frozen with Dry Ice–isopropyl alcohol and the pressure of the noncondensable gases recorded. The liquid nitrogen bath was removed and the total gas pressure recorded.

The gases were thoroughly mixed using a Toepler pump and then forced by external pressure into a gas sampler fitted with a rubber serum cap. A gas-tight Hamilton syringe was used to transfer the gas mixture to a F & M Model 700 gas chromatograph with a thermal conductivity detector.[27] Air, methane, ethane, and carbon dioxide are easily resolvable and a check was made of their separation before an unknown was measured.

After the sample had been removed, the system was evacuated and the bomb degassed a second time. The pressure was measured and added to the first pressure reading. The system was reevacuated and the total volume calculated by admitting a known volume of gas at atmospheric pressure and observing the final pressure.

The Dry Ice–isopropyl alcohol trap was rinsed with chlorobenzene and the washings were added to the main solution. For qualitative identification the solution was distilled and three fractions were collected; a 5-ml forerun, bp 25–130°; *ca.* 300 ml of chlorobenzene, bp 130°; and a high boiling residue (*ca.* 20 ml). Each of the fractions was subjected to gas chromatography (10 ft × 0.25 in. SF-96 silicone oil, 7 ft × 0.25 in. DEGS,[28] 7 ft × 0.25 in. PPE,[29] and 7 ft × 0.25 in. FFAP[30] columns). Peaks were collected and identified by comparing their infrared and nmr spectra and gas retention times with those of authentic samples.

Quantitative measurements were performed using standard solutions of known compounds. Each peak was bracketed by injecting enough of the standard solutions so that both a smaller and a larger peak than that of the unknown compound was obtained. Analyses were made using the same chromatographic conditions. All analyses were made in duplicate.

No low-boiling compounds other than methyl iodide were observed. Methyl acetate was found to be completely resolved from methyl iodide at 35° using a 7 ft × 0.25 in. DEGS column; it was not present in the product mixture.

No high-boiling compounds other than those mentioned were detected. Biphenyl, phenol, *o*- and *m*-iodochlorobenzene, *o*-iodophenyl benzoate, *p*-chlorobenzyl acetate, and *p*-chlorophenyl acetate were shown to be absent (or if present, in less than 1% yield) by control experiments.

Determination of Chlorotoluene Isomer Ratios. The chlorotoluene isomer ratios were determined by gas chromatography, using the liquid crystal technique recently developed by Dewar and Schroeder[31] and an F & M Model 700 flame ionization chromatograph at 125°. Peak height-to-composition conversion factors were determined experimentally for each isomer.

Acknowledgments. We are happy to acknowledge support of this research by the Petroleum Research Foundation and by the National Science Foundation.

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[27] Conditions: 12 ft × 0.25 in. copper column; 30–60 mesh silica gel; oven, 70–90°; detector, 80°; injector, 52°; helium, 37 cc/min; sample, approximately 30 μl.

[28] Diethylene glycol succinate.

[29] Polyphenyl ether.

[30] A specially modified Carbowax obtained from Wilkins Instrument and Research Corp., Walnut Creek, Calif.

[31] M. J. S. Dewar and J. P. Schroeder, *J. Am. Chem. Soc.*, 86, 5235 (1964).

Decarbonylation of Aromatic Carbonyl Compounds Catalyzed by Rhodium Complexes

Jochanan Blum,[1] Edna Oppenheimer, and Ernst D. Bergmann

Contribution from the Department of Organic Chemistry, Hebrew University, Jerusalem, and the Institute for Advanced Study, Princeton, New Jersey.

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Abstract: The catalytic decarbonylation of aroyl chlorides, bromides, and cyanides with chlorotris(triphenylphosphine)rhodium(I) has been investigated; particular attention has been paid to polycyclic aroyl halides. A theory of the mechanism of decarbonylation has been suggested which accounts for the observations made in this study. The essential features of the theory are the formation of V, its isomerization to VI, and the loss of carbon monoxide from the latter. Several new rhodium complexes are described.

