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FULL PAPER

Synthesis, characterization and evaluation of 5-alkylidene meldrum's acid derivatives as multifunction lubricating oil additives

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A series of 5-alkylidene Meldrum's acid derivatives were prepared by Knovenagel condensation of Meldrum's acid with different aldehydes in the presence of pipridin as a catalyst. The prepared compounds were characterized by FT-IR, ^{1}HNMR, and ^{13}CNMR. Each prepared compound (0.2% wt. /wt.) was blended with base sixty stock lubricating oil to be evaluated as anti-rust and anti-corrosive additives according to ASTM-D665, and ASTM-D130 respectively. The formulated blend of some compounds showed better anti-rust and anti-corrosion properties compared with the base oil (blank) supplied by the Midland Refineries Company/Iraq.

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KEYWORDS

Meldrum's acid; Knovenagel condensation; lubricating oil; anti-rust; anti-corrosion.

Introduction

Mineral base oil alone cannot meet all of the demands of engine oil. To increase the performance of basic oils, different types of additives are blended with the base oils to increase their performance and extend the engine's lifetime. The commonly used additives are viscosity index improvers, anti-wear, anti-rust, corrosion inhibitors, detergents, pour point depressants, dispersants, and antioxidants [1,2].

Multifunctional additives serve more than one purpose, i.e., they have many roles. Zinc dialkyl dithiophosphates act as antiwear, antioxidants, and corrosion inhibitors [3]. Polyacrylates are a type of multifunctional additive utilized as antiwear, viscosity index (V.I) improvers, and pour point (P.P) depressants. Copolymers of dodecyl acrylate with castor oil [4], copolymers of methyl acrylate with soybean oil [5], polyacrylate-magnetite nanocomposite [6], and isodecyl acrylate copolymers with peanut oil performed well as antiwear, viscosity modifiers, and pour point depressants, with excellent biodegradability [7]. Some ionic liquids have recently been used as multifunctional lubricating oil additives [8, 9]. Pentaerthritol monooleate gallate [10] pentaerythritol rosin ester [11] and over-based magnesium stearate [12,13] were senthesized and used as environmentally friendly multifunctional lubricant additives.

2,2-Dimethyl-1,3-dioxane-4,6-dione (Meldrum's acid) has been used in organic synthesis for over a century, demonstrating its utility and adaptability. Meldrum's acid and its arylidene or alkylidene derivatives are useful for the synthesis of natural products [14], and heterocyclic compounds [15], which exhibit some pharmacological activities, such as antimicrobial [16,17], antimalarial, and antioxidant [18]. Recently, Meldrum's acid was used to prepare novel polymers and thermosetting resins [19, 20]. Meldrum's acid reacts with aldehydes to produce arylidene or alkylidine derivatives according to Knoevenagel condensation, which is commonly catalyzed by pyridine or piperdine [21]. Uncatalyzed reactions were reported [22,23], and sodium ascorbate in water was used as a green catalyst [24]. Ionic liquids [25, 26] as well as nanoparticles [27] have been used as environmentally friendly catalysts for Knoevenagel condensation.

In this work, some new 5-alkylidin Meldrum's acid derivatives were synthesized and evaluated as multifunction lubricant additives such as antirust and anticorrosion.

Experimental

Materials and instruments

All chemicals used were supplied by Fluka AG, Sigma-Aldrich, Merck, and BDH chemicals. Thin-layer chromatography was performed on aluminum sheets coated with silica gel-60. The eluant was a mixture of ethyl acetate and petroleum ether (3:2). Spots were detected by Iodine vapour. Melting points were recorded using Electro thermal Stuart Scientific apparatus. Infrared spectra were recorded on the SHIMADZU-8400S Spectrophotometer at the Department of Chemistry, College of Science, University of Baghdad.

The ^{1}H and ^{13}C Nuclear Magnetic Resonance spectra were recorded on a VARIAN model at 500 MHz and 125 MHz respectively at Tehran University, Iran. Dimethyl sulfoxide (DMSO-d6) was used as the solvent and Trimethyl silane (TMS) as an internal standard.

Rust preventing characteristics test (ASTM - D665) [28]

A polished steel rod is immersed in a mixture of 300 mL of blended oil and water (30 mL) and heated at 60°C for four hours. The steel rod is then checked for rust signs. This test is carried out in duplicate, and both test rods must be rust-free to be declared successful.

Copper corrosion test (ASTM – D130) [29]

A polished copper stripe is submerged in a 30mL sample of oil blend at 100° C for three hours. At the end of the test, the copper strip is cleaned and inspected for tarnish. The stains on the copper strip are compared with the ASTM D130 color scale, which ranges from 1a to 4c.

