[Contribution from the Department of Organic Chemistry of the Hebrew University]

The Synthesis of Some Esters and Amides of β,β-Diarylacrylic Acids

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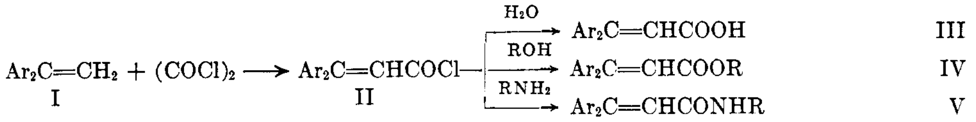
The reaction of 1,1-diarylethylenes with oxalyl chloride giving β,β-diarylacrylyl chlorides, has been utilized for the preparation of several aliphatic and aromatic esters of β,β-diarylacrylic acids as well as for the preparation of some N-alkyl- and N-aryl-β,β-diarylacrylamides.

The preparation of β,β-diarylacrylic acids (III) by the reaction of 1,1-diarylethylenes (I) with oxalyl chloride has been described previously.[1,2] The β,β-diarylacrylyl chloride (II) formed in this reaction can be used after superficial purification for the preparation of esters (IV)[3] and also of N-substituted amides (V).



$$Ar_2C{=}CH_2 + (COCl)_2 \longrightarrow Ar_2C{=}CHCOCl \begin{cases} \xrightarrow{H_2O} Ar_2C{=}CHCOOH & \text{III} \\ \xrightarrow{ROH} Ar_2C{=}CHCOOR & \text{IV} \\ \xrightarrow{RNH_2} Ar_2C{=}CHCONHR & \text{V} \end{cases}$$

I II

This paper reports the preparation of some aliphatic and aromatic esters and N-substituted amides of β,β-diphenyl-, β,β-di-(*p*-tolyl)-, and β,β-di-(*p*-anisyl)-acrylic acid. The syntheses are convenient and easy to carry out. In the standard procedure as described in the experimental section, the yields were generally not more than 50% of the theoretical (calculated on basis of the ethylene), but by using a larger excess of oxalyl chloride the yields could be improved considerably.

TABLE I

Alkyl Esters of β,β-Diphenylacrylic Acid $(C_6H_5)_2C{=}CHCOOR$

R	B.p., °C./2 mm.	n_D^{23}	Yield, %	Formula	Analysis Carbon Calc'd	Analysis Carbon Found	Analysis Hydrogen Calc'd	Analysis Hydrogen Found
Ethyl[a]	73–74	1.5973	65	$C_{17}H_{16}O_2$	80.9	80.6	6.4	6.1
Isopropyl	122	1.5886	54	$C_{18}H_{18}O_2$	81.2	81.6	6.8	6.7
n-Pentyl	145	1.5770	49	$C_{20}H_{22}O_2$	81.6	82.4	7.5	7.0
n-Heptyl	146–147	1.5620	43	$C_{22}H_{26}O_2$	81.9	82.3	8.1	7.8
n-Octyl	153	1.5466	41	$C_{23}H_{28}O_2$	82.1	82.6	8.4	8.3

[a] This compound has been prepared before by condensation of benzophenone with ethyl bromoacetate and subsequent dehydration. Rupe and Busolt, *Ber.*, **40**, 4537 (1907); Schlenk and Bergmann, *Ann.*, **463**, 237 (1928).

EXPERIMENTAL[4]

Preparation of β,β-diphenylacrylyl chloride. To 2 ml. (0.01 mole) of 1,1-diphenylethylene in a 50 ml. round-bottomed flask fitted by means of a ground-glass joint with a reflux condenser with a drying-tube, there was added 2 ml. of pure oxalyl chloride. After the subsidence of the first strongly exothermic reaction (rapid evolution of HCl) the mixture was heated on a water-bath for four hours. After cooling the excess of oxalyl chloride was removed *in vacuo* at room temperature. Then 5 ml. of dry benzene was added and removed again *in vacuo* and this operation was repeated twice more in order to remove all excess of oxalyl chloride. The resulting brown viscous residue then was dissolved in 15 ml. of dry ether. This ether solution was used in the subsequent preparation of both esters and amides.

