TRIAZOLOPYRIDINES. 15[1]. REACTIONS BETWEEN TRIAZOLO-PYRIDINIUM YLIDES AND ALKENES

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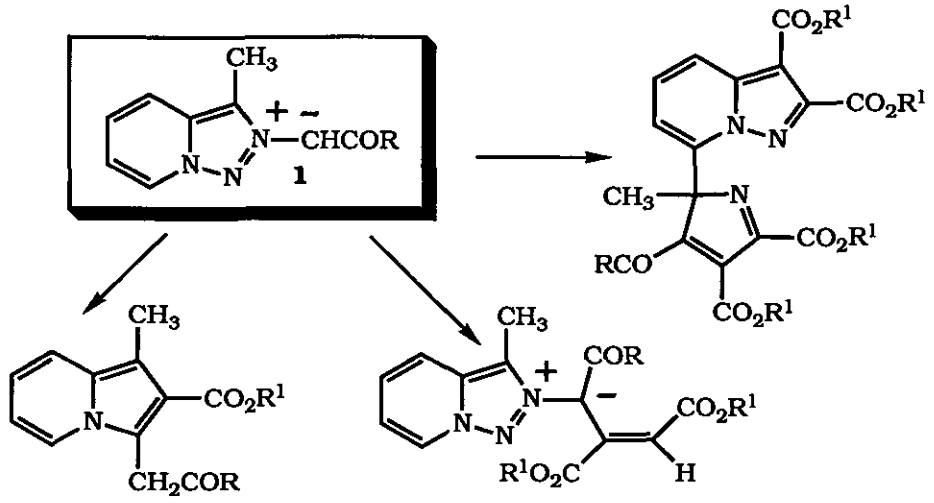
Abstract - The triazolopyridine ylides (**1**) react with acrylates (**2**) to give 3-(2-pyridyl)acrylates (**4a**) and (**4b**), the 2-pyridylcyclobutanes (**5a**)-(**5g**), the pyridylpent-1-ene (**8**) and the zwitterion (**3**). The mechanism of reaction between the ylides (**1**) and acrylates or alkynes is discussed.

We have reported[2-4] that the triazolopyridinium ylides (**1**) react with acetylenic dipolarophiles to give a range of new heterocycles (Scheme 1). We have now studied the reaction between ylides (**1**) and acrylates; the reactions are slower, but the new products give information on the reaction between ylides (**1**) and dipolarophiles.

Dedicated to Professor E.C. Taylor on his 70th birthday.



Scheme 1

Our first experiment used the ylide (**1a**) and methyl acrylate (**2a**). Reactions were throughout done in toluene solution, with a mixture of triethylamine and anhydrous potassium carbonate as base. After twelve hours at ambient temperature, the toluene soluble products were separated by Chromatotron; the major product was isolated from the toluene-insoluble salts, and shown to be the zwitterion (**3**) (74%), formed by simple hydrolysis of the ylide. From the toluene-soluble material two major and one minor products were obtained. The simpler of the major products was the 3-(2-pyridyl)acrylate (**4a**), (3%), characterised by its nmr spectra and by gc/ms. In the ^{1}H nmr spectrum typical aromatic signals were at 8.65, 7.75, 7.51, and 7.26, characteristic of an α-substituted pyridine, a one proton signal at 6.69 (q, J=1.2 Hz), showing coupling to a methyl doublet (J=1.2 Hz) at 2.62, and a methyl singlet at 3.78 due to the methyl ester. DIFNOE spectra, irradiating at 2.62 and 6.69, produced enhancement only of the pyridine β-proton signal at 7.51, thus confirming the configuration about the double bond as E. The second product (11%) was also a 2-pyridyl derivative (^{1}H nmr), with a molecular formula of $C_{14}H_{17}NO_4$. In the aliphatic region the ^{1}H nmr spectrum showed three methyl singlets, two due to methyl esters (at 3.75 and 3.39), and the third, at 1.53, due to a methyl group attached to an sp^3 quaternary carbon atom. A sequence of four signals, each due to a

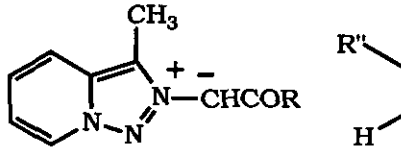
Table 1: ^{1}H Nmr data ($CDCl_3$) for Cyclobutanes (**5a**) - (**5g**)

