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The BF_3 Catalyzed Decomposition of Diazo Compounds in the Presence of Carbonyl Compounds

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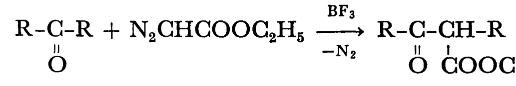
Synopsis The BF_3 catalyzed decomposition of diazo compounds such as α-diazoacetophenones, ethyl diazoacetate, and diphenyldiazomethane in the presence of cyclic β-diketones gave the corresponding enol ether. Used as a substrate, cyclohexanone gave the ring expanded homologation product.

The reactions of diazo compounds with carboxylic acids have been extensively studied as a preparative method for esters.[1] Few papers have however been published on the Lewis acid catalyzed reaction of diazo compounds with carbonyl compounds. For example, the BF_3 catalyzed decomposition of ethyl diazoacetate in carbonyl compounds was reported to give homologation products (**1**).[2–5]



$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}R + N_2CHCOOC_2H_5 \xrightarrow[-N_2]{BF_3} R{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{COOC_2H_5}{|}}{CH}{-}R}$$

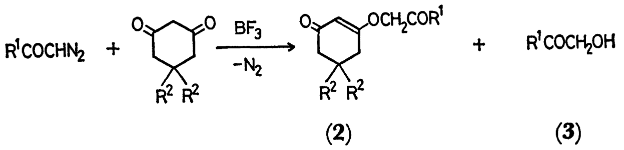
(**1**)

In this paper a further type of reaction observed in the BF_3 catalyzed decomposition of diazo compounds in the presence of β-diketones such as dimedone (5,5-dimethyl-1,3-cyclohexanedione) and 1,3-cyclohexanedione will be reported. A catalytic amount of BF_3 etherate when added to a solution of α-diazoacetophenone and dimedone (1 : 3 molar ratio) in benzene at 60 °C gave a vigorous evolution of nitrogen gas. Column chromatography (silica gel–benzene) of the reaction mixture gave two products. The first fraction was identified as α-hydroxyacetophenone (**3a**, 28%) by comparison of the IR and NMR spectra with those of authentic samples prepared by the decomposition of the diazoacetophenone in dilute sulfuric acid. The second product was characterized as 5,5-dimethyl-3-phenacyloxy-2-cyclohexene-1-one (**2a**: R^1=Ph, R^2=CH_3, 63%) on the basis of the results of elemental analysis and spectral properties. The IR spectrum shows the carbonyl band of the benzoyl group at 1700 cm^{-1} and bands of the enone group at 1650 and 1600 cm^{-1}. The NMR spectrum exhibits a singlet of the vinyl proton at δ 5.22 and three methylenes at 5.12, 2.43, and 2.22 ppm besides two methyl signals and a phenyl signal. Similar results were observed in the reactions of substituted diazoacetophenones with dimedone or 1,3-cyclohexanedione (Table 1, Runs a—f and h—j). Ethyl diazoacetate gave the corresponding enol ethers (**2g** and **2k**: R^1=OC_2H_5) in the reactions with dimedone and 1,3-cyclohexanedione.

Table 1. Yields, melting points, and analytical data of the products (**2** and **3**)

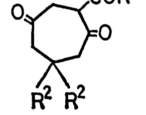
Run	R^1	R^2	**2** Yield/%	**2** Mp/°C	**2** Found (%) C	**2** Found (%) H	**2** Calcd (%) C	**2** Calcd (%) H	**2** Molecular formula	**3** Yield/%
a	C_6H_5	CH_3	63	109—110	74.18	7.06	74.39	7.02	$C_{16}H_{18}O_3$	28
b	*p*-BrC_6H_4		72	182—183	56.79	5.15	56.99	5.05	$C_{16}H_{17}O_3Br$	20
c	*p*-$NO_2C_6H_4$		60	187—189	63.32	5.66[a]	63.36	5.65	$C_{16}H_{17}O_5N$	11
d	*p*-$CH_3OH_6H_4$		65	102—105	70.97	6.92	70.81	6.99	$C_{17}H_{20}O_4$	23
e	*p*-$CH_3C_6H_4$		53	133—134	74.71	7.42	74.97	7.40	$C_{17}H_{20}O_3$	18
f	*m*-$CH_3C_6H_4$		44	57—58	74.61	7.34				29
g	C_2H_5O		55	oil						
h	C_6H_5	H	73	140—141	72.96	6.17	73.02	6.13	$C_{14}H_{14}O_3$	25
i	*p*-BrC_6H_4		49	182—183	54.15	4.26	54.39	4.24	$C_{14}H_{13}O_3Br$	43
j	*p*-$NO_2C_6H_4$		40	193—194	61.21	4.82[b]	61.09	4.76	$C_{14}H_{13}O_5N$	25
k	C_2H_5O		40	oil						

a) N: Found 4.53%, Calcd 4.62%. b) N: Found 4.92%, Calcd 5.09%.