β,β-Di-(p-tolyl)acrylyl chloride was obtained in the same manner from 1,1-di-(*p*-tolyl)ethylene and oxalyl chloride but with only 45 min. heating on the water-bath; for the preparation of *β,β-di-(p-anisyl)acrylyl chloride* from 1,1-di-(*p*-anisyl)ethylene and oxalyl chloride only 25 minutes of heating on the water-bath was necessary. In all three cases the yields diminished if the mixtures were heated for longer periods than stated.

Preparation of β,β-diarylacrylic esters (IV). The ether solution of the β,β-diarylacrylyl chloride obtained from 0.01 mole of the corresponding ethylene, was added slowly to a solution of 0.01 mole of the alcohol or the phenol in 5–10 ml. of dry ether. After about two hours the solution was refluxed on a water-bath for 15 minutes and left overnight. After removal of the solvent (and in the cases where phenols were used, after removal of the excess of the phenol by washing with 5% sodium hydroxide solution) the products were purified either by distillation or by crystallization. (Tables I-IV).

Preparation of β,β-diarylacrylyl amides. The ether solution of the β,β-diarylacrylyl chloride obtained from 0.01 mole of the ethylene was added dropwise with stirring in the course of 15 minutes to an ether solution of 0.02 mole of the amine (RNH_2 or $ArNH_2$) in ether, or, in the case of unsubstituted or N-methyl amides, dry ammonia or methylamine was bubbled through the acrylyl chloride solution until no more precipitation took place. The mixture was refluxed for one hour on a water-bath and then left overnight. After filtra-

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(1) Kharasch, Kane, and Brown, *J. Am. Chem. Soc.*, **64**, 333 (1942).

(2) Bergmann, Weizmann, Dimant, Patai, and Szmuskowicz, *J. Am. Chem. Soc.*, **70**, 1612 (1948).

(3) Weizmann, Patai, Dimant, and Bergmann, *J. Am. Chem. Soc.*, **71**, 2315 (1949).

(4) Micro-analyses by Drs. Weiler and Strauss, Oxford.

TABLE II

Aryl Esters of β,β-Diphenylacrylic Acid $(C_6H_5)_2C{=}CHCOOAr$

Ar	M.p., °C.	Recryst. Solvent	Appearance	Yield, %	Formula	Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found	N or Halogen Calc'd	N or Halogen Found
Phenyl	121	Ethanol	Needles	52	$C_{21}H_{16}O_2$	83.9	84.1	5.4	5.3		
o-Tolyl	82	Ethanol	Rhombic plates	40	$C_{22}H_{18}O_2$	84.1	84.1	5.8	5.7		
m-Tolyl	96.5	Ethanol	Needles	56	$C_{22}H_{18}O_2$	84.1	83.9	5.8	5.7		
p-Tolyl	111	Ethanol	Pink needles	57	$C_{22}H_{18}O_2$	84.1	83.8	5.8	5.5		
p-Chlorophenyl	112	Ethanol	Hexagonal plates	56	$C_{21}H_{15}ClO_2$	75.3	75.2	4.5	4.1	Cl, 10.5	11.1
2,4-Dichlorophenyl	89.5	Methanol	Needles	66	$C_{21}H_{14}Cl_2O_2$	68.3	67.9	3.8	3.5		
p-Nitrophenyl	146	Benzene-pet. ether	Grey needles	35	$C_{21}H_{15}NO_4$	73.0	73.2	4.4	4.2	N, 4.1	4.1
p-Biphenylyl	170	Benzene	Rhombic plates	44	$C_{27}H_{20}O_2$	86.2	85.9	5.4	5.5		
2-Naphthyl	140	Ethanol	Needles	74	$C_{25}H_{18}O_2$	85.7	85.6	5.2	5.2		
1,6-Dibromo-2-naphthyl	186	Dioxane-pet. ether	Needles	45	$C_{25}H_{16}Br_2O_2$	59.1	58.8	3.2	3.1	Br, 31.5	32.0