	Pyridine Ring				Cyclobutane Ring								Coupling Constants
	H6	H5	H4	H3	$H_{2\alpha}$	$H_{2\beta}$	$H_{3\alpha}$	$H_{3\beta}$	$H_{4\alpha}$	$H_{4\beta}$	Me	Other	(Hz)
5a	8.49	7.09	7.62	7.52	4.14	——	2.32	2.70	——	3.14	1.53	3.75(s,3H,C2-COOMe) 3.39(s,3H,C4-COOMe)	$J_{2\alpha,3\alpha}=J_{2\alpha,3\beta}=9.27$; $J_{3\alpha,4\beta}=J_{3\beta,4\beta}=9.03$; $J_{3\alpha,3\beta}=11.96$
5b	8.49	7.10	7.66	7.52	4.18	——	2.32	2.72	——	3.12	1.55	3.76(s,3H,C2-COOMe) 3.82(q,2H)0.96(t,3H)	$J_{2\alpha,3\alpha}=J_{3\alpha,4\beta}=J_{3\beta,4\beta}=9.03$; $J_{2\alpha,3\beta}=9.27$; $J_{3\alpha,3\beta}=11.96$
5c	8.47	7.11	7.67	7.33	————		2.32	2.86	——	3.20	1.58	4.25(q,2H)3.58(s,3H, C4-COOMe)1.34(t,3H) 0.96(s,3H)	$J_{3\alpha,4\beta}=9.27$; $J_{3\beta,4\beta}=8.30$; $J_{3\alpha,3\beta}=11.59$
5d	8.69	7.65	*	*	————		3.4	1.70	——	5.30	1.00	4.22(q,2H)1.32(t,3H) 1.30(s,3H)8.20(d,2H *ortho*)7.50-7.71(m,2H)	$J_{3\alpha,4\beta}=10.30$; $J_{3\beta,4\beta}=8.30$; $J_{3\alpha,3\beta}=11.80$
5e	8.63	*	*	*	3.88——		3.10	2.25	——	5.22	1.20	3.57(s,3H)7.00-7.80 (m,7H)	$J_{2\alpha,3\alpha}=8.60$; $J_{2\alpha,3\beta}=10.60$; $J_{4\beta,3\alpha}=J_{4\beta,3\beta}=8.40$; $J_{3\alpha,3\beta}=11.50$
5f	8.15	6.9	*	*	——	4.13	2.32	2.75	4.25	——	1.64	3.71(s,3H)7.00-7.80 (m,7H)	$J_{2\beta,3\alpha}=J_{2\beta,3\beta}=9.50$; $J_{3\alpha,4\alpha}=3.00$; $J_{3\beta,4\alpha}=9.00$; $J_{3\alpha,3\beta}=11.50$
5g	8.72	*	*	*	——	3.20	2.90	2.60	——	4.75	1.42	3.26(s,3H)7.00-7.80 (m,7H)	$J_{2\beta,3\alpha}=J_{2\beta,3\beta}=11.30$; $J_{4\beta,3\alpha}=8.40$ $J_{4\beta,3\beta}=10.30$; $J_{3\alpha,3\beta}=11.50$

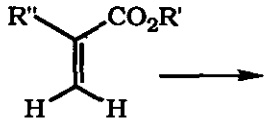
*included in other

single hydrogen, at 4.14, 2.32, 2.70, and 3.14, were shown by decoupling to be due to the sequence -CH^A-$C(H^BH^C)$-CH^D, H^B and H^C having a geminal coupling constant of 11.96 Hz. The only satisfactory formula was the cyclobutane (**5a**). The relative stereochemistry about C2, C3, and C4 of the cyclobutane was established by DIFNOE. Irradiation at 1.53 (quaternary methyl) caused enhancement of H^B and H^D; thus of the two $CHCO_2CH_3$ groups the H of only one is cis to the quaternary methyl group. A negative NOE[5] was observed for the H^C signal. The different shifts of the methyl ester groups can be explained by the shielding effect of the pyridine ring on the substituent on C4; Ziffer et al. report a similar effect.[6]

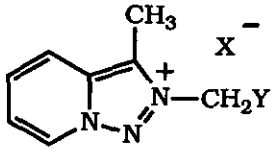
A second experiment was conducted to discover the source of the ester group in the pyridylacrylate (**4a**). When the ylide (**1b**) was treated with methyl acrylate (**2a**), the isolated acrylate was again (**4a**); hence the ester group in the acrylate originates from the methyl acrylate, not from the ylide. The major product was zwitterion (**3**) (70%).



