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Intermolecuar (4+2) π cycloadditions of 2,6–bis (3-phenylallylidene) and 2,6-bis (furan-2-ylmethylene) cyclohexanones with reactive dieneophiles under classical and microwave heating

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Abstract : Synthetic approaches towards new dispiro derivatives and bicyclic ring systems have been achieved by application of intermolecular (4+2) π cycloaddition reactions of suitably dieneophiles with the title compounds under thermal and microwave conditions. Also, the antimicrobial activity of some of the synthesized compounds was tested.

Keywords : Dispiro compounds; Bicyclic ring systems; Microwave heating.

INTRODUCTION

α-Enones underwent a variety of cycloaddition and self-condensation reactons[1-6]. They behave as building blocks in synthesis of multiply substiuted benzenes via a formal [3+3] cycloaddition[7]. As well as [2+2] photocycloaddition of chiral cyclic enones with olefins was reported[8,9]. In the previous work we utilized the title compounds in heterocyclic synthesis[10]. Herein we report an investigation of reactions of these compounds with reactive dieneophiles. Moreover, a comparison of the results obtained from classical and microwave heating was presented.

RESULTS AND DISCUSSION

In the present investigation, no reactions, of (E,Z)-2,6-bis (3-phenylallylidene)cyclohexanone (1) with electron deficient dienophiles 2-4 toke place at room temperature. However, refluxing of compound 1 with the reagents 2-4 in toluene for 25-30 hours afforded 1:2 adducts in reasonable yields. Thus, reaction of 1 with diethyl acetylenedicarboxylate (2) in toluene for 30 hours gave an adduct 5 as shown in Scheme 1. The structure of 5 was evidenced from its microanalytical and spectroscopic data that shows it is formulated as a dispiro derivative. The IR absorption bands at 1730

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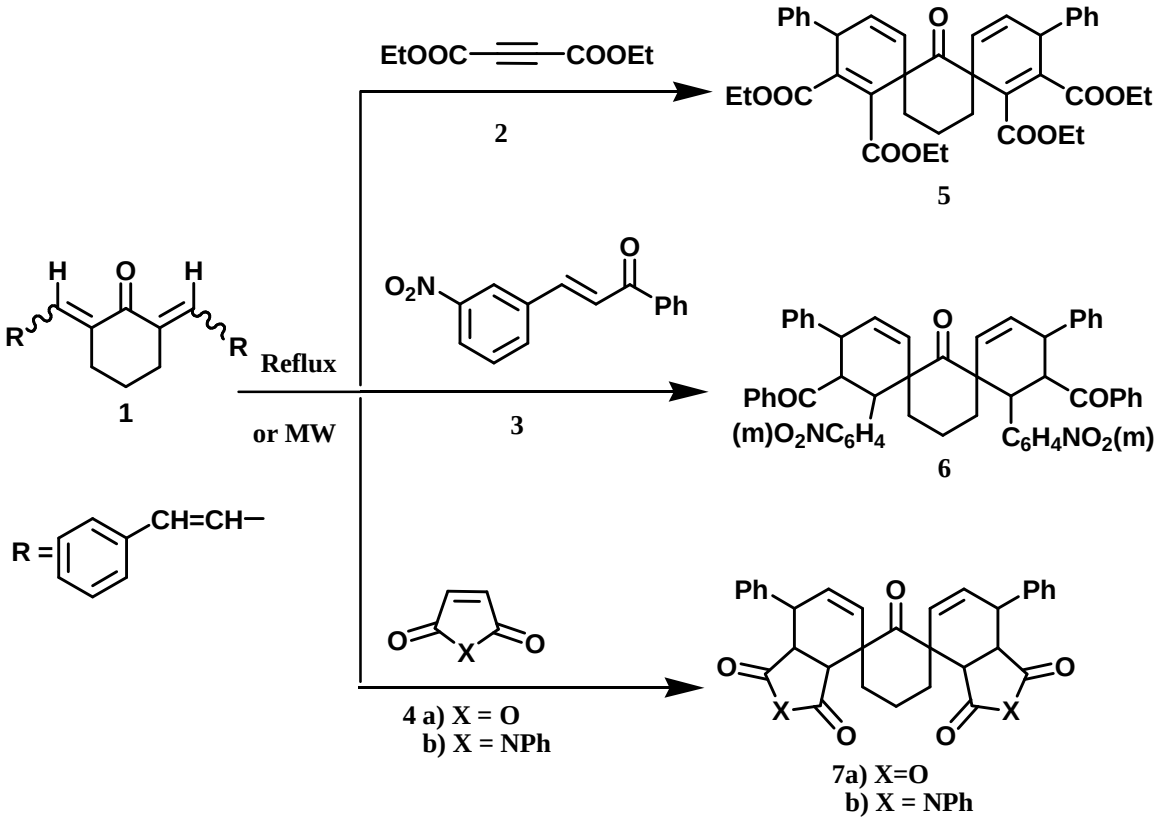
and 1661 cm^{-1} confirmed the presence of carbonyl groups of ester and ketone respectively. The ^{1}HNMR spectrum supports the structure as it shows a multiplet signal at δ 1.1-1.4 ppm corresponds to four methyl groups, two multiplets signals at 3.3-4.1 and 4.2-4.6 correspond to four methylene groups as well as signals for olefinic and aromatic protons (see Experimental). Further support for the assigned structure of 5 was given from its mass spectrum that shows the correct molecular ion and fragment peaks correspond very well with its proposed structure. The low absorption value of C=O group of cyclohexanone moiety (not conjugated C=O group) at 1661 cm^{-1} indicate the existence a trans annular conjugation between the cyclohexanone carbonyl group and one of the two C=C at carbons 2' or 2'' in compound 5. This also supported by the fact that the two spiro rings are placed in 1,3-trans axial-equatorial conformation. Moreover, the adduct 5 was prepared in 95% yield after 10 minutes of microwave heating. On the other hand the yield of 5 was 60% after 30 hours of reflux (TABLE 1). The formation of compound 5 can be rationalized on the basis of (4+2) π cycloaddition reactions.