A previous communication from this laboratory[2] reported that chlorotris(triphenylphosphine)rhodium(I) catalyzes the decarbonylation of aroyl chlorides to the corresponding aryl chlorides. Almost simultaneously, Tsuji and Ohno observed that aliphatic acyl chlorides are converted, under the same conditions, into olefins.[3] In both cases, the analogous response of acyl bromides was briefly mentioned.[3,4]

The Japanese authors suggested a mechanism for these decarbonylation reactions. This mechanism will have to be somewhat modified in view of the more extensive studies reported in the present paper.

In Table I, the results obtained with a number of benzoyl chlorides are summarized. This table also contains some examples for the decarbonylation of benzoyl and naphthoyl bromides. The last two examples in this table indicate that carbon monoxide can be extruded also from benzylic carbonyl chlorides without difficulty.[2,3] It is obvious from these data that the reaction is practically unaffected by electronic or steric influences of substituents; the seemingly accelerating effect of the α-naphthoyl residue (compare benzoyl and α-naphthoyl bromide) is most probably due to the higher temperature at which the reaction with α-naphthoyl bromide is carried out.

The behavior of the three isomeric phthaloyl chlorides deserves some comment. *o*-Phthaloyl chloride does not react at all, possibly because it has the structure of α,α-dichlorophthalide.[5] The other two isomers decompose in two distinct steps, *via* the chlorobenzoyl chlorides, into the dichlorobenzenes. This is in

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[1] To whom inquiries should be addressed at the Department of Organic Chemistry, Hebrew University, Jerusalem.

[2] J. Blum, *Tetrahedron Letters*, 1605 (1966).

[3] J. Tsuji and K. Ohno, *ibid.*, 4713 (1966).

[4] *Cf.* J. Blum, *ibid.*, 3041 (1966).

[5] F. B. Garner and S. Sugden, *J. Chem. Soc.*, 2877 (1927).

Table I. Decarbonylation of Aromatic Acid Chlorides and Bromides ("Distillation Technique")

Acid halide	Reaction time, hr	Yield of pure aryl halide, %	Acid halide	Reaction time, hr	Yield of pure aryl halide, %
C_6H_5COBr[a]	6	80	4-$(CH_3CONH)C_6H_4COCl$	0.25	Low
3-$CH_3C_6H_4COCl$[b]	20	74	1,2-$C_6H_4(COCl)_2$	10	0
4-$C_2H_5C_6H_4COCl$	15	82	1,3-$C_6H_4(COCl)_2$[d]	3.5	78 + 17
4-$CH_3OC_6H_4COCl$	10	50	1,4-$C_6H_4(COCl)_2$[d]	4.5	79 + 5
4-$C_2H_5OC_6H_4COCl$	5	59	3,4-$Cl_2C_6H_3COCl$[c]	5	76
3-BrC_6H_4COBr	2	85	2,4,6-$(CH_3)_3C_6H_2COCl$	2	55
4-BrC_6H_4COBr	0.25	95	α-$C_{10}H_7COBr$[e]	0.5	84
4-NCC_6H_4COCl[c]	4	90	$C_6H_5CH_2COCl$[a,b]	0.25	97
4-$O_2NC_6H_4COCl$[c]	8.5	79	$(C_6H_5)_2CHCOCl$	0.25	94

[a] Compare ref 3. [b] Under nitrogen. [c] A 25-cm-long Vigreux column was used. [d] The first yield figure corresponds to the chlorobenzoyl chloride, the second to the dichlorobenzene. [e] The acid bromide was prepared by refluxing α-naphthoic acid with twice its weight of phosphorus tribromide for 30 min; bp 195–196° (30 mm). This method is superior to that of Yu. A. Ol'dekop and A. M. Kalinina, *Zh. Obshch. Khim.*, **34**, 3473 (1964).