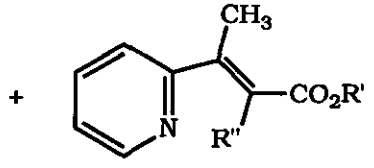
1a, R=OCH$_3$
1b, R=OC$_2$H$_5$
1c. R=C$_6$H$_5$



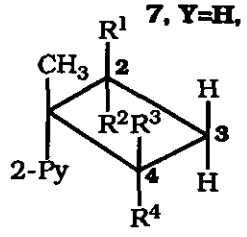
2a, R'=CH$_3$, R"=H
2b, R'=C$_2$H$_5$, R"=CH$_3$



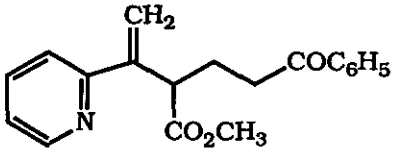
3, Y=CO$_2$
7, Y=H, X=C$_6$H$_5$CO$_2$



4a, R'=CH$_3$, R"=H
4b, R'=C$_2$H$_5$, R"=CH$_3$



5a, R^1=R^4=CO$_2$CH$_3$, R^2=R^3=H
5b, R^1=CO$_2$CH$_3$, R^4=CO$_2$C$_2$H$_5$, R^2=R^3=H
5c, R^1=CO$_2$C$_2$H$_5$, R^2=CH$_3$, R^3=H, R^4=CO$_2$CH$_3$
5d, R^1=CO$_2$C$_2$H$_5$, R^2=CH$_3$, R^3=H, R^4=COC$_6$H$_5$
5e, R^1=CO$_2$CH$_3$, R^2=R^3=H, R^4=COC$_6$H$_5$
5f, R^1=R^4=H, R^2=CO$_2$CH$_3$, R^3=COC$_6$H$_5$
5g, R^1=R^3=H, R^2=CO$_2$CH$_3$, R^4=COC$_6$H$_5$



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A new cyclobutane was isolated, containing one methoxycarbonyl and one ethoxycarbonyl group. A careful study of the chemical shifts of the cyclobutane

protons, and comparison with those of compound (**5a**) (Table 1) indicates a similar geometry. The near identity of shift of the methyl group of the methyl ester in the new cyclobutane with that assigned to the C2 ester methyl in compound (**5a**) leads to the formula (**5b**). When ethyl methacrylate (**2b**) was reacted with the ylide (**1a**), the products included two acrylates (**4a**) and (**4b**), and a single cyclobutane (10%). Again the very close similarity in chemical shift of H3$^{\alpha}$, H3$^{\beta}$, and H4 to those in compound (**5a**) (Table 1) leads to formula (**5c**). The ethoxycarbonyl group, being derived from the methacrylate, must be at C2.

Since, in each of the preceding reactions, the major product was the zwitterion (**3**) we examined the reaction of ylide (**1c**), where zwitterion (**3**) was a less likely product. Reaction of ylide (**1c**) with ethyl methacrylate (**2b**) gave a simpler mixture of products than similar reaction with methyl acrylate (**2a**) and is dealt with first. The acrylate (**4b**) and 3-methyltriazolopyridine (**6**) were easily identified. A single crystalline cyclobutane was formulated as **5d** on the basis of its nmr spectra (Table 1). DIFNOE with irradiation at 1.00 (methyl group at C1) showed enhancement of the pyridine β-signal and cyclobutane H4 doublet (5.30) proving that the benzoyl group was cis to the pyridine ring. Confirmation of this assignment was provided by irradiation at 8.20 (benzene, o-protons), causing enhancement of the pyridine β-proton, the H4 doublet, and the second methyl signal (1.32). Irradiation of the methyl signal at 1.32, caused enhancement of H3$^{\alpha}$ (3.41) with a negative NOE for H3$^{\beta}$ (1.70). The signal for H4 is further downfield than that in compound (**5a**) because of the greater deshielding of the benzoyl group. Examination of the solid toluene-insoluble material showed the presence of a substantial quantity of the quaternary benzoate (**7**).