Similar treatments of compound 1 with 3-(3-nitrophenyl)-1- phenylprop-2-en-1-one (3), maleic anhydride (4a) or N-phenylmalimide (4b) proceeded in similar manner to give dispiro compounds 6,7a and 7b respectively. It is believed that these compounds were formed via direct 4+2 cycloaddition reactions (Scheme 1). Microwave irradiation was used to facilitate these reactions by improving their yields and decreasing their reactions times as shown in TABLE 1. The structures of these products were elucidated from their microanalytical and spectral data (see Experimental).

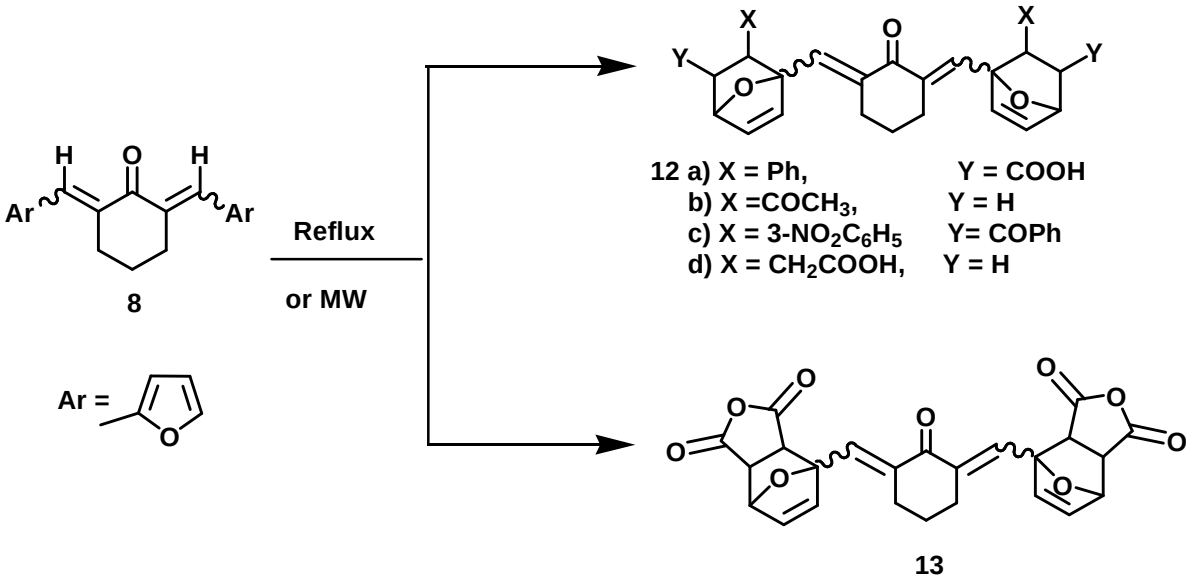
Refluxing of (E/Z)-2,6 Bis (furan-2-ylmethylene)cycohexanone (8) in toluene with cinnamic acid (9), 1-buten-3-one(10),3-(3-nitrophenyl)-1-phenyl prop-2-en-1-one (3), vinylacetic acid (11) and maleic anhydride (4a) afforded the cycloadducts 12a-d and 13 in reasonable yields (Scheme 2). The formation of compounds 12a-d and 13 is explaned on the basis of (4+2) π cycloaddition reactions. The reactive dienophiles added entirely to the activated furan ring to produce bicyclic ring systems. Since, at lower temperature, due to the lower barrier height, the formation of



