.03 g, 1%) as crystals, mp 64-66° (diethyl ether); R_f = 0.59; ir (nujol): ν 1725, 1710, 1665, 1620, 1590 cm^{-1}; uv (ethanol): λ_{max} 301, 262, 250, 204 nm; ^1H nmr (deuteriochloroform): δ 7.96 (1H, d, $J_{4,5}$ = 8.4, H-4), 7.48 (1H, d, $J_{a,x}$ = 9.4, H_a), 7.24 (1H, d, $J_{4,5}$ = 8.4 and $J_{5,7}$ = 1.4, H-5), 7.18 (1H, d, $J_{5,7}$ = 1.4, H-7), 6.04 (1H, d, $J_{a,x}$ = 9.4, H_x), 4.18 (2H, q, J = 7.2, CH_2-CH_3), 2.54 (3H, s, 6-CH_3), 1.12 (3H, t, J = 7.2, CH_3-CH_2).

Anal. Calcd. for $C_{12}H_{13}N_3O_2$: C, 62.32; H, 5.67; N, 18.17. Found: C, 62.54; H, 5.67; N, 18.25.

Characterization of compound (*Z*)-**6b** by its ^1H nmr data allowed us to assign unambigously the remaining resonances to the isomer, ethyl 3-(5-methylbenzotriazol-1-yl)propenoate (*Z*-**5b**); ^1H nmr (deuteriochloroform): δ 7.84 (1H, d, $J_{4,6}$ = 1.4, H -4), 7.63 (1H, d, $J_{6,7}$ = 8.4, H-7), 7.53 (1H, d, $J_{a,x}$ = 9.6, H_a), 7.47 (1H, dd, $J_{6,7}$ = 8.4 and $J_{4,6}$ = 1.4, H-6), 6.04 (1H, d, $J_{a,x}$ = 9.6, H_x), 4.18 (2H, q, J = 7.2, CH_2-CH_3), 2.54 (3H, s, 5-CH_3), 1.12 (3H, t, J= 7.2, CH_3-CH_2).

Reaction of 1*H*-Benzotriazole (**1a**) with Ethyl Acetoacetate.

A mixture of 2 g (16.8 mmoles) of **1a** and 4.4 g (33.6 mmoles) of ethyl acetoacetate was stirred at 180° for 68 hours. After cooling the reaction mixture was flash chromatographed, eluting with a 1:1 mixture of diethyl ether-light petroleum to give, in the order, **4a** (10% yield) and **2a** (9.3% yield), identical to the samples obtained in the reactions with diethyl ethoxymethylenemalonate and diethyl sulfate, previously described, and unreacted **1a** (78%).

Reaction of 5-Nitro-1*H*-benzotriazole (**1c**) with Ethyl Acetoacetate.

Following the same procedure reported for **1a**, starting from **1c** (1.5 g, 9.13 mmoles) and ethyl acetoacetate (2.4 g, 18.4 mmoles) were obtained, after chromatography, respectively **4c** (5.1%), **3c** (3.5%), and **2c** (9.1%), whose analytical and spectroscopic data were coincident to those of compounds obtained in the reaction with diethyl ethoxymethylenemalonate.

Reaction of 1*H*-Benzotriazole (**1a**) with Ethyl Orthoformate.

A mixture of **1a** (2 g, 16.8 mmoles) and ethyl orthoformate (5 g, 33.7 mmoles) was stirred at 140° for 30 hours. After cooling, the reaction mixture was purified by flash chromatography, using as eluent a 1:1 mixture of diethyl ether-light petroleum, to yield in the order **2a** (0.18 g, 6%), identical to the sample isolated in the reaction with diethyl ethoxymethylenemalonate, and unreacted **1a** (1.86 g, 93%).

Reaction of 1*H*-Benzotriazole (**1a**) with Ethyl Propionate.

A mixture of **1a** (2 g, 16.8 mmoles) and ethyl propionate (3.5 g, 34 mmoles) was stirred at 160° for 68 hours. After cooling, crystallization from diethyl ether of the reaction mixture gave 1.9 g (95%) of the unreacted **1a**.

X-Ray Crystallography of Compound **8**.

The structure of compound **8** was conclusively confirmed by X-ray crystallography as shown in Figure 1. The crystal data and X-ray experimental details are reported as follows: formula: $C_{28}H_{36}N_2O_8$, M = 528.6, monoclinic, space group C2/c, a = 40.581(8), b = 9.876(2), c = 30.985(5) A, b = 113.34(2)°, V = 11402(4) A^3, Z = 16, D_c = 1.23 g cm^{-3}, m (CuKα) = 7.46 cm^{-1}.

X-ray data were collected at room temperature on a Siemens AED diffractometer using CuKα radiation (λ = 1.54178 Å). The structure was solved by direct methods using SIR92 [10] and refined by full-matrix least squares on F2 with the SHELXL93 package [11] to R1 = 0.0771 (calculated on 8235 unique data having I>2s(I)) and wR2 = 0.2465 (all 10790 unique data) for 698 parameters refined. Non-hydrogen atoms were refined anisotropically, hydrogen atoms were introduced at calculated positions, with isotropic thermal parameters set to 1.2 times the one of the carrier atom, geometry calculation and drawing were performed with PARST [12] and ZORTEP [13]. There are two symmetry-indipendent molecules per asymmetric unit; the most evident feature differentiating them is the orientation of the -C=O groups at C23 and C51, which are, respectively, *trans* and *cis* to the double bond C21 = C22 and C49 = C50 (torsion angles: C21-C22-C23-O5 = 177.0(3)° and C49-C50-C51-O13 = -13.9(6)°). Minor differences are present also in the orientation of the remaining terminal ethyl groups. Otherwise, the two molecules are congruent within a mean square atomic deviation of 0.08A^2. Both molecules, the structure of one of which is illustrated in Figure 1 along with its numebring scheme, can be described on the basis of two planes, one comprising the benzimidazolic moiety, and the other the carbon backbone of the branched chain. The two planes are connected by the bond indicated as C11-C12 as shown, and form dihedral angles of 72.68(6)° and 69.78(8)° respectively. Packing is due to normal Van der Waals interactions.

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