TABLE III

Aryl Esters of β,β-Di-(*p*-tolyl-)acrylic Acid $(p\text{-}CH_3C_6H_4)_2C{=}CHCOOAr$

Ar	M.p., °C.	Recryst. Solvent	Appearance	Yield, %	Formula	Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found	Halogen Calc'd	Halogen Found
Phenyl	97	Ethanol	Needles	37	$C_{23}H_{20}O_2$	84.1	84.4	6.1	6.2		
p-Tolyl	102	Methanol	Needles	31	$C_{24}H_{22}O_2$	84.2	84.3	6.5	6.8		
p-Chlorophenyl	98	Ethanol	Needles	35	$C_{23}H_{19}ClO_2$	76.1	76.2	5.3	5.0		
2,4-Dichlorophenyl	93	Methanol	Pink needles	39	$C_{23}H_{18}Cl_2O_2$	69.5	69.4	4.6	4.8		
1,6-Dibromo-2-naphthyl	157	Benzene-Ethanol	Pink needles	33	$C_{27}H_{20}Br_2O_2$	60.5	60.6	3.8	3.7	29.8	29.7
p-Biphenylyl	160	Benzene-pet. ether	Needles	31	$C_{29}H_{24}O_2$	86.1	86.0	6.0	6.0		
2-Naphthyl	135	Ethanol	Needles	64	$C_{27}H_{22}O_2$	85.7	85.7	5.9	5.7		

TABLE IV

Aryl Esters of β,β-Di-*p*-anisylacrylic Acid $(CH_3OC_6H_4)_2C{=}CHCOOAr$

Ar	M.p., °C.	Recryst. Solvent	Appearance	Yield, %	Formula	Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found	Halogen Calc'd	Halogen Found
Phenyl	120	Ethanol	Dark grey powder	34	$C_{23}H_{20}O_4$	76.7	76.8	5.6	5.7		
p-Tolyl	104	Methanol	Needles	34	$C_{24}H_{22}O_4$	77.0	77.4	5.9	6.2		
p-Chlorophenyl	101	Ethanol	Grey needles	32	$C_{23}H_{19}ClO_4$	70.0	70.3	4.8	4.6	9.0	8.7
p-Biphenylyl	151	Benzene-Ligroin	Needles	36	$C_{29}H_{24}O_4$	79.8	79.6	5.5	5.6		
2-Naphthyl	154	Ethanol	Needles	39	$C_{27}H_{22}O_4$	79.0	79.4	5.4	5.3		

TABLE V

AMIDES OF β,β-DIPHENYLACRYLIC ACID $(C_6H_5)_2C{=}CHCONHR$

						Analyses					
						Carbon		Hydrogen		Nitrogen	
R	M.p., °C.	Recryst. Solvent	Appearance	Yield, %	Formula	Calc'd	Found	Calc'd	Found	Calc'd	Found
H	120	Dil. ethanol	Yellow needles	74	$C_{15}H_{13}NO$	80.7	80.3	5.9	5.6	6.3	6.1
Methyl	111	Dil. ethanol	Orange needles	50	$C_{16}H_{15}NO$	81.0	81.9	6.4	6.5		
Ethyl	80	Dil. ethanol	Orange needles	36	$C_{17}H_{17}NO$	81.3	81.6	6.8	6.8		
Phenyl	130	Methanol	Needles	57	$C_{21}H_{17}NO$	84.3	84.3	5.7	5.6	4.7	4.6
o-Tolyl	136	Methanol	Needles	47	$C_{22}H_{19}NO$	84.4	84.3	6.1	6.1	4.5	4.6
m-Tolyl	141	Methanol	Yellow needles	45	$C_{22}H_{19}NO$	84.4	84.5	6.1	6.2	4.5	4.7
p-Tolyl	157	Methanol	Cubes	54	$C_{22}H_{19}NO$	84.4	84.3	6.1	6.3	4.5	4.7
3-Nitrophenyl	187	Ethanol	Needles	41	$C_{21}H_{16}N_2O_3$	73.3	73.1	4.7	4.7	8.1	8.2
2-Methyl-4-nitrophenyl	190	Ethanol	Grey needles	61	$C_{22}H_{18}N_2O_3$	73.7	73.6	5.1	5.1	7.8	7.9
1-Naphthyl	164	Ethanol	Yellow needles	74	$C_{25}H_{19}NO$	85.9	85.9	5.5	5.7	4.0	4.0
2-Naphthyl	136	Methanol	Needles	49	$C_{25}H_{19}NO$	85.9	86.0	5.5	5.4	4.0	4.2