Table II. Decarbonylation of Polycyclic Aroyl Halides (without distillation)

Aroyl halide[a]	Reaction temp, °C	Yield of ArX, %	Aroyl halide[a]	Reaction temp, °C	Yield of ArX, %
Acenaphthene-5-COCl	300	81	Phenanthrene-9-COBr	300	95
Fluorene-2-COCl	280	60	Fluoranthene-3-COCl	235	84
Anthracene-2-COCl	310	81	Chrysene-6-COCl	280	48
Anthracene-9-COCl	310	24[b]	Pyrene-1-COCl	250	94
Phenanthrene-2-COCl	235	95	Pyrene-1-COBr	290	89
Phenanthrene-9-COCl	260	60	Benzo[*c*]phenanthrene-6-COCl	260	89

[a] "Ring Index" numbering. [b] And 30% of ketone X.

marked contrast to the behavior of the benzenedisulfonyl chlorides.[4]

The very low yields obtained with *p*-acetamidobenzoyl chloride are due to the very pronounced instability of the aroyl halide at the required elevated temperature.

In the decarbonylation of relatively low-boiling aroyl chlorides it has proven essential to distil off the aryl chloride as it is formed; otherwise the reaction comes to a standstill after a given period, which varies from compound to compound. As examples, *o*-, *m*-, and *p*-chlorobenzoyl chlorides, heated with a small amount (100 mg/9.9 g) of I at 217°, cease to react after 300, 40, and 10 min, respectively (the yield of the three dichlorobenzenes after these periods was 8.0, 15.3, and 1.7%, respectively). Here an influence of the distance of the carbonyl group from the substituent appears to exist. Following the theoretical concept outlined below, we assume that a rhodium complex is formed which does not participate in the decarbonylation reaction. Whatever the structure of the complex is, it must be assumed that it is stable in the presence of aroyl halides.

The "distillation technique" is not applicable to the preparation of the otherwise difficultly obtainable halogenated polycyclics in which we were particularly interested in connection with other projects of this laboratory. This is due to the relative instability of the polycyclic acid halides at elevated temperatures and the difficulty in obtaining these halides free from impurities, *e.g.*, hydrogen halide. We shall return to this point later on; here it may be said that an easy technique has been developed for the polycyclic acyl halides. They are heated at about 260° for 1–3 min in the presence of I, and the product is purified by chromatography on alumina. The results are summarized in Table II, from which it can be seen that this technique gives, *e.g.*, for 1-pyrenoyl chloride a yield of 94%, while the "distillation technique" at 230° (8–10 min) gave only 40% of 1-chloropyrene.

Table III shows some experiments with aroyl cyanides which are also decarbonylated by heating with I, yielding the nitriles of aromatic acids. This is perhaps not surprising in view of the "pseudo-halogen" character of the cyano group. Table III contains, for comparison, also two examples for the decarbonylation of aldehydes. The stoichiometric decarbonylation of aldehydes by the reaction with I has, of course, been known before.[6]

Table III. Decarbonylation of Aroyl Cyanides and Aldehydes

Aromatic carbonyl compd	Reaction time, hr	% Yield of nitrile or hydrocarbon
C_6H_5COCN	*a*	*a*
4-ClC_6H_4COCN	3.5	95
α-$C_{10}H_7COCN$	1	87
α-$C_{10}H_7CHO$	2	88
β-$C_{10}H_7CHO$	2.5	77

[a] Very slow decarbonylation. After 7 hr, 8% of benzonitrile and 91% of unchanged starting material were obtained.