Finally, reaction between ylide (**1c**) and methyl acrylate (**2a**) gave a mixture of toluene-soluble products from which only the pyridylacrylate (**4a**) could be isolated pure. Careful chromatography gave two major fractions, one containing two compounds, the second four (by gc); on standing one of the four components disappeared, with a concomitant increase in one of the others. One component was shown to be common to both fractions. The structures of the products were

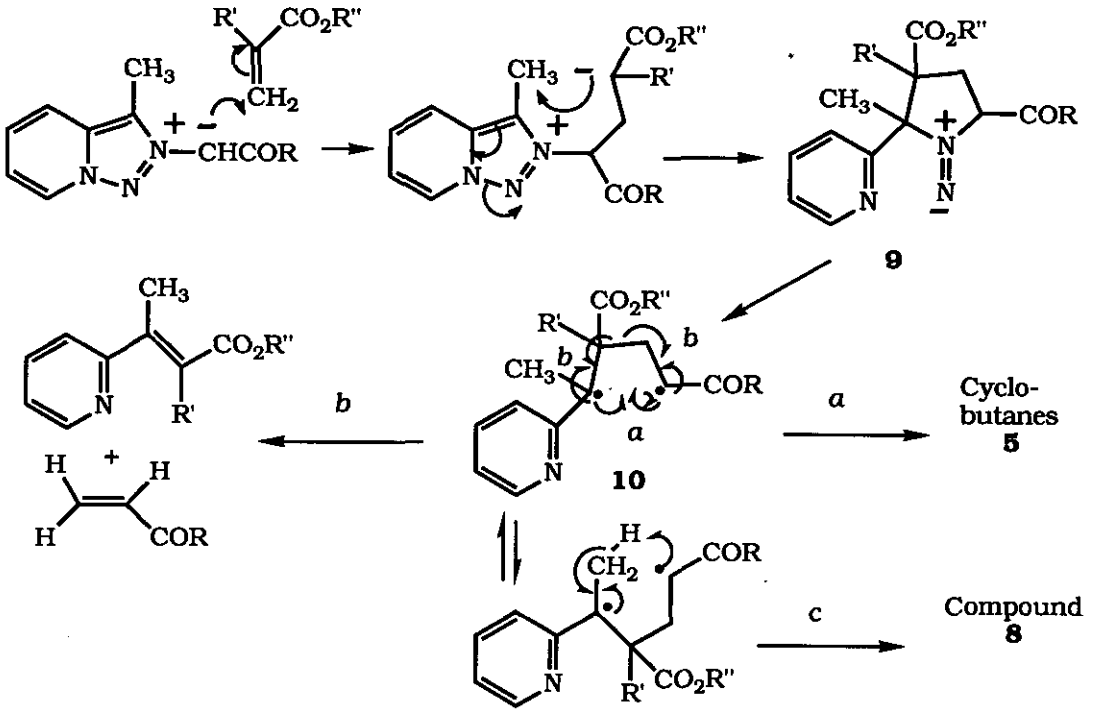
assigned by a combination of gc/ms and ^1H nmr. The fraction with two components, subjected to gc/ms, gave characteristic mass spectra, showing that the two components were isomers, $C_{19}H_{19}NO_3$; losses of 31 mu, 59 mu, and the presence of an ion at 105 mu confirmed that both compounds contained a methoxycarbonyl and a benzoyl group. The ^1H nmr spectrum showed clear signals at 2.32, 2.75, 4.13, and 4.25 for the minor component with the characteristic splitting of a cyclobutane of type (**5**). The outstanding feature of the major component of this fraction was an exo methylene group (singlets at 5.45 and 5.85, confirmed by a ^{13}C signal at 116.69). The compound also showed two methylene carbons (25.78 and 36.23) and one methine (45.90), and this subunit leads to the formula (**8**), a 5-benzoyl-2-(2-pyridyl)pent-1-ene. Traces of similar pentenes were found on careful examination of nmr spectra of the crude products from previous experiments, but none were isolated. Returning to the second fraction, now containing three isomeric products, the major one of which was the same cyclobutane (**5f**) found in the first fraction, a gc/ms separation confirmed that all had a molecular weight of 309, with very similar losses of OCH_3, and CO_2CH_3 fragments and all showed a strong ion at 105 mu for the benzoyl group. An expanded ^1H nmr spectrum of the region from 0.50 to 5.50 allowed the observation of most of the cyclobutane hydrogen signals for all three isomers (Table 1). One of the minor isomers showed signals at 2.25, 3.10, 3.88, and 5.22. Comparison with the cyclobutane signals for compounds already characterized (Table 1) allow us to assign the structure (**5e**). The other minor isomer was assigned structure(**5g**). We believe that in this isomer the pyridyl, benzoyl, and methoxycarbonyl group are on the same side of the molecule because the values of H2 (3.20) and H4 (4.75) are shielded with respect to those of compound (**5e**), and the ^{13}C shift of the methyl group, free of steric hindrance, is at 14.63 (Table 2). The chemical shifts for the cyclobutane hydrogens in the third (major) isomer are in agreement with those expected for compound (**5f**). It seems probable that the fourth component, present in the crude fraction, was the isomer with ester, methyl, and benzoyl groups in an all cis relationship, isomerizing to compound (**5e**).