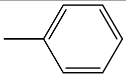
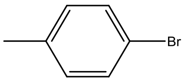
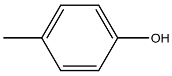
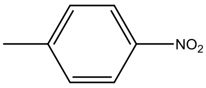
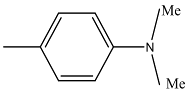
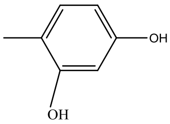
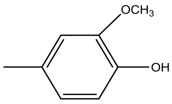
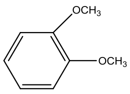
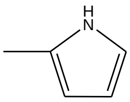
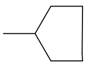
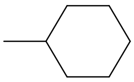
Synthesis of 2,2-Di methyl-1,3-dioxane -4,6-dione(Meldrum's acid)[30]

To a stirred suspension of malonic acid (42 g, 0.4 mol.) and acetic anhydride (50 mL, 0.5 mol.) in an ice bath, concentrated sulfuric acid (1.7 mL, 0.03 mol.) was added, followed by dropwise acetone (41 mL, 0.5 mol.). The mixture was stirred for four hours and then kept in the fridge overnight. The formed precipitate was filtered and washed with water to yield 50.7 g (87%) of Meldrum's acid as white crystals with a m.p. 94-95 C°.

Synthesis of 5-alkylidene Meldrum's acid derivatives (2a-l) [21]

A mixture of Meldrum's acid (2.88 g, 0.02 mol.) and appropriate aldehyde or ketone (0.02 mol.) in ethanol (20 mL) and two drops of piperidin were refluxed for (2-14) hours. After cooling to room temperature, the formed precipitate was filtered, and crystallized from ethanol. The physical properties of the synthesized Meldrum's acid derivatives (2a-l) are illustrated in Table 1.

TABLE 1 physical properties of the 5-alkylidene Meldrum's acid derivatives (2a-2l)

Comp. no.	R.	Compound name	Molecular weight, g/mole	Color	m.p., °C	Yield, %	Time hours	Rf.
2a		5-Benzylidene-2,2-dimethyl-1,3-dioxane-4,6-dione	232.24	Off white	178-180	62	4	0.545
2b		5-(4-bromobenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione	311.13	White	186-188	64	9	0.483
2c		5-(4-Hydroxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione	248.23	Yellow	194-196	53	8	0.314
2d		2,2-dimethyl-5-(4-nitrobenzylidene)-1,3-dioxane-4,6-dione	277.23	White	130-132	71	14	0.468
2e		5-(4-Dimethyl amino)benzylidene)2,2-dimethyl-1,3-dioxane-4,6-dione	275.30	Orange	166-168	80	2	0.617
2f		5-(2,4-dihydroxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione	264.23	Green	182-184	52	5	0.611
2g		5-(4-hydroxy-3-methoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione	278.26	Brown	Oily	79	2	0.361
2h		5-(3,4-dimethoxybenzylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione	292.29	Yellow	166-168	62	2	0.382
2i		5-((1H-pyrrol-2-yl)methylene)-2,2-dimethyl-1,3-dioxane-4,6-dione	221.21	Black	>300	55	8	0.468
2j		5-cyclopentylidene-2,2-dimethyl-1,3-dioxane-4,6-dione	210.23	Yellow	Oily	52	14	0.515
2k		5-cyclohexylidene-2,2-dimethyl-1,3-dioxane-4,6-dione	224.26	Yellow	Oily	54	14	0.666
2l		5-heptylidene-2,2-dimethyl-1,3-dioxane-4,6-dione	240.30	Yellow	Oily	58	12	0.800

Oil blend formulation [31]

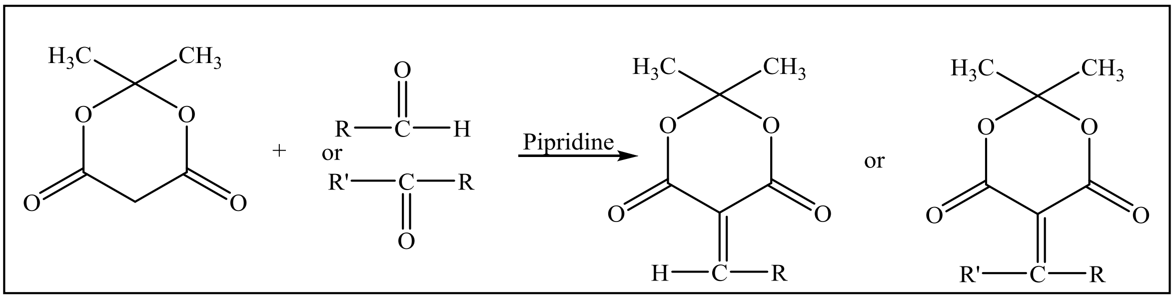
Blends of different synthesized compounds were prepared by mixiing 0.2% wt. /wt. of each compound with base oil sixty stock at 70 °C with stirring for one hour. The properties of the base oil supplied by Iraqi Midland Refineries Company were listed in Table 2.