Tsuji and Ohno[3] have assumed that the essential intermediate in the decarbonylation reaction is chlorocarbonylbis(triphenylphosphine)rhodium(II). As we shall show, this complex has a part in the scheme of the reaction, but it cannot always be an essential intermediate; it is often much less reactive as a decarbonylation catalyst than I. α-Naphthoyl chloride is converted at 290° into α-chloronaphthalene by II in 30, and by I

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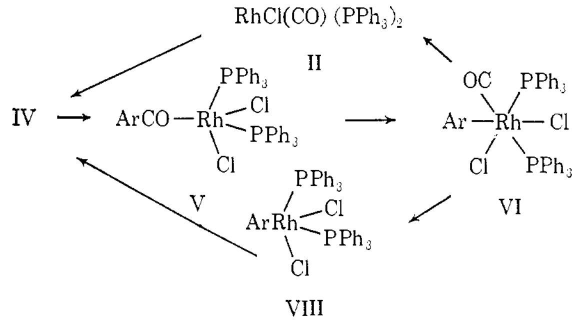
(6) J. Tsuji and K. Ohno, *Tetrahedron Letters*, 3969 (1965).

in 7 min. Furthermore, one would have to assume that II is converted, at least initially, into a complex of type III; however, we have not been able to isolate such a complex or even detect its temporary appearance by its characteristic infrared spectrum.

$$\underset{\text{I}}{RhCl(PPh_3)_3} \rightleftharpoons \underset{\text{IV}}{RhCl(PPh_3)_2} + PPh_3$$



We propose that compound I is first converted into the dimeric tricoordinate complex IV described by Bennett and Longstaff.[7] This complex reacts with the aroyl chloride to give V, which isomerizes to VI. The next step is normally the loss of carbon monoxide, leading to VII, followed by the elimination of aryl chloride. Thus IV is regenerated and the *catalytic* activity of IV (and, therefore, I) is explained. *As a side reaction*, the steps of the decomposition of VI can be reversed: elimination of the aryl chloride leads to II and subsequent liberation of carbon monoxide back to IV. This would be the mechanism proposed by Tsuji and Ohno[3] and, as already pointed out, cannot be the major component of the scheme.

In no case have we been able to isolate and identify all the intermediary stages demanded by the proposed reaction mechanism. It seems, however, supported by the observations described in the following paragraphs. When some of the substituted benzoyl chlorides, *e.g.*, *p*-chlorobenzoyl chloride, were heated very briefly with I, yellow rhodium complexes were obtained (not isolated in analytical purity) which did not show any carbonyl absorption in the infrared and are, very likely, of type VII. Benzoyl, *m*-toluoyl, and *m*-chlorobenzoyl chloride as well as *p*-bromobenzoyl bromide gave at 80 and at 200° the same type of complex, which showed no absorption characteristic of an aroyl group, but metal carbonyl peaks (in Nujol) at 2068, 2058, 2070, and 2055 cm^{-1}, respectively, indicating that the complexes are of formula VI. In analogous cases[4,8] such carbonyl peaks have been observed at 2080 and 2072 cm^{-1}. On the other hand, α-naphthoyl chloride forms, even at 250°, a complex (or rather a mixture of two isomeric complexes) which shows carbonyl absorption at 1670 and 1685 cm^{-1}, α-naphthoyl bromide gives a complex with a peak at 1675 cm^{-1}, and *o*-chlorobenzoyl chloride, a rather unstable complex with carbonyl bands at 1675 and 1715 cm^{-1}. These complexes represent examples for type V.

In one case—using β-naphthoyl chloride in boiling benzene—we have followed the transition from an isomeric mixture of pentacoordinate complexes of type V (aryl carbonyl absorptions at 1665 and 1680 cm^{-1}) to VI (Ar = β-$C_{10}H_7$), showing a characteristic metal carbonyl band at 2062 cm^{-1}.

We have also observed transitions from complexes V and VI to II, though these transitions have often been erratic in their reproducibility. When hexane or ethanol was added to a benzene solution of VI (Ar = C_6H_5),[8] II precipitated often, but not always, in quantitative yield.[2] Heating of VI (Ar = C_6H_5) *in vacuo* (20 mm) for 4.5 hr at 144° did not produce any changes, while refluxing with xylene for 3 min caused complete conversion into II.