Table 2: ^{13}C Nmr Data ($CDCl_3$) for Cyclobutanes (**5a**) - (**5g**)

	Pyridine					Cyclobutane					
	C_2'	C_3'	C_4'	C_5'	C_6'	C_1	C_2	C_3	C_4	Me	Other
5a	163.58	119.15	135.58	120.26	147.48	48.89	46.32*	42.52*	20.57	23.72	173.70(s)172.17(s)50.62(q) 50.29(q)
5b	163.62	119.13	135.48	120.24	147.50	49.74	46.57*	42.45*	20.66	23.69	173.11(s)172.25(s)50.63(q) 59.14(t)12.87(q)
5c	161.36	121.95*	136.09	121.45*	147.74	49.14	54.06	45.08	21.43	26.19	175.76(s) 175.37(s) 60.71(t) 51.16(q) 29.53(q) 14.41(q)
5d	161.43	122.16*	136.34	121.85*	147.75	48.17	53.19	40.06	27.21	22.38	201.09(s)175.24(s)137.52(s) 132.83(d)129.03(d) 128.23(d)60.62(t)19.31(q) 14.54(q)
5e	162.70	120.37*	136.12	121.82*	148.30	51.57	47.89*	45.35*	19.07	22.88	200.04(s)173.11(s)136.69(s) 132.68(d)128.21(d) 128.04(d) 51.10(q)
5f	163.43	120.00*	136.12	120.89*	148.03	51.88	48.81*	43.13*	21.62	24.45	201.91(s)173.21(s)138.15(s) 132.18(d)127.97(d)127.87 (d)51.45(q)
5g	161.90	120.05*	136.28	120.81*	149.22	51.13	46.21*	44.15*	18.90	14.63	198.59(s)172.18(s)136.36(s) 132.69(d)128.13(d) 127.99(d) 51.01(q)

* Or vice versa

We are now in a position to advance a mechanism for the cycloaddition reactions of the ylides (**1**) which can be applied to the reaction with alkenes and alkynes, Scheme 2. The first attack by the ylide on the acrylate is a Michael addition, and this is followed by a cyclization to position 3 of the triazolopyridine, with concomitant cleavage of the N-N bond to give a cyclic diazene (**9**). Such diazenes are known to fragment to give nitrogen and a diradical (**10**). Such a diradical could cyclize to cyclobutanes (route a) without the necessity for stereochemical integrity, fragment to give two alkenes (route b), or undergo hydrogen abstraction from the methyl group (route c) to give all the observed products. In the previously reported cycloadditions using alkynes, a similar mechanism was suggested to account for the formation of indolizines[4].



Scheme 2

EXPERIMENTAL

Mps were recorded on a heated stage, and are uncorrected. Nmr spectra were determined for solutions in $CDCl_3$, unless otherwise stated, on a Jeol GSX 270 MHz

spectrometer. In ^{13}C nmr off-resonance multiplicities are given in parenthesis. Ms/gc determinations were made using a Hewlett-Packard MSD. Chromatographic separations used a Chromatotron, with 2 mm silica plates, eluting with mixtures of hexane and ethyl acetate, in proportions presented thus (9:1).