TABLE 2 The properties of base oil (60 stock)

No.	Specification	Properties	Test method
1.	Kinematic viscosity, (mm^2/s) at 40 °C	58.03	ASTM D445
2.	Kinematic viscosity, (mm^2/s) at 100 °C	8.17	ASTM D445
3.	Viscosity index	105	ASTM D2270
4.	Pour point	0.0	ASTM D97
5.	Specific gravity	0.8843	ASTM D4052
6.	Flash Point	243	ASTM D92
7.	Rust Preventing	Fail	ASTM D665
8.	Copper corrosion	2a	ASTM D130

Results and discussion

Meldrum's acid was reacted with different aldehydes or ketones to synthesize 5-alkylidine and arylidine Meldrum's acid derivatives (2a-l) in the presence of pipridine as a catalyst according to the Knovenagel condensation mechanism [32] as shown in Scheme 1.



SCHEME 1 The synthetic route

The structure of the prepared compounds was characterized by FT-IR, 1H NMR, and 13CNMR spectroscopies.

The FT-IR spectra showed stretching bands at 2869.88-2987.53 cm^{-1} for CH aliphatic, while CH aromatic appeared between 3010-3109 cm^{-1}. The carbonyl groups of Meldrum's acid gave strong stretching bands between 1685.67 and 1795.6 cm^{-1}. A band in the region of 1600.81-1652.88 cm^{-1} refered to C=C. The detailed infrared spectral data is illustrated in Table 3.

The 1H-NMR spectra showed singlet signals in the region (1.18 – 1.77 ppm) for (2CH3, 6H), (7.23 – 8.39 ppm) for (=CH, 1H), while aromatic protons showed doublet-doublet signals at (6.81 – 7.85 ppm) and (6.34-7.68 ppm) for 2Ha and 2Hb respectively. 13CNMR spectra showed characteristic signals at (140.31-166.10 ppm) for the carbonyl group, (106.70-161.32 ppm) for C=CH, (60.08-111.81 ppm) for C-O-C and (110.31-140.91 ppm) for aromatic carbons. The two methyl groups of Meldrum's acid appeared between 14.59 and 28.17 ppm. Table 4 lists the NMR spectral data in further detail. The synthesized derivatives were evaluated for their anti-rust and anti-corrosion activities by mixing 0.2% weight/weight of each compound with 60 stock base oil according to ASTM-D665, and ASTM–D130 respectively.

The rust preventing test was run in duplicate for a steel rod immersed in a mixture of blended oil and water for four hours at 60 C°. After that, the rod was examined for rust signs. The majority of the blends were rust-free, with the exception of blends of compounds 2j and 2k with aliphatic rings, which failed the rust-prevention test. A copper corrosion test was performed on a polished copper strip submerged in blended oil at 100 C° for three hours. Then, a copper strip was tested for evidence of corrosion by comparing it to the ASTM D130 color scale, which ranges from 1a (freshly polished copper) to 4c (the worst corrosion staining) [33]. The results of the corrosion test for the blend oils with the prepared compounds showed good results ranging from 1a (slight staining, but barely noticeable) to 1b (slight tarnish), with the exception of the blends with 2b, 2k, and 2j derivatives, which appeared 2c (tarnish).