In many experiments leading to II, the latter was isolated as a mixture of two isomeric forms, exhibiting carbonyl absorption at 1965 and 1978 cm^{-1}; the melting points of the isomers were 204–205° and 209–210°, respectively. Previous authors[6,9] reported for II an unsharp melting point around 195° and a carbonyl absorption at 1980 cm^{-1}. As the compound absorbing at 1965 cm^{-1} predominates in these mixtures it is assumed—in accord with similar cases studied previously[9,10]—that it has the *trans* structure (mp 209–210°), while the minor isomer is assigned the *cis* configuration. Recently Chatt and Shaw reported that the *trans* isomer of II absorbs at 1961 cm^{-1}, but indicated a melting point of 189–190.5°.[11] The pure *trans* form was isolated from α-naphthaldehyde and I, the pure *cis* form, from 9-anthroyl chloride and I (after chromatography on neutral alumina); the former is partially isomerized to the latter by heating with chlorobenzene at 220° in a sealed tube. Incidentally, Tsuji and Ohno's[3] theory would imply that under these conditions II is converted into VI, which is, however, not the case.

Let us return to the reactions of polycyclic aroyl halides. It has been pointed out that their transformations are affected adversely by impurities. Moisture and hydrogen chloride may form the hydrido complex VIII[8] or compound IX (see Table IV) from I. VIII may also originate from V, by reaction with moisture: $V + H_2O \rightarrow ArCOOH + VIII$.

Both these complexes may catalyze formation of hydrocarbons from the aroyl chlorides; they may, alternatively, lose hydrogen chloride and cause Friedel–Crafts reactions. Such a reaction has, indeed, been observed in the case of 9-anthroyl chloride. Together with the expected 9-chloroanthracene, a ketone, $C_{29}H_{17}ClO$, was formed, showing a strong carbonyl absorption at 1645 cm^{-1}. It is assigned structure X on the strength of two independent syntheses: from 9-chloroanthracene and 9-anthroyl chloride, or from anthracene and 10-chloro-9-anthroyl chloride.

It is noteworthy that 9-anthroyl chloride could only be decarbonylated with catalytic amounts of I above 300°. Below this temperature, a yellow complex of formula XI was obtained, which was also formed when the two reactants were refluxed in decalin for 1 hr. The structure is in accord with the existence of two carbonyl absorptions: 1680 cm^{-1} (acyl carbonyl) and 2055 cm^{-1} (metal carbonyl).

The analyses and some other data for the metal complexes isolated in this study are summarized in Table IV.

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[7] M. A. Bennett and P. A. Longstaff, *Chem. Ind.* (London), 846 (1965). See also J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.*, 131 (1965).

[8] M. C. Baird, D. N. Lawson, J. T. Mangue, J. A. Osborn, and G. Wilkinson, *ibid.*, 129 (1966).

[9] L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

[10] L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, 83, 2784 (1961).

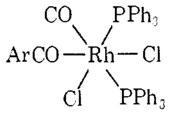
[11] J. Chatt and B. L. Shaw, *J. Chem. Soc., A*, 1437 (1966).