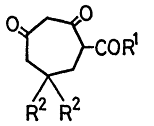


(**2**) (**3**)

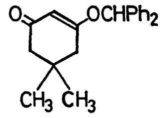
In these reactions, no ring expanded homologation product, *e.g.*, **4** or **5** was found in detectable amounts despite detailed inspection of the reaction mixture by column chromatography.



(**4**)



(**5**)



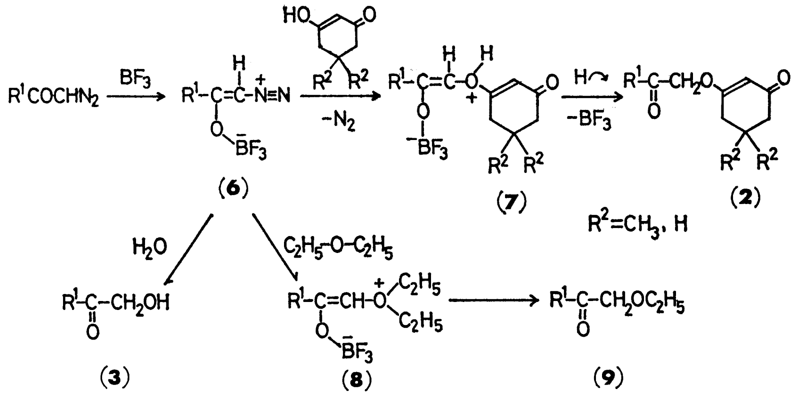
(**10**)

An excess of BF_3 etherate,[6] did not give the homologation product. In these cases **2** and **3** were accompanied by α-ethoxyacetophenone (**9**) which is thought formed by attack of the reaction intermediate (**6**) on diethyl ether through betaine (**8**). An increase in the amount of BF_3 etherate used caused a decrease in the yields of **2** and **3** an increase in the yield of **9**. The use of a five molar amount of BF_3 etherate gave only one product **9**, (69%), **2** and **3** were not detected.

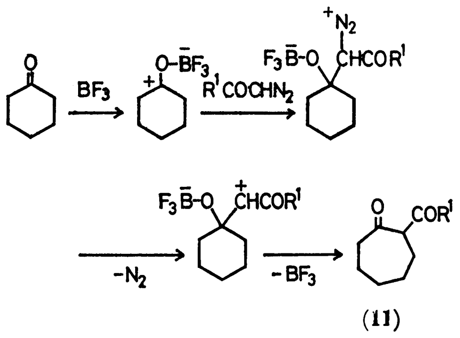
Table 2. The IR and NMR data of **2**

Compd	IR (KBr, ν/cm^{-1}) C=O	IR (KBr, ν/cm^{-1}) enone	NMR ($CDCl_3$, δ/ppm) CH_3	NMR CH_2	NMR CH_2	NMR OCH_2	NMR =CH	NMR Others[a]
2a	1700	1650, 1660	1.07	2.22	2.43	5.12	5.22	
2b	1710	1640, 1600	1.02	2.20	2.42	5.13	5.27	
2c	1710	1630, 1595	1.10	2.23	2.47	5.23	5.30	
2d	1690	1645, 1600	1.10	2.23	2.43	5.14	5.31	3.88(s) OCH_3
2e	1700	1650, 1600	1.40	2.20	2.40	5.03	5.24	2.40(s) CH_3
2f	1705	1655, 1600	1.07	2.20	2.40	5.20	5.30	2.40(s) CH_3
2g	1760	1660, 1600	1.07	2.22	2.38	4.47	5.23	1.29(t), 4.29(q) CH_2CH_3
2h	1695	1640, 1600	—	m	m	5.20	5.28	
2i	1695	1640, 1600	—	m	m	5.20	5.30	
2j	1705	1635, 1600	—	m	m	5.18	5.30	
2k	1760	1650, 1605	—	m	m	4.45	5.23	1.27(t), 4.23(q) CH_2CH_3

a) Signals of the aromatic protons have been omitted.



