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ARYLMETHYLENEMALONALDEHYDES AND THEIR HETEROCYCLIC ANALOGUES: A NOVEL GROUP OF ORGANIC LEWIS ACIDS

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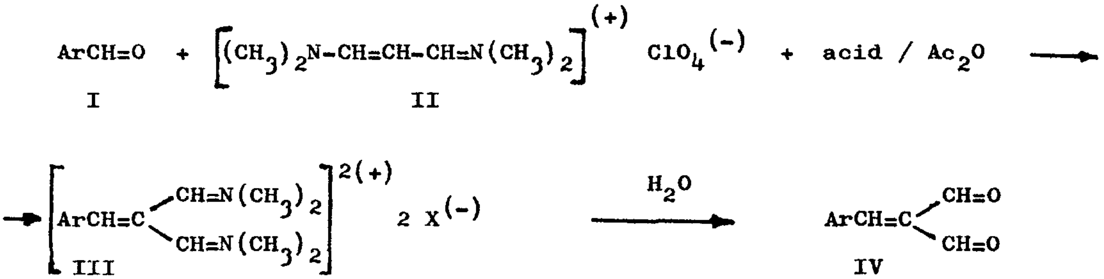
Abstract: The first general synthesis of arylmethylenemalonaldehydes and their heterocyclic analogues has been developed; some physico-chemical properties and reactions of these compounds are briefly mentioned.

No alkylidene- nor aralkylidenemalonaldehyde has been isolated and investigated so far[1] although some synthetic potentialities of this class of compounds are evident from Woodward's work dealing with Cephalosporin C synthesis[2].

Exploiting the well known reactivity of polymethinium salts against electrophilic reagents[3] we have developed a simple general synthesis of arylmethylenemalonaldehydes IV and of their heterocyclic analogues, according to the Scheme[4]. Starting substances are aromatic or heteroaromatic aldehydes (I) and a malonaldehyde derivative, 1,3-bis-dimethylaminotrimethinium perchlorate (II)[5]. In acetanhydride solution in the presence of an acid a doubly charged intermediate (III)



$$\underset{\text{I}}{ArCH{=}O} + \underset{\text{II}}{\left[(CH_3)_2N{-}CH{=}CH{-}CH{=}N(CH_3)_2\right]^{(+)}} ClO_4^{(-)} + \text{acid} / Ac_2O \longrightarrow$$

$$\longrightarrow \underset{\text{III}}{\left[ArCH{=}C\begin{matrix}CH{=}N(CH_3)_2\\ CH{=}N(CH_3)_2\end{matrix}\right]^{2(+)}} 2\,X^{(-)} \xrightarrow{H_2O} \underset{\text{IV}}{ArCH{=}C\begin{matrix}CH{=}O\\ CH{=}O\end{matrix}}$$

Scheme

is formed, the structure of which was confirmed in some cases by NMR spectra. The hydrolysis of this intermediate, which need not be isolated, takes place usually quite readily.

The variety of aldehydes used is evident from Table 1. In view of the easy availability of the starting materials the yields (mostly between 40-70%) are considered satisfactory. Most of the preparations require only slight modification of the reaction conditions given in the example[6]; in addition to strong proton acids, the Lewis acids proved efficient in the studied condensation.

Table 1 Arylmethylenemalonaldehydes IV

Ar	Yield (%)	M.p. (°C)	Ar	Yield (%)	M.p. (°C)
Ph	78	b.p. 94/25 Pa	4-MeO-Ph	61	39-41
2-Cl-Ph	58	75-76.5	4-Me_2N-Ph	47	119-121.5
2-MeO-Ph	58	34-36.6	Mesityl	12	40-43.5
3-NO_2-Ph	20	91-93.5	Ph-CH=CH-	85	79-80
3-Br-Ph	42	39-41.5	2-Thienyl	61	95-96
4-NO_2-Ph	21	130-131.5	2-Furyl	70	50-54
4-Br-Ph	65	92-94			

According to Polansky´s concept[7], the dialdehydes IV can be looked upon as organic Lewis acids. This manifests itself e.g. by strong dependence of their UV spectra on pH, allowing thus to determine their acidity lying in the region of carboxylic acids. The reactivity is governed by the strongly electron deficient CH group; the addition reactions thus proceed not only with trisubstituted phosphines or some tertiary amines, but also with 1,3,5-trimethoxybenzene etc. Very pronounced is their ability to enter as 4π-heterocomponents into Diels-Alder reaction. A full account of these and other transformations will be given elsewhere.

REFERENCES AND NOTES

1. The synthesis of tetraethyl acetals of various alkylidenemalonaldehydes has been reported (C. Reichardt, W. Pressler, E.-U. Würhwein: Angew. Chem. 88, 88 (1976), with no indication, however, that these derivatives can be converted to parent dialdehydes.
2. R.B. Woodward et al.: J. Amer. Chem. Soc. 88, 852 (1966);see also ref.in lit.[1]
3. J. Kučera, Z. Arnold: Collect. Czech. Chem. Commun. 32, 1704 (1967).
4. Z. Arnold, V. Král: Czech. Appl. 8429-80 (1980).
5. S.S. Malhotra, M.C. Whiting: J. Chem. Soc. 1960, 3812; Z. Arnold, A. Holý: Collect. Czech. Chem. Commun. 30, 47 (1965).
6. In a typical example, 70% $HClO_4$ (5 ml), followed by p-chlorobenzaldehyde (6.2 g; 0.044 mol), was added to an ice-cooled solution of the trimethinium salt II (9.1 g; 0.04 mol) in Ac_2O (60 ml). After standing for two days at laboratory temperature, the solid intermediate was precipitated and washed with dry ether, then stirred with dilute HCl (500 ml; 1:20), benzene (150 ml) and dichloromethane (75 ml) for several hours till dissolution. The product was isolated by extraction, drying the extracts over $MgSO_4$, evaporation of the solvents and crystallization of the residue from CCl_4 (16 ml). Yield 4.2 g (54%) of IV (Ar = p-Cl-Ph), m.p. 69-72°C. UV spectrum (CH_3CN), nm ($\varepsilon . 10^{-3}$): max 308(18.3), 227(13.0); NMR spectrum ($CDCl_3$), δ :10.18 (d, 1H, CH=O, $J_{CHO,CH}$ 0.5 Hz); 10.02 (s, 1H, CH=O); 8.03 (bs,1H, CH); 7.63 (m, 2H, arom.); 7.45 (m, 2H, arom.); IR spectrum ($CHCl_3$),cm^{-1}: 1743m,sh, 1704s,sh, 1681vs (C=O); 1591vs (C=C); 1600s,sh, 1565m, 1492m (arom.); 2725w, 2780vw, 2873w (C-H).
7. O.E. Polansky, P. Schuster, F. Wessely: Tetrahedron 1966, Suppl. 8, Part II, 463.

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