

PRELIMINARY COMMUNICATION

POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS
XXIII*. POLYHALODIKETONES FROM POLYHALOARYLCOPPER COMPOUNDS

SUJAN S. DUA, ANTHONY E. JUKES and HENRY GILMAN

Department of Chemistry, Iowa State University, Ames, Iowa 50010 (U.S.A.)

(Received March 4th, 1968)

This communication reports an extension of our studies on thermally stable compounds and some comparisons of polyhalogeno compounds having different halogens². Among other aspects, we have been interested in the preparation of highly halogenated chelates. One approach is through highly halogenated diketones. We have found that such compounds can be readily and conveniently prepared via polyhaloaryl-copper compounds.

Several procedures can be used for the synthesis of polyhaloarylcopper compounds, such as pentafluorophenylcopper, pentachlorophenylcopper, 2,3,5,6-tetrachloro-4-pyridylcopper, etc. Some of these are: (1) reaction of pentafluorophenylmetallic compounds (such as the lithium and magnesium types), or the corresponding pentachlorophenylmetallic compounds or 2,3,5,6-tetrachloro-4-pyridylmetallic types; (2) reactions of lithium dimethylcopper³ with the appropriate halides or hydrogen compounds such as pentafluoroiodobenzene, pentachloroiodobenzene, 4-iodotetrachloropyridine, pentafluorobenzene, pentachlorobenzene, and 2,3,5,6-tetrachloropyridine.

Tamborski and DePasquale⁴ had prepared pentafluorophenylcopper from pentafluorophenylmagnesium bromide and cuprous chloride prior to our work** on the preparations of the several polyhaloaryl compounds by some of the procedures mentioned previously in this publication. There has just appeared an announcement of a paper on *Fluorinated Organocopper Compounds* to be presented by Cairncross and Sheppard⁵ at the forthcoming National ACS Meeting.

As was to have been expected the highly halogenated arylcopper compounds are more thermally stable than the non-halogenated counterparts. This is substantiated by the several findings. Furthermore, our earlier generalizations and experimental work on the relative activities of organometallic compounds⁶ showed that such compounds would be of lesser chemical reactivity than the Grignard reagents. This has been found

* For Part XXII see Ref.1.

** An account of this work was presented at the *International Symposium on Decomposition of Organometallic Compounds to Refractory Ceramics, Metals and Metal Alloys* at Dayton, Ohio, November 28-30, 1967.

TABLE 1
PHYSICAL PROPERTIES OF SOME DIKETONES

Diketone	M.p. (°C)	Spectral data	
		Uve [λ_{\max} , m μ (e)]	IR ν (cm $^{-1}$)
C ₆ H ₅ COCOC ₆ H ₅	95	258 (18000), 384 (71)	1654 (C=O)
C ₆ F ₅ COCOC ₆ F ₅ ^a	80-80.5	255 (11000), 398 (55)	1723, 1708 (C=O); 1649, 1502 (C ₆ F ₅)
C ₆ Cl ₅ COCOC ₆ Cl ₅ ^a	320-322	288 (2250), 298 (2200), 377	1727 (C=O); 1540, 1347, 1333 (C ₆ Cl ₅)
4-C ₅ NCl ₄ COCOC ₅ NCl ₄ -4 ^a	282-284	280 (8200), 410 (57)	1727 (C=O); 1520, 1326 (C ₅ NCl ₄)
C ₆ F ₅ CO(CH ₂) ₂ COC ₆ F ₅ ^b	99-100	274 (2225)	2930 (CH ₂); 1712 (C=O); 1650, 1493 (C ₆ F ₅)
C ₆ Cl ₅ CO(CH ₂) ₂ COC ₆ Cl ₅	300-302	288 (955), 296 (950)	2945 (CH ₂); 1712 (C=O); 1543, 1350 (C ₆ Cl ₅)
4-C ₅ NCl ₄ CO(CH ₂) ₂ COC ₅ NCl ₄ -4	275-277	295 (7090)	2910 (CH ₂); 1712 (C=O); 1520, 1319 (C ₅ NCl ₄)
C ₆ F ₅ CO(CH ₂) ₄ COC ₆ F ₅ ^{c,d}	93-94	268 (2253)	2940 (CH ₂); 1710 (C=O); 1652, 1496 (C ₆ F ₅)
C ₆ Cl ₅ CO(CH ₂) ₄ COC ₆ Cl ₅	280-282	290 (1600)	2940 (CH ₂); 1713 (C=O); 1540, 1360 (C ₆ Cl ₅)
4-C ₅ NCl ₄ CO(CH ₂) ₄ COC ₅ NCl ₄ -4	182-184	293 (8675)	2950 (CH ₂); 1712 (C=O); 1535, 1322 (C ₅ NCl ₄)

^a The benzil analogs are yellow.

^b C₆H₅CO(CH₂)₂COC₆H₅ has m.p. 144-145° [lit.].

^c C₆H₅CO(CH₂)₄COC₆H₅ has m.p. 112° [lit.].

^d The ¹H NMR spectrum in CCl₄ shows multiplets at 7.15 [-C(O)CH₂-] and 8.23 (-CH₂-) τ , relative to TMS.

^e In THF. The *n*- η^D absorption for some of the diketones was not observable. Measured on a Carey 14R spectrophotometer.

^f Fluorolube mull. Recorded on a Perkin-Elmer Model 21 spectrophotometer.

to be the case, and as with the organocadmium⁶★ compounds or their complexes one could predict that reactions with acid halides or anhydrides might be expected to provide as useful route to ketones.

Reactions have been carried out with adipyl chloride, succinyl chloride and oxalyl chloride. Some of the properties are described in Table 1, and details on these and other polyhalogenated-arylcopper compounds will be forthcoming.

ACKNOWLEDGEMENTS

This research was supported by the United States Air Force under Contract F 33615-68-C-1251 monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

REFERENCES

- 1 F.W.G. Fearon and H. Gilman, *J. Organometal. Chem.*, (1968) in press.
- 2 G. Fearon, T. Brennan, I. Haiduc, A.E. Jukes and H. Gilman, *Fourth International Symposium on Fluorine Chemistry*, Estes Park, Colorado, July 24-28, 1967.
- 3 H. Gilman, R.G. Jones and L.A. Woods, *J. Org. Chem.*, 17 (1952) 1630; H.O. House, W.L. Respass and G.M. Whitesides, *J. Org. Chem.*, 31 (1966) 3128; E.J. Corey and G.H. Posner, *J. Am. Chem. Soc.*, 89 (1967) 3911.
- 4 C. Tamborski and R.J. DePasquale, Private communication and *Chem. and Ind.*, (1968) in press.
- 5 A. Cairncross and W.A. Sheppard, *155th National ACS Meeting* to be held in San Francisco, March 31-April 5, 1968, to be presented.
- 6 H. Gilman and J.F. Nelson, *Rec. Trav. Chim.*, 55 (1936) 518; H. Gilman, in H. Gilman (Ed.), *Organic Chemistry - An Advanced Treatise*, Wiley, New York, 1938, p.435.
- 7 D.A. Shirley, *Organic Reactions*, 8 (1954) 28.

★ For a general account of the formation of ketones from reaction of aryl halides with organo-metallic compounds such as those of cadmium, see Ref.7.