Scheme 1

the product with endo configuration is allowed (Kinetic control). At higher temperature, both of the barriers with significantly different energies can be overcome, but the endo mechanism will be reversible (Thermodynamic control), thus the more stable exo product is expected to be formed in a larger quantity[11,12].

As shown in Scheme 2, since compound 8 has furan ring substituted at position 2 by a conjugated group, this will raise its HOMO energy and lower its LUMO energy. As well as, dienophiles are substituted by electron withdrawing groups; these will decrease both the HOMO and LUMO energies, so the optimum interaction will be between HOMO furan LUMO dienophile. The regeoselectivity of the reaction is explained by consideration of the effect of substituents on the coefficient of diene and dieanophiles, this shows that furan has the largest coefficient on C-5 (in HOMO) and dienophiles 10 and 11 the largest coefficient on the unsubstituted carbon of alkene, leading to reaction between C-5 furan and the unsubstituted carbon of the alkene. In case of dienophiles 3, 4 and 9 being symmetrical alkenes no such regeoselectivity is expected. The structures of the obtained compounds were proved by their microanalytical and spectral data (see Experimental). Inspection of the ^{1}HNMR of compound 12d reveals two absorption signals correspond to two OH protons at δ 11.4 and 11.9 ppm, as well the two olefinic protons of the side chain appear at two different positions (at δ 6.6 and 6.9 ppm), similarly those inside the bicyclic-ring system appear at δ 5.8-6 and 6.1-6.3 ppm, this suggests that compound 12d not symmetrical and may be exists in two different environments. Microwave irradiation was used to facilitate these cycloadditions. The reaction time is reduced to few minutes with an improvement of the isolated yields (TABLE 1).



Scheme 2

TABLE 1 : Comparison between reaction times and yields of the products obtained from classical and microwave heating

Compd	Classical heating		Microwave	
	yield %	Time (min)	yield %	Time (min)
5	60	1800	95	10
6	63	1500	93	15
7a	75	1700	96	20
7b	72	1600	93	12
12a	66	1720	89	18
12b	64	1500	86	25
12c	77	1750	92	26
12d	68	1800	87	24
13	77	1800	90	19

BIOLOGICALACTIVITY

The antimicrobial screening of some of the synthesized compounds was done using the agar plate diffusion method[13]. The possible antimicrobial activity of compounds 6, 7a, 12a and 12d was investigated to eight standard organisms including the Gram positive bacteria: *Staphylococcus aureus* (Sa) and *Bacillis subtilis* (Bs); Gram negative bacteria: *Pseudomonas*

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aeruginosa (Pa) and *Escherichia coli* (Ec); and fungi: *Candida albicans* (C), *Aspergillus fumigatus* (A), *Penicillium italicum* (P) and *Syncephalastrum racemosum* (S). The obtained results are presented in TABLE 2. The reference standard Terbinafin was used as a standard antifungal agent while Chloramaphenicol was used as a standard antibacterial agent.

ANTIBACTERIAL ACTIVITY

Various concentrations of the tested compounds 6, 7a, 12a and 12d (1, 2,5 and 5 mg mL^{-1}) dissolved in dimethylsulfoxide (DMSO) were added to each filter paper disc and DMSO was used as control. Plates were incubated at 37 °C and examined for zone of inhibition around each disc after 24 hr (TABLE 2). The antibacterial activity was evaluated by measuring the zone of inhibition against the test organisms. The results were compared with commercial standard Chloromphenicol (St).