Scheme 1.



Scheme 2.

The reactions are explained in terms of the attack of the diazonium ion type intermediate (**6**) on the enol oxygen of the β-diketones to give the intermediate **7** which by the elimination of BF_3 and hydrogen migration gives the product **2**. An alternative mechanism which can not be excluded is the attack by **6** on the carbonyl oxygen of the keto form of the β-diketones. The formation of α-hydroxyacetophenones (**3**) may be explained by the attack of **6** on the water contained in the reaction system. Diphenyldiazomethane also gave the corresponding enol ether (**10**, 44%) in a similar reaction accompanying benzhydryl alcohol and tetraphenylethylene. Cyclohexanone however changes the mode of the reaction. The decomposition of p-methoxydiazoacetophenone in cyclohexanone in the presence of catalytic amounts of BF_3 occurs vigorously even at temperatures as low as 0 °C, affording the homologation product (**11**: $R^1=p\text{-}CH_3OC_6H_4$, 92%). A small broad singlet at 16.6 ppm in the NMR spectrum shows the partial existence of the enol form in **11**. This reaction may be initiated by the attack of BF_3 on the oxygen of cyclohexanone as shown in the following Scheme 2.

The difference in reaction between cyclohexanone and the cyclic β-diketones may be attributed to differences in affinity of these ketones to BF_3. The affinity appears to be in the order: cyclohexanone> diazoacetophenone>dimedone≈1,3-cyclohexanedione.

Experimental

All melting points are not corrected. The IR spectra were measured on a Hitachi Spectrometer Model 215. The ^{1}H-NMR spectra were recorded in $CDCl_3$ solution at 60 MHz on a Varian Spectrometer Model EM-360 using TMS as an internal standard.

Materials. All diazo compounds were prepared by the methods described in the literature.[7,8]

General Procedure of the BF_3 Catalyzed Decomposition of Diazoacetophenones in the Presence of Cyclic β-Diketones.
To a benzene solution (50 ml) of diazoacetophenone (5 mmol) and the carbonyl compound (15 mmol) a catalytic amount of BF_3 etherate (20 mg) was added under magnetic stirring at 60°C. Vigorous evolution of N_2 occurred and the reaction mixture changed from yellow to dark red. The reaction mixture was added to water (50 ml) and the benzene layer washed with H_2O (10 ml), dried over Na_2SO_4, and column chromatographed on silica gel.

The BF_3 Catalyzed Decomposition of Diphenyldiazomethane in the Presence of Dimedone. To a benzene solution (50 ml) of diphenyldiazomethane (0.51 g, 2.6 mmol) and dimedone (0.63 g, 4.5 mmol) two drops of BF_3 etherate were added and the mixture stirred at room temperature. After the evolution of N_2 ceased, the reaction mixture was treated as described above. Column chromatography of the reaction mixture gave three products. Benzhydryl alcohol (35%) and tetraphenylethylene (8%) were characterized by direct comparison with authentic samples. Enol ether (**10**): colorless crystals; yield 44%; mp 57—58°C; IR (KBr) 1650, 1600 cm^{-1} (enone); NMR ($CDCl_3$) δ 1.03 (s, 6H, CH_3), 2.17 (s, 2H, CH_2), 2.45 (s, 2H, CH_2), 5.41 (s, 1H, =CH), 6.17 (s, 1H, OCH), and 7.33 ppm (s, 10H, Ph). Found: C, 82.10; H, 7.31%. Calcd for $C_{21}H_{22}O_2$: C, 82,37; H, 7.24%.

Reaction of p*-Methoxydiazoacetophenone with Cyclohexanone.* To a solution of p-methoxydiazoacetophenone (0.53 g, 3 mmol) in cyclohexanone (5 ml) three drops of BF_3 etherate were added. After the usual workup, 2-(p-anisoyl)cycloheptanone (**11**: $R^1=p\text{-}CH_3OC_6H_4$) was obtained; yield 92%, colorless needles; mp 125.0—126.5°C; IR (KBr) 1700, 1670 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.2—2.9 (m, 10H, CH_2), 3.85 (s, 3H, OCH_3), 4.5 (broad t, 1H, CH), 6.95, 7.97 (ABq, 4H, Ar), and 16.6 ppm (broad s, 0.1H, enol-H). Found: C, 72.94; H, 7.32%. Calcd for $C_{15}H_{18}O_3$: C, 73.14; H, 7.37%.

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