General Procedure for Reaction between Ylide (1) and Acrylate (2): A suspension of the appropriate salt (preparation previously described[7]) (0.007 mol) in anhydrous toluene (30 ml) with triethylamine (1 ml) and anhydrous potassium carbonate (1 g, 0.0072 mol) was stirred vigorously at room temperature (4 h) during which a yellow paste formed. Methyl acrylate **or** ethyl methacrylate (0.007 mol) was added, and stirring continued (1-7 days). The mixture was filtered, the filtrate was evaporated under reduced pressure and the residue was separated by Chromatotron. The solid, separated in the filtration, was exhaustively extracted with methanol to give the zwitterion (**3**) with the ylides (**1a**) and (**1b**), and the quaternary benzoate (**7**) with ylide (**1c**). The zwitterion (**3**) was crystallized from isopropanol, mp 183-184°C *(decomp.)*. The zwitterion could not be obtained free of traces of inorganic salt, and was characterized by nmr spectra. ^1H Nmr (D_2O) 2.75 (3H, s), 5.38 (2H, s), 7.66-7.81 (2H, m), 8.17 (1H, d, J=9.04 Hz), and 8.93 (1H, d, J=6.8 Hz). ^{13}C Nmr (D_2O) 20.02 (q), 43.52 (t), 109.00 (d), 112.55 (d), 115.20 (d), 118.90 (d), 123.25 (s), 123.98 (s), 159.49 (s). Individual products are listed with their physical properties.

Methyl (E)3-(2-pyridyl)but-2-enoate (**4a**). Obtained from ylide (**1a**) and methyl acrylate (**2a**) in 3% yield after chromatography (9:1) as an oil. A sample gave a single peak on gc/ms, and showed m/z 177 (M^+, shown by appearance potential, 17%), 162 (15%, M^+-CH_3), 146 (22%, M^+-CH_3O), 145 (39%, M^+-CH_3OH), 119 (9%), 117 (100%, M^+-CH_3CO_2H), 91 (15%), 90 (19%), 89 (12%), 78 (21%, $C_5H_4N^+$). ^1H Nmr 2.60 (3H, d, J=1.38 Hz), 3.77 (3H, s), 6.69 (1H, q, J=1.38 Hz, H2), 7.25 (1H, ddd, J=7.00, 4.77, and 0.95 Hz, H5'), 7.55 (1H, ddd, J=8.00 1.00, and 1.00 Hz, H3'), 7.75 (1H, ddd, J=8.00, 7.00, and 1.79 Hz, H4'), 8.65 (1H, ddd, J=4.77, 1.79, and 0.95 Hz, H6'). ^{13}C Nmr 15.88 (q), 51.17 (q), 118.92 (d), 121.06 (d), 123.70 (d), 136.86 (d), 149.42 (d), 153.55 (s), 158.14 (s), 167.61 (s).

2β,4α-Bismethoxycarbonyl-1β-methyl-1α-(2-pyridyl)cyclobutane (**5a**). Obtained from ylide (**1a**) (9:1) and methyl acrylate (**2a**) (4 days) in 11% yield as an oil (from the Chromatotron). (Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.46; N, 5.32. Found: C, 63.95; H, 6.57; N, 5.27). m/z 263 (19%, M^+), 204 (89%, M^+-CO_2CH_3), 177 (65%, 2-pyridyl-C(CH_3)=$CHCO_2Me^+$), 146 (56%), 118 (63%), 117 (100%).

4α-Ethoxycarbonyl-2β--methoxycarbonyl-1β-methyl-1α-(2-pyridyl)cyclobutane (**5b**): obtained from ylide (**1b**) and methyl acrylate (**2a**) (1 day), in 5.4% yield as an oil from the Chromatotron (9:1). (Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.93; H, 6.85; N, 5.05%. Found: C, 64.67; H, 7.08; N, 4.87) . m/z 277 (40%, M^+), 218 (100%, M^+-CO_2CH_3).