ANTIFUNGAL ACTIVITY

The antifungal bioassay was tested by the disc method in potato-dextrose agar (PDA) medium with various concentrations (1, 2.5 and 5 mg mL^{-1}). The fungi test plate was incubated for 72 hours at 28 °C (TABLE 2). The antifungal activity was evaluated by measuring the zone of inhibition against organisms. Terbinafin was used as commercial standard (St).

TABLE 2 : Mean diameters of inhibition Zone (mm) coused by 100 µL of antibacterial and antifungal activities in the agar plate diffusion method

Compd No.	Conc mg /ml	Gram positive bacteria		Gram negative bacteria		Fungi			
		Sa	Bs	Pa	Ec	C	A	P	S
6	1	5	4	0	4	0	3	0	0
	2.5	8	8	0	6	0	7	0	0
	5	11	10	0	9	9	16	0	0
7a	1	4	6	0	8	0	0	0	0
	2.5	7	8	0	11	0	5	3	0
	5	11	15	0	15	6	9	7	0
12a	1	5	7	0	0	0	3	0	0
	2.5	9	10	0	0	0	5	0	0
	5	12	17	0	7	7	11	5	0
12d	1	5	9	0	8	0	0	0	0
	2.5	8	13	0	10	0	4	3	0
	5	11	18	0	13	8	6	5	0
st	1	4	11	0	13	6	11	4	9
	2.5	6	18	5	20	10	18	9	13
	5	15	22	11	27	19	24	19	21

Well diameter 6 mm (100 µL of each concentration was tested). 0 = zone of inhibition reflecting no inhibition growth.

Data in TABLE 2 emphasized the fact that the chemical agents symbolized 6, 7a, 12a and 12d exhibited various degrees of activities against Gram positive bacteria. Aganist *staphylococcus aureus* (Sa) they exhibit strong activities at both high concecentration (5 mg/mL^{-1}), and low concentrations (2.5 or 1 mg/mL^{-1}). For *bacillus subtilis* (Bs) compounds 12a and 12d exhibit moderate activities at both high concentration (5 mg/mL^{-1}), and low (2.5 or 1 mg/mL^{-1}). On the other hand compound 7a exhibit moderate activity at high concentration and low activity at low concentration while 6 shows low activities at both high and low concentrations. For Gram negative bacteria: *pseudomonas aeruginosa* (Pa), the tested compounds exhibit no activities at all. For *Escherichia coli* (Ec) they exhibit low activities at both high and low concentrations except compound 12a didn't show any activity at low concentration. For fungi: the tested compounds show weak activity at high concentration against *Candida albicans* (C), while they reflect no inhibition of growth at low concentrations. The compounds show weak activity against *Aspergillus fumigatus* (A) at both concentrations except 7a and 12d show no activity at the concenteration 1 mg/ml. For *Penicillium italicum* (P) compounds 7a, 12a and 12d show low activity at high concentrations and low to no activities at low concentrations. Compound 6 didn't show any activity at all. For *Syncephalastrum racemosum* (S) the tested compounds didn't show activity..

EXPERIMENTAL

Melting points were determined in open capillary tubes on a Gallenkemp melting point apparatus and were uncorrected. The elemental analyses were done on Perkin-Elemer 2400 CHN elemental analyser. The IR spectra were recorded on Perkin Elmer spectrometer RXIFT-IR systems using KBr discs. The ^{1}HNMR spectra were measured on Varian Gemini 200 MHz instrument with chemical shift (δ) expressed in ppm downfield from teramethylsilane (TMS) as internal standard, in

deuterated chloroform ($CDCl_3$). Mass spectra (MS) were recorded on Shimadzu GC-MS, QP 1000 EX instrument operating at 70 eV. Thin layer chromatography (TLC) was carried out for the monitoring of the progress of all reactions and homogeneity of the synthesised compounds. TLC was performed using TLC aluminum sheet silica gel F_{254} (Merck). Microwave irradiations were performed in Sharp R-23 IF microwave oven 800 W.

Reaction of (E,Z)-2,6-bis(3-phenylallylidene)- and (E,Z)-bis(furan-2-ylmethylene)cyclohexanones 1 and 8 with diwneophiles

(a) General procedure (A)

To a solution of compounds 1 and / or 8 (3 mmole) in dry toluene (30 ml) diethyl acetylenedicarboxylate (2) (3 mmole) was added. The reaction mixture was refluxed for 30 hours and cooled to room temperature. The precipitated solid was filtered, washed with light petroleum 60-80 °C, and recrystallised from ethanol to give compound 5. The same procedure was done with 3-(3-nitrophenyl)-1-phenylprop-2-en-1-one (3), maleic anhydride (4a), N-phenylmalimide (4b), cinnamic acid (9), 1-buten-3-one (10), or vinylacetic acid (11). The progress of all reactions and homogeneity of the synthesised compounds were monitored by TLC. The solid obtained in each case was recrystallized from a suitable solvent to give the corresponding compounds 6, 7a,b, 12a-d and 13.

