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ALKYLATION OF METAL DERIVATIVES OF 1,3-DIPHENYL-1,3-PROPANEDIONE WITH 1,2-DIPHENYL-3,3-DICHLOROCYCLOPROPENE

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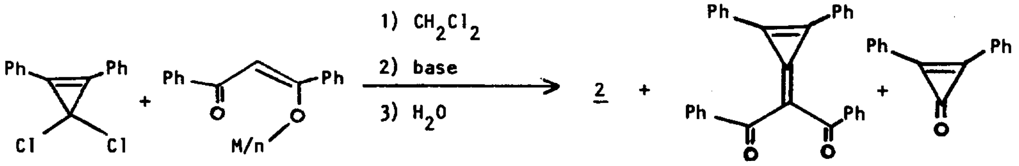
Reactions of halocyclopropenes include hydrolysis to cyclopropenones and acrylic acids, halogen exchange, salt formation, and conversion to quinocyclopropenes.[1,3] Little is known about the reaction of these compounds with enolate anions and related systems. We have studied the reaction of 1,2-diphenyl-3,3-dichlorocyclopropene (1) with metal derivatives of 1,3-diphenyl-1,3-propanedione (2).[4] When 1 and the metal salt or chelate of 2 are allowed to react under anhydrous conditions[5] in methylene chloride, the observed products after aqueous workup are the dibenzoylmethylenecyclopropene 3, diphenylcyclopropenone (4), and 2. The results are summarized in Table 1. The structure of 3 was confirmed by comparison of spectral data (see Table 2) to that observed for similar systems.[6,7]



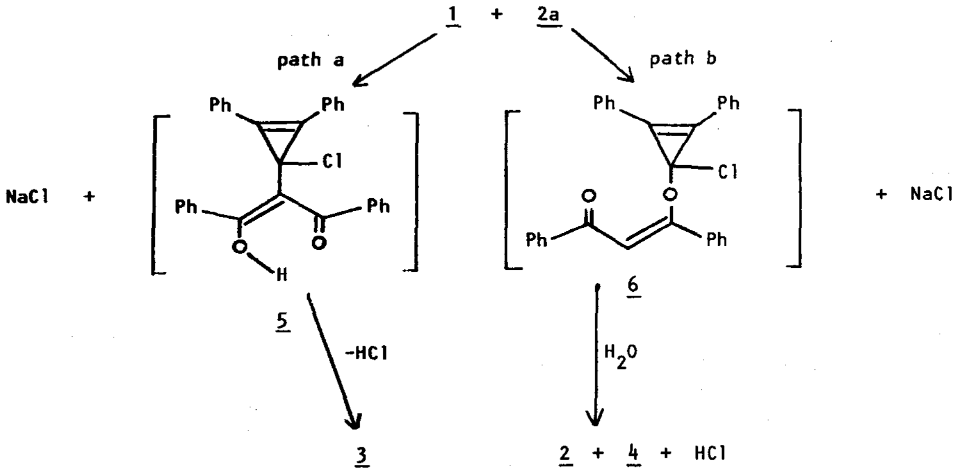
1 2a-d 3 4

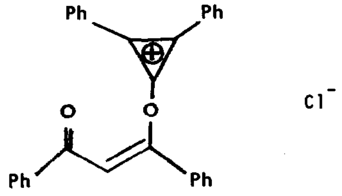
Table 1
Reaction of 1 and Metal Derivatives of 2

Compound	M	n	Base	Yields path a (3)	 path b (2 and 4)[a]
2a	Na[b,c]	1	none	19	81
2a	Na[b,c]	1	2,6-lutidine	21	79
2b	Cu[b]	2	none	15	85
2c	Zn[b]	2	none	26	74
2d	Cr[d]	3	none	no reaction	

a. average yield of 2 and 4
b. The initial reaction was complete within 15 min.
c. Use of diglyme as solvent made little difference in the reaction rates or yields.
d. refluxing for 15 hr

In each case where reaction occurs the yield of 3 is quite low compared to the average amount of 2 and 4. For the sodium salt 2a, two paths (a and b) are believed to be operative, with products arising from C- and O- alkylation of the enolate anion.[8] Loss of HCl from 5 is facile; addition of 2,6-lutidine to the reaction mixture makes no difference in the overall yield of 3. The results are consistent with the structure shown for the water sensitive intermediate 6, or with certain charge separated structures such as 7.





7

Reaction of 1 with the copper and zinc chelates (2b and 2c) results in rapid destruction of the chelates with formation of the corresponding metal halide. The yields of 2-4 in these reactions indicate that there is little difference in the overall reaction path once the chelate is destroyed. This result contrasts with the reaction of 1,2-diphenyl-3-ethoxycyclopropenylium tetrafluoroborate with Cu and Zn chelates; alkylation, rather than decomposition of the chelates is observed.[7] The sensitivity of copper chelates to acid chlorides has been demonstrated in previous work.[9] The chromium chelate 2d is known to have greater stability[10]; no reaction with 1 is observed in this case.

Table 2

Spectral Properties of 3, mp 186-188°

ir ($CHCl_3$)	3080, 3040(w), 1826(m), 1625(sh), 1600(s), 1575(m), 1495(m), 1465(vs), 1445(vs), 1375(m), 1325(s), 1295(m), 900(m) cm^{-1}
uv (EtOH)	323 mμ (ε 16,500), 255 mμ (ε 20,600), 240 mμ (sh)
nmr ($CDCl_3$)	8.75 ppm, 4H, multiplet; 7.90 ppm, 16H, multiplet

hrms[11]	m/e	elcomp	rel. int.
	412.1455	$C_{30}H_{20}O_2$	100 (molecular ion)
	383.1436	$C_{29}H_{19}O$	45[12]
	335.1053	$C_{24}H_{15}O_2$	27
	105.0329	C_7H_5O	91
	77.0391	C_6H_5	30

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2. B. Föhlisch and P. Bürgle, Ann. Chem. 701 67 (1967).
3. R. West, Accounts Chem. Res. 3 130 (1970).
4. Reaction of the parent compound with 1 gives a very low yield of 3.
5. The dichlorocyclopropene 1 is very easily hydrolyzed to diphenylcyclopropenone.
6. T. Eicher and A. Loschner, Z. Naturforschg. 21b 295 (1966).
7. T. Eicher and A. Loschner, Z. Naturforschg. 21b 899 (1966).
8. The theoretical amount of NaCl was isolated. Hydrochloric acid released could account in part for eventual isolation of 2 and 4.
9. W. J. Barry, J. Chem. Soc. (1960) 670.

10. J. Collman, R. Moss, H. Maltz, and C. C. Heindel, J. Amer. Chem. Soc. 83 531 (1961).

11. Provided kindly by the laboratory of K. Biemann, Massachusetts Institute of Technology.

12. The origin of this peak is under investigation.