Ethyl 2-Methyl-(E)3-(2-pyridyl)but-2-enoate (**4b**): obtained in 7% yield from ylide (**1a**) and ethyl methacrylate (**2b**) as an oil, purified by Chromatotron (9:1), and characterized only by nmr spectra. ^1H Nmr 1.30 (3H, t, J=7.0 Hz), 1.70 (3H, q, J=1.4 Hz), 2.30 (3H, q, J=1.4 Hz), 4.25 (2H, q, J=7.0 Hz), 7.00-7.30 (2H, m), 7.40-7.75 (1H, m), 8.60 (1H, d, α-pyridine, J=5 Hz). ^{13}C Nmr 14.29 (q), 17.11 (q), 21.35 (q), 60.61 (t), 122.01 (d), 122.91 (d), 136.30 (d), 148.37 (s), 149.48 (d), 160.98 (s), 161.90 (s), 169.69 (s).

2β-Ethoxycarbonyl-1β,2α-dimethyl-4α-methoxycarbonyl-1α-(2-pyridyl)cyclobutane (**5c**). Obtained in 10% yield from ylide (**1a**) and ethyl methacrylate (**2b**) (1 day), and purified by chromatotron (9:1) as an oil. (Anal. Calcd for $C_{16}H_{21}NO_4$: C, 65.97; H, 7.21; N, 4.81. Found: C, 65.84; H, 7.38; N, 5.00). m/z 291 (15%,M^+),232(100%,M^+-CO_2CH_3),177(36%,2-pyridyl-C(CH3)-$CHCO_2CH_3^+$), 146(43%), 118(32%), 117(49%).

4α-Benzoyl-2β-ethoxycarbonyl-1β,2α-dimethyl-1α-(2-pyridyl)cyclobutane(**5d**): Obtained from ylide (**1c**) and ethyl methacrylate (**2b**)(7 days) in 7.3% yield, as a solid, mp 84-85°C (from petroleum ether). (Anal. Calcd for $C_{21}H_{23}NO_3$: C, 74.77; H, 6.85; N, 4.15. Found: C, 74.62; H, 6.79; N, 4.10). m/z 337 (2%, M^+), 232 (100%, M-C_6H_5CO).

Cyclobutanes (**5e**), (**5f**), and (**5g**) were present in the two major fractions obtained by chromatography from the reaction between ylide (**1c**) and methyl acrylate (**2a**); both were oils.

4α-Benzoyl-2β-methoxycarbonyl-1β-methyl-1α-(2-pyridyl)cyclobutane(**5e**). Separated by gc/ms; m/z 309 (9%, M^+), 250 (82%, M^+-CO_2CH_3), 232 (46%, M^+-C_6H_5), 204 (59%, M^+-C_6H_5CO), 172 (27%), 146 (39%), 145 (46%), 144 (50%), 130 (20%), 118 (36%), 117 (69%), 105 (100%, $C_6H_5CO^+$) 78 (22%, $C_5H_4N^+$) 77 (77%, $C_6H_5^+$).

4β-Benzoyl-2α-methoxycarbonyl-1β-methyl-1α-(2-pyridyl)cyclobutane(**5f**) Separated by gc/ms. m/z 309 (6%, M^+), 250 (73%, M^+-CO_2CH_3), 204 (75%, M^+-C_6H_5CO), 146 (24%), 145 (20%), 144 (39%), 118 (20%), 117 (40%), 105 (100%, $C_6H_5CO^+$), 78 (17%, $C_5H_4N^+$) 77 (55%, $C_6H_5^+$).

4α-Benzoyl-2α-methoxycarbonyl-1β-methyl-1α-(2-pyridyl)cyclobutane(**5g**) Separated by gc/ms. m/z 309 (5%, 251 (20%), 250 (100%, M^+-CO_2CH_3), 204 (55%, M^+-C_6H_5CO), 177 (21%), 145 (33%), 144 (39%), 130 (20%), 118 (27%), 117 (43%), 107 (24%), 105 (96%, $C_6H_5CO^+$), 78 (19%, $C_5H_4N^+$), 77 (67%, $C_6H_5^+$).

5-Benzoyl-3-methoxycarbonyl-2-(2-pyridyl)-pent-1-ene (**8**). Separated by gc/ms. m/z 309 (5%, M^+), 278 (15.8%, M^+-OCH_3), 250 (100%, M^+-CO_2CH_3), 232 (42%, M^+-C_6H_5), 204 (60.5%, M^+-C_6H_5CO), 144 (34%), 143 (50%,), 117 (42%), 105 (71%, $C_6H_5CO^+$), 77 (47%, $C_6H_5^+$).

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