(b) General procedure (B)

In 25 mL beaker the title compounds 1 and / or 8 (1 mmole) and dienophiles 2, 3, 4a, 4b, 9, 10 or 11 (1 mmole) are dissolved in 5 mL DMF. The beaker with its contents is put in the middle of the microwave oven. Time is adjusted at the beginning for 1 min. and the reaction time is checked by TLC. A solid product was obtained after cooling which was washed with ethanol, filtered off and recrystallised from a suitable solvent to give the same products 6, 7a,b, 12a-d and 13.

2,6(Spiro[2.1']-2',3'-diethoxycarbonyl-4'-phenyl-2',5'-cyclohexadiene-spiro[6.1'']-2",3"-diethylcarbonyl-4"-phenyl-2",5"cyclohexadiene) cyclohexan-1-one (5)

Yellow crystals; m.p 162-164 °C (ethanol); IR (KBr) υ: 3060, 3029 (CH_{arom}),2980, 2939 (CH_{aliph}), 1730 (CO_{ester}), 1661 (CO), 735, 699 (δ_{5H}) cm^{-1}; ^{1}HNMR ($CDCl_3$) δ: 1.1-1.4 (m, 12H, 4 $COOCH_2CH_3$), 1.8-2.1 (m, 6H, $CH_2CH_2CH_2$), 3.3-4.1 (m, 4H, 2 $COOCH_2CH_3$), 4.2-4.6 (m, 6H, (2 CHPh +2 $COOCH_2CH_3$)), 6.6-6.8 (m, 4H. 4CH=), 7.2-7.6 (m, 10H, Ar-H); MS (70 eV) *m/z* (%): 666 ($M^{+\cdot}$, 2), 653 (8), 562 (8),529 (8), 340 (3), 333 (7), 215 (4), 191 (11), 129 (35), 91 (100); Anal. Calcd. For $C_{40}H_{42}O_9$ (666.76): C, 72.05; H, 6.35. Found: C, 71.62; H, 6.28%.

2,6(Spiro[2.1']-4'-phenyl-5'-benzoyl-6'-(3-nitrophenyl)-2'-cyclohexene-spiro[6.1'']-4''-phenyl-5''-benzoyl-6''-(3-nitrophenyl)-2''-cyclohexen)cyclohexan-1-one (6)

Orange crystals; m.p 130-132 °C (benzene); IR (KBr) υ: 3070 (CH_{arom}), 2920, 2850 (CH_{aliph}), 1661 (CO), 1605, 1593 (C=C), 756, 682 (δ_{5H}) cm^{-1}; ^{1}HNMR ($CDCl_3$) δ: 1.6-1.9 (m, 6H, $CH_2CH_2CH_2$), 3.8-4.3 (m, 6H), 5.8 (d, 2H, J = 9.4 Hz), 6.1 (d, 2H, J = 8.5 Hz), 7.0-8.6 (m, 28H, Ar-H); MS (70 eV) *m/z* (%): 832 ($M^{+\cdot}$, 0), 502 (1), 385 (4) 384 (9), 383 (4), 265 (2), 222 (3), 105 (100); Anal. Calcd. For $C_{54}H_{44}N_2O_7$ (832.94): C, 77.87; H, 5.32, N, 3.36. Found: C, 77.52; H, 5.08; N, 3.78%.

2,6(Spiro[2.1']-4'-phenyl-5',6'-dicarboxylic anhydride-2'-cyclohexene-spiro[6.1'']-4''-phenyl-5'',6''-dicarboxylic anhydride -2''-cyclohexen) cyclohexan-1-one (7a)