Table IV. Analytical Data for Rhodium Compounds

Compd	Mp (dec), °C	Carbon, % Found	Carbon, % Calcd	Hydrogen, % Found	Hydrogen, % Calcd	Cl, Br, % Found	Cl, Br, % Calcd
$C_{37}H_{30}ClOP_2Rh$ (*cis*-II)	204–205	64.3	64.3	4.4	4.3	5.4	5.1
$C_{37}H_{30}ClOP_2Rh$ (*trans*-II)	209–210	64.4	64.3	4.6	4.3	5.4	5.1
$C_{37}H_{31}OP_2Rh$ (IX)[a]	Softens at 195	61.2	61.1	4.4	4.3	9.5	9.8
$C_{43}H_{34}Br_3OP_2Rh$ (XII)	185–186	53.1	53.2	3.7	3.5	25.1	24.7
$C_{43}H_{35}Cl_2OP_2Rh$ (VI, Ar = C_6H_5)[b]	215–218	64.1	64.3	4.4	4.4	9.2	8.8
$C_{47}H_{37}Br_2OP_2Rh$ (XIII)	174–176	60.2	59.9	4.3	3.9	17.5	17.0
$C_{47}H_{37}Cl_2OP_2Rh$ (V, Ar = α-$C_{10}H_7$)	220–222	65.9	66.1	4.6	4.3	8.3	8.3
$C_{47}H_{37}Cl_2OP_2Rh$ (V, Ar = β-$C_{10}H_7$)[c]	145	66.2	66.1	4.4	4.3	8.5	8.3
$C_{47}H_{37}Cl_2OP_2Rh$ (VI, Ar = β-$C_{10}H_7$)[d]	177–180	66.2	66.1	4.6	4.3	8.3	8.3
$C_{66}H_{48}Cl_2O_2P_2Rh$ (XI)[e]	195	71.4	71.6	4.0	4.3	6.0	6.4

[a] Rh–H absorption at 2095 cm^{-1}; carbonyl band at 1960 cm^{-1}. *Cf.* L. Vaska, *J. Am. Chem. Soc.*, **88**, 4100 (1966). [b] *Cf.* ref 8. [c] Not isomerically pure; contaminated with VI (Ar = β-$C_{10}H_{71}$); carbonyl bands at 1665 (vs), 1680 (vs), and 2062 (w) cm^{-1}. [d] $\bar{\nu}_{CO}$ 2062 (vs) cm^{-1}. [e] Recrystallized from a mixture of benzene–hexane.

In conclusion, some comment is due on the reaction of aroyl *bromides* (Tables I, II) with the *chloro* complex I. Experiments at relatively low temperatures have shown that in these reactions the original metal chlorine atom is partly or completely replaced by bromine. For example, *p*-bromobenzoyl bromide gave with I in boiling benzene (30 min) a complex which could be recrystallized from benzene–hexane, absorbed at 2055 cm^{-1}, and had thus the structure XII, which is confirmed by the analysis. XII is thus an analog to the complex of type VI. α-Naphthoyl bromide, under the same conditions, on the other hand, gave an orange five-coordinate complex, which after recrystallization from benzene showed aromatic carbonyl absorption (at 1675 cm^{-1}) and was thus XIII, corresponding to V.



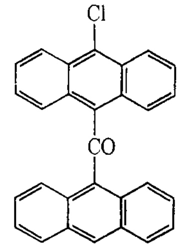
III

$HRhCl_2(PPh_3)_3$

VIII

$HRh(CO)Cl_2(PPh_3)_2$

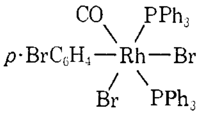
IX



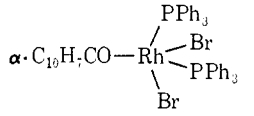
X

$(Ar{\cdot}CO)RhCl(CO)(PPh_3)_2(ArCl)$

XI, Ar = 9-anthryl



XII



XIII

Experimental Section

The different techniques used for the decarbonylation reactions are illustrated by the following examples.

***m*-Dibromobenzene from *m*-Bromobenzoyl Bromide.** A mixture of 14.0 g of *m*-bromobenzoyl bromide (Eastman Organic Chemicals) and 50 mg of I was heated in a Claisen flask equipped with a 25-cm-long Vigreux column, so as to permit distillation of the dibromobenzene formed at 214–216°. After 1 hr the evolution of carbon monoxide practically ceased, and an additional portion of 15 mg of I was added to the reaction mixture. This process was repeated four times in intervals of 15 min (until decarbonylation was complete). The crude distillate was washed with alkali, neutralized, and dried in the usual manner and redistilled at 215–216°, yielding 10.6 g (85%) of pure *m*-dibromobenzene.