TABLE 3 FTIR spectral data (cm-1) of alkylidine meldrums acid derivatives (2a-2l)

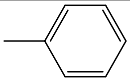
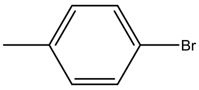
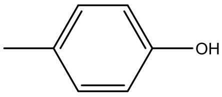
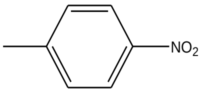
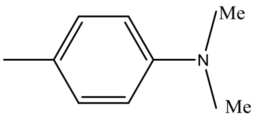
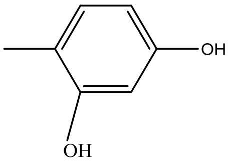
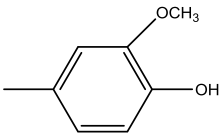
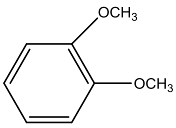
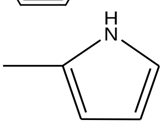
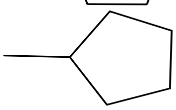
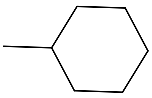
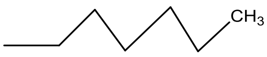
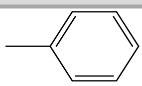
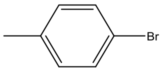
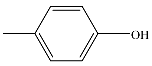
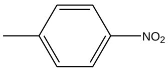
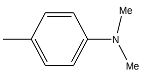
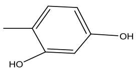
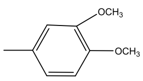
Comp. no.	R.	νCH arom.	νCH aliph.	νC=O	νC=C	δ(o-o-p)	Other bands
2a		3001.03	2904.60 2950.89	1739.67 1776.32	1602.74	773.40 709.76	
2b		3066.61	2931.60 2981.74	1731.96 1795.60	1633.59	Di subs.1,4 821.62	νC-Br 577.39
2c		3001.03	2948.96 2900.74	1749.32 1697.24	1606.59	Di subs.1,4 840.91	ν O-H 3272.98
2d		3029.96	2939.31 2916.17	1712.67 1776.32	1645.17	Di subs.1,4 827.41	ν NO_2 1515.94 asym. 1342.36 sym.
2e		3089.75	2979.82 2908.45	1728.10 1699.17	1612.38	Di subs.1,4 819.69	$-N(CH_3)_2$ 2827.45
2f		3097.47	2947.03 2869.88	1712.67 1685.67	1616.24	Tri subs 1,2,4 819.69 883.34	ν O-H 3444.63 3483.20
2g		3068.53	2981.74 2937.38	1722.31	1650.95	Tri subs. 1,2,4 825.48 889.12	ν O-H 3419.56
2h		3010.67	2981.74 2908.45	1708.81 1747.39	1652.88	Tri subs. 1,2,4 879.48 811.98	
2i		3109.04	2987.53 2921.96	1714.60 1730.03	1650.95		ν N-H 3442.70
2j		3082.75	2954.74 2921.96	1726.17	1600.81	-	
2k		3055.03	2948.96 2927.74	1735.81	1610.45	-	
2l			2947.73 2858.31	1735.81	1618.17	-	

TABLE 4 ^{1}HNMR & ^{13}CNMR spectral data of alkylidine meldrums acid derivatives (2a-2h)

Comp. no.	R.	^{1}HNMR (δ ppm) =CH singlet	CH aromatic Doublet 2Ha	2Hb	2CH$_3$(6H) Singlet	others	^{13}CNMR(δ ppm) C=O	Aromatic carbons	C=CH	O-C-O	2CH$_3$	others
2a		7.99	7.48	7.29	1.75		162.92	133.27 128.91`	116.25 157.03	105.07	27.49	
2b		7.23	7.66	7.68	1.62		140.31	122.62	106.70 131.99	60.08	28.17	C-Br 127.88
2c		8.24	8.04	7.92	1.71	OH 10.91	163.80	138.35 123.49 110.31	116.27 157.45	104.34	27.30	C-OH 160.68
2d		8.39	6.84	7.59	1.26		166.10	140.91 129.87 124.35	122.90 148.49	60.85	14.59	C-NO$_2$ 142.22
2e		8.15	8.24	6.79	1.68	N(CH$_3$)$_2$ 3.12	164.58	139.08	119.64 161.32	104.55	27.17	C-N 157.07 N-CH$_3$ 103.52
2f		8.45	7.62	6.79 6.72	1.18	OH 9.89	164.63	131.62 110.93	114.60 147.35	102.28	22.67	C-OH 157.05 158.92
2h		8.29	7.85	7.12 8.06	1.72	- (OCH$_3$)$_2$ 3.79 3.83	163.70	111.80 131.74 154.67	116.69 157.35	104.53	27.34	-OCH$_3$ 56.43 55.98

Conclusion

A series of 5-alkylidene Meldrum's acid derivatives were successfully synthesized by Knovenagel condensation of Meldrum's acid with various aldehydes. The synthesized derivatives were assessed as antirust, and corrosion inhibitors for engine lubricating oil by blending 0.2 percent with base oil (60 stock). Most of the blends showed good antirust, and anticorrosive properties.

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