Yellow crystals; m.p 170-172 °C (Toluene); IR (KBr) υ: 3029 (CH_{arom}),2936 (CH_{aliph}), 1773, 1706 ($CO_{anhydride}$)1663 (CO), 754, 646 (δ_{5H}) cm^{-1}; ^{1}HNMR ($CDCl_3$) δ: 1.6-2.1 (m, 6H, $CH_2CH_2CH_2$), 2.6-2.8 (m, 2H, CHCO), 3.5-3.6 (m, 2H, CHCO), 3.8-3.9 (m, 2H, CHPh), 6.0 (m, 2H), 6.6 (d, 1H, J = 11.0 Hz), 6.8 (d, 1H, J = 10.4Hz), 7.3 (m, 8H, Ar-H), 7.6 (m, 2H, Ar-H); MS (70 eV) *m/z* (%): 522 ($M^{+\cdot}$, 1), 507 (10), 478 (4) 353 (5), 226 (3), 187 (8), 182 (7), 91 (100); Anal. Calcd. For $C_{32}H_{26}O_7$ (522.54): C, 73.55; H, 5.02. Found: C, 73.86; H, 4.98%.

2,6(Spiro[2.1']-4'-phenyl-5',6'-dicarboxylic-N-phenylimide-2'-cyclohexene-spiro[6.1'']-4''-phenyl-5'',6''-dicarboxylic-N-phenylimide-2''-cyclohexen)cyclohexan-1-one (7b)

Yellow crystals; m.p 138-140 °C (ethanol); IR

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(KBr) υ: 3060 (CH_{arom}),2930 (CH_{aliph}), 1760-1712 (br.CO_{imide})1668 (CO), 754, 696 (δ_{5H}) cm^{-1}; ^{1}HNMR ($CDCl_3$) δ: 1.6-1.9 (m, 6H, $CH_2CH_2CH_2$), 2.9-3.4 (m, 4H, CHCON), 3.8-3.9 (m, 2H, CHPh), 5.8 (d, 2H, J = 8.9 Hz), 6.3 (d, 2H, J = 8.3 Hz), 7.0-7.7 (m, 20H, Ar-H); MS (70 eV) *m/z* (%): 672 ($M^{+\cdot}$, 0), 403 (2), 348 (7) 244 (4), 208 (3), 175 (26), 105 (43), 93 (100), 91 (86); Anal. Calcd. For $C_{44}H_{36}N_2O_5$ (672.77): C, 78.55; H, 5.39, N, 4.16. Found: C, 78.23; H, 4.79, N, 3.86%.

(2 E/Z, 6 E/Z)-2,6-bis ((5-carboxy-7-oxa-6-phenyl-bicyclo[2.2.1]hept-2-en-1-yl)methylene)cyclohexanone (12a)

Brown crystals; m.p 222-224 °C (ethanol); IR (KBr) υ: 3300-2300 (br. OH), 1682 (CO), 1592 (C=C), 756, 696 (δ_{5H}) cm^{-1}; ^{1}HNMR ($CDCl_3$) δ: 1.6-1.9 (m, 6H, $CH_2CH_2CH_2$), 3.2-3.4 (m, 4H, CH), 4.2-4.3 (m, 2H, CH-O), 6.1 (d, 2H, J = 11.6 Hz), 6.3 (d, 2H, J = 10.9 Hz, 2CH=), 6.9 (s, 2H, 2CH=), 7.4-7.9 (m, 10H, Ar-H), 11.9 (br. s, 2H, 2OH, excheangeable with D_2O); MS (70 eV) *m/z* (%): 550 ($M^{+\cdot}$, 3), 508 (1), 462 (4) 438 (11), 280 (23), 132 (32), 85 (43), 77 (100); Anal. Calcd. For $C_{34}H_{30}O_7$ (550.6): C, 74.17; H, 5.49. Found: C, 73.87; H, 5.64%.

(2E/Z,6E/Z)-2,6-bis((6-acetyl-7-oxa-bicyclo[2.2.1]hept-2-en-1 yl)methylene)cyclohexanone (12b)

Pale brown crystals; m.p 280-282 °C (ethanol); IR (KBr) υ: 2938 (CH_{aliph}), 1703 (CO), 1594 (C=C) cm^{-1}; ^{1}HNMR ($CDCl_3$) δ: 1.7-1.9 (m, 6H, $CH_2CH_2CH_2$), 2.1 (s, 6H, CH_3CO), 2.4-2.7 (m, 6H, $2CH_2CHCOCH_3$), 4.2-4.4 (m, 2H, CH-O), 5.8 (d, 2H, J = 10.3 Hz), 6.1 (d, 2H, J = 9.5 Hz), 6.9 (s, 2H); MS (70 eV) *m/z* (%): 394 ($M^{+\cdot}$, 6), 377 (2), 356 (12), 302 (23), 165 (56), 123 (64), 44 (100); Anal. Calcd. For $C_{24}H_{26}O_5$ (394.46): C, 73.08; H, 6.64. Found: C, 73.24; H, 6.39%.