α-Naphthonitrile from α-Naphthoyl Cyanide. A mixture of 9.0 g of α-naphthoyl cyanide (mp 101–102°; prepared by refluxing α-naphthoyl chloride with an equal amount of cuprous cyanide at 190° for 1 hr) and 0.1 g of I was heated for 45 min in a Claisen flask, so that the product distilled off as formed (bp 294°). The product was distilled again (during 10 min) with 0.02 g of I. Thus 6.6 g (87%) of α-naphthonitrile (mp 37°) was obtained. The nitrile was identical with an authentic sample.

α-Chlorodiphenylmethane from Diphenylacetyl Chloride. A quantity of 6.5 g of freshly distilled diphenylacetyl chloride [bp 185–187° (20 mm)] and 0.1 g of I were placed in a Claisen flask mounted with two thermometers and connected to a variable vacuum system. The mixture was heated at 210–230° (internal temperature), and a suitable vacuum was applied, so that the product distilled off during 15 min. On redistillation at 137–138° (2 mm) there was obtained 5.4 g (94%) of colorless α-chlorodiphenylmethane, identical with a product prepared from benzhydrol.[12]

6-Chlorobenzo[*c*]phenanthrene. A mixture of 1.45 g of 6-benzo[*c*]phenanthroyl chloride[13] and 0.1 g of I was heated in a test tube, under exclusion of moisture, at 260° (internal temperature) for 1–3 min. After this time the evolution of carbon monoxide had ceased. Chromatography on alumina, *n*-hexane serving as eluent, yielded 1.15 g (89%) of 6-chlorobenzo[*c*]phenanthrene from *n*-hexane as colorless needles, mp 85–86°, λ_{max}^{EtOH} (mμ (log ϵ)) 219 (4.71), 232 (4.38), 245 (4.15), 276 (4.71), 285 (4.79), 310 (4.00), 318 (4.02), 330 (3.57), 361 (2.57), and 380 (2.38). *Anal.* Calcd for $C_{18}H_{11}Cl$: C, 82.4; H, 4.2; Cl, 13.4. Found: C, 82.2; H, 4.1; Cl, 13.5.

Decarbonylation of 9-Anthroyl Chloride. A quantity of 2.34 g of 9-anthroyl chloride was heated, in a test tube, with 0.1 g of I at 310° for 3 min. Chromatography on alumina, benzene serving as eluent, yielded, as the first fraction, 0.49 g (24%) of pale yellow 9-chloroanthracene (mp 102–104°) identical with the product prepared from anthracene and cupric chloride.[14]

A second fraction from the chromatography afforded, on recrystallization from benzene and ethanol, 0.60 g (30%) of X as deep yellow crystals, mp 260–262°. *Anal.* Calcd for $C_{29}H_{17}ClO$: C, 83.6; H, 4.1; Cl, 8.5; mol wt, 416. Found: C, 83.8; H, 4.1, Cl, 8.9; mol wt, 416 (mass spectrum).

9-Anthryl 10-Chloro-9-anthryl Ketone (X) by Friedel–Crafts Acylation. a. Following the known route for the preparation of 9-benzoylanthracene, 2.8 g of 9-chloroanthracene, 3.5 g of 9-anthroyl chloride, 1.8 g of aluminum chloride, and 50 ml of carbon disulfide were refluxed for 48 hr. After the usual work-up, the oily residue was chromatographed on alumina, yielding 0.8 g of X, mp 260–262°.

b. In a similar manner, anthracene and 10-chloro-9-anthroyl chloride were treated with aluminum chloride in carbon disulfide, giving X in 21% yield, identical with the samples obtained by the two preceding methods.

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(12) A. M. Ward, *J. Chem. Soc.*, 2285 (1927).

(13) M. S. Newman and J. Blum, *J. Am. Chem. Soc.*, **86**, 1835 (1964).

(14) D. C. Nonhebel, *Org. Syn.*, **43**, 15 (1963).