TABLE VI

AMIDES OF β,β-DI-(*p*-TOLYL)ACRYLIC ACID $(p\text{-}CH_3C_6H_4)_2C{=}CHCONHR$

						Analyses					
						Carbon		Hydrogen		Nitrogen	
R	M.p., °C.	Recryst. Solvent	Appearance	Yield, %	Formula	Calc'd	Found	Calc'd	Found	Calc'd	Found
H	150	Ethanol	Amorph. powder	48	$C_{17}H_{17}NO$					5.6	5.4
Methyl	185	Dil. ethanol	Yellow powder	57	$C_{18}H_{19}NO$	81.5	81.0	72.	7.1	5.3	5.3
Phenyl	170	Ethanol	Needles	36	$C_{23}H_{21}NO$	84.4	83.8	6.5	6.4	4.3	4.3
m-Tolyl	150	Methanol	Tan plates	40	$C_{24}H_{23}NO$	84.4	84.2	6.8	6.8	4.1	4.0
p-Tolyl	155	Ethanol	Tan plates	31	$C_{24}H_{23}NO$	84.4	84.3	6.8	6.9	4.1	4.2
1-Naphthyl	187	Ethanol	Red powder	37	$C_{27}H_{23}NO$					3.7	3.7
2-Naphthyl	175	Methanol	Red needles	33	$C_{27}H_{23}NO$					3.7	3.9

TABLE VII

AMIDES OF β,β-DI-(*p*-ANISYL)ACRYLIC ACID $(p\text{-}CH_3OC_6H_4)_2C{=}CHCONHR$

						Analyses					
						Carbon		Hydrogen		Nitrogen	
R	M.p., °C.	Recryst. Solvent	Appearance	Yield, %	Formula	Calc'd	Found	Calc'd	Found	Calc'd	Found
H	125	Dil. ethanol	Orange needles	32	$C_{17}H_{17}NO_3$	72.1	72.1	6.0	6.1	4.9	4.7
Phenyl	108	Dil. ethanol	Grey needles	44	$C_{23}H_{21}NO_3$	76.9	76.5	5.9	5.8	3.9	4.2
m-Nitrophenyl	103	Benzene-pet. ether	Grey needles	54	$C_{23}H_{20}N_2O_5$	68.3	68.6	5.0	4.8	6.9	7.3
p-Nitrophenyl[a]	101	Benzene-pet. ether	Grey needles	48	$C_{29}H_{26}N_4O_7$	64.2	63.9	4.8	4.7	10.3	10.3
1-Naphthyl	140	Ethanol	Scarlet rhombic plates	30	$C_{27}H_{23}NO_3$	79.2	79.0	5.7	5.6	3.4	3.3

[a] This amide precipitated as a stable compound with *p*-aminonitrobenzene, which remained unaffected by the standard procedure of purification.

tion, the precipitate was washed several times with dilute hydrochloric acid and with water in order to remove any unchanged amine and amine hydrochloride. The solids were generally purified by crystallization from ethanol or methanol (Tables V–VII).

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