(2E/Z,6E/Z)-2,6-bis((5-benzoyl-6-(3-nitrophenyl)-7-oxa-bicyclo[2.2.1]hept-2-en-1-yl)methylene)cyclohexanone (12c)

Orange crystals; m.p 115-117 °C (ethanol); IR (KBr) υ: 3072 (CH_{arom}),2940 (CH_{aliph}), 1664 (CO), 1604 (C=C), 738, 684 (δ_{5H}) cm^{-1}; ^{1}HNMR ($CDCl_3$) δ: 1.7-1.9 (m, 6H, $CH_2CH_2CH_2$), 3.6-3.7 (m, 4H), 5.0-5.2 (m, 2H, CH-O), 6.4 (d, 2H, J = 8.0Hz), 6.5 (d, 2H, J = 8.3 Hz), 6.6 (s, 1H), 6.7 (s, 1H), 7.6-7.9 (m, 10H, Ar-H), 8.1-8.3 (m, 6H, Ar-H), 8.7 (s, 2H, Ar-H); MS (70 eV) *m/z* (%): 760 ($M^{+\cdot}$, 0), 639 (22), 613 (6) 492 (32), 240 (19), 186 (16), 123 (44), 105 (100), 77 (86); Anal. Calcd. For $C_{46}H_{36}N_2O_9$ (760.79): C, 72.62; H, 4.77, N, 3.68. Found: C, 73.02; H, 4.54; N, 3.22%.

(2E/Z,6E/Z)-2,6-bis((6-carboxymethyl-7-oxa-bicyclo[2.2.1]hept-2-en-1-yl)methylene)cyclohexanone (12d)

Pale brown crystals; m.p 140-142°C (ethanol); IR (KBr) υ: 3404-2800 (br. OH),1700, 1674 (CO), 1592 (C=C) cm^{-1}; ^{1}HNMR ($CDCl_3$) δ: 1.4-1.6 (m, 4H, CH_2-CH), 1.7-1.9 (m, 6H, $CH_2CH_2CH_2$), 2.1-2.2 (m, 2H, $CH-CH_2$), 2.6-2.8 (m, 4H, $2CH_2COOH$), 4.3-4.5 (m, 2H, CH-O), 5.8-6.0 (m, 2H), 6.1-6.3 (m, 2H), 6.6 (s, 1H), 6.9 (s, 1H), 11.4, 11.9 (br.s, 2H, 2OH, excheangeable with D_2O); MS (70 eV) *m/z* (%): 426 ($M^{+\cdot}$, 0), 382 (9), 340 (11), 312 (36), 284 (18), 204 (27), 123 (56), 66 (100), Anal. Calcd. For $C_{24}H_{26}O_7$ (426.46): C, 67.59; H, 6.15. Found: C, 67.87; H, 6.34%.

(2E/Z,6E/Z)-2,6-bis((5,6-dicarboxylic anhydride-7-oxa-bicyclo[2.2.1]hept-2-en-1-yl)methylene)cyclohexanone (13)

Brown crystals; m.p 180-182°C (ethanol); IR (KBr) υ: 2933 (CH_{aliph}),1714, 1660 (CO), 1598 (C=C) cm^{-1}; ^{1}HNMR ($CDCl_3$) δ: 1.6-1.9 (m, 6H, $CH_2CH_2CH_2$), 2.9-3.2 (m, 4H, CH), 4.7-4.9 (m, 2H, CH-O), 5.8 (d, 2H, J = 8.8 Hz), 6.1 (d, 2H, J = 8.7 Hz), 6.8 (s, 2H); MS (70 eV) *m/z* (%): 450 ($M^{+\cdot}$, 3), 404 (6), 378 (16), 354 (23), 262 (38), 176 (100), 136 (46), 106 (76),; Anal. Calcd. For $C_{24}H_{18}O_9$ (450.39): C, 64.00; H, 4.03. Found: C, 64.19; H, 3.78%.

CONCLUSION

In the present investigation thermal (4+2) π Diels-Alder reaction for the title compounds with different dienophiles afforded dispiro derivatives and bicyclic ring systems. Microwave heating save time and improve the yields of the products. Some of the obtained products are biologically active.

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